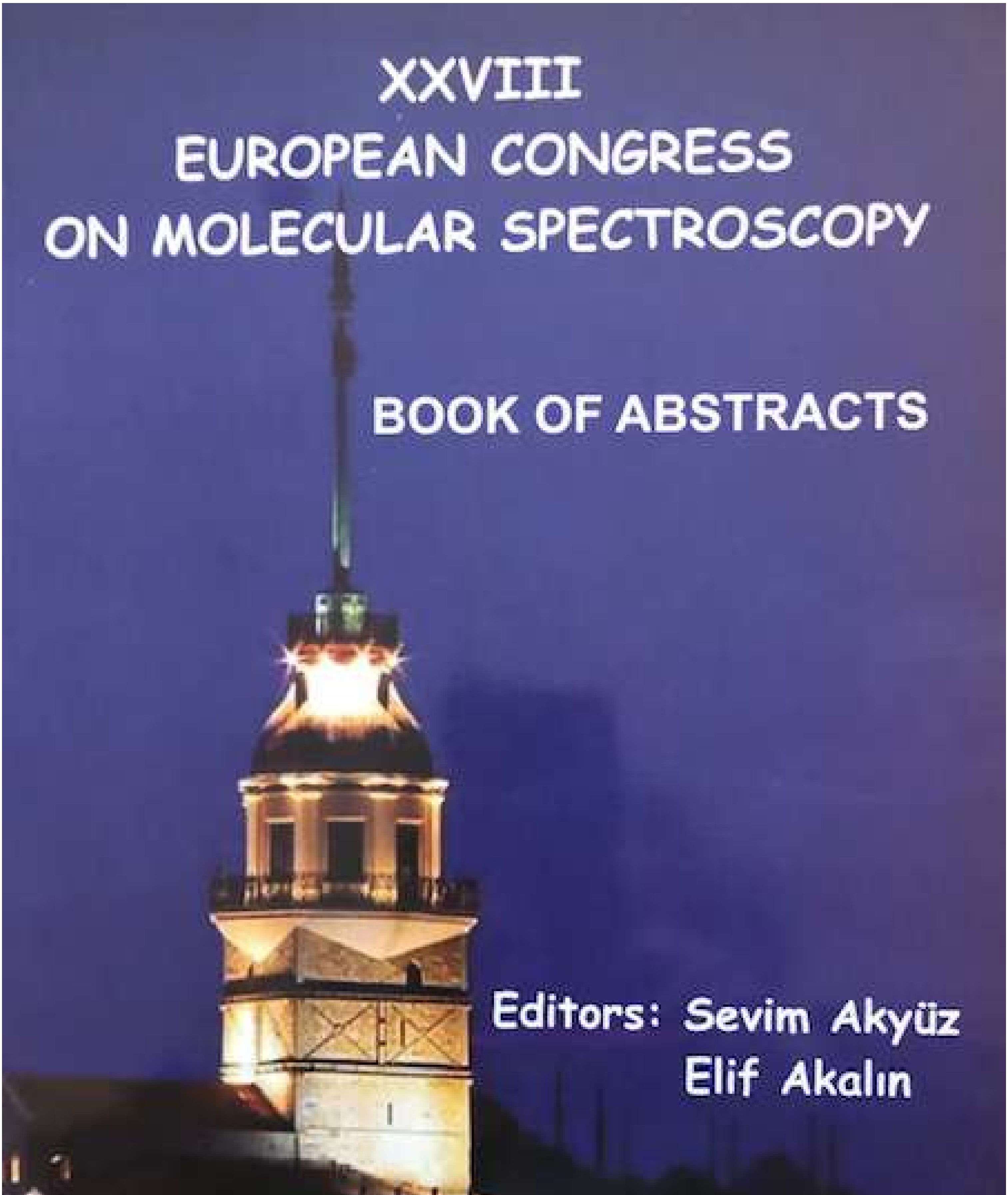
XXVIII
EUROPEAN CONGRESS
ON MOLECULAR SPECTROSCOPY

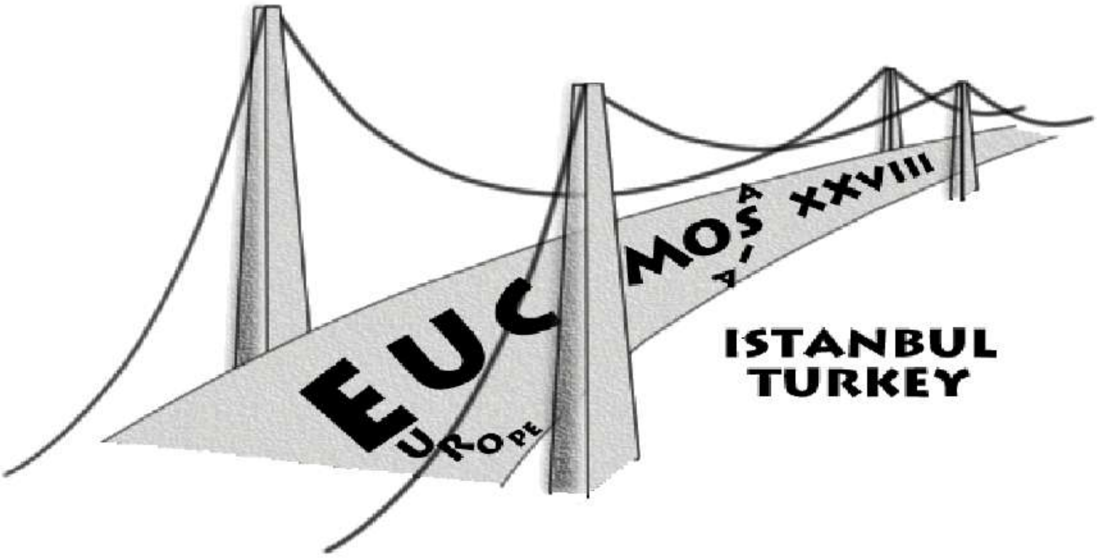


BOOK OF ABSTRACTS

Editors: Sevim Akyüz
Elif Akalın

September 3-8, 2006 İstanbul University, İstanbul, Turkey

XXVIII EUROPEAN CONGRESS ON MOLECULAR SPECTROSCOPY



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İstanbul, Turkey

WELCOME TO EUCMOS XXVIII

On the behalf of the International Steering Committee, the Scientific Program Committee and the Local Organising Committee of EUCMOS-28, we would like to welcome all congress participants to

XXVIII European Congress on Molecular Spectroscopy

The European Congress on Molecular Spectroscopy (EUCMOS) is an important biennial meeting attended by molecular spectroscopists in diverse branches from all over the world. For over 50 years EUCMOS has brought together spectroscopists from Basel in 1951 to Krakow in 2004. For the first time EUCMOS will be held in İstanbul, Turkey. It is our pleasure and pride to host the XXVIII European Congress on Molecular Spectroscopy in İstanbul University. İstanbul is one of the world's famous historical cities. It lies at the junction of the Bosphorus and the Marmara Sea. It contains a wealth of architectural treasures - Topkapı Palace, the Blue Mosque, Saint Sophia, Galata Tower and Sultan Süleyman Mosque - as well many interesting places such as the Grand Bazaar, the Golden Horn and the Roman underground water reservoir.

The congress has been organised by the science faculty of İstanbul University. İstanbul University is one of the oldest universities in the world. It was founded in 1453. The university has campuses on either side of the city of İstanbul, i.e., in both Europe and Asia. The oldest, the Beyazıt Campus, is within the walled city of İstanbul, on the European side. It is surrounded by many buildings and sites which date from the Byzantine and Ottoman Empires. The congress will be held on the Beyazıt Campus.

We hope that you will enjoy the congress, and that the mix of interesting participants will provide you with a truly rewarding intellectual and social experience.

It is both a privilege and a pleasure for me, as chairperson of EUCMOS XXVIII, to extend a warm invitation to you to attend the congress, and I wish you a fruitful, simulating and enjoyable week in İstanbul.

Welcome to İstanbul!

Professor Sevim Akyüz

Chairperson of EUCMOS XXVIII

THE ORGANISING COMMITTEES OF EUCMOS XXVIII GRATEFULLY ACKNOWLEDGE SUPPORT FROM

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The Organising Committees of EUCMOS XXVIII thank very much the lecturers and participants for their valuable contributions to the scientific program.

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Portugal
Romania
Russia
Serbia and Montenegro
Slovakia
Spain
South Africa
Turkey
Ukraine
United Kingdom
United States of America

CONGRESS SCHEDULE

Sunday September 3		
12.00-18.00	**Registration**	
18.00-20.00	**Get-together party**	
Monday September 4		
8.45 - 9.15	Opening Ceremony	
OPENING LECTURES		
9.15 -10.15	**OL1** Laurence D. Barron	
10.15-11.15	**OL2** Henry H. Mantsch	
11.15-11.45	**Coffee break**	
PLENARY LECTURES		
11.45-12.30	**KN1** C. Domingo	
12.30-13.00	**PL1** J. Durig	
13.00-14.30	**LUNCH**	
ORAL PRESENTATIONS		
	Hall A	Hall B
	Session 2	**Session 5**
14.30-14.50	**OA-01** K. Volka	**OB-01** R. Kolos
14.50-15.10	**OA-02** O.F. Nielsen	**OB-02** V.I. Korepanov
15.10-15.30	**OA-03** G. Tosi	**OB-03** L. Krim
15.30-15.50	**OA-04** J. Lojewska	**OB-04** J.G. Phillis
15.50-16.10	**OA-05** E. Bogomolny	**OB-05** A.Loewenschuss
16.10-16.40	**Coffee Break**	
	Hall A	Hall B
	Session 2	**Session 10**
16.40-17.00	**OA-06** J.C. Lopez	**OB-06** O. Dopfer
17.00-17.20	**OA-07** A. Kamnev	**OB-07** E. Kleinpeter
17.20-17.40	**OA-08** J.L. Alonso	**OB-08** M.H. Palmer
17.40-18.00	**OA-09** S. Stavrov	**OB-09** A. Virdi
Tuesday, September 5		
PLENARY LECTURES		
8.30 - 9.15	**KN2** R.J.H. Clark	
9.15 -10.00	**KN3** H.G.M. Edwards	
10.00-10.30	**PL2** T. A. Ford	
10.30-11.00	**PL3** L. Pejov	
11.00-11.30	**Coffee break**	
11.30-12.15	**KN4** S. Sanchez-Cortes	
12.15-12.45	**PL4** B. Vlckova	
12.45-14.45	**LUNCH**	
ORAL PRESENTATIONS		
	Hall A	Hall B
	Sessions 6 and 12	**Session 8**
14.45-15.05	**OA-10** D.K. Breitinger	**OB-10** C. Naudin
15.05-15.25	**OA-11** O. Boyarkin	**OB-11** S. Kirillov
15.25-15.45	**OA-12** N. Westwood	**OB-12** P. Matejka
15.45-16.05	**OA-13** R. Bohn	**OB-13** I. Zawisza

16.05-16.25	**OA-14** G. Zachmann	**OB-14** Y. Chikishev
16.25-16.55	**Coffee Break**	
16.25-18.30	**Poster Presentation-Session 2, 6 and 9**	
Wednesday, September 6		
PLENARY LECTURES		
8.30 - 9.15	**KN5** R. Fausto	
9.15 - 10.00	**KN6** M. Gerhards	
10.00 - 10.30	**Coffee Break**	
10.30 - 11.15	**KN7** G. Zerbi	
11.15 - 11.30	**Packet Lunch**	
11.30 - 19.00	**Conference Trip (Miniaturk Park-Dolmabahce Palace- tea at Emirgan Grove)**	
Thursday, September 7		
PLENARY LECTURES		
8.30 - 9.15	**KN8** H. Ratajczak	
9.15 - 10.00	**KN9** H. Takahashi	
10.00 -10.30	**PL5** B. Minceva-Sukarova	
10.30 -11.00	**PL6** G. Topçu	
11.00 -11.30	**Coffee Break**	
11.30 -12.15	**KN10** O. Dopfer	
12.15 -14.15	**LUNCH**	
ORAL PRESENTATIONS		
	Hall A	Hall B
	Sessions 1, 3 and 7	**Session 4**
14.15 -14.35	**OA-15** H.M.Heise	**OB-15** E.M.S. Maçôas
14.35 -14.55	**OA-16** Z. Jurasekova	**OB-16** E.S Stoyanov
14.55 -15.15	**OA-17** J. Mohn	**OB-17** M. Rozenberg
15.15 -15.45	**Coffee Break**	
15.15 -17.15	**Poster Presentation-Sessions 1, 3, 4, 5, 7, 8, 10**	
17.15 -23.00	**Bosphorus Tour and Conference Dinner**	
Friday, September 8		
PLENARY LECTURES		
8.30 - 9.15	**KN11** P. Carmona	
9.15 -10.00	**KN12** G. Buntinx	
10.00 -10.30	**PL7** J. Laane	
10.30 -11.00	**PL8** S Turrell	
11.00 -11.30	**Coffee Break**	
CLOSING LECTURE		
11.30 -12.00	**CL** S. Music and K. Furic	
12.00 -12.30	**Closing Ceremony**	
12.30 -14.30	**LUNCH**	

LIST OF LECTURES AND POSTERS

PLENARY LECTURES

ORAL CONTRIBUTIONS-A

ORAL CONTRIBUTIONS-B

POSTERS

Session 1 - Analytical Spectroscopy

Session 2 - Biospectroscopy and Spectroscopy of Macromolecules

Session 3 - Environmental Applications of Spectroscopy

Session 4 - Hydrogen Bonding

Session 5 - Low Temperature Spectroscopies- Jet Spectroscopy, Matrix Isolation (including quantum matrices), Liquid Noble Gas Spectroscopy

Session 6 – Molecular Structure

Session 7 – Nanomaterials

Session 8 – Surface Spectroscopies - Infrared, Raman, Fluorescence, Plasmon Surface

Session 9 – Time Resolved Spectroscopies

Session 10–Theoretical spectroscopy/Computational methods in Spectroscopy

PLENARY
LECTURES

RAMAN OPTICAL ACTIVITY: AN INCISIVE PROBE OF MOLECULAR CHIRALITY AND BIOMOLECULAR STRUCTURE

L. D. Barron

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Chirality, meaning right- or left-handedness, pervades much of modern science.[1] Raman optical activity (ROA) is a novel form of polarization-sensitive Raman spectroscopy that probes molecular chirality. It may be measured either through a small difference in the intensity of Raman scattering in right- and left-circularly polarized incident light, or through a small circular component in the scattered light using unpolarized incident light (Fig.1).[1-3]

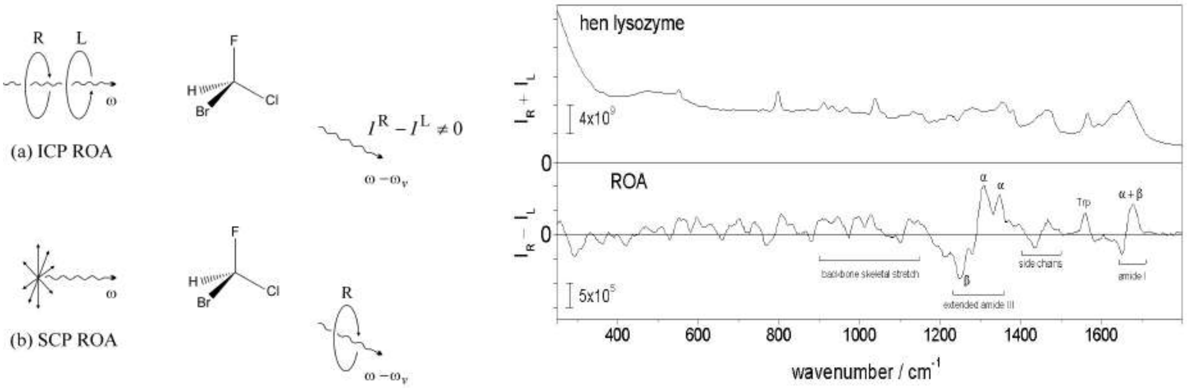

Fig. 1: Incident circular polarization (ICP) and scattered circular polarization (SCP) ROA experiments, together with the SCP ROA (bottom) and Raman (top) spectra of the protein hen lysozyme in aqueous solution.

Whereas UV-visible optical rotation and circular dichroism measure *electronic* optical activity, ROA measures *vibrational* optical activity and so provides much more structural/stereochemical information. It may be applied to a vast range of chiral molecular structures, from small organics to large biopolymers like the protein lysozyme (Fig. 1). For small chiral molecules, comparison of experimental with ab initio computed ROA spectra provides the complete three-dimensional structure (conformation and absolute configuration), a recent example being the determination of conformational populations of sugars in aqueous solution.[4] The plethora of structure-sensitive bands in protein ROA spectra makes the application of multivariate analysis methods ideal for extracting structural information, including the tertiary fold in addition to secondary structure.[5] ROA can even provide information about polypeptide and carbohydrate structure of intact glycoproteins,[5] and protein and nucleic acid structure of intact viruses.[1,3]

This talk will review the theoretical and experimental background to ROA followed by some recent applications to molecular structure and biomolecular science.

[1] L.D. Barron, Molecular Light Scattering and Optical Activity, 2nd ed., Cambridge University Press, Cambridge (2004).
[2] W. Hug in J.M. Chalmers and P.R. Griffiths (Eds.), Handbook of Vibrational Spectroscopy, Vol. 1, Wiley, Chichester 2002, p. 745.
[3] L.D. Barron, L. Hecht, I.H. McColl, E.W. Blanch, Mol. Phys. 102 (2004) 731.
[4] N.A. Macleod, C. Johannessen, L. Hecht, L.D. Barron, J.P. Simons, Int. J. Mass Spectrom. doi:10.1016/j.ijms.2006.01.031.
[5] F. Zhu, N.W. Isaacs, L. Hecht, G.E. Tranter, L.D. Barron, Chirality 18 (2006) 103.

MOLECULAR SPECTROSCOPY AFTER GERHARD HERZBERG

Henry H. Mantsch

National Research Council of Canada
Science Counsellor at the Canadian Embassy in Germany,
Leipziger Platz 17, 10117 Berlin, Germany (at present)

This talk is a tribute to the grandmaster of Molecular Spectroscopy, Gerhard Herzberg, who was cozily know to his friends and colleagues only as GH. His books, published half a century ago, have remained the “Bible” of Molecular Spectroscopy even today. When GH received the Nobel Prize for Molecular Spectroscopy in 1971, he was most surprised to receive it in Chemistry and not in Physics. At heart GH always remained a “physicist”, yet he understood that Molecular Spectroscopy is not a prerogative of physics and that it also serves other disciplines like chemistry, the life sciences and even the arts. In fact, when at the age of 90 he visited our lab at the Institute for Biodiagnostics in Winnipeg, GH marveled at how far we had taken “his” Molecular Spectroscopy.

To all of us who had the privilege to work with GH at the National Research Council in Ottawa, he was not only a great scientist, but also a true row model of a human being. In my talk I hope to reach many young people who are at the beginning of their career in science. Through the example of Gerhard Herzberg I will demonstrate to them the constructive influence of such a mentor. Besides, today Molecular Spectroscopy has penetrated all aspects of our daily life and thus it constitutes a first-class example of interdisciplinary research.

RAMAN SPECTROSCOPY FOR CHARACTERIZATION OF CARBON NANOTUBES AND RELATED COMPOSITES

C. Domingo

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Carbon nanotubes (CNTs) are very important systems both from fundamental research as well as for their potential applications in different fields[1]. In particular, these singular one-dimensional (1D) systems have exceptional mechanical, thermal and electrical properties which make them excellent candidates for being included in composites to improve the characteristics of the base material[2]. Additionally, CNTs (especially Single-wall SWNTs) show very interesting optical properties largely due to the 1D confinement of their electronic and phonon (vibrational) states, resulting in the so-called van Hove singularities (vHSs) in the nanotube density of states (DOS).

Among all the physical methods employed for characterizing CNTs[3], Micro-Raman spectroscopy has become a standard tool as it is a non-destructive, preparationless technique which provides first and second order Raman bands from where precise information about sample purity, NTs structure (diameter distribution, chirality and aggregation state) and electronic (**ME**tallic/**S**emi**C**onducting) character can be extracted[4]. Moreover, as the Raman effect in CNTs is a resonant phenomena, the corresponding spectra are very much enhanced, thus even single isolated nanotubes can be studied.

In this Lecture, the physical processes giving rise to the characteristic Raman bands of the **S**ingle- **D**ouble- and **M**ultiwalled CNTs, will be briefly described. Special attention draw: *I)* the first order low-frequency *RBM* (*R*adial *B*reathing *M*odes), crucial for determining the structural parameters of SWNts (and DWNTs) mentioned above; *II)* the *D* (*D*isorder induced) and *G* (Tangential mode) bands and their intensities relation, for concluding about CNTs purity and ME/SC character; and *III)* the second order *G'*~ 2D Raman band.

Some outstanding results, including non routine Raman imaging and Near-Field Raman on isolated SWNTs, showing the state-of-the-art, will be reviewed. Furthermore, some changes observed in the Raman bands when the CNTs are embedded/dispersed in polymer-composites will also be illustrated[5].

(Resonant) Raman spectroscopy and CNTs are strongly linked, as CNTs constitute an incomparable system for the study of Raman spectra of one-dimensional systems and Raman spectroscopy has provided a remarkably powerful tool for the characterization of SWNTs.

[1] M.S. Dresselhaus, G. Dresselhaus and Ph. Avouris, Springer Series in Topics in Applied Physics, Vol. 80, Springer, Berlin (2001)
[2] E.T. Thostenson, Z. Renb and T.-W. Choua, Composites Sci. Tech. 61 (2001) 1899.
[3] T. Belin and F. Epron, Mat. Sci. Eng. B 119 (2005) 105.
[4] M.S. Dresselhaus, G. Dresselhaus, R. Saito and A. Jorio, Phys. Rep. 409 (2005) 47.
[5] M.C. García-Gutiérrez, A. Nogales, D.R. Rueda, C. Domingo, J.V. García-Ramos, G. Broza, Z. Roslaniec, K. Schulte, R.J. Davies and T.A. Ezquerra, Polymer 47 (2006) 341.

CONFORMATIONAL STABILITY DETERMINATIONS FROM TEMPERATURE-DEPENDENT FT-IR SPECTRA OF NOBLE GAS SOLUTIONS OF SEVERAL 3- AND 4-MEMBERED RINGS

James R. Durig

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Variable temperature (–55 to –145°C) studies of the infrared spectra (3500 to 100 cm^{-1}) of cyclopropylmethyl isocyanate, c-$C_3H_5CH_2NCO$ have been carried out. By analyzing six conformer pairs in xenon solutions, an enthalpy difference of 193±19 cm^{-1} (2.31±0.23 kJ/mol) was obtained with the *gauche*-*cis* rotamer the more stable form where the first designation indicates the orientation of the CNCO group with respect to the three-membered ring and the second designation indicates the relative orientation of the NCO group with respect to the bridging C–C bond. Only this form was present in polycrystalline solid. The abundance of the *cis-trans* conformer present at ambient temperature is 16±1%. The potential function governing the conformational interchange has been obtained from B3LYP/6-31G(d) calculations and the two-dimensional potential has been obtained. From MP2 *ab initio* calculations utilizing various basis sets with diffuse functions, the *gauche-cis* conformer is predicted to be more stable by 223 to 269 cm^{-1}, which is consistent with the experimental results. However, without diffuse functions the predicted conformational energy differences are much smaller (77 to 166 cm^{-1}). Similar diffuse function dependency affects density functional theory calculations by the B3LYP method to a lesser extent.

These studies have been compared to similar studies[1] of cyclopropylmethyl isothiocyanate, c-$C_3H_5CH_2NCS$ where the enthalpy difference was found to be 228±23 cm^{-1} with a slightly smaller amount of *cis-trans* conformer present at ambient temperature of 14±2%. These results are in marked contrast to what has been found[2] for the corresponding cyanide c-$C_3H_5CH_2CN$ where the abundance of the *cis* conformer was found to be 25% and the replacement of the cyanide by the ethynyl group[3] was found to result in the *cis* conformer being more stable than the *gauche* form. The reasons for these significant differences will be presented. Some similar studies have recently been undertaken for the corresponding 4-membered rings with a variety of substituents. Some of these studies are in progress with near completion expected in the next few weeks. As time permits, results for these molecules will be provided.

[1] C. Zheng, G. A. Guirgis, W. A. Herebout, B. J. van der Veken, C. J. Wurrey, and J. R. Durig, J. Phys. Chem., submitted.
[2] C. J. Wurrey, S. Shen, X. Zhu, H. Zhen, J. R. Durig, J. Mol. Struct. 449 (1998) 203.
[3] G. A. Guirgis, C. J. Wurrey, Z. Yu, X. Zhu, J. R. Durig., J. Phys. Chem. A 103 (1999) 1509.

THE SCIENTIFIC INVESTIGATION OF ARTWORK AND ARCHAEOLOGICAL ITEMS: RAMAN MICROSCOPY, PIGMENTS AND THE ATTRIBUTION OF ARTWORK

Robin J. H. Clark

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The identification of pigments on works of art and archaeological materials is fundamental to furthering our understanding of an object's history or an artist's techniques, to solving certain conservation and restoration problems, and to providing evidence for dating and attribution issues. Raman microscopy has emerged as probably the single most effective technique for these purposes as it is non-destructive, non-invasive and can be applied in situ. It has the further advantages of high reproducibility, high spatial resolution (<1 micrometre) and high spectral resolution <1 cm^{-1}. Moreover the introduction of portable instruments means that it is now possible, albeit with some loss of performance and convenience, to move the instrument to the object rather than the object to the instrument [1].

The lecture will concentrate upon several high profile studies carried out recently. These studies include the critically important establishment of the palettes of the following works of art:

- Highly valuable Anglo-Saxon manuscripts such as the Lindisfarne Gospels c. 715 AD.
- An Arabic Treatise containing early maps end celestial diagrams c. 1200 AD [2].
- Eight Gutenberg Bibles c. 1455 AD [3].
- A painting recently reattributed to Vermeer, partly on the basis of Raman-based pigment studies, and sold at auction in 2004 for £16.2 million [4].

Other studies have led to or contributed to the realisation that a significant proportion of so-called works of art are forgeries, for instance:

- Egyptian papyri, supposedly dating from 1250 BC, but shown to be illuminated with several 20th century pigments including copper phthalocyanine blue.
- Postage stamp forgeries, Mauritius 1847, Hawaii 1859 [5].

The need to check scientifically by Raman microscopy and other techniques as to whether or not works of art contain any pigments or other features which indicate lack of authenticity, particularly those offered for sale at auction houses, cannot be overstressed.

Further Raman and other scientific studies have opened up the field of archaeology [6], for example the analysis of American ceramics of the Puebloan period from archaeological sites [7] and of metal inclusion or corrosion products etc. [8]. Notable is the study of an 1837 Russian three rouble coin of impure platinum metal which led to the identification of inclusions within the coin of magnetite and iron-deficient magnetite (thereby accounting for the magnetism) and of haematite [8]. The intense Raman band of magnetite at 668 cm^{-1} is sensitive to the oxidation state of the iron. The spectroscopic study of artwork and archaeological items is expected to develop rapidly in the future as the appropriate techniques become better appreciated.

[1] R.J.H. Clark in Scientific Examination of Art, National Academies Press, Washington D.C., 2005, pp. 162-185.
[2] T.D. Chaplin, R.J.H. Clark, A. McKay, S. Pugh, J. Raman Spectrosc. 37 (2006) in press.
[3] T.D. Chaplin, R.J.H. Clark, D. Jacobs, K. Jensen, G.D. Smith, Anal. Chem. 77 (2005) 3611-3622.
[4] L. Burgio, R.J.H. Clark, L. Sheldon, G.D. Smith, Anal. Chem. 77 (2005) 1261-1267.
[5] T.D. Chaplin, A. Jurado-Lopez, R.J.H. Clark, D.R. Beech, J. Raman Spectrosc. 35 (2004) 600-604.
[6] G.D. Smith, R.J.H. Clark, J. Archaeolog. Sci. 31 (2004) 1137-1160.
[7] J. van der Weerd, G.D. Smith, S. Firth, R.J.H. Clark, J. Archaeolog. Sci. 31 (2004) 1429-1437.
[8] J. van der Weerd, T. Rehren, S. Firth, R.J.H. Clark, Materials Characteriz. 53 (2004) 63-70.

RAMAN SPECTROSCOPY OF EXTREMOPHILES FROM HOT AND COLD DESERTS : AN ASTROBIOLOGICAL JOURNEY FROM MARS OASIS, ANTARCTICA , TO PLANET MARS

H.G.M. Edwards

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The survival strategies of extremophilic organisms in terrestrially stressed locations and habitats are critically dependent upon the production of protective chemicals in response to desiccation , low wavelength radiation insolation , temperature and the presence of toxins[1]. The adaptation of life to the prevailing conditions involves the control of the substratal geology ; the interaction between the rock and the organisms is critical and the biological modification of the geological matrix plays a significant role in the overall survival strategy[2,3,4] . The identification of the these biological and biogeological chemical molecular signatures in the geological record is ,therefore, a crucial stage in the recognition of the presence of extinct or extant life in terrestrial and extraterrestrial scenarios.

Raman spectroscopic techniques have been identified as valuable instrumentation for the detection of life extraterrestrially because of the use of non-invasive laser-based excitation of organic and inorganic molecules and molecular ions with high discrimination characteristics ; the interactions effected between biological organisms and their environments are detectable through the molecular entities produced at interfaces , for which the vibrational spectroscopic band signatures are unique. Combination of spectroscopic and microscopic data acquisition from Raman microscopes gives an additional information category which is essential for the desription of heterogeneous specimens ; for geological specimens of significant transparency , the use of confocal microscopy for the spectroscopic analysis of subsurface inclusions in crystals is a significant development for the analytical detection of halotrophs[5] . A very important attribute of Raman spectroscopy is the acquisition of experimental data using remote optical flexible probes without the need for chemical or mechanical pre-treatment of the specimen ; this has been a major factor in the proposal for the adoption of Raman instrumentation on robotic landers and rovers –and this is now being advocated for the ExoMars programme [6].

In this paper , the merits of using Raman spectroscopy for the recognition of key molecular biosignatures from several terrestrial extremophile specimens will be illustrated and some recommendations made for the technical requirements of a miniaturised system and its evaluation for Martian exploration . The data and specimens used in this presentation have been acquired from Arctic and Antarctic cold deserts , a meteorite crater , and from a hot desert saltpan evaporite locations from which it will be possible to assess the advantages and current limitations of Raman spectroscopic techniques for the detection of extraterrestrial extremophilic life signatures.

References

[1] C.S. Cockell and J.R. Knowland , Biol.Revs. 74 (1999) 311.
[2] D.D. Wynn-Williams and H.G.M. Edwards, Planetary Space Sci. 48 (2000) 1065.
[3] D.D.Wynn-Williams and H.G.M. Edwards, Icarus 144 (2000) 486.
[4] S.E. Jorge Villar , H.G.M. Edwards and C.S. Cockell , Analyst 130 (2005) 156.
[5] H.G.M. Edwards , S.E. Jorge Villar , J. Parnell , C.S. Cockell and P.Lee, Analyst 130 (2005)917.
[6] S.E.Jorge Villar and H.G.M. Edwards , Analytical & Bioanalytical Chemistry 217(2006)100.

AB INITIO STUDIES OF THE PROPERTIES OF THE MOLECULAR COMPLEXES OF BORON TRIFLUORIDE WITH METHANOL AND METHANETHIOL. COMPARISON WITH SOME RELATED OXYGEN AND SULPHUR BASES

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The structures, interaction energies and vibrational spectra of the electron donor-acceptor complexes of boron trifluoride with methanol and methanethiol have been determined by means of *ab initio* calculations, at the level of second order Møller-Plesset perturbation theory, using the 6-311++G(d,p) basis set. The shifts of the wavenumbers of the intramolecular modes of the Lewis acid fragment have been calculated, for comparison with those measured in cryogenic matrices, when such results become available.

The computed properties of these complexes have been compared with those of the analogous adducts of boron trifluoride with water, hydrogen sulphide, dimethyl ether and dimethyl sulphide. Some relationships have been observed between the calculated intermolecular geometries, interaction energies and vibrational wavenumber shifts of the complexes and some physical properties of the Lewis bases, including their gas phase basicities, ionization energies and mean polarizabilities.

SOME ASPECTS OF NON-COVALENT BONDING IN VAN DER WAALS AND HYDROGEN-BONDED MOLECULAR CLUSTERS AND THE CORRESPONDING SPECTROSCOPIC MANIFESTATIONS - A THEORETICAL INSIGHT

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Studies of intermolecular interactions leading to formation of non-covalently bonded molecular clusters are of certain relevance to contemporary chemical physics. The main reason for this is that such systems in a sense bridge the gap between the isolated molecules and the condensed phases they form. On the other hand, it appeared that besides the weak character of these interactions, they may play the central role in molecular recognition and other phenomena relevant to biochemical sciences. To understand these phenomena of weak bonding at a fundamental level, combining the most sophisticated experimental and theoretical approaches is required. In this lecture, several types of intermolecular interactions studied by the author are reviewed, such as blue-shifting hydrogen bonding[1], dihydrogen bonding[2], π-type hydrogen bonding[3-5], purely electrostatic bonding etc. To illustrate the mentioned interactions, the following systems are considered: CF_3H-H_2O, CF_3H-HCOH, CF_3H-CH_3CN, CF_3H-$(CH_2)_2O$, CH_3OH-C_6H_5F, indole dimer, pyrrole dimer, indole-pyrrole, phenol-CO, phenol-C_2H_2, $(\text{phenol})_2^+$, phenol-benzene cation, phenol-boranetrimethylammine (phenol-BTMA), 2-pyridone-BTMA, C_6F_6-CO. Besides the structural aspects concerning the minima located on various potential energy hypersurfaces of the mentioned species, special attention is paid to the spectroscopic manifestations of these interactions. It is demonstrated that sufficiently high level of theory is required to reproduce the experimentally measured vibrational frequency shifts of particular modes induced by the interaction, and that the harmonic approximation may only lead to a fortuitous agreement with the experiment, due to cancellation of errors. It is therefore necessary to calculate the anharmonic vibrational frequency shifts for these purposes. On the basis of this approach, however, in some cases even reinterpretation of experimental observations may be suggested. Performing a more in-depth analysis of the anharmonic vibrational potentials of the relevant intramolecular modes, including partitioning of the interaction energy for sampled points on the potential energy curve, allows in most cases a profound insight into the physics behind the vibrational frequency shifts to be acquired. By combination of electrostatics reasoning, based on multipole expansion techniques, with the contemporary quantum chemical methods, existence of rather peculiar (at least from a classical “chemical” viewpoint) molecular clusters may be understood.

[1] Lj. Pejov, K. Hermansson, J. Chem. Phys. 119 (2003) 313.
[2] Lj. Pejov, Gj. Ivanovski, Chem. Phys. Lett. 399 (2004) 247.
[3] Lj. Pejov, Chem. Phys. Lett. 358 (2002) 368.
[4] Lj. Pejov, Chem. Phys. Lett. 339 (2001) 269.
[5] Lj. Pejov, Int. J. Quantum Chem. 92 (2003) 516.

SURFACE-ENHANCED SPECTROSCOPY ON FUNCTIONALIZED METAL NANOSTRUCTURES

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Surface-enhanced optical spectroscopies (SEOS) have become very useful analytical methods for chemical and biochemical detection and analysis in the last times. These techniques are based on the giant electromagnetic enhancement observed in the vicinity of metal nanoparticles, due to the plasmon resonance. Among these techniques, SERS (Surface-enhanced Raman spectroscopy) has been largely employed and studied due to the larger enhancement of Raman scattering on metal nanostructures in comparison to IR and fluorescence. However, in the last years an increase in the application of the SEIR (Surface-enhanced infrared) and SEF (Surface-enhanced fluorescence) also occurred.

SEOS techniques require the presence of metal nanoparticles. Thus, their application have depended on the development of the nanotechnology associated to the preparation of nanostructured metal particles and aggregates. In this work we have carried out a comparative study of metal nanoparticles prepared by different methods concerning their application in SEOS. Apart from the metal nature and morphology, other important issues to take into account in these surface techniques are the molecular adsorption and the physico-chemical properties of the interfaces.

SERS, in particular, requires the close proximity of the scattering molecule to the surface in order to undergo an enhancement of its vibrational spectrum. We have studied a large list of adsorbates with different structures, concluding that there are three main adsorbate groups regarding the adsorption strength on a metal surface: non active molecules, which do not adsorb wee on the surface, molecules adsorbed onto the surface (mainly those molecules chemisorbed undergo a higher enhancement), and molecules which are so strongly attached that undergo a catalytic modification induced by the metal. The major part of SERS studies has been carried out on the second group. However many hazardous pollutants such as the polycyclic aromatic hydrocarbons (PAHs) and pesticides represents an important group of compounds which cannot approach the metal surface, and, consequently, can not be detected by neither SERS nor SEIRA.

The affinity of these pollutants can be increased by a proper functionalization of the metal surface with host molecules. The formation of self-assembled monolayers of bifunctional molecular adsorbates is a good procedure to enhance the spectroscopic sensitivity and the molecular selectivity of metal nanostructures. These features are, indeed, very important in the design of chemical sensors based on SEOS.

In this work we show the results obtained by surface functionalisation of Ag nanoparticles with different host molecules: calixarenes, cationic aromatic hosts, carbon nanotubes, humic acids. We have seen that the sensitivity and selectivity of the metal-host functionalised systems can be modulated by modifying the chemical groups existing in the lower and upper rims of the host.

In conclusion, the results derived from our study are of great interest for the fabrication of metal-host systems with a high sensitivity and selectivity in the detection of pollutants, and whose specificity can be easily modulated by changing the chemical groups. The information derived from this study can be applied in the design of advanced chemical sensor based on surface-enhanced optical techniques.

SINGLE MOLECULE SERS: PERSPECTIVES OF ANALYTICAL APPLICATIONS

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Recent challenging development in SERS and SERRS spectroscopy is associated with the discovery of its single molecule sensitivity [1]. Achievement of single molecule level of SERS (Surface-Enhanced Resonance Raman Scattering) and/or SERRS (Surface-Enhanced Resonance Raman Scattering) spectral detection is conditioned by localization of detected molecules into strong nanoscale-localized optical fields (dubbed hot spots [2]). Recent theoretical treatments predict SERS enhancement factors as high as 1×10^{15} for chromophoric molecules (in particular rhodamine 6G) located in the hot spot amidst two Ag nanoparticles of a suitable size [3]. Several pathways to experimental realization of such optimal nanoparticle geometries have been explored and single molecule SERS and/or SERRS spectra were reported [4]. Owing to a combination of single molecule sensitivity with the fingerprint selectivity inherent to methods of vibrational spectroscopy, single molecule SERS spectroscopy offers unprecedented possibilities of analytical applications. On the other hand, one of the most challenging questions is whether the perspectives of single molecule detection are open to all kinds of molecular species as the prospective analytes. A possible limitation in a widespread use of single molecule SERS could stem from surface-enhanced and/or surface-induced photochemical processes which may obstruct a reliable analyte detection on a single molecule level. In addition to that, several important questions related to single molecule SERS experiments remain to be answered. For example, the origin of temporal fluctuations of SERS signal (called blinking and frequently observed in single molecule SERS) has not yet been fully explained.

The highlights and possible limitations of single molecule SERS will be discussed on the basis of the results recently obtained in our laboratories in comparison to those recently published by other research groups. We will compare several strategies by which dimers and small aggregates of silver (Ag) nanoparticles are assembled and by which molecules are localized into hot spots created by an external laser excitation in the interstices between the nanoparticles. One of our recently elaborated approaches is based on an idea that molecules linking together two or more Ag nanoparticles will be automatically located in hot spots. Dimers and small aggregates of Ag nanoparticles linked together by several types of bifunctional linkers (e.g. 4,4'-diaminoazobenzene) have been assembled on chemically functionalized supporting surfaces suitable for combined TEM-SERS micro-Raman studies. Temporally fluctuating SERS signals of linker molecules measured from a selected single dimer or small aggregate are interpreted in terms of molecular dynamics of a single or a very few molecules, which, in turn, is specific for each of the linkers. Furthermore, we demonstrate that although some of the linker molecules undergo a photochemical decomposition, a rapid acquisition of SERS spectra as a function of time in 1s intervals provides us with one or more spectra in which the characteristic spectral bands of the unperturbed linkers can be identified.

Finally, several prospective pathways towards decreasing the risks of thermal and/or photochemical decomposition of molecules localized in strong optical fields in the course of single molecule SERS experiment will be outlined.

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[1] K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, and M. S. Feld, Phys. Rev. Lett. 78 (1997) 1667.
[2] M. Moskovits, L. L. Tay, J. Yang, and T. Haslett, Topics Appl. Phys. 82 (2002) 215.
[3] Johansson, H. Xu, and M. Kall, M. Phys. Rev. B 72 (2005) art. No. –035427.
[4] For example: A. M. Michaels, M. Nirmal, and L. E. Brus, J. Am. Chem. Soc. 121 (1999) 9932. H. Xu, E.J. Bjerneld, M. Kall and L. Borjenson, Phys. Rev.Lett. 83 (1999) 4357. M. Sladkova, B. Vlckova, P. Mojzes, M. Slouf, C. Naudin, and G. Le Bourdon, *Faraday Discuss*. 107 (2006), in press.

PHOTOCHEMISTRY OF MATRIX-ISOLATED HETEROCYCLES: SELECTED EXAMPLES

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When used together with conventional spectroscopic methods (*e.g.*, FTIR spectroscopy), matrix isolation constitutes a very powerful technique to investigate the photochemistry of single molecules. In matrix-isolation spectroscopy the sample to be studied is prepared by deposition under high vacuum conditions of the necessary amounts of the target substance and support gas (usually an inert gas such as argon) on a suitable optical substrate cooled at a temperature of a few degrees Kelvin. Under these conditions the spectral resolution strongly increases due to the band narrowing effects associated with both the extreme low work temperature and matrix rigidity (molecular diffusion as well as rotational and vibrational hot transitions are suppressed). Once a matrix of a given substance has been prepared, selective *in situ* irradiation can be undertaken in order to promote diverse types of photochemical processes such as conformational isomerization [1,2], tautomerization [3] or fragmentation (including photo-degradation) [4].

In this talk, a brief description of the matrix isolation method, highlighting its advantages over other sampling methods for the investigation of molecular structure and photochemical reactivity will be given, followed by the presentation of a series of illustrative examples of application of the method to the study of some selected heterocyclic compounds. These include photochemically induced conformational isomerizations and tautomerizations, ring-opening reactions and photofragmentation processes.

References

[1] IR-Induced Photoisomerization of Glycolic Acid in Low Temperature Matrices, I. Reva, S. Jarmelo, L. Lapinski and R. Fausto, *J.Phys.Chem. A*, 108 (2004) 6982.
[2] Rotational Isomerism in Acetic Acid: The First Experimental Observation of the High-Energy Conformer, E.M.S. Maçôas, L. Kriachtchev, M. Pettersson, R. Fausto and M. Räsänen, *J.Amer.Chem.Soc.*, 125 (2003) 16188.
[3] Photochemical □-Cleavage in Pyran-2-Thione: Generation of Aldehyde-Thioketene and Thioaldehyde-Ketene Photoproducts, S. Breda, I.D. Reva, L. Lapinski and R. Fausto, *Chem.Phys.Chem.*, 6 (2005) 602.
[4] Conformational Isomerism and Photodecomposition of Carboxylic Compounds Studied by Matrix Isolation Infrared Spectroscopy, R. Fausto, in “Low Temperature Molecular Spectroscopy”, Ed. R. Fausto, NATO-ASI Series C, Kluwer, Amsterdam, 483 (1996) 125.

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PEPTIDES AND PEPTIDE AGGREGATES IN THE GAS PHASE: WHAT DO WE LEARN ABOUT SECONDARY STRUCTURES FROM ISOMER SELECTIVE IR/UV SPECTROSCOPY

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Secondary structures play an important role to explain the function of proteins. There are different important binding motifs like β-sheets, α-helices, β-turns or γ-turns. These structures are stabilized by intra- or intermolecular hydrogen-bonds. In order to figure out the influence of an individual H-bond on the structure and to learn more about the driving forces to form secondary structures, isolated di- up to pentapeptides and peptide aggregates are analyzed by mass-, isomer-, and state selective combined IR/UV techniques, i.e. for each isomer of a given peptide or peptide aggregate an individual IR-spectrum can be recorded in a molecular beam experiment (IR/R2PI). The different isomers are selected by ionization after resonant UV excitation which differ for each isomer (R2PI). This process is very efficient for peptides containing an aromatic amino acid (phe, tyr, and trp). Due to our development of a new narrow band-width and high power IR laser we are able to obtain IR/R2PI-spectra in the complete region from 1000 – 4000 cm^{-1} for each selected isomer. In combination with force field and ab initio calculations the IR spectra yield the structural binding motifs of all isomers as well as the strength of the individual H-bonds. By adding water gradually the influence of a microsolvation shell on the secondary structure can be investigated. Not only water but also templates can form aggregates with peptides. The chosen templates are important to inhibit pathogenic β-sheets, especially the aggregation of templates to a peptide sequence responsible for Alzheimer disease will be discussed.

Π-Π DELOCALIZATION: FROM VIBRATIONAL SPECTROSCOPY TO DEVICE DEVELOPMENT

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It is known fact that when in a molecule pi electron delocalization takes place over long distances (polyconjugation) the vibrational spectra are strongly affected (both frequencies and intensities) and produce spectra which even escape the traditional group frequency correlations used in chemical diagnosis. Raman spectra are the source of interesting data on the electronic properties of polyconjugated molecules in their “pristine” (i.e. undoped) state while the infrared spectra are extremely useful when the same systems are “doped” in a state which is electrically conducting. We have contributed to the understanding of these peculiar vibrational spectra by proposing the so called ECC (Effective Conjugation Coordinate) theory which tries to account for the contribution to the Raman scattering /IR absorption by the delocalized pi electrons.

The peculiar physics which makes these molecules relevant for materials science and technology includes consideration of their peculiar optical properties. We focus in this talk on the reversible optical properties of a class of photochromic organic materials (oligomers and polymers) originally synthesized and characterized in our group. These studies have paved the way to the development of optical devices offered to the astrophysical community.

In this talk we will show the relevant contribution by Raman spectroscopy, through ECC theory (and also quantum chemical calculations), to the understanding of the electronic configurations of the two reversibly interconverting species which are the basis of the photochromism of these materials. From these studies interesting technologically relevant innovative developments can be derived. First we consider innovations in optical imaging based on our photochromic materials. The writing and erasing of the information is achieved with UV and visible radiations respectively while the reading (with no erasing!) is achieved in the IR region using specific absorption bands. Devices have been obtained and in particular focal plane masks for optical telescopes have been produced and actually tested on a telescope; to our knowledge this goal has never been reached before.

The second application being developed, based on the photochromism monitored by Raman spectra, is the writing and erasing of optically written erasable optical gratings. The efficiency of the grating could be maximized only by maximizing the change of the refractive index of the two photoactivated interconverting molecules. Also with the help of spectroscopy and quantum chemistry suitable photochromic molecules have been synthesized, characterized and used for the fabrication of such optical gratings. The optical fatigue turns out to be extremely.

In this talk we will present: i) the theoretical aspects of the vibrational spectra of polyconjugated molecules, ii) the Raman spectra of several of the photochromic molecules used and iii) the optical devices developed and successfully tested.

VIBRATIONAL SPECTROSCOPY OF HYDROGEN-BONDED SYSTEMS: THEORY AND EXPERIMENT

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The profiles of hydrogen stretching infrared bands of hydrogen-bonded systems in gas phase, liquids and solids will be presented and discussed on the basis of recently developed theories (1-3). Infrared spectra of hydrogen-bonded systems in the range of the ν(XH) stretching vibrations are very complicated.The bands are broad with many sub-maxima.It will be demonstrated that the main mechanisms responsible for the genaration of complicated profiles of hydrogen stretching bands are the anharmonic coupling between the high-frequency stretching vibration, ν(XH), and low-frequency vibrations of the X-H...Y bridge in the gas phase and solutions, or with low-frequency lattice phonons in solids.

In addition one has to take into account Fermi resonances between states involving the ν(XH) stretching and overtones or combinations of some internal modes and Davydov resonances in solids.

The application of the Car-Parrinello Molecular Dynamics Simulation Method to study the broad protonic infrared absorption in a short intramolecular hydrogen bond will be presented too.

References:
1.S.Bratos, J-Cl.Leicknam, G.Gallot and H.Ratajczak in *"Ultrafast Hydrogen Bonding Dynamics and Proton Transfer Processes in the Condensed Phase*, edited by T.Elsaesser and H.J.Bakker, Kluwer Academic Publishers, 2002 p.5
2.H.Ratajczak and A.M.Yaremko, J.Mol.Structure (THEOCHEM), 500 (2000) 413
3.A.M.Yaremko, H.Ratajczak, J.Baran, A.J.Barnes, E.V.Mozdor and B.Silvi, Chem.Phys.,306(2004)57

TIME-RESOLVED SPECTROSCOPY OF ELECTRONIC EXCITED STATES AND PHOTO-GENERATED TRANSIENT SPECIES

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In order to understand the mechanism of photochemical reactions, it is of utmost importance to clarify the structure and dynamics of electronic excited states and photo-generated short-lived transient species which play vital roles in the physical and chemical processes involved. In this study picosecond and nanosecond time-resolved resonance Raman and UV-visible absorption spectroscopies and nanosecond time-resolved IR spectroscopy were utilized with the purpose of obtaining information on the structure and dynamics of electronic excited states and photo-generated transient species of a few compounds having photochemical interest.

Structural changes in the electronic excited states: (1) The ground state structure of benzil is known to be in a skewed configuration about the central C-C bond both in the crystalline state and in solutions. Nanosecond time-resolved IR spectra and picosecond and nanosecond time-resolved Raman and absorption spectra of the S_1 and T_1 states of benzil and its isotopically substituted analogues indicated that in the S_1 state, benzil changed its structure from a skewed configuration about the C-C bond of the Franck-Condon state to the trans-planar configuration of the relaxed state. The structure of the T_1 state is also in the trans-planar configuration. (2) 5-dibenz[b,f]azepine exhibited extremely rapid changes of the absorption spectra in the picosecond time domain (less than 20 ps in methanol). The spectral changes can be attributed to conformational changes in the singlet manifold of the electronic excited states from the bent configuration of the Franck-Condon state to the planar configuration of the relaxed S_1 state.

Vibrational cooling in the T_1 state: It was found that 5H-dibenzo[a,d]cyclohepten-5-one exhibited vibrational cooling in the T_1 state with the decay time of 16.2 ps. This is the first observation of the vibrational cooling in the T_1 state. The T_1 state of this compound has a π–π^* character, while the S_1 state of this compound has an n–π^* character. The observation of the vibrational cooling in the T_1 state can be attributed to the extremely rapid $S_1(n-\pi^*) \rightarrow T_1(\pi-\pi^*)$ intersystem crossing (allowed transition according to the El-Sayed rule).

Competition between photo-ionization and photo-deprotonation: Nanosecond time-resolved absorption and Raman spectra of carbazole in acetonitrile and its isotopically substituted analogues revealed that the photo-protonation and photo-ionization of carbazole occurred competitively through different biphotonic processes on excitation with 308 nm light: the photo-ionization to generate cation radical occurred in the singlet manifold of the electronic excited state, while the photo-deprotonation to produce carbazyl radical by the cleavage of the N-H bond proceeded through the triplet manifold.

Photo-induced intramolecular proton transfer: *Ortho*-nitrobenzyl compounds are known to exhibit photochromism in solution through reversible proton transfer from the methylene group to proton-accepting sites in the molecule. In the case of 4-(2'-nitrobenzyl)pyridine, an absorption band was observed at 423 nm with a shoulder at 392 nm at 100 ns after UV irradiation. At 10 μs these bands disappeared while new bands appeared at 379 and 544 nm. The band at 423 nm is assignable to the aci-nitro acid generated through direct transfer of a methylene proton to the *ortho*-nitro group. The shoulder at 390 nm is attributed to the aci-nitro anion produced in the dissociation of the aci-nitro acid. The bands at 379 and 544 nm are assigned to the N-H quinoid isomer generated through an indirect transfer of a methylene proton to the 4-pyridyl group.

HOFMANN TYPE CLATHRATES – SPECTROSCOPIC STUDIES

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Hofmann type clathrates are one of the most thoroughly studied families of inclusion compounds. Their general formula is $M(NH_3)_2M'(CN)_4{\cdot}2G$, where $M \in \{Ni, Co, Zn, Fe, Mn, Cd\}$, $M' \in \{Ni, Pd, Pt\}$, while G is benzene, thiophene aniline, pyrrole, dioxane or byphenyl. These inclusion compounds have attracted significant attention because of their structural peculiarities, such as orientation of particular guest molecules, nature of the host-guest interactions, differences in the enclathration energies, but also because of their practical application. The cage structure and the inclusion character of these compounds can be used for storage, exchange, separation and scavenger for organic substances in polluted aqueous or organic medium.

This work comprises the results from the spectroscopic investigation of the series of Hofmann type clathrates highlighting the most important segments of our experimental and theoretical work on these compounds. Three main points of these spectroscopic studies will be discussed: *(i)* spectroscopic evidence of the host-guest interaction *(ii)* assignment of the mid-infrared and Raman bands due to the host lattice and the gust molecule and to the *(iii)* assignment of the far-infrared and Raman bands in the low frequency region.

(i) The host-guest interactions were studied through (a) the changes in the bands due to the CH out-of-plane bending modes in the guest (benzene) molecule and through (b) the changes in the symmetric bending $\delta_s(NH_3)$ and/or rocking, $\gamma(NH_3)$ modes due to the host lattice. The magnitude of the observed splitting of the ν_{19} CH out-of-plane mode due to the guest (benzene) molecule at LNT served as a measure of the host-guest interaction and was correlated with the volume of the tetragonal unit cell of the Hofmann type clathrates and with the effective ionic radii of octahedrally coordinated metal M, and square-planar coordinated metal, M'. This interaction was also recognized with the quantum theoretical models. The changes observed in the symmetric bending $\delta_s(NH_3)$ modes due to the host lattice were detected by the gradual abandoning of the guest molecules from the host lattice. The magnitude of the observed splitting of the bending $\delta_s(NH_3)$ modes and their ratio of intensities is strongly dependant on the volume of the tetragonal unit cell of the Hofmann type clathrates.

(ii) The mid-infrared and the corresponding Raman bands due to the guest molecules and the host lattice were assigned and correlated with other published data.

(iii) The far-infrared and the corresponding Raman bands of the vibrational spectra in the low frequency region, originating from the host lattice: $M(NH_3)_2M'(CN)_4$, were assigned to the stretching and deformational vibrations of (a) the $M(NH_3)_2$ ligands: $\nu(M\text{-}N)$ and $\delta(NMN)$ and of (b) the $M'(CN)_4$ groups: $\nu(M'\text{-}C)$, $\delta(M'CN)$, $\delta(CM'C)$.

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ELUCIDATION OF ORGANIC COMPOUNDS FROM NATURAL SOURCES USING 1- AND 2-D NMR TECHNIQUES

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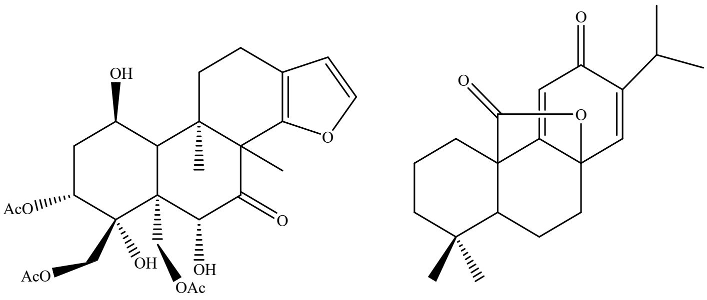
Identification of organic structures is mainly based on spectroscopic techniques. UV, IR, Mass, X-ray and particularly NMR are commonly used spectroscopies and various 1- and 2-D NMR techniques have been used for elucidation of natural organic compounds.

In this presentation, structure elucidation of some bioactive natural compounds obtained from Lamiaceae family plants, such as *Teucrium, Salvia* and *Sideritis* species will be given. Their structure elucidation was based on namely 1- and 2-D NMR techniques as well as UV, IR, MS and when possible X-ray, and their cytotoxic activities were investigated against a series cell line.



Alysine B

Wiedelactone

Fig. 1

[1] A. Ulubelen, G. Topçu, Diterpenoids from *Salvia* species and their pharmacological activities, in Advanced in Natural Product Chemistry, Atta-Ur-Rahman (Ed.), Harwood Academic Publishers, USA, 363-381 (1992).
[2] G. Topçu, C. Eriş, A. Ulubelen, M. Krawiec, W.H. Watson, New rearranged neo-clerodane diterpenoids from *Teucrium alyssifolium*. Tetrahedron 51, 11793-11800 (1995).

IR SPECTRA OF MASS SELECTED IONS AND CLUSTER IONS: STRUCTURE & REACTIVITY

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Ions and ion-ligand interactions play a crucial role for many processes in physics, chemistry and biology (e.g., chemical reaction mechanisms, plasma and combustion processes, planetary and interstellar chemistry, biomolecular recognition). The fundamental understanding of these phenomena at the molecular level requires the knowledge of the potential energy surface of the molecular ion and its interaction with the surrounding solvent molecules. To this end, we characterize isolated cluster ions of the type X^+-L_n, in which a central cation (X^+) is microsolvated by a variable number (n) of neutral ligands (L). The methods are mass spectrometry and spectroscopy on the experimental side and quantum chemical techniques on the theoretical side. The fruitful combination of these approaches has proven to provide the most detailed access to the desired potential energy surfaces.[1] The clusters are generated in a supersonic plasma expansion, which is obtained by electron impacting a pulsed molecular beam. IR spectra are then obtained by the very sensitive and selective technique of single-photon photodissociation spectroscopy (IRPD) in a tandem mass spectrometer using a high-resolution OPO laser in the spectral range of 2500-7000 cm^{-1}.[2] In addition, some experiments have also been conducted using the intense IR free electron laser CLIO (500-2500 cm^{-1}) in combination with a FT-ICR mass spectrometer, which allows to dissociate strongly bound ions via IR multiphoton photodissociation (IRMPD).[3] Recent applications include the characterization of:

(1) Protonation and microsolvation of protonated aromatic molecules (short-lived reactive intermediates in electrophilic aromatic substitution);[4,5]
(2) Aromatic ion-ligand interactions of biophysical interest;[6,7]
(3) Elementary $C_nH_m^+$ carbocations;[2]
(4) S_N2 reaction intermediates;[3,8]
(5) Proton wires of interest for biochemical proton transfer catalysis and proton conductivity in solution.[7,9]

In the presentation, selected results will be presented to demonstrate the potential of the combined experimental and theoretical approach.

[1] E.J. Bieske and O. Dopfer, Chem. Rev. 100 (2000) 3963.
[2] O. Dopfer, Int. Rev. Phys. Chem. 22 (2003) 437.
[3] O. Dopfer, J. Phys. Org. Chem. 19 (2006) in press.
[4] N. Solca and O. Dopfer, Angew. Chem. 114 (2002) 3781; ibid. 115 (2003) 1575; J. Am. Chem. Soc. 125 (2003) 1421; ibid. 126 (2004) 1716; Chem. Eur. J. 9 (2003) 3154; J. Chem. Phys. 120 (2004) 10470; ibid. 121 (2004) 769; Chem. Phys. Chem. 6 (2005) 434.
[5] O. Dopfer et al., J. Phys. Chem. A 109 (2005) 7881; Int. J. Mass Spectr. 249-250 (2006) 149.
[6] O. Dopfer, Z. Phys. Chem. 219 (2005) 125.
[7] H.-S. Andrei, N. Solca, O. Dopfer, Chem. Phys. Chem. 7 (2006) 107.
[8] U. Lorenz, N. Solca, O. Dopfer, Chem. Phys. Lett. 406 (2005) 321.
[9] N. Solca, O. Dopfer, J. Am. Chem. Soc. 126 (2004) 9520; J. Phys. Chem. A 109 (2005) 6147.

BIOMOLECULAR INTERACTIONS IN HCV NUCLEOCAPSID-LIKE PARTICLES AS REVEALED BY VIBRATIONAL SPECTROSCOPY

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Hepatitis C virus (HCV) is a major cause of chronic hepatitis, liver cirrhosis and hepatocellular carcinoma. It contains a 9.6-kb plus-strand RNA genome composed of a 5' noncoding region (5'NCR), a long open reading frame (ORF) encoding a polyprotein precursor of about 3,000 amino acids and a 3' NCR. The HCV polyprotein precursor is co- and posttranslationally processed to yield the mature structural and non-structural proteins. The structural proteins include the core protein, which forms the viral nucleocapsid. This protein is a highly basic, RNA-binding protein whose structure is poorly characterized. A better understanding of the structural properties of core protein and viral RNA is essential to provide a framework for elucidation of HCV nucleocapsid assembly and to further evaluate the core molecular interactions with numerous host compounds. We provide here novel insights into the structure of core protein and viral 5'NCR RNA in reconstituted HCV nucleocapsid particles.

We have first found *in vitro* particles of pure protein, having similar morphology and size distribution of those of nucleocapsids found in sera from HCV-infected patients. Overall, our spectroscopic results reveal that the secondary structure of these protein particles involve β-sheet enrichment in relation to its protein monomer.[1] Tertiary/quaternary structure has been also studied using the dynamics of H/D exchange.[2] With this aim infrared spectra were measured as a function of H/D exchange time and subsequently analysed by principal component analysis and two-dimensional correlation spectroscopy. Temporal dynamics of exchange for these protein particles were as follows: arginine residues exchanged first, followed by turn and unordered structures, followed by β-sheets which may act as linkers of protein monomers. Solvent accessibility of protein arginine residues is consistent with ionic protein-nucleic acid interactions which provide nucleocapsid stability. FTIR-monitored H/D exchange of the viral nucleic acid reveals the presence of $A{*}A{\cdot}U$ triplets, and the vibrational coupling between the ribose ether C-O stretching and 2'OH bending motions suggests that helical regions of 5'UTR RNA are characterized by hydrogen bonding between the 2'OH ribose groups and the ether oxygen atoms of neighbouring ribose residues.

[1] A. Rodríguez-Casado, M. Molina, P. Carmona, Biopolymers (in press).
[2] A. Rodríguez-Casado, M. Molina, P. Carmona, Anal. Bioanal. Chem. (in press).

TIME-RESOLVED ABSORPTION INVESTIGATION OF PHOTOPHYSICAL AND PHOTOCHEMICAL PROCESSES IN SOLUTION

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In the last decades, time-resolved spectroscopies have played a crucial role in the understanding of ultrafast photophysical and photochemical processes in condensed phase. In this field, transient absorption and emission spectroscopies are the most widely used techniques. Fluorescence spectroscopy has very high sensitivity and provides essentially information about the first excited singlet state S_1 of molecules and its dynamics but is unable to probe non fluorescent excited states (triplet state) and ground state intermediates (cations, anions, radicals…). On the contrary, ultrafast absorption spectroscopy can provide information about most of the intermediates involved in the photochemical and photophysical processes provided theses intermediates absorb in the spectral windows under study. Although the sensitivity of this technique is lower than that of fluorescence, it is still good enough to probe low concentrated transient species in solution. We have developed in our laboratory an ultrafast absorption spectrometer which exhibits a 100 fs time-resolution, a high sensitivity (detection of absorption variation down to 0.1 mOD) in the 300-700 nm spectral range. This setup has been applied to the study of numerous photo-induced chemical reactions. In this talk, we will give some recent results obtained for photochromic compounds and for hydroxyquinolines.

Photochromism is a reversible phototransformation of chemical species between two forms showing different absorption spectra. This effect can result from various types of chemical reaction (cis-trans isomerization, electrocyclic or cycloaddition reactions, tautomerization, photodissociation processes…). We have investigated by transient absorption spectroscopy different substituted spirooxazines and 2H-chromenes for which the photochromism proceeds via a C-O bond cleavage followed by isomerization, and some quinolone-ketones for which the photochromism is based on intramolecular hydrogen atom transfer. Pertinent new information about the photochromism reaction pathway and about the role of the substituent in the photochromism efficiency was collected. In the case of spirooxazines and 2H-chromenes, new deactivation routes of the initially populated singlet state, parallel and concurrent with the photocoloration reaction, were evidenced and characterized.

Hydroxyquinolines are amphoteric compounds characterized in the ground state by weak acidic (hydroxyl) and basic (imine) functions. The acidity and basicity of these molecules are strongly enhanced in the lowest excited singlet state where tautomerization takes place. We have investigated the photoinduced process of tautomerization of various hydroxyquinolines in acidic, alkaline and neutral aqueous solutions and for comparison in aprotic solvents. We have characterized the hydroxyl deprotonation and imine protonation dynamics in the excited state. For all the investigated molecules, the deprotonation rate constant is higher than the protonation one.

LASER INDUCED FLUORESCENCE SPECTRA AND VIBRATIONAL POTENTIAL ENERGY SURFACES OF COUMARAN AND 1,4-BENZODIOXAN IN THEIR GROUND AND EXCITED ELECTRONIC STATES

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The fluorescence excitation spectra (FES) and the single vibrational level fluorescence spectra (SVLF) of jet-cooled coumaran and 1,4-benzodioxan have been analyzed. These data have been complemented by infrared and Raman spectra and by *ab initio* and DFT calculations. A detailed energy map of the low-frequency modes was determined for coumaran for both S_0 and S_1 (π,π^*) states. The ring-puckering data showed that the ground state has a barrier to planarity of 154 cm^{-1} and energy minima at puckering angles of ± 25°. In the S_1 excited state, the barrier drops to 34 cm^{-1} and the puckering angle becomes ± 14°. 1,4-Benzodioxan is a twisted molecule in both its S_0 and S_1 states. Analysis of the ring-twisting and ring-bending motions shows that the barrier to inversion is 5000 ± 2000 cm^{-1} in the ground state and 3600 ± 2000 cm^{-1} for the S_1 (π,π^*) state. The large uncertainties arise from the fact that data extend to less than 1000 cm^{-1} above the ground states. The *ab initio* calculations predict twisting angles of 30° and 28° for the ground and excited states, respectively.

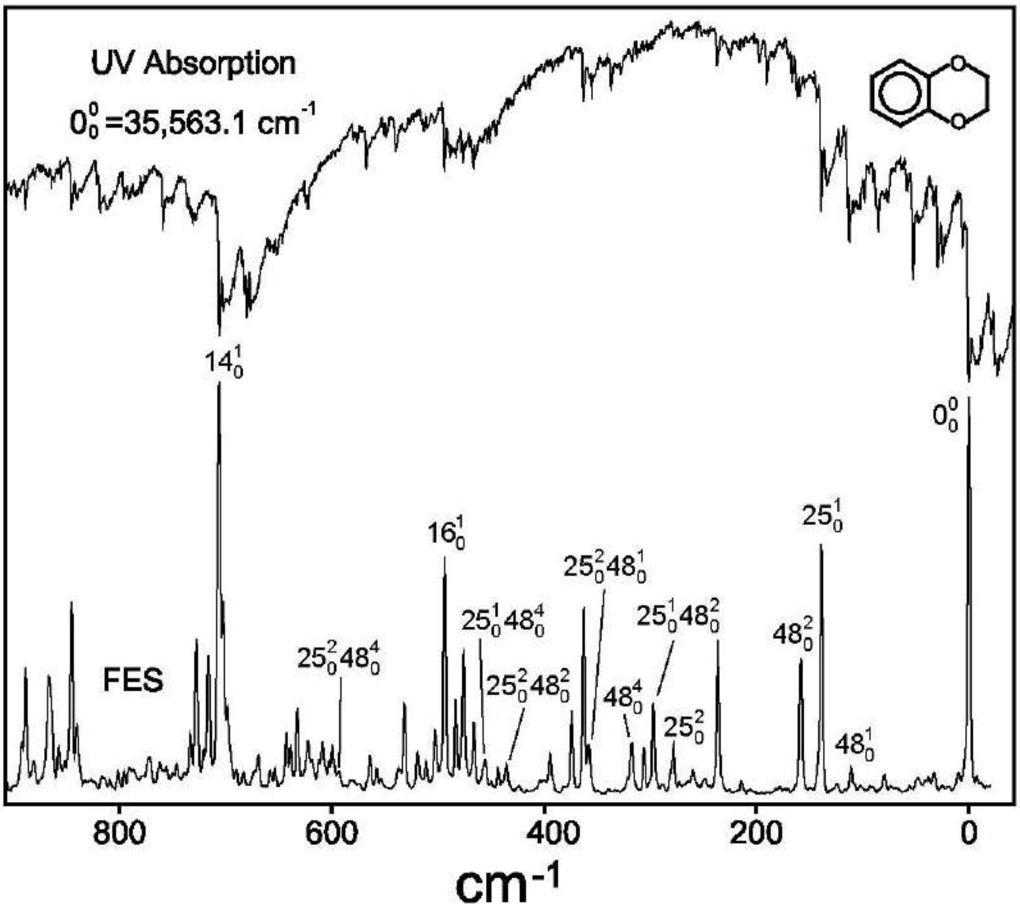

Figure 1. Fluorescence excitation spectrum of jet-cooled 1,4-benzodioxan and ultraviolet absorption spectrum at ambient temperature.

WAVEGUIDE RAMAN AND PHOTOLUMINESCENCE STUDIES OF ZIRCONIUM AND TITANIUM OXIDE THIN FILMS DOPED WITH SEMICONDUCTOR NANOCRYSTALS

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Materials doped with semi-conductor nanocrystals (NC) or codoped with rare earth (RE) ions attract much attention at the moment. This interest results from the surge of development of techniques for integrated optics and the search for new and better optical amplifiers, non-linear systems and optical waveguides. Zirconium and titanium oxide materials are of wide interest as host matrices because of their excellent mechanical, thermal and optical properties. Doping these materials with semiconductor nanoparticles (SC-NP), such as CdS or PbS, can confer an appreciable enhancement of the third order optical non-linearity. Moreover, codoping them with SC-NP and RE may result in a considerable increase of the RE emission. However, since optical properties are closely related to the microstructure, an understanding of the relation between the doping species and the host matrix is essential for every preparation technique. To date, very few publications have been devoted to structural studies of either nanoparticle-doped ZrO_2 films or to systems codoped with NC such as silicon, CdS or ZnS and RE ions such as Er^{3+} or Eu^{3+}.

In the present work, CdS, ZnS and ZnS/ Eu^{3+} doped structures have been prepared by sol-gel processing in the form of optical planar waveguides. The quality of the thin films was determined by optical loss measurements and waveguide Raman spectroscopic (WRS) studies. Luminescence and WRS spectroscopies were used to follow structural changes within the glass matrices resulting from different heat treatments and from the presence of doping species. Micro-Raman spectroscopy was used to demonstrate the nanometric size of the CdS crystallites. For the ZrO_2 films, the influence of the NC on the emission of RE ions was studied using luminescence spectroscopy. When excited at 350 nm in the presence of the NC, the Eu^{3+} emission was enhanced by a factor of 13 at 293K.

DESTINATION CROATIA: LIFE AND SCIENCE

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Croatia is the organizer of the forthcoming European Congress on Molecular Spectroscopy, to be held at Opatija on the Adriatic coast of Croatia. In our brief address we'll try to give some facts about Croatia, its people and their contribution to science and technology. Croatia is both a Central European and a Mediterranean country, and owing to its geographical position it is culturally diverse. Croats came down to the Adriatic Sea thirteen centuries ago. Originally a Slavic people, they founded a new homeland where they met the Illyrians, the Romans and the Greek colonists. The tradition and culture of these ancient peoples left significant traces in the history of Croatia. For many centuries Croatia has been surrounded by different cultures, Italian, German, Hungarian, and partly exposed to the Oriental influence through the Turkish presence for a few centuries. Thus Croatia became a unique destination in Europe for many tourists from all over the world. Croatia is also a country with a long-standing industrial tradition. There are several universities, the oldest among them the University of Zagreb, founded in 1669, and many scientific institutions, notably the "Ruđer Bošković" Institute located in Zagreb. Educated people, men of letters and science in the spirit of their times first emerged in the Middle Ages in the Croatian towns along the Adriatic, under the influence of Venice and specifically the Italian Renaissance. Of the many towns in that age one stands out in particular as the pearl of the Mediterranean: the city of Dubrovnik, which for many centuries was known as the Republic of Dubrovnik. The poet Marko Marulić of Split was a central figure of the period. His epic poem *Judith* written in the Croatian language marks the birth of the Croatian literature. Herman Dalmatin, active in Spain and France at the beginning of the twelfth century, is considered to be our first scientist. Ivan Česmički-Pannonius (a poet with interests in astronomy and astrology), Pietro Buono (a theoretical alchemist, in Trogir), Gjin Gazilli-Gazulus (an astrologist, in Dubrovnik) and Federico Grisogono (a physician, in Zadar) also contributed to the sciences of that period. In the seventeenth century Croatia gave several great scientists, such as Marin Ghetaldić (optics, in Dubrovnik), Marko Antun Dominis (theory of the rainbow; the telescope, Split), and Faust Vrančić (a famous constructor and engineer, in Šibenik and Padua). Ruđer Bošković, the greatest of them all, was born in Dubrovnik in the eighteenth century, and active in Rome, Milan and Paris. His concepts of the structure of the matter published under the title *Theory of Natural Philosophy* had a strong influence on the development of physics of the time, and we consider this a most valuable Croatian contribution to the world of science. In the 19th century, Bishop Josip Juraj Strossmayer founded the Academy of Arts and Sciences of all South Slavs (today: Croatian Academy of Sciences and Arts) in Zagreb. Nikola Tesla, born in Smiljan, was our greatest representative in the field of technical sciences, and it is impossible to imagine today's world without his inventions in the late 19th and early 20th centuries. He is the single scientist from all Slavic nations after whom a physical unit was named (tesla, for magnetic flux). In the twentieth century Lavoslav Ružička (of Vukovar) and Vladimir Prelog (of Osijek) were awarded Nobel Prizes for chemistry. We must not forget Andrija Mohorovičić (Moho discontinuity) who is one of the most prominent earth scientists of the 20th century. Advances in spectroscopy by a new generation of scientists in Croatia are then the continuation of the Croatian scientific lineage.

ORAL
CONTRIBUTIONS

ELECTRONIC AND VIBRATIONAL CIRCULAR DICHROISM SPECTROSCOPIC STUDY OF NON-COVALENT INTERACTIONS OF 5,10,15,20-TETRAKIS(1-METHYLPYRIDINIUM-4-YL)PORPHYRIN WITH (dG-dC)$_{10}$ AND (dA-dT)$_{10}$

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The non-covalent interactions of (dG-dC)$_{10}$ and (dA-dT)$_{10}$ with 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin (TMPyP) were studied using the combination of electronic circular dichroism (ECD), vibrational circular dichroism spectroscopy, and UV-VIS and IR absorption spectroscopy at different ratios of both components [oligonucleotide]/[TMPyP] = 2/1 – 10/1, where [oligonucleotide] and [TMPyP] are the amount concentrations of oligonucleotide per base-pair and TMPyP, respectively. It was shown that TMPyP with (dG-dC)$_{10}$ provided intercalative binding mode and this binding did not decay even at 90°C. TMPyP with (dA-dT)$_{10}$ provided three binding modes: (i) external binding to the phosphate backbone, (ii) external minor groove binding for the ratios >6/1, and (iii) external major groove binding associated with B- to Z- transition for the ratios <4/1. In the (dA-dT)$_{10}$ – TMPyP complexes, the external binding to the phosphate backbone accompanied by self-stacking of porphyrins along the phosphate backbone chain is preferred at temperatures higher than 40°C.

Financial support of Ministry of Education, Youth and Sports of the Czech Republic (grant MSM 6046137307) is gratefully acknowledged.

LOW-WAVENUMBER NIR-FT-RAMAN STUDIES OF WATER STRUCTURE IN HUMAN AND ANIMAL SKIN: BIOMEDICAL ASPECTS

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Water is a major constituent of all living systems. Human skin contains around 70% of water. Raman spectroscopy with cw-laser excitation reflects the dynamics on a pico-second time scale and faster. Thus Raman spectroscopy gives a snapshot of an interacting water/biomolecule system. The water stretching and bending vibrations are only slightly perturbed by differences in water hydrogen bonding. The low-wavenumber region is much more sensitive, because this part of the spectrum depends directly on the intermolecular hydrogen bonds. However, Rayleigh scattering yields a very intense band extending to Raman shifts of several hundred wavenumbers (cm^{-1}). This band tends to hide weaker bands from intermolecular water vibrations. By use of the so-called $R(\bar{\nu})$-representation the band due to Rayleigh scattering is converted to a plateau, and weak vibrational features of water below 400 cm^{-1} are more easily seen[1-4]. ^{2}H-, ^{17}O- and ^{18}O- isotopic substitution in water showed that a band with a maximum around 180 cm^{-1} in the $R(\bar{\nu})$-representation was caused solely by oxygen displacements[1,3]. A water molecule with four neighbouring molecules exhibits a vibrational motion. The corresponding band is observed at 180 cm^{-1} in the $R(\bar{\nu})$-representation and this is a characteristic band for water with a bulk-like structure. NIR-FT-Raman spectra were recorded with excitation at 1064 nm.

Animal skin is used as model for human skin in laboratory studies of skin properties. Thus it is essential to characterize the water content and structure in animal and human skin. Raman spectra of skin from pig ear, guinea pig and mouse were compared to human skin. A comparison of the total water content was performed from the OH-stretching region around 3250 cm^{-1}. An estimate of the amount of water with a bulk-like structure was performed for the low wavenumber Raman spectrum in the $R(\bar{\nu})$-representation. The water content and structure of pig ear and guinea pig were closer to human skin than mouse skin. The same technique was used to follow the loss of water in human skin samples after freezing and thawing.

Human skin biopsies of normal skin were compared to biopsies of skin with malignant melanoma, basal cell carcinoma, pigmented nevi and seborrheic keratosis. The low-wavenumber spectra in the $R(\bar{\nu})$-representation revealed an increase of water with a bulk-like structure in malignant skin tumours.

[1] O. Faurskov Nielsen, Chem. Phys. Lett. 60 (1979) 515.
[2] O. Faurskov Nielsen, Annu. Rep. Prog. Chem., Sect. C, Phys Chem., 90 (1993) 3 and 93 (1997) 57.
[3] O. Faurskov Nielsen, C. Johansson, K. L. Jakobsen, D.H. Christensen, M.R. Wiegell, T. Pedersen, M. Gniadecka and P. Westh, Proceedings of SPIE 4098 (2000) 160.
[4] O. Faurskov Nielsen, in I.R. Lewis and H.G.M. Edwards (Eds), Handbook of Raman Spectroscopy, Marcel Dekker, Inc., New York, Basel 2001, Chapter 15, p. 593.

FT-IR MICROSCOPY IMAGING ON ORAL CAVITY TUMORS, III

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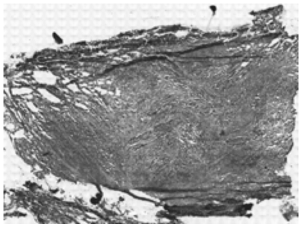
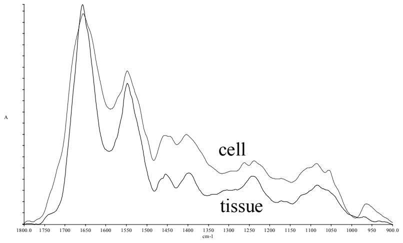
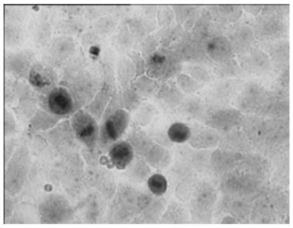
The potential role of conventional as well as synchrotron Infrared and Raman micro spectroscopy in the study of tumours in cells and tissues has been highlighted in a large number of reports[1,2]. The occurrence of oral cavity neoplastic changes (oral squamocellular carcinoma, OSCC) is remarkable in the pathological states of neck and head tumours. The clinical behaviour of these tumours is difficult to predict based only on histopathological parameters. Studies on biochemical and morphological changes between control and pathological tissues of these tumours, have been monitored drawing three-dimensional chemical maps of the main vibrational modes in the regions of interest[2]. The aim was, based on histopathological parameters as well as Microscopy FT-IR procedures, to add further insight in the prognosis of OSCC[3,4]. Spectral determinations were performed with Perkin-Elmer Spectrum GX1 and Spot Light spectrometers equipped with Perkin-Elmer Autoimage microscopes at 25x25 and 10x10 µm spatial resolution, respectively. For data processing, Galactic AI and Pirouette software packages were used. Spectroscopic data from normal mucosa, displastic lesions and OSCC in tissue sections of the oral cavity, were processed and the spectroscopic data were used to generate a statistically significant protocol to distinguish neoplastic and displastic lesions from healthy tissues. Chemometric procedures allowed to find characteristic spectral patterns of control and neoplastic areas that were also assessed by drawing custom maps between cell lines and tissues[2]. The evaluation of the ratio between representative bands of important cellular components, nucleic acids, proteins, glycogen, resulted helpful to discriminate among various states and were in agreement with our previous results on these pathologies.[1,3] Supervised and unsupervised cluster analysis, to achieve good separation of even subtle spectral differences, resulted in a satisfactory accordance (higher than 90%) between spectroscopic and histopathological findings. A comparison of the results from tissues with those obtained from cellular lines representative of various regions of the mouth, was satisfactory taking into account that some differences, in the spectroscopic pattern of the tissues, could derive from the environment (Figures).







[1] H.H. Mantsch et al., J. Mol. Struct., 661-2, 397 (2003).
[2] 1st DASIM Workshop (Diagnostic Applications of Synchroton Infrared Microspectroscopy), Daresbury Lab.s, Manchester, July 2005; RSC Faraday Division. Faraday Discussion 126, Nottingham (2003).
[3] G. Tosi et al., J. Mol. Struct., 744-7, 187 (2005).
[4] M. Tobin et al., RSC Faraday Division. Faraday Discussion 126, 41 (2004).

OPERANDO FTIR IN MODELLING CELLULOSE DEGRADATION MECHANISM

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Despite numerous examples of the use of FTIR technique in diverse fields connected with cellulose chemistry its potential does not seem to be completely exploited yet. Vibrational spectroscopy has already been applied to resolve cellulose structure, crystalline phases and hydrogen bonds network. However, since cellulose is a ubiquitous biopolymer that is widely used as a rough material for a great many applications either in a pure or chemically modified form, new challenges that emerged in material and preservation science have evoked new questions to be answered. Our research is targeted at cellulose stability in paper, still the most ubiquitous information carrier, and especially that which has been produced using so called acidic technology utilizing ground wood, rosin and alum. Its introduction around 1850 year brought about dramatic changes in cellulose stability due to acid catalysed hydrolysis of glycosidic bonds. Now, the problem of paper rapid deterioration concerns around 80% of libraries and archives collections. To prevent it we should be able to evaluate current paper condition and its longevity and understand the chemistry that is behind observed collapse of mechanical properties.

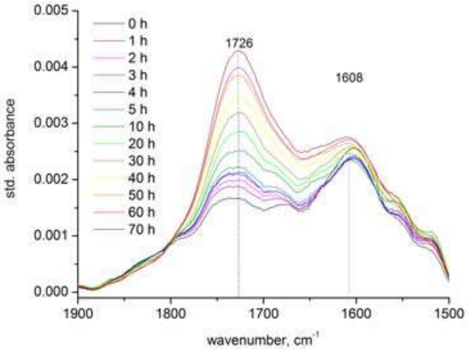

Fig. 1: Time evolution of bands of cellulose aged in dry air at 150°C .

Our study [5-7] deals with modelling cellulose degradation kinetics through hydrolytic and oxidative reaction paths by operando FTIR spectroscopy. The experiments of accelerating ageing of cellulose samples were performed in situ under various conditions (temperature, gas mixture) to be able to possibly discriminate between occurring reaction routes. The focus was mainly on the spectra between 1500-1900 cm^{-1}, where the products of paper ageing under various conditions appear in form of carbonyl groups of various degrees of freedom at changing potential environment. A procedure of spectra standardization allowed combining the bands area with conversion of carbon atoms in cellulose. An example of the results is presented in Figure 1. From the time evolution of the bands overall kinetic curves were generated. The positions of the carbonyl bands were verified by independent experiments and theoretical calculations (DFT method). Basing on this a combined model involving hydrolysis and oxidation has been put forward and tested on the available data sets.

[1] J. Łojewska, P. Miśkowiec, T. Łojewski, L.M. Proniewicz. Polym. Deg. Stab., 88 (2005) 512-520.
[2] J. Łojewska, A. Lubańska, T. Łojewski, P. Miśkowiec, L.M. Proniewicz, , e-Preservation Science 2 (2005). 1-11.
[3] J. Łojewska, H. Lubańska, P. Miśkowiec, T. Łojewski, L.M. Proniewicz, Applied Physics A, in press

EARLY SPECTRAL CHANGES IN CELLULAR MALIGNANT TRANSFORMATION USING VIBRATIONAL SPECTROSCOPY

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Fourier transform infrared microspectroscopy (FTIR-MSP) is potentially a powerful analytical method for identifying the spectral properties of biological activity in cells[1]. The implementation of FTIR-MSP was studied for early spectral changes accompanying cellular malignant transformation. As a model for this purpose we used cell cultures infected with Murine Sarcoma Virus (MuSV) which induces malignant transformation. In order to follow the transformation's progress as a function of time, it was necessary to find and validate consistent and significant spectral parameters (biomarkers)[2,3], which can clearly distinguish between normal and cancerous cells. We classified the transformation level by an array of spectral biomarkers using cluster analysis. The results indicate that the spectral changes were detectable much earlier than the first morphological signs of malignant transformation. The parameters associated with nucleic acids were found most effective for early detection (Fig. 1)

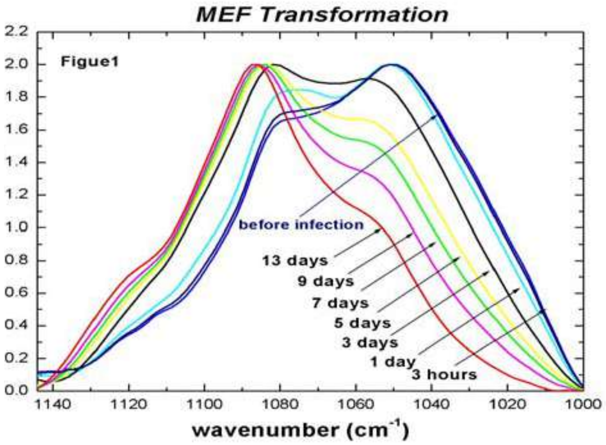

Figure 1 : Typical spectral transformation in the wavenumber region of 1000-1185 cm^{-1} (dominated by glycogen and phosphodiester absorbance bands) at various post infection time intervals indicating a clear and gradual variations of the associated macromolecules absorbance.

The present FTIR- MSP results are promising for early detections of malignancy.

[1] M.Diem et al, *Appl. Spectroscopy*, 53, 148A-161A, (1999)
[2] R.Sahu et al, J Biomed Opt. Sep-Oct;10(5):054017 (2005)
[3] R.Sahu et al, Tech. in Cancer Res. & Treat Vol 3(6) 629-638,2004.

GAS PHASE STRUCTURE OF AMINO ACIDS: LASER ABLATION JET-COOLED ROTATIONAL STUDIES.

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The structural analysis of natural amino acids using rotational spectroscopy was hindered in the past by the high melting points and thermal fragility of these compounds. Recently, these studies have received an important impulse with the introduction of a technique which combines laser ablation with Fourier transform microwave spectroscopy in supersonic jets[1] (Laser-ablation molecular-beam Fourier transform microwave spectroscopy, LA-MB-FTMW). Using this technique we have studied under isolation conditions in gas phase proline[2], alanine,[3] valine,[4] hydroxyproline,[5] serine, cysteine, leucine, isoleucine[6], aspartic acid, γ-aminobutiric acid (GABA), N,N-Dimethylglycine,[7] β-alanine,[8] phenylglycine,[9] etc. Several conformers (up to six for serine, cysteine, and aspartic acid and five for GABA) have been detected in the jet-cooled rotational spectrum and their rotational and N-nuclear quadrupole coupling constants determined; the latter are crucial to distinguish unequivocally between conformations with similar rotational constants. The observed conformers present different intramolecular hydrogen bonds involving the –COOH, –NH2, –OH and –SH groups which influence their stability. In 4-hydroxyproline, β-alanine and GABA n-π* interactions have been found also to contribute to the stability of certain conformers.

The first observation of the 1:1 complex of glycine-water[10] is also presented. The water molecule has been reliably located in the complex from the analysis of several isotopomers. The complex is stabilized by two intermolecular hydrogen bonds formed between the carbonyl group and one of the hydrogen atoms of water (O_w-H···O=C) and between the hydroxyl group and the electron lone pair at the oxygen atom of water (O_w···H-O-C)).

[1] Lesarri, A.; Mata, S.; López, J.C.; Alonso J. L. ***Rev. Sci. Instrum***. 2003, *74,* 4799.
[2] Lesarri, A.; Mata, S.; Cocinero, E. J.; Blanco, S.; López, J. C.; Alonso, J. L.; ***Angew. Chem. Int. Ed.*** 2002, *41*, 4673.
[3] Blanco, S; Lesarri, A.; López, J. C.; Alonso, J. L. ***J. Am. Chem. Soc***. 2004, 126,11675.
[4] Lesarri, A.; Cocinero, E. J.; López, J. C.; Alonso, J. L. ***Angew. Chem. Int. Ed***. 2004, *43*, 605.
[5] Lesarri, A.; Cocinero, E. J.; López, J. C.; Alonso, J. L. ***J. Am. Chem. Soc***. 2005, 127,2572.
[6] Lesarri A.; Sanchez, R:; Cocinero E. J.,;Lopez, J. C.; Alonso, J. L.; ***J. Am. Chem. Soc***. 2005, 127, 12952.
[7] Lesarri,A; Cocinero,E.J.; López J.C.; Alonso J. L.; ***ChemPhysChem***.2005,6,1559
[8] Sanz, M. E; Cortijo, V.; Caminati, W.; López, J. C.; Alonso, J. L.; ***Chem.Eur.J***. 2006 12, 2564
[9] Sanz, M. E; Lesarri, A; Peña ,I.; Vaquero, V.; Cortijo, V.; López, J. C.; Alonso, J. L., ***J. Am. Chem. Soc***. , *128*, 3812
[10] Alonso, J. L.; Cocinero, E. J.; Lesarri, A.; Sanz, M. E; López, J. C. ***Angew. Chem. Int. Ed***. (2006) In Press
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FTIR SPECTROSCOPIC DETECTION AND STUDY OF BIOSPECIFIC INTERACTIONS USING FUNCTIONALISED GOLD NANOPARTICLES

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Biospecific interactions ("recognising molecule – target molecule") of various kinds comprise a wide range of processes highly important for molecular recognition and signalling, that span from an intracellular level to symbiotic or pathogenic relations between organisms. The interacting systems include such kinds as antigen–antibody (representing a large variety of immunochemical interactions), lectin–polysaccharide, enzyme–substrate, avidin–biotin, actin–myosin, *etc*. Many of these systems involve biopolymers either as recognising or target molecules, or both.

Since in most cases such interactions result in chemical (covalent) and/or structural modifications of the reacting biomolecules, their investigation may (and in many cases does) benefit from using spectroscopic techniques, in particular, vibrational spectroscopy. Moreover, as has been shown in the last decades, surface-enhanced vibrational spectroscopy (SERS or SEIRA; see, e.g. [1, 2] and references cited therein) can be useful analytical methodologies. Whereas in Raman the enhancement factors can be very high [1], in IR they usually range from units up to hundreds [2]. Nevertheless, SEIRA is easily applicable and, with different physical factors governing peak intensities, can still be highly informative [3].

In this work, we comparatively studied the FTIR-SEIRA spectroscopic effects of conjugation of gold nanoparticles (AuNP) with different proteinaceous biopolymers. The observed similarities in spectroscopic changes for different proteins upon their conjugation with AuNP point to common mechanisms underlying these processes.

Further, using different pairs of specifically interacting biopolymers, either one of which in a pair was conjugated with AuNP, we identified the characteristic SEIRA spectroscopic changes accompanying the interactions of AuNP-conjugated proteins with their specific target molecules. The data obtained provide a basis for rapid, simple and sensitive SEIRA spectroscopic detection of both immunochemical reactions (which is to be termed “spectroimmunochemistry” [4]) and other types of biospecific interactions using AuNP functionalised by conjugation. Using this novel methodology, some natural molecular biosystems were studied related to plant–bacterial interactions, involving plant root lectin and various cell-surface biopolymers from plant-growth-promoting rhizobacteria.

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[1] A. Ibrahim, P.B. Oldham, D.L. Stokes, T. Vo-Dinh, B.H. Loo, J. Mol. Struct. 735-736 (2005) 69-73.
[2] R.F. Aroca, D.J. Ross, C. Domingo, Appl. Spectrosc. 58 (2004) 324A-338A.
[3] K. Ataka, F. Giess, W. Knoll, R. Naumann, S. Haber-Pohlmeier, B. Richter, J. Heberle, J. Amer. Chem. Soc. 126 (2004) 16199–16206.
[4] A.A. Kamnev, L.A. Dykman, P.A. Tarantilis, M.G. Polissiou, Biosci. Rep. 22 (2002) 541-547.

GAS PHASE ROTATIONAL STUDIES OF NUCLEIC ACID BASES

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Spectroscopic studies of biomolecules in gas phase are directed to the conformational and structural analysis of the building blocks of life, providing a picture of their intrinsic molecular properties free of intermolecular interactions imposed by the biological environment. The nucleic acid bases are particularly appealing and questions like their structure, planarity, tautomer equilibria and their multiple character of proton acceptors/proton donor are of interest since these are of fundamental importance to the structure and function of Nucleic Acids. These bases, like almost all biomolecules, have high melting points and thermal fragility which imposes serious difficulties to their vaporization. We have recently built an experimental set up which combines laser ablation with Fourier transform microwave spectroscopy in supersonic jets[1] (Laser-ablation molecular-beam Fourier Transform microwave spectroscopy, LA-MB-FTMW). Using this technique we have studied under isolation conditions in gas phase the rotational spectra, structure and conformational equilibria of more than 15 amino acids.[2-8]

In the present work we present the first studies of the rotational spectra of uracil, thymine and cytosine at the very high resolution provided by Fourier transform microwave spectroscopy, which has allowed to completely resolve their complex ^{14}N-nuclear quadrupole hyperfine patterns. The uracil structure has been derived on the basis of all ^{13}C, ^{15}N and ^{18}O isotopomers observed in their natural abundance. The analysis of the methyl group internal rotation splittings observed in thymine allowed to determine a V_3 barrier of 1.87 Kcal.mol^{-1}. Four tautomeric species of cytosine have been observed in the gas phase. The assignment of the spectra to the various species is unambiguously based on the markedly different values of the quadrupole coupling constants of the three ^{14}N nuclei, which act as finger prints for the identification of the various species. The relative energies of the various species are estimated from the relative intensities of the spectra. First results on adenine and Guanine are presented.

These studies show that LA-MB-FTMW[1] Spectroscopy is emerging as a precious tool for the conformational and structural analysis of biological molecules in gas-phase.

[1] Lesarri, A.; Mata, S.; López J.C.;.Alonso J.L. ***Rev. Sci. Instrum***. **2003**, *74,*4799.
[2] Lesarri, A.; Mata, S.; Cocinero, E.J.; Blanco, S.; López, J.C.; Alonso, J.L. ***Angew. Chem. Int. Ed.*** **2002**, *41*, 4673.
[3] Blanco, S; Lesarri, A.; López, J. C.; Alonso, J. L. ***J. Am. Chem. Soc***. **2004**, 126,11675.
[4] Lesarri, A.; Cocinero, E. J.; López, J. C.; Alonso, J. L. ***Angew. Chem. Int. Ed***. **2004**, *43*, 605.
[5] Lesarri, A.; Cocinero, E. J.; López, J. C.; Alonso, J. L. ***J. Am. Chem. Soc***. **2005**, 127,2572.
[6] Lesarri,A; Cocinero,E.J.; López J.C.; Alonso J,L.; ***ChemPhysChem*.2005**,6,1559
[7] Sanz,M.E;Cortijo,V.;Caminati,W.;López,J.C.;Alonso,J.L.; ***Chem.Eur.J***. **2006**, *12*, 2564
[8] Sanz,M.E; Lesarri, A;Peña,I.;Vaquero,V.;Cortijo,V.;López,J.C.;Alonso,J.L., ***J. Am. Chem. Soc***. **2006,** *128*, 3812

WHY IS GREEN FLUORESCENCE PROTEIN SO BRIGHT?

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The green fluorescence protein (GFP) is intensively used to study very diverse problems in molecular biology, medicine, biochemistry and cell biology. Its usage takes advantage of the presence of an internal chromophore, which generates a very effective and intense fluorescence and is isolated from the solvent by the very rigid protein environment.

To reveal the causes of the strong fluorescence the emission spectra of GFP and the model of its chromophore *p*-Hydroxybenzylidenedimethylimidazolone (*p*-HBDI) in glycerol/water 60/40 v/v solution were obtained in the wide interval of temperatures, 80 – 300 K. The protein spectra consist of a progression of well resolved narrow bands, which broaden and shift to the red upon the heating. The model compound spectra are very wide and have no structure at all temperatures.

The temperature dependence of the GFP spectra was interpreted using theory of optical absorption bandshape[1]. The progression was shown to be a manifestation of the linear coupling of the electronic transition to a number of the chromophore modes. The linear red shift of the protein spectra was shown to be caused by the presence of the chromophore coordinate Q, which is quadratically coupled to the electronic transition under consideration and most probably corresponds to the *cis-trans* isomerization of the chromophore. Taking into account of the distribution of the model molecules along both the types of the coordinates allowed us to reconstruct the HBDI spectrum at different temperatures[2].

The interpretation brought us to conclude that in the model compounds in liquid solvent the very effective radiationless decay of the excited electronic state along this coordinate takes place; it strongly reduces the quantum yield of the fluorescence. In the glassy matrix this motion is hindered and the quantum yield is larger. In native GFP this motion is arrested by the rigid protein environment at all temperatures; this makes the quantum yield of the fluorescence close to 1.

[1] K.K. Rebane, Impurity Spectra of Solids. Elementary Theory of Vibrational Structure, Plenum Press, New York, 1970.
[2] S.S. Stavrov, K.M. Solntsev, L.M. Tolbert and D. Huppert, J. Am. Chem. Soc., 128 (2006) 1540.

VIBRATIONAL SPECTRA OF HALOGENO SULFITO MERCURATES(II) $M^I[XHgSO_3]$ (M^I = NH_4, ALKALI METAL; X = Cl, Br)

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In connection with structural and spectrometric studies of sulfito complexes of noble metals ([1], and references therein) we turned our attention anew to sulfito complexes of mercury, especially to mixed halogeno sulfito complexes $M^I[XHgSO_3]$. Here, we present optical vibrational spectra (IR and Raman) of species with M^I = NH_4 and alkali metals, and X = Cl and Br.

The crystal structure of the compound $NH_4[ClHgSO_3]$ has been determined (*Pnma*, *Z* = 4) [2]. It contains bent $ClHgSO_3$ entities (S-coordination) linked to ribbons parallel to the ***b***-axis by secondary donor-acceptor bonds S–O···Hg; these ribbons in turn aggregate to layers around the ***bc***-plane. The layers stack along the ***a***-axis with inter-layer distances of *a*/2 (771.5 pm). The NH_4 cations are placed between the layers on sites with symmetry *m*, as are the $ClHgSO_3$ anions within the layers. Thus, all original degeneracies of vibrations of both entities should be lifted. The full unit-cell group analysis based on the structure predicts further splitting of all internal vibrations due to correlation coupling; *e g* the $\nu_{as}(SO_3)$ ($\sim$1100 cm^{-1}) and $\delta_{as}(SO_3)$ ($\sim$500 cm^{-1}) should occur in all species of the unit cell, *viz* in A_g, B_{1g}, B_{2g}, B_{3g}, A_u (inactive), B_{1u}, B_{2u}, B_{3u} (the mutual exclusion rule applies).

The only paper with some few IR data for $NH_4[ClHgSO_3]$ [3] gives partly wrong assignments and more bands than found in the corresponding region of our reproducible IR spectra, which are deceptively simple. Thus, the above vibrations of the SO_3 groups appear as doublets in both IR and Raman spectra. This simplification is probably due to suppression of correlation coupling between the widely spaced layers (see above), in other words to restriction of this coupling to the layers or even ribbons. Under these conditions as a good approximation a partial symmetry analysis for the ribbons (band or rod group (***b***)·2_1:*m* (Shubnikov notation, see [4]) or $p12_1/m1$) should be sufficient. In fact, analysis at this level yields two species each with gerade (Raman) and ungerade parity (IR).

The valence vibrations of the heavy-atom skeleton X–Hg–S strongly appear in both Raman and IR spectra (X = Cl: $\sim$310 and $\sim$230 cm^{-1}; X = Br: $\sim$200 and $\sim$140 cm^{-1}) and the bending mode clearly in the IR spectra (90 cm^{-1}; 63 cm^{-1}).

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[1] H. Meinberg, D.K. Breitinger, J. Mol. Struct. 563/564 (2001) 389.
[2] M. Weil, D.K. Breitinger, G. Liehr, J. Zürbig, to be published.
[3] J.I. Bullock, D.G. Tuck, J. Chem. Soc. (1965) 1877.
[4] A.V. Shubnikov, V.A. Koptsik, Symmetry in Science and Art, Plenum Press, New York-London 1974, Chapter 6, Table 6, p. 116.

OA-11

STATE RESOLVED SPECTROSCOPY OF VERY HIGH VIBRATIONAL LEVELS OF WATER

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Water is a key molecule in our life, particularly in atmospheric photophysics, as it is involved to the sunlight absorption, energy transfer etc. Modeling of these processes requires knowledge of rotational-vibrational energy levels of water in the electronic ground state with high precision and up to its dissociation limit. High level *ab initio* calculations provide a potential energy surface (PES), yielding the first guess for the energy levels. The PES then has to be fitted, so that the calculated energy levels match the available experimental data. This surface then can be used to calculate levels with high confidence within the energy intervals, where it's been fitted. Over last 20 years the progress in this procedure has been limited due to a lack of experimental data for the energy levels above 25500 cm^{-1}. This is primarily because of difficulty in accessing high vibrational levels through overtone transitions, as they have extremely small absorption cross-sections. We use a double resonance laser spectroscopic scheme to access high vibrational states of water molecules from single rotational-vibrational states. Our recent results provide accurate positions of several rovibrational levels above 27000 cm^{-1}. Fitting the water PES using these data extends the high-precision calculation of any energy levels in water, currently, to 35000 cm^{-1}.

We have also performed a direct measurement of one of the key fundamental thermochemical value - the dissociation energy of the O-H bond in water molecule- with the accuracy that by orders of magnitude exceeds all previously reported and accepted results. The dissociation continuum has been reached by a triple-resonance laser excitation of H_2O molecules in single quantum states.

PHOTOELECTRON, VIBRATIONAL (INFRARED, RAMAN) AND AB INITIO STUDY OF THE PARENT FUROXAN

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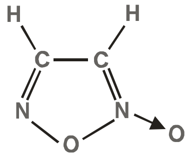
The parent furoxan (1,2,5-oxadiazole 2-oxide), an electron rich compound with an exocyclic oxygen atom,



is the key to understanding the structure, properties, and thermolytic cycloreversion reactions of substituted furoxan species (see, for example, references[1,2]).

Unknown until relatively recently,[3] we have synthesized this species from glyoxime and NO_2 (g) and have investigated it in the gas phase by FT-infrared and HeI photoelectron spectroscopy and in the liquid phase by FT-Raman. The ground-state geometry has been obtained from both single and multi-reference quantum-chemical calculations, *viz*. B3LYP, MPn (n=2-4), CCSD, CCSD(T), RSPT2, RSPT3, MRCI and MR-AQCC, using 6-311++G(2d,2p) and cc-pVTZ, cc-PVQZ basis sets. The furoxan is predicted to be planar, with the calculated structure depending upon the method employed, indicative of the difficulty in accurately representing the structure of furoxans. From various aromaticity indices, furoxan is nearly as aromatic as furan and furazan. The furoxan ring opening has been investigated at the MRCI and MR-AQCC//B3LYP levels and compared to (U)B3LYP calculations. The ring-opening process is found to involve open-shell dinitrosoethylene-like intermediates. Unlike the methyl- and cyano-substituted furoxans, the parent furoxan, upon thermolysis, does not yield the monomer nitrile oxide but leads to HNCO, CO_2, and H_2O as major products.

[1] B. Havasi, T. Pasinszki, N.P.C. Westwood. J. Phys. Chem. A. 109 (2005) 3864.
[2] T. Pasinszki, N.P.C. Westwood. J. Phys. Chem. A. 105 (2001) 1244.
[3] T. I. Godovikova, S.P. Golova, Y.A. Strelenko, M. Yu. Antipin, Y.T. Struchkov, L.I. Khmel'nitskii. Mendeleev Comm. (1994) 7.

CONFORMATIONS OF SUBSTITUTED ACETYLENES

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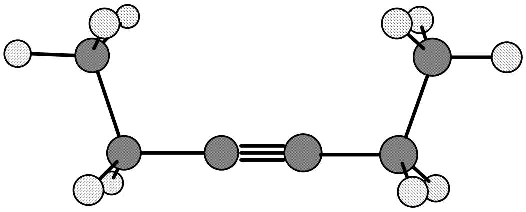
Conformations of alkanes have been well studied and occur in anti and gauche configurations. Similarly in alkenes, stable conformations have an adjacent bond, either C-C or C-H, eclipsing a C=C bond. Using microwave spectroscopy and quantum chemical calculations, we have determined the molecular structures of a variety of compounds where the organic groups have been separated by a cylindrically symmetrical spacer, a C≡C triple bond. The structural results have revealed surprises. For example, butane exists in anti C_{2h} and less stable gauche C_2 conformations. When the ethyl groups are separated by C≡C (3-hexyne), the conformation is syn heavy-atom-planar C_{2v} as shown[1].

3-Hexyne, observed structure, syn C_{2v}



3-Hexyne can be called diethyl acetylene. We have carried out similar studies on substituted acetylenes with an ethyl group at one end and n-propyl, 2-propenyl, formyl, acetyl, and phenyl groups at the other. In the case of ethyl n-propyl acetylene (3-heptyne) two conformers are observed, syn heavy-atom-planar with the propyl group anti and nearly syn planar when the propyl group is gauche. Ethyl 2-propenyl acetylene (2-methyl-1-hexene-3-yne) exists in two conformations, one planar and another apparently pseudo-planar. The shorter analog, 2-methyl-1-butene, also exists in two conformations but each has either a C-C or C-H bond eclipsing the C=C double bond. The formyl and acetyl ethyl acetylenes each display a single planar conformer although the shorter analogs, propanal and butanone, each have two stable conformers with an adjacent C-C or C-H bond eclipsing the carbonyl C=O bond. Ethyl phenyl acetylene is heavy-atom-planar but the shorter analog, ethyl benzene, has the plane containing the ethyl C-C bond orthogonal to the phenyl plane.

1. R. K. Bohn, J. Phys. Chem. A, 108 (2004) 6814

INNOVATIVE INTERFEROMETER DESIGN OF A NEW RESEARCH VACUUM FT-IR SPECTROMETER

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When the bar for research FT-IR spectrometers was set, we knew that some day we would feel obliged to raise it. For the new VERTEX 80v Bruker Optics provides an innovative interferometer concept and a very flexible vacuum optics layout, which is the culmination of everything that have been pioneered and developed in over 30 years. The new research vacuum FT-IR spectrometer is based on the true-aligned UltraScan™ interferometer (see fig. 1), which provides the highest spectral resolution achievable on a bench top FT-IR spectrometer. The precise linear air bearing scanner and high quality optics guarantees the ultimate sensitivity and stability.

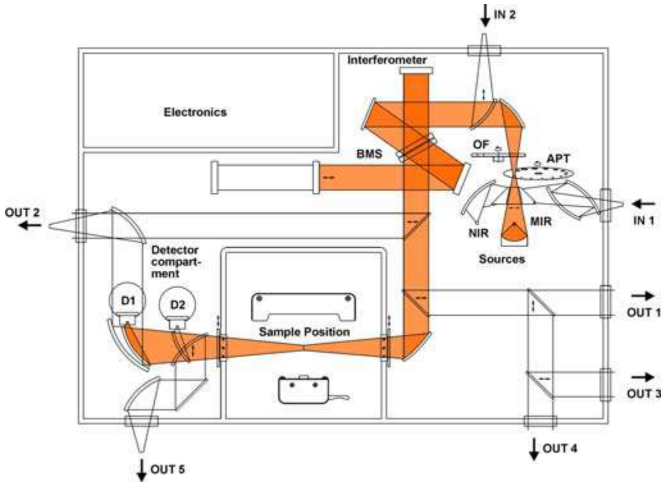

Fig.1 Optics layout of the new vacuum research FT-IR spectrometer VERTEX 80v.

The rugged and stable cast aluminium optics bench enables demanding experiments such as high spectral resolution (better than 0.07 cm^{-1}), ultra fast time resolved spectroscopy (msec down to few nsec temporal resolution), or ultra-violet spectral range (up to 50,000 cm^{-1}) measurements. The two optional external detector ports accommodate liquid He dewars of bolometer and/or hot electron-detectors (see beam exits OUT 2 and OUT 5 in fig.1). In combination with the external water cooled high power Hg-arc source, the recently discovered terahertz spectral range is accessible (down to less than 5 cm^{-1}). The evacuated optics bench eliminates atmospheric moisture absorptions and provides extreme sensitivity and stability, especially in the far IR spectral regions.

In this paper we will demonstrate the instruments resolving power $\nu/\Delta\nu$ of better than 300.000:1 on iodine vapour absorption lines in the visible spectral range. In addition from the area of nano-science research air water vapour free IR spectra of less than 10^{-3} molecular mono layers on gold surfaces will be presented which are achieved by use of a vacuum optics bench only [1].

[1] A. Schlapka, U. Käsberger, D. Menzel, and P. Jakob, Surface Science 502-503 (2002) 129-135.

CALIBRATION EFFORT FOR PLS AND CLS-MODELS FOR IR-SPECTROSCOPIC ANALYSIS OF DIALYSATES OBTAINED BY CONTINUOUS MICRO-DIALYSIS OF SUBCUTANEOUS ADIPOSE TISSUE

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For clinical research, in-vivo blood glucose monitoring is an ongoing important topic to improve glycemic control in patients with non-adequate blood glucose regulation. In particular, for critically ill patients the intensive insulin therapy treatment is advantageous as established for diabetic patients. Continued interest is in infrared spectroscopic techniques for glucose monitoring. Its application has been reported for glucose determination in whole blood, serum and dialysates using transmission or ATR techniques with liquid or dried down samples. However, the development of an automated, micro-fluidics coupled infrared system for continuous long-term monitoring of glucose using a subcutaneous microdialysis probe is a new application.

A bed-side device with an FTIR-mini-spectrometer, coupled to a micro-dialysis probe and a fluidic system for intermittent sample transport to a micro-cell for transmission spectroscopy was developed for continuous glucose monitoring.[1, 2] Measurements on several healthy and diabetic test persons were carried out with experiments lasting up to 8 hours. Multivariate calibration is required for glucose quantification due to the complex composition of dialysates obtained from interstitial body fluids. In addition to glucose, other components identified in the interstitial fluid include bicarbonate, lactate, urea, acetate and phosphate.

The on-line measured spectra were evaluated by partial least-squares (PLS) calibration models for prediction of the glucose concentration values or using the classical least squares (CLS) approach, which allows the simultaneous determination of multi-components. For optimal PLS-quantification of glucose, spectral data from 1180 – 950 cm^{-1} were used without previous spectral processing. For the CLS-approach, spectral data from 1500 – 1000 cm^{-1} were used. All dialysate components were included for spectral fitting, but further refinement was required due to the spectral variance arising from temperature and pH dependency of the dialysate compound spectra. For analysing these effects, principle component analysis (PCA) was employed, providing factor spectra for improving the calibration reference spectra set and leading to robust calibration models. Using PLS-models, the interstitial glucose concentration was determined with a standard error of prediction (SEP) of 0.16 mM. Alternatively, the optimal CLS calibration model yielded an SEP of 0.18 mM. However, the CLS-advantage is the reduced calibration effort with the option for a multi-component quantification.

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[1] H.M. Heise, U. Damm, O. Vogt, V.R. Kondepati, Vib. Spectrosc, in press (2006).
[2] H.M. Heise, U. Damm, V.R. Kondepati, Proc. SPIE. 6093 (2006) 21.

SURFACE-ENHANCED VIBRATIONAL STUDY OF FLAVONOIDS OF INTEREST FOR THE CULTURAL HERITAGE

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Paintings and textiles represent an essential part of Cultural Heritage having an important artistic and historical significance. The analysis of organic molecules employed as pigments or dyes is crucial to carry out studies on their conservation. Artworks are in general very complex objects and the organic pigments are often present only in very small quantities, thus, their study is difficult and a large effort has been devoted to find analytical non-destructive method to allow the *in situ* study of art objects without their destruction.

Vibrational spectroscopy (Raman and infrared (IR) spectroscopy) is a very useful tool for specific identification of molecules with very good spatial resolution. In particular the Surface-enhanced Raman spectroscopy (SERS) technique represented a remarkable improvement in the detection. These pigments are in many cases highly fluorescent, display a relative small Raman cross-section and are practically insoluble in water. All these facts make more difficult their study by normal Raman. SERS technique implies the use of nanostructured Ag or Au surfaces to enhance both the incident and scattered light resulting from the studied molecules.

In this work we present preliminary results derived from the application of SERS and Surface-enhanced Infrared spectroscopy (SEIR) to the flavonoids quercetin, luteolin, apigenin and kaempferol. This is the first time that surface-enhanced vibrational techniques are applied in the study of these compounds. Flavonoids are organic colouring materials known since the antiquity which have been used traditionally to prepare artist's pigments and textiles dyes. These compounds also have important biological activity. A previous assignation of Raman and IR vibrational spectra of flavonoids was made on the basis of the different position of the –OH groups existing in these molecules. SERS spectra of flavonoids display many differences when compared to normal Raman of solid and solution suggesting that these molecules undergo a clear chemical change upon adsorption on the metal surface. We have found that the chemical degradation depends on the flavonoid structure and it can also be modulated by changing the pH. The laser irradiation line employed as excitation also seems to have an influence in the pigment degradation on the metal surface.

Acknowledgements: This research project has been supported by a Marie Curie Early Stage Research Training Fellowship of the European Community's Sixth Framework Programme under contract number MEST-CT-2004-513915. Authors also acknowledge grant FIS2004-00108 from *Dirección General de Investigación, Ministerio de Educación y Ciencia* (Spain) and *Comunidad Autonoma de Madrid* project number GR/MAT/0439/2004 for financial support. This work also received support from the *Red Temática del Patrimonio Histórico* (C.S.I.C.).

ATMOSPHERIC TRACE GAS AND δ^{13}C-CO_2 ANALYSIS BY FTIR SPECTROSCOPY

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Fourier Transform Infrared (FTIR) spectroscopy is a powerful technique, widely used for gas analysis in both laboratory and field studies. Due to its high methodological flexibility applications are widespread from real-time measurement of industrial processes to environmental monitoring of trace gases [1, 2]. The quality of the analytical result, however, is strongly dependent on task-specific optimization of the system which includes hardware configuration, quantification algorithm and calibration strategies.

Here we present a newly developed method based on a portable, commercially available, 0.5 cm^{-1} resolution FTIR spectrometer which allows simultaneous on-line analysis of most important atmospheric trace gases (CO_2, CH_4, N_2O, CO) as well as the $^{13}C/^{12}C$ isotopic ratio of ambient CO_2 ($\delta^{13}C$ - CO_2). The optimized instrumental setup yields high temperature and pressure stability and an exceedingly good spectral signal to noise ratio.

With this novel FTIR method a precision of 0.06-0.10 ‰ for CO_2, CH_4, N_2O and 0.19 ‰ for CO was obtained, which is competitive with accepted single-component trace gas measurement techniques. For $\delta^{13}C$ - CO_2 we designed a calibration procedure that is distinctly different from the concepts published so far [3], using a set of multicomponent standards that were prepared from CO_2 emission sources with characteristic isotopic composition and quantified by Isotope Ratio Mass Spectrometry (IRMS). For the quantification with an optimized non-linear partial least square (PLS) algorithm we obtained a precision of 0.2‰. Further validation was performed in various laboratory and field studies using well established methods such as GC-FID/ECD, laser spectroscopy and IRMS.

[1] J. Mohn, U. Beck, K. Zeyer and L. Emmenegger, J. Mol. Struct. 744 (2005) 247.
[2] J. Mohn, A.M. Forss, S. Bruhlmann, K. Zeyer, R. Luscher, L. Emmenegger, P. Novak and N. Heeb, Int. J. Environ. Pollut. 22 (2004) 342.
[3] M.B. Esler, D.W.T. Griffith, S.R. Wilson and L.P. Steele, Anal. Chem., 72 (2000) 216.

ISOMERS OF CYANODIACETYLENE: PREDICTIONS FOR THE ROTATIONAL, INFRARED AND RAMAN SPECTROSCOPY

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Following a preliminary DFT study, and the selection of seven most stable isomeric species of the C_5HN stoichiometry, further CCSD(T), MP4 and B3LYP calculations on these molecules yielded the:

- energies and structures,
- equilibrium electric dipole moments,
- fundamental frequencies (also for ^{2}H- and ^{15}N- isotopomeres),
- infrared absorption intensities,
- Raman scattering activities,
- vibration-rotation coupling constants,
- rotational constants.

Cyanodiacetylene (cyanobutadiyne; H-CC-CC-CN) is one of the key astrochemical molecules, first detected 30 years ago, in clouds of interstellar matter [1]. An efficient laboratory synthesis of this species has recently been reported [2]. Present predictions should be helpful in the interpretation of laboratory experiments and of astronomical observations, the former including ongoing studies on the photochemistry of low temperature matrix-isolated cyanodiacetylene.

[1] L.W. Avery, N.W. Broten, J.M. MacLeod, T. Oka, and H.W. Kroto, Astrophys. J. Lett., 205 (1976) 173
[2] Y. Trolez, J.-C. Guillemin, Angew. Chem. Int. Ed. 44 (2005) 2

SPECTROSCOPY OF FULLEROPYRROLIDINES: EXPERIMENTAL AND DFT STUDY OF ELECTRONIC AND VIBRATIONAL SPECTRA

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The majority of fullerene-based photovoltaic, photosynthetic and photoelectronic device prototypes have common structure: fullerene is covalently linked to a donor unit through a pyrrolidine bridge. Spectroscopy of such compounds is a very interesting and challenging scope of an inquiry. Absorption and fluorescence spectra of fullerene and their derivatives in the visible range exhibit complex vibrational structure. At the best of our knowledge no attempts were made to study vibronic structure of C_{60} derivatives. In Raman and infrared spectra of fulleropyrrolidines, both pyrrolidine and fullerene lines should be observed, the latter revealing much more features then pristine fullerene because of the I_h symmetry disturbance.

In this work we present the complex spectroscopic study of N-methyl fulleropyrrolidine (C_{60}-NMP) as a model compound for explanation of spectroscopic features of C_{60} dyads and employ our method to a couple of substituted fulleropyrrolidines. Low-temperature (2 K) electronic spectra of C_{60}-NMP are studied and vibronic structure is analyzed by means of DFT and TD-DFT calculations. The spectral pattern is adequately described in terms of Franck-Condon mechanism.

To analyze ground state vibrational spectra, we employed scaled DFT force fields. Raman and infrared spectra of the studied compounds were interpreted in terms of C_{60} and NMP normal modes and detailed vibrational assignments were proposed. In particular, splitting and appearance of originally forbidden fullerene modes, mixing of C_{60} and NMP vibrations, and changes in the vibrational modes of pyrrolidine-bridged functional substituents are discussed.

VIBRATIONAL SPECTRA AND STRUCTURE OF NO-H_2O, NO-HDO AND NO-D_2O COMPLEXES. AN IR MATRIX ISOLATION AND DFT STUDY.

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The infrared spectra of H_2O + NO isolated in solid neon at low temperature have been investigated. The H_2O + NO system is remarkable due to its propensity to form NO-H_2O, $(NO)_2$-H_2O, NO-$(H_2O)_2$ and NO-$(H_2O)_n$, and IR spectroscopy reveals a variety of phenomena far from being fully understood. We will focus here on the NO-H_2O and NO-$(H_2O)_2$ species.

Low concentration studies (0.01 % - 0.2%) and subsequent annealing leads to the formation of one NO-H_2O complex in which NO is weakly bonded to H_2O. All Vibrational modes of this complex have been detected. In addition, spectra of D_2O + NO and HDO + NO have also been recorded. A detailed vibrational analysis of deuterated species shows that two species NO-$D_2O(\alpha)$ and NO-$D_2O(\beta)$ have been observed. One species NO-$D_2O(\alpha)$ is similar to the observed NO-H_2O and another species NO-$D_2O(\beta)$, which structure has been predicted by DFT calculations, where the water deuterium and the NO nitrogen are weakly bonded. The NO-$H_2O(\alpha)$ and NO-$D_2O(\alpha)$ potential surface was explored systematically at the B3LYP level but no stable species reproducing the experimental data could be found. This shows that the structure of the observed NO-$H_2O(\alpha)$ and NO-$D_2O(\alpha)$ species results from columbic attractions between the water and NO and is stabilized only in neon matrix.

CYCLOPROPYLBENZENE: A REMPI STUDY OF THE $S_1 \leftarrow S_0$ TRANSITION

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The $S_1 \leftarrow S_0$ transition of cyclopropylbenzene (CPBZ) was studied in a supersonic jet by resonance enhanced multiphoton ionization, one-photon and two-photon spectra. Vibrational analysis-assignments are presented and the comparison of these two spectra with the analogous spectra of other benzene derivatives shows that only one conformer is present. This result is in agreement with all previous experimental investigations (NMR, microwave spectroscopy, gas-phase electron diffraction). Ab initio calculations[1] HF, MP2 and B3LYP, indicate that the internal rotation barrier, separating the bisected conformer (most stable) from the perpendicular one, is less than 1 kcal mol^{-1}. The REMPI spectra are mass-resolved and show that trans-β-methylstyrene is an impurity in the commercially available sample of CPBZ.

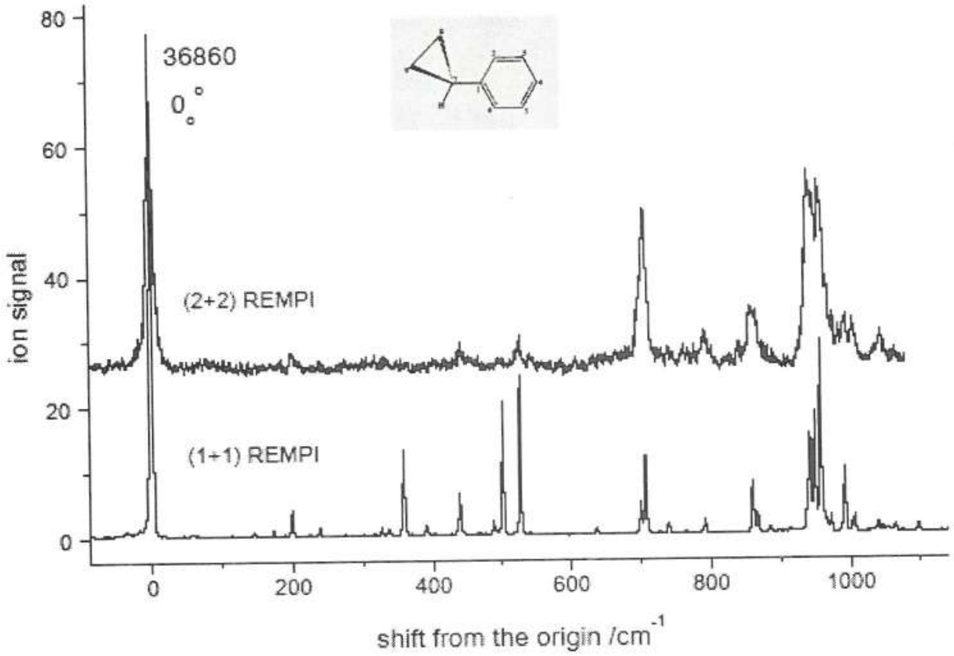

Fig. 1: Two-photon and one-photon spectra of the $S_1 \leftarrow S_0$ transition of cyclopropylbenzene

[1] Q. Shen, C. Wells, M. Traetteberg, R.K. Bohn, A. Willis and J. Knee, J. Org. Chem. 66 (2001) 5840.

FTIR AND COMPUTATIONAL STUDIES OF PURE AND WATER CONTAINING SO3 SPECIES IN SOLID ARGON MATRICES

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The FT infrared spectrum in the 4000 - 400 cm^{-1} range of SO_3 vapors, matrix isolated in argon and in water doped argon solid layers, is reported. Vibrational bands are assigned to pure SO_3 monomeric and polymeric species and to $SO_3 \cdots H_2O$ complexes, on the basis of theoretical B3LYP and MP2 calculations employing the aug-cc-pVTZ basis sets. The spectroscopic evidence suggests that in addition to monomer, both the dimeric and the cyclic trimeric $(SO_3)_n$ complexes are only present in the matrix. The spectra also indicates the presence of the 1:1 and the 1:2 $SO_3 \cdot\cdot H_2O$ complexes as well as both H_2SO_4 and $H_2S_2O_7$, but no evidence for a stable 2:1 $SO_3 \cdot\cdot H_2O$ complex was found. The occurrence of the various species is discussed in the light of their calculated energies.

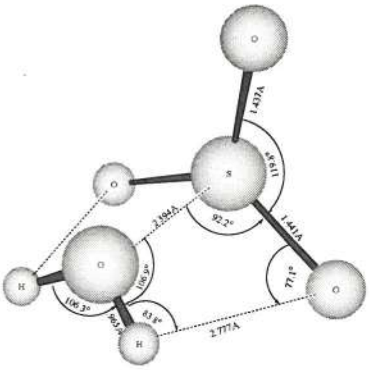

Figure 1: Caculated structure of the 1: 1 SO_3*H_2O complex.

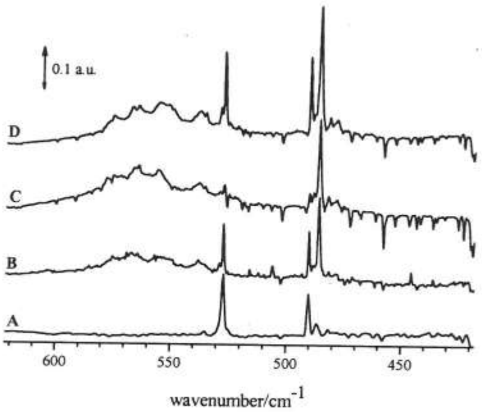

Figure 2: Water fraction and annealing effects on the SO_3 spectrum in Ar/H_2O matrices.

A. No water in the sample, as deposited at 17 K.
B. Argon:H_2O=300:1, as deposited at 17 K.
C. Argon:H_2O=150:1, as deposited at 17 K.
D. Layer C temperature cycled to 35 K

IR SPECTRUM OF THE ETHYL CATION ($C_2H_5^+$): NONCLASSICAL VERSUS CLASSICAL STRUCTURE

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The competition between classical and nonclassical geometries is a fundamental issue for carbocations. The ethyl cation ($C_2H_5^+$, protonated ethene) represents the most simple example for protonation of a C=C double bond. Calculations predict the nonclassical structure to be slightly more stable than the classical structure (see Fig. 1). However, experimental evidence for this conclusion is still lacking.

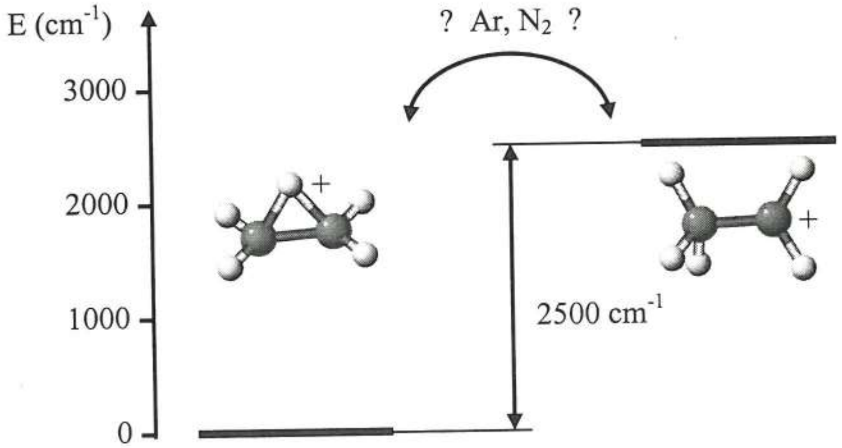

Fig. 1: Relative stability of the classical versus the nonclassical structure of $C_2H_5^+$

The present work reports IR photodissociation spectra[1] of size-selected clusters of the ethyl cation with Ar and N_2. The IR spectra recorded in the CH stretching range provide detailed information on the degree of delocalization of the excess proton between the two C atoms. Significantly, the position of the additional proton is strongly influenced by the microsolvation environment. Whereas Ar is a negligible perturber, leaving $C_2H_5^+$ in the most stable nonclassical geometry, the stronger interaction with N_2 induces a switch from a nonclassical to a classical $C_2H_5^+$ ion core (Fig. 2). The latter ligand appears to form a weak covalent bond to one C atom of the ethyl cation. The interpretation of the IR spectra is supported by rotational line profile simulations and ab initio calculations.

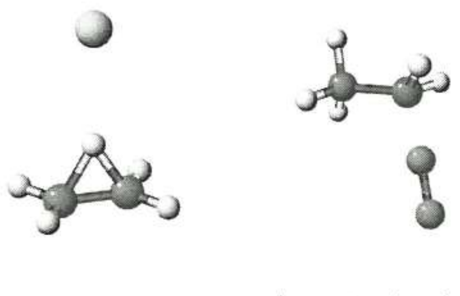

Fig. 2: Most stable isomers of $C_2H_5^+$-Ar and $C_2H_5^+$-N_2 obtained at the MP2/6-311G(2df,2pd) level

[1] O. Dopfer, Int. Rev. Phys. Chem. 22, 437 (2003).

QUANTIFICATION OF THE *PUSH-PULL EFFECT* IN TOLANES – ALSO A RE-EVALUATION OF FACTORS AFFECTING THE ^{13}C CHEMICAL SHIFTS OF CARBON ATOMS OF THE C≡C TRIPLE BOND

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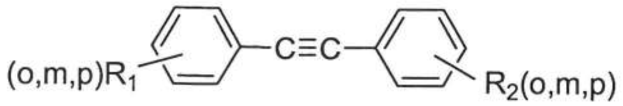
For the first time, the presence of the *push–pull effect* in disubstituted acetylenes (tolanes 1) was studied. The successful correlation of the occupation quotient π*/π of the π-orbital of the C≡C triple bond in resonance with the substituted phenyl moieties of tolanes vs. the bond length of the C≡C triple bond proves this effect, well studied for push-pull ethylenes,[1,2] to be also active in this kind of compounds.



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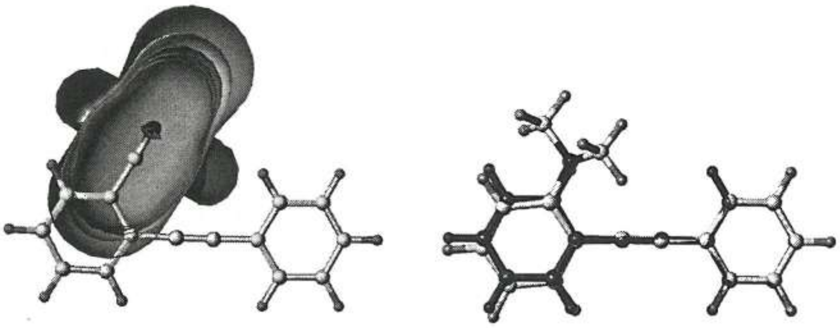
In addition, the influences of *ortho* phenyl ring substituents on the ^{13}C chemical shifts of the triple bond carbon atoms, which were estimated by Rubin et al.[3] to be "inapplicable for describing triple bond polarization", were re-evaluated leading to the conclusion that whilst anisotropic effects of *ortho* substituents are negligible, the steric *ortho-substituent effects* do in fact dominate the deviations obtained. A detailed theoretical ab initio MO/NBO/NCS study has been employed to illuminate the facts of this case.



$\Delta\delta(^{13}C_\alpha\equiv^{13}C_\beta)$: anisotropy effect negligible *but* steric hindrance relevant

(1) Kleinpeter, E.; Klod, S.; Rudorf, W.-D. *J. Org. Chem.* **2004**, *69*, 4317.
(2) Kleinpeter, E.; Schulenburg. A. *Tetrahedron Lett.* **2005**, *46*, 5995.
(3) Rubin, M.; Trofimov, A.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*, 10243.

HIGH-RESOLUTION INFRARED AND THEORETICAL STUDIES OF 5-MEMBERED RING HETEROCYCLES

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This Paper brings together the results of both Fourier transform gas-phase IR spectrum of the title compounds, generally recorded with a resolution of ca. 0.0030 cm^{-1} in the region 600–1400 cm^{-1}, and compares with the results with *ab initio* and density functional theoretical (DFT) values for the anharmonic frequencies. The experimental data for the series of C_{2V} and C_S symmetry molecules have been analysed using the Watson model, and the series of harmonic and anharmonic frequencies, and derived vibrational energy surfaces determined. Both ground and upper state rotational and quartic centrifugal distortion spectroscopic constants have been derived experimentally. Rotation constants (RC), harmonic and anharmonic frequencies, and vibration-rotation constants (alphas, $\alpha_{v}^{A,B,C}$) have been predicted theoretically using a cc-pVTZ basis and both MP2 and B3LYP levels of methodology. The MP2 values for the RC are often marginally closer to the experimental values, while the B3LYP frequencies and alphas are generally closer to experiment. The values for Δ_J, Δ_K, δJ and δK are close to experiment by both MP2 and B3LYP methods.

The examples chosen are isoxazole, oxazole, isothiazole, 1,2,5-oxadiazole, 1,2,5-thiadiazole and 1,2,5-selenadiazole. In the last case, both the isotopologues $C_2H_2N_2{}^{80}Se$ and $C_2H_2N_2{}^{78}Se$ were analysed by experimental IR spectroscopy and the theoretical methods.

AB INITIO STUDIES ON CONFORMATION, VIBRATIONAL AND ELECTRONIC SPECTRA OF 3-SUBSTITUTED METHYL-2-PROPENOATES

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Rotational isomerism in methyl propenoate derivatives (X-CH=CH-COOH; X=Cl, Br) and their properties in the ground (S_0) and first excited (S_1) electronic states have been studied by spectroscopic and quantum chemical techniques such as Density Functional Theory (DFT) with B3LYP functionals and RHF using extended basis sets like 6-31G** and 6-311+G**. In RHF calculations, electron correctional effects have been included at the Moller-Plesset MP2 level. As the E-isomer of methyl propenoate derivatives has been found to be more stable than the Z-isomer, the calculations have been limited to the E-isomer. The molecules were treated as a two rotor systems in which rotation about C-C and C-O bonds may give rise to rotational isomerism, with an additional possibility of hindered rotation of the methyl group about C-O bond. Four possible conformers Cc, Tc, Cc, Tc have been identified. Conformations in which the carbonyl and methoxy groups are in *cis* position are the most stable with the methyl group having staggered conformation relative to the carbonyl group. Plot of potential energy curves for rotation about C-C bond in the S_0 and S_1 states shows two energy minima corresponding to the s-*cis* and s-*trans* orientations of the ethylenic and carbonyl groups. While, in the ground state, the Cc conformer, in which the C=C and C=O bonds are in s-*cis* position, is more stable than the Tc, their relative stabilities get reversed in the first excited (S_1) state. Fully optimized geometries of the two stable conformers in the S_0 and S_1 states are being reported by RHF/ 6-31G** and RHF/6-311+G** basis sets. Based on suitably scaled RHF/6-31G** and DFT/6-311G** calculations, assignments have been provided to the fundamental vibrational bands of both the Cc and Tc conformers in terms of frequency, form and intensity of vibrations and potential energy distribution across the symmetry coordinates in the S_0 state. A complete interpretation of the electronic spectra of Cc and Tc conformers of methyl propenoate derivatives (X-CH=CH-COOH; X=Cl, Br) in terms of nature, energy and intensity of electronic transitions has been provided on the basis of time-dependent density functional theory (TDDFT) using BLYP functionals and 6-31G basis set.

RAMAN SPECTROSCOPIC IMAGING: OPTIMISATION OF COLLECTION SPEED AND SPATIAL RESOLUTION WITH RESPECT TO INFORMATION CONTENT.

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Raman Microspectroscopy enables to analyze materials with a high spatial resolution which is observed to be higher than a micrometer at the surface (x,y) of the sample. In addition, the confocal configuration is an optical design which enables to reach a high axial discrimination in the z direction, achieving a resolution better than 2μm at the top surface.

However, for increased spatial resolution mappings, the acquisition speed can become an issue. There are many key parameters in the sampling method, hardware and software configurations that can affect the speed of data collection. Various options will be considered to reduce the overall mapping time without compromising the information content.

Examples will be provided in the field of pharmaceuticals applications. In this domain, the acquisition speed must often be balanced with the need for highly informative spectra on one hand and accurate maps on the other hand, giving an insight into the homogeneity of the active ingredients distribution.

The possibility of mapping a sample at the submicron scale by UV Raman spectroscopy creates a great interest for observing very small patterns. Semiconductor applications provide a wide panel of examples. The influence of the XY automated stage's accuracy on the contrast and quality of Raman images will be discussed.

The recent coupling of Atomic Force Microscopy (AFM) with Raman Spectroscopy will also be mentioned. This set-up opens new possibilities to further enhance spatial resolution, aiming at a resolution of about 100nm and below by implementing Near Field Optical Microscoy (NSOM) and tip-enhanced Raman scattering (TERS).

SORPTION OF CATIONS ONTO SURFACES OF OXIDES: IR STUDIES IN THE OH VIBRATION REGION

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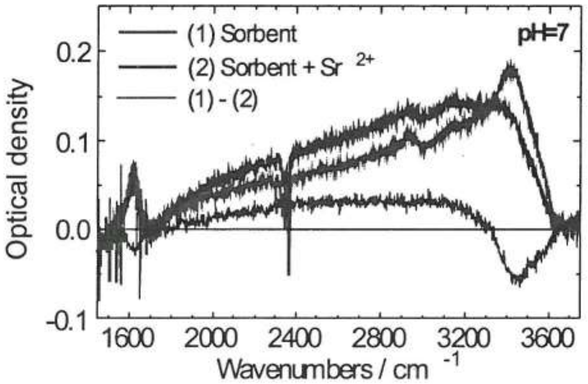
Studies of sorption of organic molecules and complex inorganic anions are well established fields of vibrational spectroscopy. However, much less is known about the spectroscopic response to sorption of the simplest, spherical cations onto the surface of oxide adsorbents. Since spherical cations do not have vibrational degrees of freedom, their sorption could be discerned by means of specific changes in the region of the stretching and bending vibrations of the OH bonds of water molecules and the OH groups of the surface of a sorbent. Such changes may reflect (i) reactions where OH of the surface of a sorbent S disappear and water molecules are formed,

$$S\cdots O{-}H + M^{n+} + OH^{-} = S\cdots O{-}M^{(n-1)+} + H_2O,$$

and (ii) variations in the number of water molecules present at the surface due to adsorption/desorption of hydrated cations. Surprisingly, such effects are out of the field of vision of spectroscopists, and the first studies of hydration of surfaces have been performed very recently by means of the so-called vibrational sum frequency spectroscopy (see, e.g., Ref. 1).

In this presentation we demonstrate potentialities of common IR spectroscopy in the studies of sorption of various cations onto the surface of oxides. As an example, in Fig. 1 we demonstrate spectroscopic data regarding sorption of the Sr^{2+} cations onto a mixed TiO_2-MnO_2 oxide at pH=7 revealing a decrease of the OH groups of the surface and an increase of the amount of surface water brought with the hydrated cations.



[1] S. Kataoka, M. C. Gurau, F. Albertorio, M. A. Holden, S.-M. Lim, R. D. Yang, and P. S. Cremer, *Langmuir* **20** (2004) 1662.

FT-RAMAN SPECTRAL MAPPING: DETECTION AND ASSESSMENT OF THIN ORGANIC LAYERS ON METAL SUBSTRATE

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Surface enhanced Raman scattering (SERS) spectroscopy is an optimal method for analysis of thin organic films attached to SERS-active metal surfaces (gold, silver etc.).

The most important goal of this work is to assess the homogeneity of both organic monolayers and consequently multilayers formed by specific molecular interactions or covalent bonds. However, measured Raman signal is influenced by both the homogeneity of deposited layer and the factor of surface enhancement. Therefore, to elucidate the information on layer homogeneity from spectral mapping of sample, a uniform and repeatable surface enhancement is a prerequisite, i.e. the homogeneity of metal surface properties (distribution of active sites, morphology and thickness of metal layer).

Recently, we have reported electrochemically prepared SERS-active surface[1]. In this study we optimized preparation procedure (i.e. potentials, current densities and current sequences used) to obtain similar enhancement factor in wide surface area. We obtained surface that have suitable surface morphology with uniform microstructure and that is almost homogeneous from macroscopic point of view. Surface morphology was viewed by scanning electron microscopy.

For reliable description of sample layers, measured Raman signal was processed and evaluated by various mathematical methods (both commonly used and developed ones). Specific types of finite impulse response filtration were performed for filtration of spectral interferences. Principal component analysis and cluster analysis were used for transformation of data to obtain hidden spectral information. Various mapping techniques were then used for visualization. Results obtained from electrochemically prepared surface were compared with results measured on commercially available SERS-active surface with systematically designed regular nanometer scale patterning.

Spectroscopic experiments were performed on FT-Raman spectrometer with FT-Raman mapping stage accessory (Bruker Optics). An appropriate sample holder of metal targets was designed and used.

Financial support of Ministry of Education, Youth and Sports of the Czech Republic (grant MSM 6046137307) is gratefully acknowledged.

[1] Kamil Záruba, Pavel Matějka, Radko Volf, Karel Volka, Vladimír Král and Jonathan L. Sessler, *Langmuir* **18** (2002) 6896.

OB-13

IN SITU POLARIZATION MODULATION INFRARED REFLECTION ABSORPTION SPECTROSCIC AND ELECTROCHEMICAL STUDIES OF THE ELECTRIC FIELD DRIVEN TRANSFORMATIONS IN A PHOSPHOLIPID BILAYER

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Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM IRRAS) combined to electrochemical interface was employed to investigate structural rearrangements in phospholipid bilayers exposed to the electric field. The Langmuir-Blodgett vertical withdrawing and the Langmuir-Schaefer horizontal touch methods were used to form a DMPC bilayer on a Au(111) electrode surface. Phsopholioid bilayers were transferred in the liquid expanded (LE) and the liquid condensed (LC) states at the surface pressure of 9.3, 18.7, 28.0 and 42 mN m^{-1}. Electrochemical experiment has shown that the DMPC bilayer is adsorbed directly on the electrode surface at charges $-10 > \sigma_M > 5\ \mu C\ cm^{-2}$. At charges lower than $-10\ \mu C\ cm^{-2}$ and $E < -0.55$ V vs. Ag/AgCl the bilayer undergoes same rearrangements leading to its desorbtion from the electrode surface. In order to recognize the structure and the nature of rearrangements occurring in the thin organic layer on the electrode surface the spectroscopic techniques have to be employed jointly with electrochemistry. The IRRAS is a powerful tool to study the orientation of molecules in the thin organic film assembled at the interface. When the IRRAS is used to investigate organic films adsorbed at the electrode surface *in situ* one has to employ either a potential or photon polarization modulation technique to subtract the signal due to the solvent and to differentiate between the molecules adsorbed at the electrode surface from those present in the solution. The PM IRRAS is the technique, where a ratio of the difference between reflectivites for *s*- and *p*- polarized light $\left|R_s - R_p\right|$ divided by the average reflectivity signal $\left(R_s + R_p\right)/2$ are measured. R_s is used as a background to subtract absorbance by the solvent and solution species from R_p that carries the spectrum of molecules adsorbed at the electrode surface.

The PM IRRA spectra in the stretching region of hydrophobic hydrocarbon chains and of the polar head group were collected in the adsorption-desoprtion process of the DMPC bilayer. The electric field driven adsorption of the DMPC bilayer is related to two simultaneous processes: the hydration of the polar head group and the structural rearrangements involving whole lipid molecule. At the adsorption potential the tilt of the hydrophobic hydrocarbon chains with respect to the normal to the electrode is largest and close to 27°. The position of the CH stretching bands confirms different physical states of DMPC bilayers transferred at low and high surface pressures. DMPC bilayers, both in liquid and gel phases adsorbed on the electrode surface are well hydrated and the ester C=O group arrange in the plane of the bilayer. The orientation and conformation of the polar head group (phosphate and choline) depends on the physical state of the lipid bilayer. The transition from the LE to the LC state is accompanied by the *trans* to *gauche* isomerization of the choline group. Desorption of the bilayer is connected with dehydration and simultaneous decrease of the tilt angle of chains to 17°.

FOXING STAINS ON OLD PAPER: ATR-FTIR SPECTROSCOPY AND LASER CLEANING

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There has been considerable recent interest in the problems of conservation and restoration of the cultural heritage, including old books, manuscripts, drawings, and prints. The main reason for the destruction of old paper lies in the oxidation of the paper materials, which leads to the paper yellowing and gives rise to foxing stains (yellowish or dark-brown spots). The nature of foxing stains is still debated in spite of an extensive study of the problem.

We employ an ATR-FTIR method to study and characterize the foxing stains and compare the spectra of foxing stains and normal paper. We demonstrate that the ATR-FTIR spectra of a conventional cotton paper, old paper (outside foxing stains), and foxing stains are different in the spectral intervals 1500-1800 cm^{-1} and 2800-3000 cm^{-1} (Fig. 1).

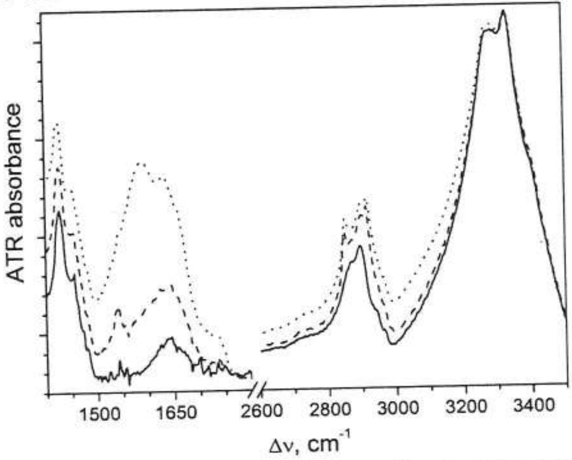

Fig. 1: ATR-FTIR spectra of (solid line) pure cotton paper, (dashed line) German map printed in 1846 (outside foxing stains), and (dotted line) dark-brown foxing stains on the map.

To clean the paper, we use the second (λ=532 nm) and third (λ=355 nm) harmonics of the Q-switched Nd:YAG laser radiation. The pulse duration and repetition rate are 5 ns and 10 Hz, respectively. The diameter of the laser spot on the sample is 5 mm and the laser power on the sample is varied. The most developed spectral changes related to the laser cleaning of paper were also observed in the spectral intervals 1500-1800 cm^{-1} and 2800-3000 cm^{-1}.

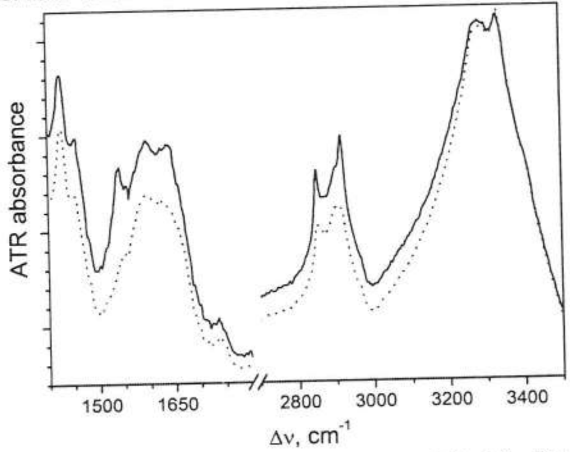

Fig. 2: ATR-FTIR spectra of foxing area on German map printed in 1846 (solid line) prior to and (dotted line) after 20-min laser cleaning at a wavelength of 532 nm, and a power of 3 W.

OB-15

MATRIX ISOLATION EXPERIMENTS AND ANHARMONIC VIBRATIONAL CALCULATIONS ON H_2O...CO AND ITS DEUTERATED ISOTOPOMERS

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Experimental low-temperature matrix isolation technique and anharmonic quantum chemical calculations are combined to study the vibrational properties of the H_2O...CO hydrogen-bonded complex and its deuterated isotopomers. This complex is an example of a relatively weakly bound hydrogen-bonded complex but which is easily prepared by *in situ* photolysis from formic acid. [1,2] Experimentally, many overtone and combination transitions of the hydrogen-bonded complex are observed. The assignment of the complex structures applies computational predictions of the transitions and their estimated vibrational shifts upon complexation. Up-to-now, only harmonic vibrational calculations have been used for this purpose.[3] Here, an anharmonic vibrational method (CC-VSCF [4,5]) is employed to describe the complex spectrum. The capability of the computational method to yield information beyond the harmonic approximation is demonstrated and its usefulness to support experimental assignment is highlighted.

References:

[1] J. Lundell M. Räsänen, J. Phys. Chem. 99 (1995) 14301.

E. M. S. Maçôas, L. Khriachtchev, M. Pettersson, J. Lundell, R. Fausto and M. Räsänen, Vib. Spectrosc. 34 (2004) 73.

[3] J. Lundell, J. Phys. Chem. 99 (1995) 14290.

[4] J.O. Jung and R. B. Gerber, J. Chem. Phys. 105 (1996) 10332; *ibid.* 105 (1996) 10682.

[5] G.M. Chaban, J.O. Jung and R.B. Gerber, J. Chem. Phys. 111 (1999) 1823.

IR SPECTRA AND MOLECULAR STATE OF H_3O^+ AND $H_5O_2^+$ HYDRONIUM IONS IN ORGANIC SOLUTIONS AND SOLID PHASE

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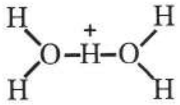
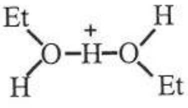
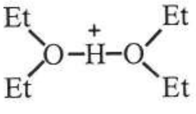
Until recently, the molecular states of the H_3O^+ and $H_5O_2^+$ cations in aprotic solvents have been studied using IR spectroscopy only under conditions of solvation by relatively basic oxygen-containing compounds such as crown ethers [1], tributyl phosphate (TBP) [2] or phosphine oxides [3]. This solvation stabilizes these hydronium ions and prevents their direct interaction with counterion. As a result, compounds of type $[H_3O^+\cdot 3X]$ (or $[H_3O^+\cdot 6X]$ in case of 18-crown-6) and $[H_5O_2^+\cdot 4X]$ are formed, where X = oxygen atom of the solvating molecule.

In this work we present the results of our IR spectroscopic investigation into the nature of mono- and di-hydrates of undecachloro-carborane acid, $H(CHB_{11}Cl_{11})$, the strongest known Lewis-free Brønsted acid [4]. These hydrates are soluble in weakly basic, aprotic solvents such as dichloromethane, benzene and dichloroethane (DCE) forming solvated ion pairs with symmetrical $[H_3O^+\cdot 3Solv]$ and $[H_5O_2^+\cdot 4Solv]$ cations that are very weakly influenced by the carborane anion. The structure of $[H_3O^+\cdot 3C_6H_6]$ cation with $CHB_{11}Cl_{11}^-$ counterion was determined by X-ray crystallography and has been shown, using IR spectroscopy, to be the same as that in benzene solution [5]. The O-H groups form π-bonds to benzene. The value of OH stretching vibrations of $[H_3O^+\cdot 3Solv]$ cation, where Solv = dichloromethane, benzene and DCE (~2900-3000 cm^{-1}), indicate on formation the strong H-bonds by H_3O^+ even with these weakly basic solvents.

The regular changes of the IR spectra of $[H_5O_2^+\cdot 4Solv]$ cation in solutions with increasing the basicity of the solvent in the row CH_2Cl_2, benzene, DCE, diethyl ether, TBP, phosphin-oxides are discussed. The low frequency shift of OH stretching vibrations of the peripheral OH groups of $H_5O_2^+$ cation, compared with those for the gas phase, are changed from ~170 cm^{-1} for CH_2Cl_2, to ~800 cm^{-1} for phosphinoxide. In contrast, the frequencies associated with the bridging proton vibrations of the OH^+O unit of the $H_5O_2^+$ cation (in the 800-1700 cm^{-1} range) are insignificantly changed, even when compared to the gas phase spectrum of bare $H_5O_2^+$. Moreover, when the four peripheral OH groups of $H_5O_2^+$ are progressively substituted by ethoxy groups in the ethanol and diethylether complexes:







the main features of vibration spectra of OH^+O group are retained. This indicates a high stability of the IR spectral fingerprint of the central OH^+O unit in proton disolvates $L\text{-}H^+\text{-}L$.

The experimental results are compared with quantum chemical simulations of IR spectra of $H_5O_2^+$ cation.

[1] E.S. Stoyanov, C.A. Reed. J. Phys. Chem. A 108 (2004) 907.
[2] E.S. Stoyanov, J. Chem. Soc. Faraday Trans., 93 (1997) 4165.
[3] E.S. Stoyanov, I.V. Smirnov. J. Mol. Struct., 740 (2005) 9.
[4] M. Juhasz, S. Hoffmann, E. Stoyanov, K. Kim, C.A. Reed. Angew. Chem. Int. Ed. 43 (2004) 5352.
[5] E.S. Stoyanov, S.P. Hoffman, K.C. Kim, F.S. Tham, C.A. Reed. J. Amer. Chem. Soc. 127 (2005) 7664.

EMPIRICAL CORRELATIONS OF SPECTROSCOPIC, THERMODYNAMIC AND STRUCTURAL PARAMETERS OF HYDROGEN BONDING

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The changes in IR spectra- the intensification, the red shift of the stretching (ν_1) and the blue shift of out of plane (ν_4) AH vibrational modes were previously correlated with experimentally measured enthalpies of the reaction of hydrogen bond AH•••B (HB)formation, mainly for binary H-complexes in solutions [A.V. Iogansen. Spectrochimica Acta, A55 (1999) 1585]. The availability of neutron scattering structures in HB crystals provides a way for correlation of these spectral parameters of HB with the H•••B length. The broad correlation of the red shift ($\Delta\nu$ = 20-2500 cm^{-1}) of the ν_1 proton mode with H•••B distance ($r_{H\cdots B}$= 0.30-0.12 nm) is established as $\Delta\nu \propto r^{-6}$; it includes now more than hundred HB of different AH-groups, including from complex HB networks of biological interest[1-3]. The combination of this correlation with those mentioned above for solutions leads to the general empirical correlation of the enthalpy - energy ($-\Delta H \equiv D$) with r(H•••B) as $D \propto r^{-3}$, which is confirmed with independent experimental data for binary gas phase HB complexes.

[1] M. Rozenberg, A. Loewenschuss, Y. Marcus, PCCP, 2 (2000) 2699-2702.
[2] M Rozenberg, C.Jung, G. Shoham, PCCP, 5 (2003) 1533-1535.
[3] M. Rozenberg, G.Shoham, I.Reva, R. Fausto, PCCP, 7 (2005) 2376 – 2383.

POSTERS

FLUORESCENCE SPECTROSCOPY TECHNIQUE TO INVESTIGATE THE BINDING PROCESS IN IMPRINTED GELS

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In the last 20 years many theoretical and experimental researches have been done on the imprinted gels which can do molecular recognition.[1-3] One of the main problems in the recognition process is to understand that the target molecule was captured by the host or not. Mainly spectroscopic methods, especially absorption measurements, have been used so far to monitor this process by measuring the total concentration of the target molecules diffused into the gel.[2] But extraction of information about the target molecules were captured by the hosts or not is not possible from these measurements. In our study we used Pyrenetetrasulfonic acid tetra sodium salt (P4) molecules as target molecules and methacrylamidopropyl trimethylammonium (MAPTAC) as host molecules synthesized in thermo sensitive gel NIPA. The P4 molecule has 4 SO_3^- group around it and is bound by the 4 positive MAPTAC molecules by coulombic interactions. We observed that the maxima of the peaks in the fluorescence spectra of the P4 shift as the number of the bound sites increase (Fig.1). This shift is towards blue and red for the releasing and the capturing processes, respectively. As a conclude we propose that the fluorescence spectroscopy technique can be used to investigate the capturing and releasing processes.

[1] Nicholas A. Peppas and Yanbin Huang, *Pharmaceutical Research,* Vol. 19, No. 5, (2002)
[2] Guney O, Yılmaz Y and Pekcan O, Sensors and Actuators B Vol. 85, pp. 86-89 (2002)
[3] Taro Oya, Takashi Enoki, Alexander Yu. Grosberg, Satoru Masamune, Yukikazu Takeoka, Kazunori Tanaka, Guogiang Wang, Yaşar Yılmaz, Toyoichi Tanaka, Science, Vol. 286, Iss. 5444, pp. 1543-1545 (1999).

VIBRATIONAL SPECTROSCOPY STUDY OF THE OXIDATION OF DIFFERENTLY STERILISED UHMWPE EXPLANTED ACETABULAR CUPS

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Ultra high molecular weight polyethylene (UHMWPE) is used from more than 40 years as acetabular cup in total hip joint prosthesis. In order to improve the longevity of the implants, in 1991 Hylamer™ was patented and marketed by the DePuy-DuPont Orthopaedics joint venture. Hylamer™ is a hot isostatically pressed material with high crystallinity (65-71%) and density. Despite the good pre-clinical results, since 1996 some Authors have shown early loosening[1] due to extensive oxidation[2] and phase transformation[3]. In order to analyze the reasons of the high tendency to oxidation of this type of cups, we have examined differently γ- sterilised (air and N_2) explanted acetabular cups at different distances from the surface using FT-IR spectroscopy. The oxidation is reported as oxidation index (OI), calculated from the ratio between the area of the carbonyl peak (1670-1850 cm^{-1}) and the area of the reference peak (1327-1394 cm^{-1}).

The results obtained indicate that the air-sterilised acetabular cups are more oxidated than the N_2 ones. The oxidation of the N_2-sterilised cups is only due to the in vivo environment (presence of the typical esther band at 1738 cm^{-1}) while the oxidation of the air-sterilised cups is due both to the environment and the γ rays (presence of the cheton band at 1717 cm^{-1}). In the more oxidated sections of the air-sterilised cups we have observed a PE delamination. Moreover, a correlation between OI and crystallinity of the cups (calculated by differential scanning calorimetric measurements) can be observed (see Fig. 1).

Our results show how sterilization method can change the PE properties. In particular, the cups sterilized in air demonstrated a severe oxidation caused by both sterilization and *in vivo* permanence. Oxidation has been associated to a great crystallinity increase together with a deterioration of the material properties.

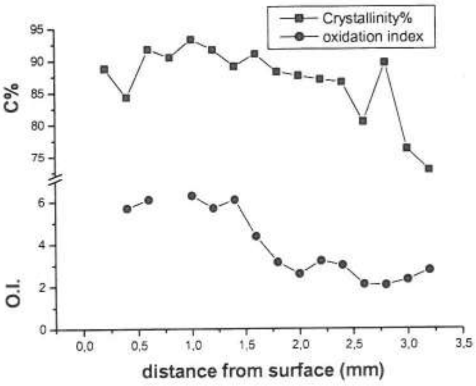

Fig. 1: Comparison between crystallinity% (■) and O.I (•) of the air sterilised cups

[1] M.J. Chmell, R. Poss, W.H. Thomas, C.B. Sledge, J. Arthroplasty, 11 (1996) 351.
[2] A. Wang, A. Essner, V.K. Polineni, C. Stark, J.H. Dumbleton, Tribo. In., 31 (1998) 17.
[3] M. Reggiani, A. Tinti, P. Taddei, M. Visentin, S. Stea, M. De Clerico, C. Fagnano, J. Mol. Struct. 785 (2006) 98.

DETERMINATION OF ENANTIOMERIC PURITY BY NMR SPECTROSCOPY

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Enantiomeric purity is a characteristic physical feature for the chirality of natural compounds. NMR spectroscopy and chromatography are the main methods for the determination of enantiomeric purity. In this study the enantiomeric purity of hydroxy methyl esters with different chain lengths and hydroxy positions is determined by ^{1}H-NMR-shift studies.

Chiral hydroxy esters are the main constituents of lipids and brain cerebrosides and essential biological molecules as well as intermediates for organic synthesis. Hydroxy aliphatic acids possess at least one stereogenic carbon atom and this chiral center gives the molecule a biological activity. The biological activity of the enantiomers is symbolized as *R* and *S* enantiomers. *R* enantiomer is found to be useful in nature, on the other hand S enantiomer can be harmful and same applies in the opposite manner as well. Therefore, the control of the enantiomeric excess (%ee) is very important, especially in medicine and food industries.

In this work, monohydroxy methyl esters carrying the hydroxy group at the ends and at the middle of the chain were synthesized as their *R* and *S* enantiomers. Their enantiomeric excesses (ee %) were determined by NMR with shift reagent Eu(tfc)$_3$.

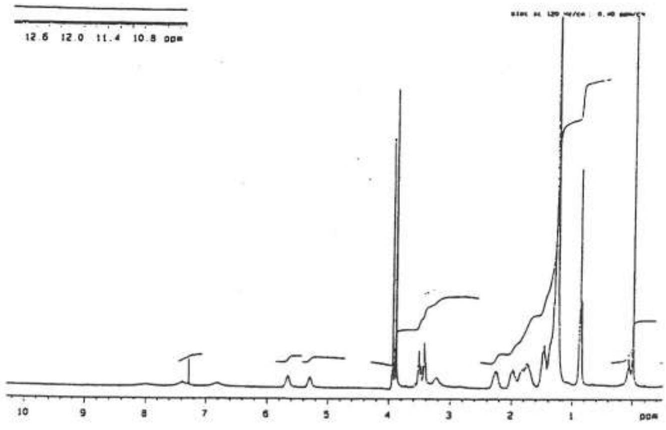

Fig. 1: H-NMR-shift spectra

^{1}H-NMR spectra analysis showed similar results for all samples. *R* and *S* enantiomers were distinguishable by the –OCH$_3$ signals. The difference of the methoxy signals of the *R* and *S* enantiomers was 15 MHz for the hydroxy position at the beginning and at the end of the chain lenghts and about 6 MHz in the middle.

AN EPR STUDY OF CU^{2+} IONS IN $[ZN(PICOL)_2(H_2O)_2].2H_2O$ SINGLE CRYSTALS

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In this work, electron paramagnetic resonance of Cu^{2+} doped $[Zn(picol)_2(H_2O)_2]$. $2H_2O$ ($C_{12}H_{18}N_2O_8Zn$) single crystals and powder are examined at room temperature. It crystallizes in monoclinic symmetry. In order to find the g and hyperfine values, we have used an iterative numerical technique. **g** and **A** tensors are constructed and diagonalized to find principal values and are found to be nearly axially symmetric[1-2]. The results are given in Table 1. The Cu^{2+} ions substitute with Zn^{2+} in the host lattice. The ionic radius of Zn^{2+} (75 pm) is enough for the substitution of Cu^{2+} (72 pm). Powder EPR spectrum of Cu^{2+} doped $[Zn(picol)_2(H_2O)_2]$ is shown in Fig 1. The EPR data from the powder gives almost the same values on single crystals, Table 1. The covalancy parameter, mixing coefficients and Fermi-contact term of the complex were obtained, and the ground-state wavefunction of the Cu^{2+} ion in the lattice has been constructed[3]-[4].

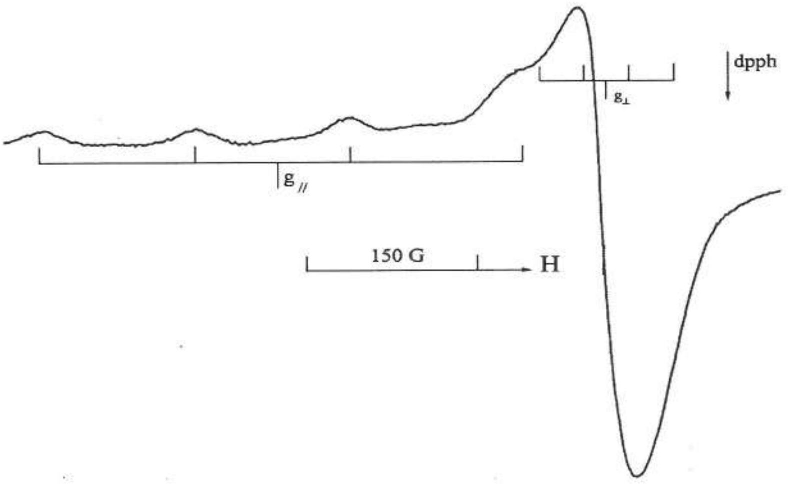

Figure 1Powder spectrum of Cu^{2+} doped in $[Zn(picol)_2(H_2\dot{O})_2]$

Table 1. Spin Hamiltonien parameters of Cu^{2+} ions in $[Zn(picol)_2(H_2O)_2]$

Site	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}
I	2.088	2.087	2.310	62.9G	53.5G	153.7G
II	2.095	2.083	2.308	68.9G	51.8G	150.6G
Powder	2.075	2.075	2.295	52G	52G	151G

[1] Atherton N. M., *Electron Spin Resonance Theory and Applications,* Jhon-Wiley and Sons, New York.(1973).
[2] B. Karabulut and R. Tapramaz, Radiat. Phys. and Chem.55 (1999) 331.
[3] T.B. Rao and M. Narayana, Phys. Stat. Sol. B 106 (1981) 601.
[4] JL. Rao,R.M. Krishna, SVJ. Lakshman, and P. Chand, J. Phys. Chem. Solids 51 (1990) 313.

CHARACTERIZATION OF EFFLORESCENCE IN FRESCOS USING INFRARED SPECTROSCOPY AND TARGET FACTOR ANALYSIS

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Efflorescence is white crystalline or powdery, often fluffy/fuzzy deposit found on the surface of materials. Its formation is caused by water penetrating through the object. The water dissolves salts inside the object while moving through it, and then evaporates leaving the salt on the surface. The accepted definition of the term *efflorescence* is "water-soluble compounds, which are at least partly derived from the substrate materials, migrate through the substrate to the surface where they react with compounds in the environment or change their state of hydration to form visible clusters". This effect causes damage and deterioration of the art objects and is serious treat to the preservation and conservation of the frescos and wall paintings in churches. Conservation treatments of these objects are highly dependent on well-established knowledge of the present salts in the efflorescence. On the other hand, identified salts could indicate the degree of degradation processes as well as the origin of the efflorescence.

An attempt is made, using target factor analysis (TFA), to develop simple and practical approach to this problem, convenient for use in everyday conservators work. Common technique for identification of the salts in efflorescence is infrared spectroscopy. Generally, the mixtures of salts give similar infrared spectra. It requires knowledge of an expert in the field of infrared spectroscopy for appropriate interpretation of these results. In this work TFA is applied to determine of composition of the infrared spectra, instead of empirical assignation.

The development of the TFA model for prediction of qualitative composition of wall painting/fresco salts requires creation of infrared spectra database of substances often found in the efflorescence. For this purpose total number of eighteen infrared spectra of commercially available and synthesized substances was recorded. The procedure was tested on different binary, ternary and quarterly mixtures of salts, mimicking the efflorescence found in the frescoes. Since the TFA showed excellent results on these artificially prepared mixtures, in the next stage, the same procedure was successfully applied in determination of the qualitative composition of samples collected from the frescos in the churches at different sites in Republic of Macedonia. The TFA procedure consists of two stages: (1) determining the number of components in the mixtures and (2) comparison of the obtained spectra with the ones, stored in the database. In case of uncertainty in determining the number of components in the mixtures by TFA, simple visual comparison of the generated spectra of pure components with those stored in the created database of spectra of pure substances could help in unambiguous determination of the exact composition of efflorescence.

MOLAB, A EUROPEAN MOBILE LABORATORY FOR *IN-SITU* NON-INVASIVE SPECTROSCOPICAL STUDIES OF CULTURAL HERITAGE.

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Relevant applications of material science to the study and conservation of artworks often involve European Transnational Access programmes to large scale facilities such as synchrotrons, neutron sources, laser laboratories, or computer centres. Recently, medium size facilities, specifically addressed to artwork studies and conservation have become also available to the scientific community of Europe and associated countries. They are AGLAE (*Accelerateur Grand Louvre d'Analise Elementaire*) and MOLAB (Mobile Laboratory).

AGLAE is the Ion Beam facility, located in the *Pavilion du Louvre* in Paris, where European researchers can carry out measurements by PIXE, PIGE, RBS, μ-PIXE elemental mapping, and other techniques.

MOLAB is of a unique collection of fourteen portable equipments, belonging to three joint Italian institutions (namely *Centre* SMAArt *of the University of Perugia, I;* OPD - *Opificio delle Pietre Dure, Firenze, I;* CNR - *Istituto per la Conservazione e Valorizzazione dei Beni Culturali, Firenze, I* and *Istituto Nazionale di Ottica Applicata, Firenze, I*), suitable to carry out non-invasive *in-situ* measurements, i.e. in the same place where the artwork is located such as a museum room, a church, a restoration workshop, etc.. *In-situ* measurements are advantageous because they ensure immediate results, eliminate any risk connected with the transportation of artworks into a laboratory, and reduce ensurance costs.

Both MOLAB and AGLAE are accessible through peer review selection of proposals and are part of the activities of the Eu-ARTECH Integrated Infrastructure Initiative (Access, Research and Technology for the conservation of the European Cultural Heritage) within the 6th F.P. of the European Community.[1]

The pool of MOLAB equipments is composed by a light fiber optic mid-FT-IR spectrometer, a compact micro-Raman, a portable UV-Vis fluorescence system, a portable XRF system, an NMR relaxometer (EUREKA-MOUSE), a scanning IR-colour reflectograph, a laser micro-profilometer, etc.. Starting from July 2004, MOLAB activities have made possible *in-situ* non-invasive studies of precious masterpieces of Michelangelo, Caravaggio, Raphael, Leonardo, and others.[2,3] Examples of spectroscopical studies carried out by MOLAB users will be given.

[1] for more information, see the website: *www.eu-artech.org*
[2] C.Ricci, C.Miliani, B.G.Brunetti, A.Sgamellotti, Ta*lanta*, 69 (2006) 1221.
[3] F.Rosi, I.Borgia, P.Benedetti, B.G. Brunetti, A.Sgamellotti, *Appl. Spectr.* (*in the press*)

NEW AND USER RELEVANT ADVANCES IN MICROANALYSIS BY RAMAN SPECTROSCOPY

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Up to know dispersive Raman microscopy was not very established for routine analysis of micro samples in chemical and pharmaceutical industry. The main reason for this was the wavelength instability and the problem of fluorescence with many samples. With the new SURECAL^{TM} technology the wavelength stability of dispersive Raman spectrometers is almost the same as for FT-Raman systems. Using this new technology the Raman spectrum is permanently corrected for any shifts of the laser excitation wavelength. To diminish the fluorescence background signal of any sample the AUTOFLUORESCENCE REJECTION^{TM} technology was developed. Here, in principle the background is automatically subtracted from the Raman spectrum by a modulated change of the laser excitation wavelength.

Both techniques will increase the robustness and applicability of dispersive Raman spectroscopy significantly. In this contribution several biochemical and pharmaceutical applications will be shown in order to demonstrate the effect of these new features in modern instrumentation.

INTERACTION INDUCED ABSORPTION IN INFRARED SPECTRA OF DIPHENYLACETYLENE AND DIPHENYLDIACETYLENE

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In infrared spectra of diphenyldiacetylene (DPDA) an unusual phenomenon has been observed going from solid to solution. In the solid state of DPDA in the region of triple bond stretching only one band has been observed at ~ 2150 cm^{-1} which describes an IR allowed antisymmetrical stretching of the acetylenic bridge. On the contrary, in solution and in melt, an extra IR band appears at ~2220 cm^{-1}. A band at the same position has also been observed in Raman spectra and assigned to the symmetrical stretching of the acetylenic bridge. Likewise, in IR spectra of melted and solvated diphenylacetylene (DPA) a band occurs at ~2219 cm^{-1} which is a consequence of the analogous normal mode.

In order to explain this behaviour (Fig. 1), IR spectra of melted DPA and DPDA at different temperatures and IR spectra of DPA and DPDA in various solvents and concentration ranges have been recorded.

Using solvents with different characteristics like polarities or donor/acceptor number, it has been noticed that the forbidden band exhibits different behaviour than the allowed bands. First, while in polar solvents the forbidden band decreases, in nonpolar solvents it increases with an increase of concentration. Second, in solutions where concentration of DPA and DPDA has been kept constant but a molar ratio of polar and nonpolar solvent has been changed, the forbidden band showed greater increase with an increase of polarity of mixture than allowed bands. No significant wavenumber shift of the discussed band has been noticed.

Since the average value of the square of the internal field is different from zero in seemingly isotropic surroundings, it affects the integrated absorption intensity of the observed IR forbidden band, which is proportional to it. However, the major reason for appearing of the forbidden band is great polarizability change during symmetrical stretching of the acetylenic bridge.

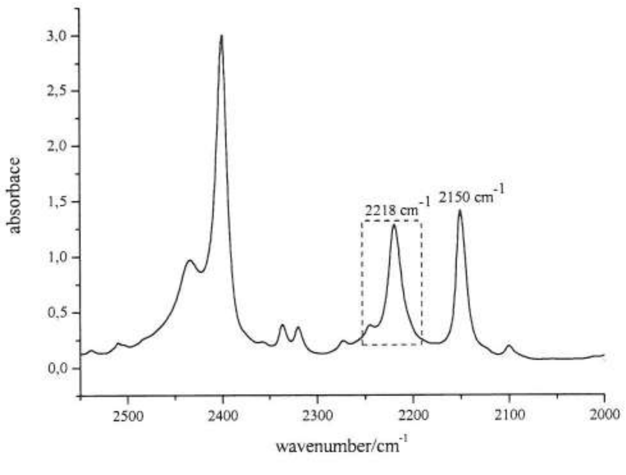

Figure 1. Spectra of 1,0 M DPDA in $CHCl_3$

AN EPR STUDY OF VO^{2+} IONS in ARSANILIC ACID [$C_6H_4ASNO\ (H_2O)_2$] SINGLE CRYSTALS

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Electron paramagnetic resonance of VO^{2+} arsanilic acid [$C_6H_4AsNO\ (H_2O)_2$] single crystals and powder are examined at room temperature. It crystallizes in monoclinic symmetry and the unit cell dimensions are $a=7.23\overset{0}{\mathrm{A}}$, $b=6.19\overset{0}{\mathrm{A}}$, $c=8.63\overset{0}{\mathrm{A}}$ and $\beta = 101.16^0$. There are two molecules in a unit cell[1]. The angular variation of the EPR spectra have shown that two different VO^{2+} complexes are located in different chemical environments, and each environment contains two magnetically inequvalent VO^{2+} sites in distinct orientations occupying interstitial positions in the lattice and show very high angular dependence(Figure 1). Crystalline field around the VO^{2+} ion is nearly axial. The principal g, and the hyperfine (A) values of two sets of VO^{2+} complexes groups are determined[2]. Both g and A values of each sites are found to be axial symmetry The results show that two sets of VO^{2+} ions are in the order of $g_{//} < g_{\perp} < g_e$ and $|A_{//}| > |A_{\perp}|$, which confirms than V^{4+} ions in arsanilic acid exist as VO^{2+} ions in octahedral coordination with tetragonal distortion and the trend $g_{//} < g_{\perp} < g_e$ shows the presence of unpaired electron in the d_{zy} orbital. The powder spectrum also clearly indicates two different VO^{2+} groups, confirming the single crystal analysis. The EPR data from the powder gives almost the same values on single crystals.

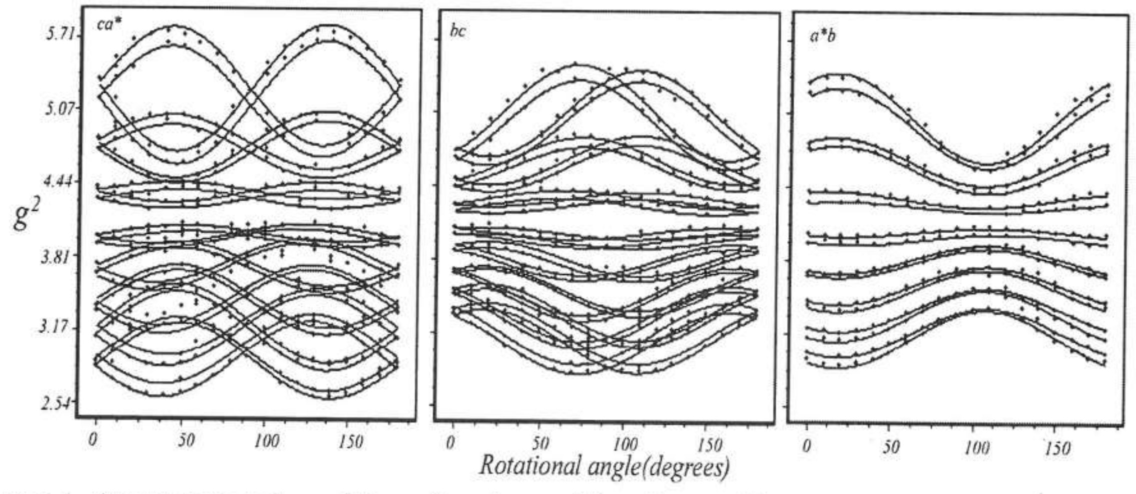

Figure 1. Angular variation of the g^2 values of four lines of in arsanilic acid single crystal at room temperature.

[1] B. Karabulut and R. Tapramaz, Radiation Physics and Chemistry., **55** (1999) 331.

[2] Atherton N. M., *Electron Spin Resonance Theory and Applications,* Jhon-Wiley and Sons, New York.(1973).

ANKA-IR BEAMLINE: DESIGN CONSIDERATION AND APPLICATION POSSIBILITIES

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The major advantages of the electron synchrotron radiation compared to the thermal or plasma radiation sources used in commercial FT-IR spectrometers are very well known: the very intense brightness and the highly collimated beam. Especially in the longer wavelengths range, the mid and far infrared, a smaller and much more intense measurement spot with a low angle of beam opening is available. Glowbar or Hg arc lamp may provide similar dimensions of the measurement spot only by suffering strong intensity losses. These synchrotron radiation properties are of high advantage for dedicated applications in the infrared spectral range: IR-microscopy, high pressure analysis, ellipsometeric studies [1], photo-acoustic spectroscopy, highest spectral resolution and time resolved measurements, by which we have named the major ones.

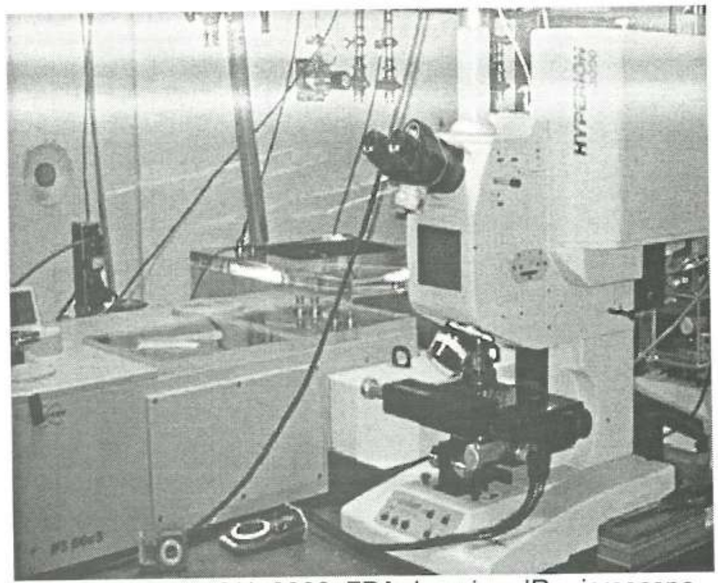
Fig. 1. *HYPERION 3000* FPA imaging IR-microscope adapted to the IFS 66v/S FT-IR spectrometer at the ANKA IR-beamline.

On the example of the IR beamline at the Angström-source Karlsruhe (ANKA) electron synchrotron facility in Germany, we will describe in this paper the principles of the optical IR beamline adaptation, the FT-IR spectrometer set-up coupled with a far IR ellipsometer and a microscope for the mid and far IR spectral range equipped with a bolometer detector. Measurement data acquired at the ANKA-IR beamline with the recently installed Focal Plane Array (FPA) IR microscope will be presented as well as results achieved at different synchrotron facilities throughout the world. We will demonstrate the current application possibilities and the outstanding performance potential of an electron -synchrotron for extreme high lateral, spectral and temporal resolutions.

[1] C.Bernhard, J.Humlicek, and B.Keimer, *Thin Solid Films*, **455** (2004), 143

P1-11

CONTINUOUS MONITORING OF INTERSTITIAL BUFFER SYSTEMS USING MICRO-DIALYSIS AND INFRARED SPECTROMETRY

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The human body maintains the blood pH around 7.4, but for severe pH level changes, acidosis or alkalosis can lead to serious health problems. With intracellular pH variation, the interstitial and plasma pH will also change, but of lesser magnitude. Three different buffer systems exist: bicarbonate, phosphate and protein buffering systems. The bicarbonate and phosphate buffer can be described by the following equations (pK values under physiological conditions were recently given by Jungas[1]):

$$CO_2 + H_2O \leftrightarrow H_2CO_3 + H_2O \leftrightarrow HCO_3^- + H_3O^+$$
$$H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$$

The buffer systems with their components including pH value can be monitored quantitatively by mid-infrared spectroscopy using a bed-side quasi-continuous monitoring system developed by us recently for clinical application. Besides a mini-spectrometer, the developed technology includes a micro-dialysis probe and a fluidic system.[2] The infrared spectra of the bicarbonate and phosphate buffer components are pH dependent. By using the CO_2 and HCO_3^- bands of the bicarbonate spectra, the pH of the harvested interstitial fluid can be predicted using the Henderson-Hasselbalch equation. Using aqueous bicarbonate solutions, the absorption band maxima of dissolved CO_2 and HCO_3^- at different pH values were recorded. By applying Henderson-Hasselbalch equation, good correlation between reference and infrared predicted pH values was observed. However, for ex-vivo measurements, strict gas tightness of the fluidic system is needed for the sample transport to the transmission cell. The performance for in-vitro and in-vivo analysis and problems due to microdialysis recovery will be discussed.

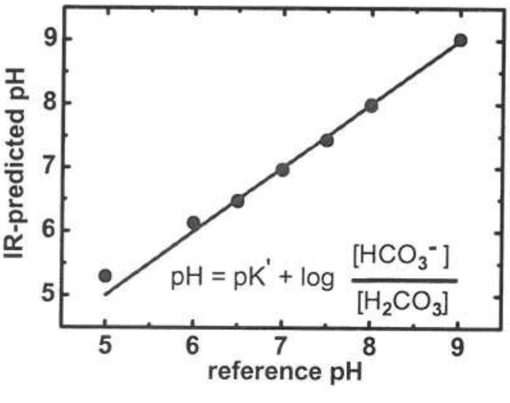

Fig. 1: IR-predicted pH using Henderson-Hasselbalch equation based on integral band absorbances of pCO_2 and bicarbonate.

Financial support by the European Commission with the CLINICIP project (contract no. 506965, 6th Framework Programme) is gratefully acknowledged.

[1] R.L. Jungas, Anal. Biochem. 349 (2006) 1.
[2] H.M. Heise, U. Damm, V.R. Kondepati, Proc. SPIE. 6093, (2006) 21.

LDA AND NEURAL NETWORK CLASSIFICATION OF PURE AND ADULTERATED OLIVE OIL SAMPLES BY USING FT-RAMAN SPECTROSCOPY

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Fourier Transform (FT) Raman spectroscopy has been evaluated for the analysis of extra virgin olive oil samples from various Mediterranean sites adulterated by sunflower oil. Recently, a quantitative assay was based on multivariate PLS calibration models using different strategies for optimal wavelength selection.[1] Compared to infrared spectroscopic studies using fiber-optic probes in contact with the vegetable oil,[2] Raman measurements can be carried out non-invasively through a glass vessel, which has been realized here. A simple classification is required for fast assessment of adulteration, which can be approached by using supervised methods such as linear discriminant analysis (LDA) or artificial neural networks (ANN).

Raman measurements were available for 92 olive oil samples in a set covering one year's harvest from different Greek sites. The 69 spiked samples contained 2, 5 and 10 % by weight of sunflower oil. A second harvest population with 48 samples with a wide regional distribution was also used for classification (18 pure samples, others contained 1 % and 5 % of sunflower oil). Spectral characteristics of the extra virgin olive oil and sunflower oil samples have been described earlier.[1] Previously, a spectral intensity normalization using the C-H stretching band at 2903 cm^{-1} improved the quantitative results significantly, since the band is a fine indicator for the overall amount of fatty acid glycerol esters being probed by the laser. Thus, raw and intensity scaled spectra were processed. Interval optimisation and wavelength selection using LDA and ANN in combination with various cross-validation schemes led to the use of optimal spectral ranges. The use of the spectral fingerprint information had best classification results for the first series using raw spectral data: all samples were correctly classified using LDA including sample packages up to 9 samples for cross-validation. The use of the C-H stretch region alone showed misclassification for the same two outliers, which proved to be problematic also within the previous PLS regression studies. Using the ANN approach, three samples were maximally incorrectly assigned by using the spectral intervals of 3100-2600 cm^{-1}, 1780-1600 cm^{-1}, and 1500-560 cm^{-1}. Slight deteriorated results were obtained for the second, but smaller population of olive oil samples.

[1] H.M. Heise, U. Damm, P. Lampen, A.N. Davies, P.S. McIntyre, Appl. Spectrosc. 59 (2005)1286
[2] L. Küpper, H.M. Heise, P. Lampen, A.N. Davies, P. McIntyre, Appl. Spectrosc. 55 (2001) 563

MONO-, DI-, AND TRI-TERTBUTYL ETHERS OF GLYCEROL. A SPECTROSCOPIC STUDY.

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Biodiesel is one of the leading alternatives to fossil fuels in transportation. Over its life cycle, the use of biodiesel releases 78% less carbon dioxide than regular diesel [1]. It also results in substantial reductions in most air pollutants that contribute to urban air problems. In the European Union, about 1.4 milion tons per year of biodiesel is produced [2], while in the same time in the US above 100 milion tons is generated [3]. In consequence of increasing production of biodiesel, a considerable excess of glycerol appears on the chemical market. Glycerol has numerous applications in different industrial processes; yet, its recovery and purification contribute to high production costs and energy consumption. Therefore, new methods of glycerol utilization are desirable. One of the methods is glycerol ethers synthesis. The ethers are excellent oxygen additives for diesel fuel [4, 5] and they are of importance to both: environmental compliance and efficiency of diesel engines [6].

The main objective of our study has been to develop a technology of catalytic synthesis of high value glycerol ethers, primarily di- and tritertbutyl ethers of glycerol, directly from glycerol and isobutene contained in the cracking derived fraction. Here, we present the spectroscopic and compound identification problems that have appeared during technology developing and analysis of the main products, i.e., mono-, di-, and tri-*t*-butyl ethers of glycerol. The molecular spectra of the title compounds were not published, so far.

To solve the analytical and spectroscopic problems the following techniques have been used: GC, GC-MS (in PCI and NCI modes), NMR, FT-IR and Raman, as well as DFT calculations. The GC was used to perform the glycerol etherification control and optimization. The GC-MS was necessary to assign most of the GC peaks. This task was possible only by using a chemical ionization mode, because such a technique enabled to observe the molecular peaks and to assign the fragment-ion contributions in the chromatographic peaks. The ^{1}H and ^{13}C NMR spectra were used to determine unambiguously the mono-, di-, and tri *t*-butyl glycerol ethers. The NMR analysis confirmed that the 1,3-di-*t*-butyl ether dominated over the 1,2-isomer which can be detected by GC-MS in minute amounts. It is interesting that in the 2D NMR spectrum a correlation peak originating from the OH proton and tertiary C-atom can be observed. This indicates the presence of an intramolecular OH...O hydrogen bond when the diether is dissolved in an inert solvent. The IR and Raman spectra of the title compounds were interpreted and change in the spectra upon successive glycerol etherification were discussed. The most striking change in the IR spectra upon successive *t*-butyl etherification of glycerol is decrease of intensity and shift of the ν(OH) stretching, γ(OH) out-of-plane, and δ(OH) bending vibration bands. The region between 1150 and 900 cm^{-1} is also very informative. In this very region there are placed both: the intense alcoholic ν(C-O) stretching vibrations bands (1130-1030 cm^{-1}) and the asymmetric (intense, 1100-1000 cm^{-1}) and symmetric (medium intensity, ca. 850 cm^{-1}) ν(C-O-C) stretching vibrations bands. However, a detailed interpretation of the bands of the studied compounds in the ν(C-O) region is a difficult task because three C-O vibrators couple to one another and to ν(C-C-C) modes in different ways in each of the molecule and in each of its conformer. The DFT calculated vibrational spectra and PED interpretation [7] were helpful in assignments of the experimental bands.

[1] National Renewable Energy Laboratory, http://www.nrel.gov/docs/legosti/fy98/ 24089.pdf (10 October 2004).
[2] Chemical Market Reporter, February 7, 2005
[3] G. A. Olah, U.S. Pat. No. 5,520,710, 1996
[4] H. Noureddini, US Pat. 6,174,501, 2001
[5] C. Dewattines, H. Hinnekens, EU Pat. 0 649 829, 1995
[6] A. Behr, L. Obendorf, Eng. Life. Sci., 2(2003)185.
[7]M.H. Jamróz,Vibrational Energy Distribution Analysis:VEDA 4 program, Warsaw,2004

^{57}Fe MÖSSBAUER, FT-IR AND FE SEM INVESTIGATION OF THE FORMATION OF HEMATITE AT HIGH pH VALUES

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Hematite (α-Fe_2O_3) is widely used in technology as a red pigment, adsorbent, catalyst or starting chemical in the solid state production of ferrites, etc. It is also present in various soils and sediments, and often associated with goethite (α-FeOOH), especially in warmer climate regions. Hematite particles are theoretically relevant in colloidal and surface chemistry, due to their acid/base surface properties and a possibility to obtain them in different geometrical shapes and sizes. In the laboratory researchers are trying to control the properties of hematite particles by changing the route and parameters of chemical synthesis. In the present work we have focused on the hydrothermal synthesis of hematite particles, as well as the mechanism of their formation. ^{57}Fe Mössbauer and Fourier transform infrared (FT-IR) spectroscopies and thermal field emission scanning electron microscopy (FE SEM) were utilized in characterizations of the samples. A ferrihydrite suspension with the final concentration of 1M $FeCl_3$ was prepared at pH~13.2, then autoclaved. No visible transformation of ferrihydrite was present up to 30 min of autoclaving at 160 °C, whereas hematite and a small amount of goethite as an associated phase were present after 40 min of autoclaving. After 50 min of autoclaving the content of goethite started to dissolve rapidly on account of hematite particles growth. The influence of Fe^{3+} concentration on the formation of hematite, with the other experimental parameters unchanged, was also investigated. FE SEM showed morphological and particle size changes in dependence on the experimental conditions. The mechanism of the formation of hematite at high pH values will be discussed.

FLUORESCENCE TECHNIQUE FOR *IN-SITU* MONITORING OF THE ACRYLAMIDE POLYMERIZATION

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A novel method, based on the binding of pyranine *((8-hydoxypyrene-1,3,6 trisulfonic acid, trisodium salt), $(Py)_3OH$)* to the polymer chains (as a fluoroprobe) via multiple point interactions during the acrylamide (AAm) polymerization, was used for *in-situ* monitoring of the free radical polymerization of polyacrylamide. $(Py)_3OH$ binds covalently to the functional ends of the growing polymer chains over -OH groups via radical edition, a considerable blue-shift, from 515 to 406 nm in maxima, occurs in the emission spectra, thus the intensity of the short wavelength peak increases as the polymerization progresses. At the same time, three SO_3^- groups on the probe molecule interact with the regions of excess positive charges appeared along the acrylamide chains. These electrostatic interactions cause a gradual red-shift in the maxima of the short wavelength peak, as seen in Figure 1.

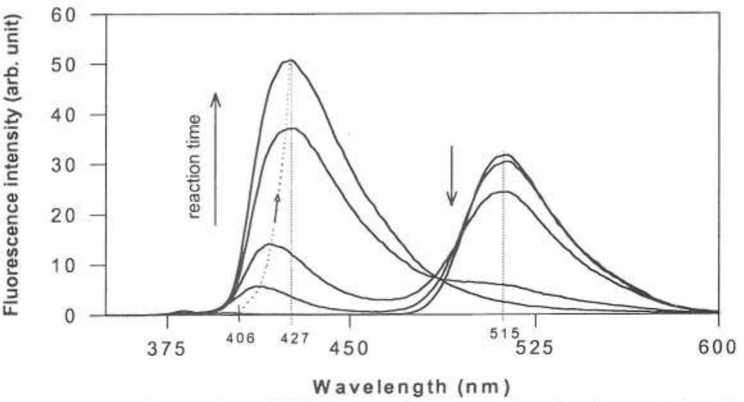

Fig. 1: Fluorescence intensity shifts from 515 nm to short wavelegths during the polymerization

The shift in the short wavelength peak during the polymerization counts the number of SO_3^--monomer contacts, and thus carry the information about the evolution of the microstructure of the polymerization. Using the fluorescence intensities (I_{510} and I_{430}) measured during the course of polymerization, we have calculated some kinetic parameters like weight average degree of polymerization, propagation rate constant and activation energy.

[1] Y. Yılmaz, Y. Yagcı and Ö. Pekcan, *J. Macromol. Sci-Pure Appl. Chem.*, **A38(7)**, 741 (2001).
[2] Y. Yılmaz, *Phys. Rev. E*, **66**, 05801(2002).
[3] D. Kaya, Ö. Pekcan and Y. Yılmaz, *Phys. Rev. E*, **69**, 016117 (2004)
[4] Y. Yılmaz, A. Erzan,and Ö. Pekcan, *Phy. Rev. E.*, **58**, 7487 (1998).
[5] Y. Yılmaz, A. Alemdar, *Applied Clay Science*, **30**, 154 (2005).

ANALYSIS OF PROTONATION AND DEPROTONATION OF PHENAZINE DERIVATIVES BASED ON CHANGES IN THEIR ABSORPTION AND FLUORESCENCE SPECTRA

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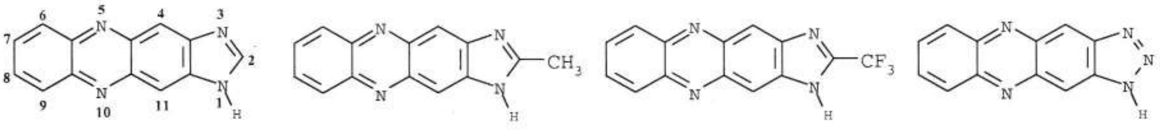
The visible electronic absorption and fluorescence spectra as well as fluorescence polarization degrees of four phenazine derivatives (see Fig.1) and their glycosides, were investigated in aqueous buffered solutions over the pH range of 0 – 12.



F1 **F2** **F3** **F4**

Fig 1. Molecular structure of phenazine derivatives: imidazo(4,5-d)-phenazine (F1), 2-methylimidazo(4,5-d)-phenazine (F2), 2-trifluoridemethylimidazo(4,5-d)-phenazine (F3), 1,2,3-triazole(4,5-d)-phenazine (F4). The numeration of atoms included in aromatic system is given according to the case F1.

The analysis of protonation and deprotonation effects on spectral properties of the dyes was made. The ranges of pH where individual ionic species are predominant were determined. The fluorescence was found only for neutral species of investigated dyes being quenched for their ionic forms. The deprotonation and protonation pK_a values were evaluated from experimental data. It was shown that donor-acceptor properties of the substitute group in the second position of the pentagonal ring substantially affect the values of the deprotonation constants and the character of protonation for chromophore. A substitution of a hydrogen atom in NH- group by the sugar residue blocks the formation of the anionic species, and results in enhancement of the dye emission intensity. The character of the dependence of F1 and F1rib emission on pH in the range of 0 - 7 with ratio of $I_{pH7}/I_{pH1} = 60$ allows to propose them as possible indicator dyes in luminescence based pH sensors for investigation of processes accompanied by acidification, e.g. as gastric pH-sensors. Comparative analysis of dyes studied has shown that F4gl is the most perspective compound as a fluorescent probe for investigation of molecular hybridization of nucleic acids.

This work was supported by Science and Technology Center in Ukraine (Project #3172).

FT-IR AND MICRO-RAMAN SPECTROSCOPIC STUDY OF DECORATED POTTERIES FROM VI AND VII CENTURY BC, EXCAVATED IN ANCIENT AINOS-TURKEY

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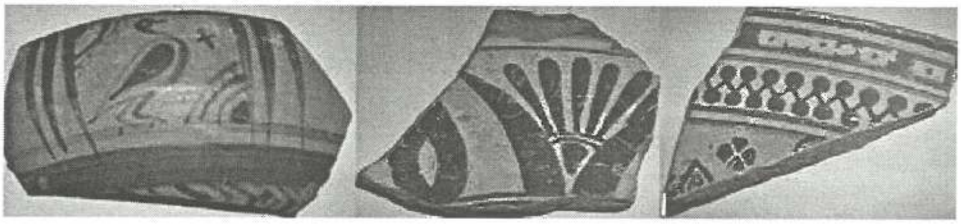
Ancient Ainos (Enez), in the Northern Coast of the Aegean Sea, has been described as one of the most important archaeological sites in Turkey. The first residents of Ainos have not been known yet but the found remains show that first residents were dated back to 7300 years from now and life in here has continued till today.

The identification of pigments used for archeological objects is important for their restoration, conservation, dating and authentication. In this study we report the Ft-IR and micro-Raman spectra of decorated pottery fragments belong to VI and VII century BC, excavated in Enez archaeological site.The experimental results allowed us to identify the peculiar components of the ceramic body and the main pigments of the decoration. Spectroscopic study revealed abundance of TiO_2 (as rutile and anatase), hematite and iron oxide on the red coloration. The brown decoration consists of pure hematite.

Performed analyses provided useful information about the analytical composition which may leads to the assignment to an historical and geographical provenance.



Some examples of decorated pottery fragments, excavated in ancient Ainos

Acknowledgement

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RADIATION STERILIZATION OF BENZYDAMINE-HCl: AN ESR STUDY

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Benzydamine-HCl (1H-Indazole, 1-benzyl-3-(3-(dimethylamino)propoxy) is one of the widely prescribed non-steroidal anti-inflammatory drugs (NSAIDs) having analgesic, antipyretic, and anti-inflammatory activities which is needed to be sterilized. The use of radiation for the sterilization of pharmaceutical raw materials and dosage forms is an attractive alternative method for sterilization recognized by all major pharmacopeias. Electron Spin Resonance (ESR) technique appears to be well suited for determination of the radicals produced in the drugs after irradiation. Thus, an ESR study was performed under different experimental conditions on solid benzydamine-HCl gamma irradiated at room temperature in the dose range of 3-34 kGy. ESR spectrum of benzydamine-HCl consisted of 8 weak resonance peaks spread over a magnetic0 field range of 130 G. The most intense resonance line appearing just at the center of the spectrum was calculated to have a g value of 2.0039 and a peak to peak width of 12.5 G. Variations of the observed peak heights with applied microwave power, temperature, storage time, annealing temperature and time were evaluated to determine structural, spectroscopic and kinetic features of the radicals induced in gamma irradiated benzydamine-HCl. G value representing the radiosensitivity of irradiated compounds was calculated to be 0.02 ± 0.01 for benzydamine-HCl. This value is fairly small compared to that obtained for solid alanine (G=1) which is used as a dosimetric material in ESR-alanine dosimetry. Basing on the results obtained in the present work, it was concluded that benzydamine-HCl was a radioresistant material. Thus, it could be sterilized by radiation and ESR spectroscopy could be used as a potential technique to monitor its radiosterilization.

INFLUENCE OF COPPER IONS ON PRECIPITATION OF GOETHITE AND HEMATITE IN HIGHLY ALKALINE MEDIA

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Metal ions have strong influence on the process of precipitation of *iron oxides* (group name for iron oxyhydroxides and oxides) in highly alkaline media. The properties of synthetic *iron oxides* can be significantly changed upon incorporation of metal cations into their crystal structure. Over the past years the properties of doped *iron oxides* were studied from the academic standpoint, as well as their role in industrial applications. In the present work we have focused on the influence of copper ions on the precipitation of goethite (α-FeOOH) and hematite (α-Fe_2O_3) in highly alkaline media and the formation of solid solutions as a function of the initial concentration ratio r = [Cu]/([Cu] + [Fe]). Precipitations were performed by adding a proper volume of the 25% w/w TMAH (tetramethylammonium hydroxide) solution to the solution of Fe^{3+} and Cu^{2+} ions, then the suspensions were autoclaved at 160 °C for 2 h. The samples were characterized by ^{57}Fe Mössbauer and FT-IR spectroscopies, thermal field emission scanning electron microscopy (FE SEM) and energy dispersive X-ray analyser (EDS). Mössbauer spectra were fitted taking into account hyperfine magnetic field distribution. Only the solid solutions α-(Fe, Cu)OOH were obtained up to r = 0.0291. The solid solutions α-(Fe, Cu)OOH + α-(Fe, $Cu)_2O_3$ were obtained between r = 0.0385 and 0.0566, whereas for $r \geq 0.0698$ only the solid solution α-(Fe, $Cu)_2O_3$ was obtained. FE SEM showed a gradual increase in the length of doped α-FeOOH crystallites along the c-axis with an increase in Cu-substitution. α-(Fe, $Cu)_2O_3$ particles showed a much better geometrical shape and uniformity at an increased r, specifically when precipitated as a single phase. The concentrations of copper ions incorporated into α-(Fe, $Cu)_2O_3$ particles were determined by the EDS technique.

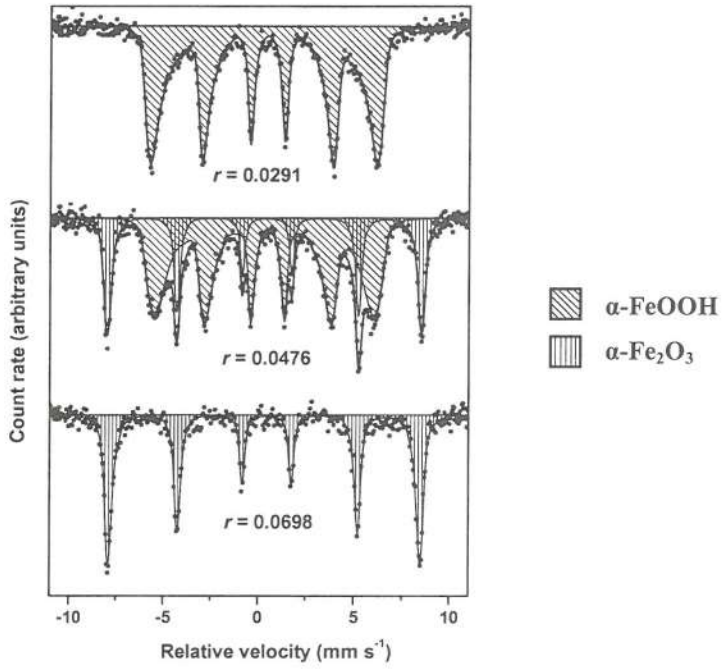

Fig. 1: ^{57}Fe Mössbauer spectra of characteristic samples

SPECTROPHOTOMETRIC DETERMINATION OF THE pK_a OF 2,3,4,6′-TETRAHYDROXY-3′-SULPHOAZOBENZENE

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Azo compounds have been used dyes for long time[1]. Since azo compounds are an important and valuable multifunctional dye with pure chromophoric properties high molar extinction coefficient, and fine staining qualities, these are commonly used in spectrophotometric determinations of metals[2]. 2,2′-Dihydroxyazo compounds which used the determination of metal ions is known the best[3-5]. In the same time, azo compounds are used as acid-base indicators.

We have synthesized 2,3,4,6′-tetrahydroxy-3′-sulphoazobenzene (THSA) (Fig. 1) that a new tetrahydroxyazo compounds and we have determined of the pK_a of THSA by spectrophotometric method. Furthermore, this structure has been investigated by using the semi-empirical quantum chemical calculated method AM1. These results have been compared between empirical pK_a and semi-empirical quantum chemical calculated pK_a.

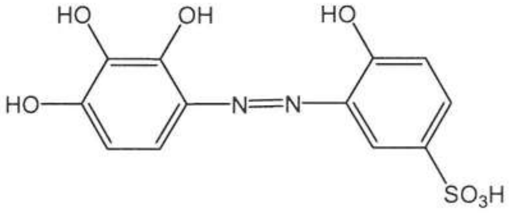

Fig. 1: 2,3,4,6′-tetrahydroxy-3′-sulphoazobenzene (THSA).

[1] A.T. Peters, E. Chisowa, Dyes and Pigments 22 (1993) 223.
[2] J. Liu, Z. Chen, S. Yuan, Jzus 6B(6) (2005) 584
[3] Z. Marczenko, Spectrophotometric Determination of Elements, Wiley, New York. 1976, p.110
[4] E. Yıldız, H. Boztepe, Turk. J. Chem. 26 (2002) 897
[5] A.A. Huseyinli, F. Köseoğlu, U.D. Uysal, Anal. Sci. 17 (2001) 793

SITE- AND STATE-SELECTIVE SPECTROSCOPY OF CIRCULAR BACTERIOCHLOROPHYLL ANTENNA COMPLEXES

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Apart from fundamental interest, considerable effort is focused recently on quasi-one-dimensional nano-materials due to their potential applications in nano-electronics, nano-photonics, and nano-sensorics. The peripheral light-harvesting (LH) 2 complex from purple photosynthetic bacteria has a known spatial structure refined to 0.2 nm. The photoactive part of this complex is a circle of ~5 nm diameter of 18 tightly packed bacteriochlorophyll *a* molecules. The core LH1 antenna forms similar but larger circle comprising 32 molecules. The apparent one-dimensional pigment organization and availability of well-developed biochemical preparation/modification techniques makes these fixed-size natural pigment-protein complexes very attractive for model investigations of molecular nano-aggregates, free from edge effects.

Here, the nature of excitations produced by light in LH1 and LH2 complexes isolated from the photosynthetic purple bacteria *Rhodobacter sphaeroides* and *Rhodopseudomonas acidophila* has been studied at 5 K by various spectrally selective techniques, including persistent spectral hole-burning, fluorescence line-narrowing, difference fluorescence line-narrowing (ΔFLN), and polarized fluorescence excitation spectroscopy. A great advantage of the ΔFLN technique is that the zero phonon lines, being typically obscured by scattered laser light in fluorescence line narrowing, are virtually free from the scattering artifacts in case of ΔFLN [1]. The thus obtained total fluorescence band shapes allow a straightforward determination of the electron–phonon and electron–vibrational coupling parameters in the spectra. It is shown that spectral selectivity of the fluorescence properties of the antenna complexes is preserved deep in the corresponding absorption bands revealing not only the exciton bandwidths (1600 - 2200 cm^{-1}, depending on the complex), but also the exciton band structure for these complexes. A dual nature of the emission bands in LH1 and LH2 complexes was confirmed, formerly assigned to the nearly free excitons weakly coupled to lattice vibrations and to the strongly coupled self-trapped excitons [2]. An analysis based on diagonally disordered excitonic polaron model [3] shows that the ground-state energies of the two distributions of excitonic polarons are shifted relative to each other by about 70 cm^{-1}. From the two, the distribution for the strongly coupled excitonic polarons is more red-shifted, being also significantly broader. Variations of the exciton characteristics under external high hydrostatic pressure up to 6 kbar have also been investigated. A compression of the antenna structures leads to (i) a considerable stabilization of the self-trapped excitons, reflected in a relative red-shift and broadening of their fluorescence band shape; (ii) up to 30% increase of the exciton absorption band width and, consequently, of the exciton coupling energy; (iii) up to 30% widening of the inhomogeneous distribution functions.

We believe that by these studies a consistent picture of the spectroscopy of the circular antenna complexes is obtained for the first time.

[1] K. Timpmann, M. Rätsep, C.N. Hunter and A. Freiberg, J. Phys. Chem. B **108** (2004) 10581.
[2] A. Freiberg, M. Rätsep, K. Timpmann, G. Trinkunas and N. W. Woodbury, J. Phys. Chem. B **107** (2003) 11510.
[3] G. Trinkunas and A. Freiberg, J. Luminescence **1112** (2005) 420.

STRUCTURAL CHANGES IN LIPIDS AND PROTEINS OF SARDINE (*Sardina Pilchardus*) MUSCLE DURING ICE STORAGE

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Determination of moisture, protein and fat accounts for the majority of applications of food analysis. Sardine forms part of the raw material used by the food industry, so an in situ knowledge of the batch quality is highly desirable. The use of FTIR spectroscopy for quality assessment is an attractive possibility since it would provide a non-destructive and rapid line analysis in the industrial production chain. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used to evaluate the changes in composition and structure of components in moisture of chilling sardines over the time in relation with quality an freshness properties.

Different batches of sardine (*Sardina Pilchardus*) were stored on ice soon after caught and investigated over the next thirteen days. The study was focused on the gradual changes produced on the lipids and proteins structure since they are the principal components in fish muscle. Spectra were recorded from sardine muscle varying over the storage time. In addition, cooled fish quality parameters such as water holding capacity, concentration of total volatile nitrogen bases, dimethylamine and formaldehyde were determined [1]. The most significant results obtained from spectroscopic data, dependent on the number of the storage days, are the following: *(i)* Lipidic oxidation degree increases as revealed by the decreasing intensities of the υ_{C-H} bands of =C-H olefinic bonds and by frequencies downshifting of the $\upsilon_{C=O}$ band; *(ii)* According to the significant changes over the Amide II band profile, it takes place β-sheet formation in the secondary protein structure over the storage period; *(iii)* Increase of the intensity of the band located towards 1400 cm^{-1}, attributable to a decrease of the concentration of salt bridges due, among other causes, to protein denaturation [2].

, It is important to point out that these results show that FTIR spectroscopy is not only susceptible to detect structural changes associated with deterioration in of sardine muscle but also is able to detect those changes produced on the second day of storage on ice. We demonstrate here that some of those changes can be used in the development of applications for the evaluation of the quality of sardine species, as a tool to determinate these parameters of sardine fresh or in studies of the aptitude of certain technological treatments.

[1] A. Macagnano, M. Careche, A. Herrero, R. Paolesse, E. Martinelli, G. Pennazza, P. Carmona, A. D'Amico, C. Di Natale, *Sensors and Actuators B* **111–112** (2005) pp. 293–298.
[2] A. Rodríguez-Casado, P. Moreno, P. Carmona, C. Di Natale, A. Macagnano, M. Careche *Journal of Agricultural and Food Chemistry* (submitted).

SITE-SPECIFIC BINDING RNA-CORE PROTEIN LEADS TO A WAY TO PREVENT SELF-ASSEMBLY OF HEPATITIS C VIRUS NUCLEOCAPSID

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The hepatitis C virus (HCV) core is a viral structural protein contains the first 191 amino acids of its viral precursor polyprotein. Although self-assembles forming the nucleocapsid it also participates in some cellular processes, including transcriptional regulation. However, the mechanisms of self-assembly core is poorly understood. The HCV core protein has three conserved clusters of highly basic residues in the first 120 amino acids and the ability of the core protein to bind RNA has been localized to amino acids 1 to 75 [1]. Although it is assumed that hepatitis C virus core protein binds with viral RNA to form a nucleocapsid, here we show that truncated 120 HCV core protein can efficiently self assemble *in vitro* into nucleocapsid-like particles lacking viral RNA. These particles are similar in size and shape to those assembled *in vivo* [2]. However, to clarify the binding features of core protein and the viral RNA for the encapsulation and morphogenesis of HCV, the specific interaction of core protein with the genomic RNA synthesized *in vitro* was examined in an *in vitro* system by spectroscopic methods. We utilized mainly Raman and infrared spectroscopies to study the structural basis of the affinity and the preference of the HCV core protein and the 5' untranslated region (5'UTR) of the viral genome.

The results regarding to the ribose-phosphate backbone reveal that the percentage of nucleobases involved in double helix-loop junctions is 19 ± 1% (theoretical model 18.7%) proposed on the basis of comparative sequence analysis and thermodynamic modelling. In addition, about 68 ± 2% of the bases are helically ordered having *C(3')-endo* ribofuranose pucker [3]. Concerning the truncated 120 HCV core protein, the results reveal that the secondary structure of the nucleocapsid like particle involve β-sheet enrichment in relation to the protein monomer. Subsequent application of principal component analysis and two-dimensional correlation spectroscopy reveal that arginine residues exchange first, followed by turns and random coil structures and finally by β-sheets that may be potential linkers of protein monomers. The solvent exposure of protein arginine residues is consistent with ionic protein-nucleic acid interactions through arginine-phosphate groups which can lead to stronger nucleocapsid stability.

The results suggest that the HCV core protein interacts with viral genomic RNA at a specific region to form nucleocapsids by interacting with the 5'UTR. These results provide novel opportunities to delineate protein-protein and protein-RNA interactions critical for HCV assembly to perform high-throughput screening of assembly inhibitors.

[1] M. Kunkel, M. Lorinczi, R. Rijnbrand, S.M. Lemon and S.J. Watowich. *Journal of Virology* 75(5);2119–2129 (2001).
[2]. A. Rodríguez-Casado, M. Molina, P. Carmona. *Proteins* (submitted).
[3]. A. Rodríguez-Casado, M. Molina, P. Carmona. *Biochimica et Biophysica Acta* (submitted).

SERUM ALBUMIN AFFINITY CHANGES FOR ASPIRIN INDUCED BY FATTY ACID

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Since a last few years the binding a various fatty acids (FA) with serum albumin (SA) is widely investigated. It was found that in vivo 0.1 – 2 moles are complexed with albumin. In vitro studies showed that one macromolecule can bind up to 8 FA molecules [1].

The comparison of albumin-fatty acid complex and defatted indicates the significant changes in albumin structures [2]. Those changes can affect the affinity of SA for various drugs.

The influence of fatty acids on drug binding may cause pharmaceutical implications in case of hyperlipidemia. High blood lipids level as well as platelet aggregation is one of the main risk factors of cardiovascular disease (CVD). Hence, our intention was to investigate the alterations of serum albumin affinity for anti-aggregant agent –aspirin (acetylic acid, ASA) induced by myristic acid (MYR C14:0) at various molar ratios.

For this purpose the albumin fluorescence changes in the presence of the ligands were used. Interactions of serum albumin with each ligand separately were investigated in the first step. Then, changes in SA-MYR and SA-ASA complexes with SA-MYR-ASA complex were compared.

The obtain results indicate conformational changes of the albumin molecule induced by MYR binding. These changes are SA/MYR molar ratio depended.

Although the relationship between fatty acid concentration and ASA binding were determined during in vitro studies, but it also may have implications in CVD treatment and prevention.

[1] Bhattacharya AA, Curry S, Franks NP. J. Biol. Chem. 275 (2000) 38731
[2] Zunszain PA, Ghuman J, Komatsu T, Tsuchida E, Curry S. BMC Struct. Biol. 3:6 (2003)

EFFECT OF TEMPERATURE ON THE METHOTREXATE – BSA INTERACTION. SPECTROSCOPIC STUDY.

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Rheumatoid arthritis (RA) is an autoimmune and chronic inflammatory disease which affects about one percent of the world's population.

Methotrexate (4-amino-10-methylfolic acid; MTX) also known as amethopterin is commonly used to treat rheumatoid arthritis (RA). It is transported in the circulatory system as a complex with serum albumin.

The aim of this study was to investigate the interactions of MTX with transporting protein using the spectroscopic methods.

The binding of MTX to bovine serum albumin (BSA) was studied by monitoring the changes in emission fluorescence spectra of protein in the presence of MTX at excitation wavelength of 280 nm and 295 nm. The quenching of protein fluorescence at temperature range from 298 K to 316 K was observed. Molar ratio MTX:BSA at which energy transfer between methotrexate and fluorophores contained in the serum albumin structure was found.

The relative fluorescence intensity decreases with increase of temperature. Similar results were observed for BSA excited with 280 nm and 295 nm at the same range of temperature. Temperature dependence of the binding constant has been presented. The binding and quenching constants for equilibrium complex were calculated using Scatchard and Stern – Volmer method, respectively.

The results show that MTX forms π-π complex with aromatic amino acid residues of BSA. The binding site for MTX on BSA was found to be situated in the hydrophobic IIA subdomain (where the Trp 214 was located). The thermodynamic parameters were calculated.

MODELS FOR THE DETERMINATION OF THE HUMAN URINARY CALCULI COMPOSITION USING TRANSMISSION AND DIFFUSE-REFLECTION INFRARED SPECTRA

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The transmission Fourier-transform infrared (FTIR) spectroscopy is the most often used technique for the analysis of urinary calculi. However, using suitable accessories diffuse-reflectance infrared Fourier-transform (DRIFT) spectroscopy could be used for the same purpose. Nowadays this technique is considered as very reliable for the development of methods for quantitative analysis. The simple and less time-consuming procedure for sample preparation is its main advantage over the techniques based on transmission FTIR spectra.

In this study, using counter-propagation neural networks (CPNM) as a modeling tool the performances of the models developed using DRIFT and transmission FTIR spectra were compared.

The DRIFT spectra were expressed in log(1/*R*) and Kubelka-Munk units. After this, the spectra from all three data sets (those using: log(1/*R*), Kubelka-Munk and the transmission spectra) were suitably preprocessed and CPNM were used for modeling of the concentration of the constituents of samples composed of calcium oxalate monohydrate, calcium oxalate dihydrate and carbonate apatite. The best network parameters and the network sizes were searched using genetic algorithms.

The F-test was applied in order to determine whether there is a statistically significant difference between different models. At the 0.95 level of significance, differences were indeed found between the performances of the model based on the Kubelka-Mink spectra and the other two models. The differences between obtained and expected values after standard addition were smaller then 0.100 (w/w) which makes the proposed methods based on CPNM suitable for analyses of urinary calculi in clinical laboratories.

EPR AND CALORIMETRIC STUDIES OF THE THERMOTROPIC PHASE BEHAVIOR OF MEMBRANE PHOSPHOLIPIDS

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The EPR spectroscopy was used to determine a structure and physicochemical properties of liposomes prepared from DL-α-phosphatidylcholine dimyristoyl (1,2-ditetradecanoyl-rac-glycerol-3-phosphocholine) (DMPC) by the modified reverse-phase evaporation method (mREV). EPR study was carried out in the temperature range from 284K to 310K i.e. below and above the phase transition temperature T_C of DMPC. On the basis of EPR spectra of spin marker 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) incorporated into liposome, the parameters *f* were determined. Thus TEMPO can be used to observe the change in partition between aqueous and fluid lipid regions. The change in the relative values of *f* determined for DMPC as a function of temperature shows that, this phospholipid undergoes a transition from a "gel phase" to a lamellar smectic liquid crystalline phase in the presence of excess water. The EPR study of TEMPO allowed to determine transition temperature T_C. The results have been compared with those obtained with DSC method. Transmission electron micrographs (TEM) showed that the liposome vesicles, obtained with the use the modified (mREV) method, were spherical in shape and in majority they were less than 100 nm in diameter. Temperature, cholesterol and pH dependent structural changes of liposome were also described.

Acknowledgements
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HEMATOPORPHYRIN BINDING WITH SERUM ALBUMIN IN PHOTODYNAMIC THERAPY

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The binding of hematoporphyrin (HP) to human (HSA) and bovine (BSA) serum albumin has been studied using UV-VIS absorption and fluorescence quenching.

The difference UV-VIS spectra confirm formation of the HP-serum albumin complexes.

Hematoporphyrin quenches the fluorescence of serum albumin excited at 295 and 280 nm. The interaction of HP with serum albumin alters the microenvironment around tryptophan and tyrosine residues of the polypeptide chain. The degree of quenching is larger for excitation 280 than 295 nm. The results point at a conformational alteration inside the subdomains where the fluorophores are located. HP gives a 1.2:1 complex with albumin with binding site in IIA subdomain. It is also shown that both tryptophanyl and tyrosyl residues participate in the HP-serum albumin complex. The binding constant is about 10^6 M^{-1}as determined by Scatchard plot after estimation of the bound HP that causes quenching of fluorescence emitted by the protein. This interaction is affected by pH: at 6.6 - two binding sites while at the physiological pH (pH 7.4) only one binding site is observed.

MEASURING THE FRACTAL DIMENSION OF LINEAR POLYMERS AND GELS VIA *IN SITU* FLUORESCENCE EXPERIMENTS

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In the first time we applied the fluorescence technique for measuring the fractal dimension of linear polymers and polymeric gels below, at, and above the gelation threshold. The linear polymers that are able to dissolve in water were prepared with trace amount of some fluorescent molecule that is able to bind to the polymer stands during the polymerization. The fluorescence intensity of the bonded probes changes proportionally to the mass of the polymer cluster in the region illuminated by the excitation light. For the bulk polymers and gels another type of probe that does not bind to the polymer chains was used. In that case, when the probe molecules are trapped in the glassy regions of the gelling system they illuminate, and thus measure the mass of the glassy regions. Thus the expression

$$M \sim R^{D_f} \tag{1}$$

relating the mass, M, fractal dimension, D_f and the scale parameter, R takes the form

$$I \sim L^{D_f} \tag{2}$$

where I and L are the fluorescence intensity and slit width of the excitation light, respectively.

The slope of log-log plot of Eq. (2) gives the fractal dimension of the polymeric system as represented in below figure.

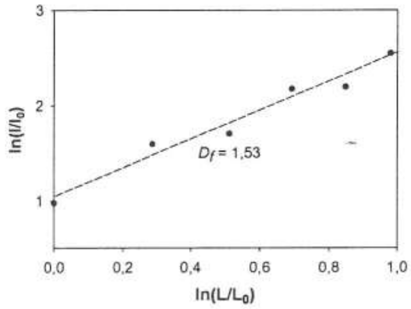

Fig. 1: log-log plot of normalized intensity (I/I_0) versus normalized slit width (L/L_0)

The result showed that the fractal dimension changes,$1 < D_f < 3$, depending on the polymer concentration, the polymerization stage and the swelling degree of the gels. But the bulk gels near the gelation threshold have the fractal dimension about 2.5, which agree best with the literature. .

References

[1] D. Stauffer and A. Aharony, *Introduction to Percolation Theory*,Taylor and Francis, London, 1992.
[2] Y. Yılmaz, *Phys. Rev. E*, **66**, 05801(2002).
[3] D. Kaya, Ö. Pekcan and Y. Yılmaz, *Phys. Rev. E*, **69**, 016117 (2004)
[4] Y. Yılmaz, A. Erzan,and Ö. Pekcan, *Phy. Rev. E.*, **58**, 7487 (1998).
[5] Y. Yılmaz, Ö. Pekcan ve A. Erzan, *Euro. Phys. J. E*, **9**, 135-141 (2002).
[6] Y. Yılmaz, D. Kaya and Ö. Pekcan, *Euro. Phys. J. E* , **15**, 19-25 (2004).

MICRO FTIR SPECTRAL IMAGING OF LYMPH NODE TISSUES

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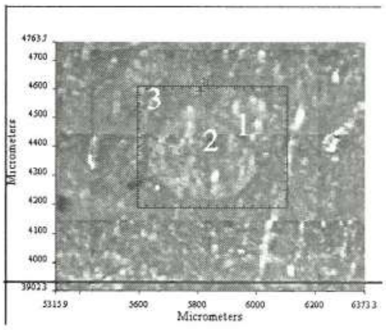
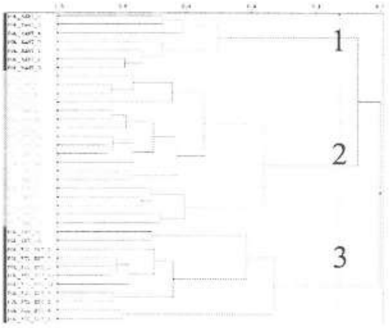
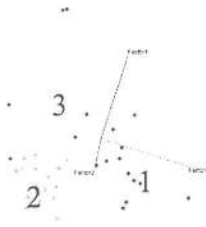
In the past decade, infrared micro spectroscopy has greatly advanced into areas of clinical study demonstrating a potential role to detect and understand pathological changes in cells and tissues. More recently, spectral images data can be obtained more rapidly by using focal plane array detectors[1,2]. Non-Hodgkin lymphomas constitute about 4% of all human malignancies. They usually involve lymphoid organs but can also primarily be present in a leukemic form. Morphological analysis coupled to immunohistochemistry is the most widely used approach for their classification, but these analyses are somehow prone to subjective interpretation. An automated technique such as FTIR microscopy could bring the benefits of objective tissue evaluation, together with the possibility to use this technique as a first-line screening methodology to distinguish normal versus neoplastic samples. Data regarding this possible application in lymphoid tissues are very scanty. We therefore compared the emitted spectra of various compartments of reactive lymph node samples and neoplastic samples (follicular lymphoma, mantle cell lymphoma). Neoplastic samples were classified according to the WHO 2001 classification of lymphoid neoplasms1 by morphology and immunohistochemistry, and included samples of mantle cell lymphoma (MCL) and samples of follicular lymphoma (FL)[3]. Non-neoplastic samples included reactive lymph nodes characterised by a marked follicular hyperplasia. Thick sections were contemporary analysed with Bruker Vertex 70 and Perkin-Elmer Spectrum GX1 spectrometers equipped with image microscopes at 10x10 and 25x25 μm spatial resolutions. In the presence of very similar spectra between the various zones, chemometric procedures (Pirouette and Opus software packages) allowed to isolate characteristic spectral patterns of the various zones (1 mantle, 2 internal and 3 external) in healthy and cancerous samples (figures)[3,4]. To our knowledge, this is the first study of this kind on this type of tissue, and demonstrates both the feasibility of the approach and the informative content of this analysis.







[1] M. Jackson, H.H. Mantsch, Pathology by Infrared and Raman Spectroscopy, in Handbook of Vibrational Spectrosc., J.M.Chalmes, P.R. Griffiths, Wiley, Chichester, 2002, Vol. 5, 3227-3245.

[2] M.J. Romeo, M. Diem, Vibrat. Spectrosc., 38 (2005) 115.

[3] E. Jaffe, N. Harris, H. Stein (editors): WHO classification of tumours: pathology and genetics of tumours of haematopoietic and lymphoid tissues. Lyon, France, IARC Press, 2001

[4] C. Conti, E. Giorgini, T. Pieramici, C. Rubini, G. Tosi, J. Mol. Struct., 744-7, 187 (2005).]; 1st DASIM Workshop (Diagnostic Applications of Synchroton Infrared Microspectroscopy), Daresbury Lab.s, Manchester, July 2005; RSC Faraday Division. Faraday Discussion 126, Nottingham (2003).

ELECTRONIC SPECTROSCOPY STUDY AND MOLECULAR DOCKING SIMULATION OF THE INTERACTION OF TERTHIOPHENE WITH DNA

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In the last years, many scientific efforts have been focused to the development of new conjugated molecules with applications in chemical therapy against an increasing number of diseases. Discovery of a new chemotherapeutic molecule requires a deep knowledge of its structure and how it interacts with its biological targets (structure/activity relationships). In this sense, DNA is a primary target in anti-tumour strategies, since alteration of its structure usually affects to cell proliferation.

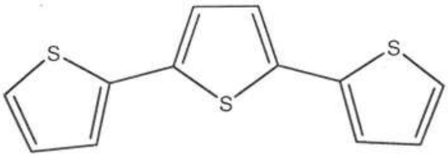

Figure 1. Chemical structure of terthiophene (TT).

Oligothiophenes are a class of molecules widely studied in the field of conjugated molecules. Currently, they are being also studied by their abilities to interact with DNA, which has been used for different applications ranging from biosensor devices to anti-cancer therapies. In these studies, information about the binding modes with DNA is of interest. The present work is aimed to investigate the interaction of terthiophene (TT, Fig. 1) with DNA. Thermal denaturing experiments showed us that the melting point of highly-polymerized calf-thymus DNA increased by 4.8 °C in the presence of a concentration 5 μM of TT, thus meaning that this molecule is interacting with DNA. In order to seek structural specificities in this interaction, we studied the electronic absorption and emission fluorescence spectra of TT in the presence of the 15-mer double-stranded oligonucleotides ds(dG-dC)$_8$ and ds(dA-dT)$_8$, at different molar ratios and physiological conditions of pH and ionic strength. Fluorescence spectra in presence of the classic intercalator ethidium were also recorded. Molecular docking simulations using the GRAMM 1.03 program evaluated intermolecular energies of different TT-oligonucleotides complexes. They suggested that intercalation is a more favourable interaction than groove binding, especially for AT sequences. Docking results also indicated preferential interaction of TT by AT-rich minor grooves and by GC-rich major grooves.

TRANSITIONS IN POLY(rA)·POLY(rU) INDUCED BY HEATING AND METAL IONS. UV-, IR- AND VCD SPECTROSCOPIC STUDY

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UV and IR absorption and vibrational circular dichroism (VCD) spectroscopy were used to study conformational transitions in the double-stranded poly(rA)·poly(rU)(AU) and its components – single-stranded poly(rA) and poly(rU) in buffer solution (pH6.5) with 0.1M Na^+ and different Mg^{2+}, Ni^{2+} and Cd^{2+} (10^{-6} - 10^{-2}M) concentrations. Transitions were induced by elevated temperature that changed from 10 up to 96°C. IR absorption and VCD spectra in the base-stretching region were obtained for duplex, triplex and single-stranded forms of AU at $[Me^{2+}]/[P]=0.3$.

A search for adequate conditions in experiments with nucleic acids by methods of ultraviolet and vibrational spectroscopy is an important and complex problem. For its decision VCD and IR-measurements of AU solutions with the constant $[Mg^{2+}]/[P]$ ratio but with different polymer concentrations (and, consequently, of metal ions) were performed. Also, with this purpose thermodynamic analysis of phase diagrams for this system was carried out and Me^{2+} binding constants (and amounts of metalbound nucleic acid) were determined.

For single-stranded polynucleotides the kind of conformational transition (ordering → disordering → compaction, aggregation) is conditioned by the dominating type of the Me^{2+}-polymer complex that in turn depends on the ion concentration range. The AU phase diagrams obtained by UV method have a triple point ($[Me^{2+}]\sim10^{-4}$M) at which the helix-coil (2→1) transition is replaced with a disproportion transition 2AU→ poly(rA)·2poly(rU) +poly(rA) (2→3) and the subsequent destruction of the triple helix (3→1). 2→1 transitions occur in the narrow temperature interval of 2° to 5°. Unlike 2→1 and 3→1 melting, the disproportion 2→3 transition is a slightly cooperative one and observed over a wide temperature range. At $[Me^{2+}]\sim10^{-3}$M the temperature interval of A2U stability is not less than 20°C. In comparison with Ni^{2+} ions, higher constants of the Cd^{2+} binding to bases of single-stranded polynucleotides[1] change radically the form of the phase diagram of AU. While the rise of the Ni^{2+} concentration over the critical point induces the broadening of the temperature range of the triplex existence mainly due to the T_{m3-1} increase, the extension of the triplex region in the case of Cd^{2+} results from the T_{m2-3} decrease (at practically constant T_{m3-1}). The conformational balance is conditioned with relationships of binding constants of ions for different phases of the polymer.

[1] S. Massoud, H.Sigel, Eur J.Biochem 179 (1989) 451.

RAMAN SPECTROSCOPY AND ATOMIC FORCE MICROSCOPY STUDY OF CELLULAR DAMAGE IN HUMAN KERATINOCYTES TREATED WITH HGCL$_2$

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Raman microspectroscopy and Atomic Force Microscopy (AFM) have been used to detect structural changes in cultured human keratinocytes as a consequence of mercury exposure. In fact, the affinity of mercury ions to thiol (-SH) groups in proteins causes cellular damage due to chemical and structural modifications. Common environmental sources of mercury are thermometers, fluorescent lamps, insecticidal products, etc. Mercury poisoning can result from vapour inhalation, ingestion or absorption through the skin. So it is interesting the study of cellular damage in epidermal cells as keratinocytes, because they are directly exposed to environmental mercury sources.

Keratinocytes cultured cells have been treated with $HgCl_2$ at a concentration of 10^{-5}M for 24 h. Both control and treated cells have been analysed by means of Raman microspectroscopy and AFM. We have found that important structural and biochemical changes occur in treated keratinocytes. In particular, Hg cations often form complexes with S species, as revealed by the presence of a Raman peak at 260 cm^{-1}, which can be attributed to Hg-S stretching mode. We also found that the $HgCl_2$ treatment causes a decrease of the phenylalanine peak at 1005 cm^{-1}, indicating either a general decrease of protein content inside the treated cells or the breakdown of phenyl group. In addition, the magnitude of a 785 cm^{-1} feature corresponding to DNA characteristic vibrations is drastically reduced in treated cells, indicating specific DNA damage. Cellular damage is also confirmed by AFM measurements: in particular, the three-dimensional images of keratinocyte surfaces evidences that the mercury treatment induces the formation of buds and roughness on the cell membrane.

ANN EXPERT SYSTEM SCREENING FOR ILLICIT AMPHETAMINES USING MOLECULAR DESCRIPTORS

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The goal of this study was to develop an artificial neural network (ANN) able to classify illicit amphetamines. The system is necessary for testing new molecular structures for epidemiological, clinical, and forensic purposes. The system was built using a database formed by 146 compounds representing drugs of abuse (mainly central stimulants, hallucinogens, sympathomimetic amines, narcotics and other potent analgesics), precursors, or derivatized counterparts. Their molecular structures were characterized by computing 38 constitutional descriptors (CDs), 69 topological descriptors (TDs) and 160 3D-MoRSE descriptors (3DDs). An ANN system was built for each category of descriptors. All three networks (CD-NN, TD-NN and 3DD-NN) were trained to distinguish between stimulant amphetamines, hallucinogenic amphetamines, and nonamphetamines. A selection of variables was performed when necessary. The efficiency with which each network identifies the class identity of an unknown sample was evaluated by calculating several figures of merit. The results of the comparative analysis are presented.

Keywords: Amphetamines; Artificial neural networks; Drugs of abuse; Constitutional descriptors, topological descriptors, 3D-MoRSE descriptors

P2-15

COMPARATIVE ANALYSIS OF ANN AND PATTERN RECOGNITION EXPERT SYSTEMS SCREENING FOR ILLICIT AMPHETAMINES BASED ON GC-FTIR SPECTRA

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Two expert systems, an artificial neural network (ANN) and a system built with the pattern recognition technique were built to identify the molecular structure of illicit amphetamines acording to their toxicity. Such a system is necessary for speeding up the tests for epidemiological, clinical, and forensic purposes. The system was built using a database formed by the GC-FTIR spectra of 159 compounds representing drugs of abuse (mainly central stimulants, hallucinogens, sympathomimetic amines, narcotics and other potent analgesics), precursors, or derivatized counterparts. Both systems were trained to distinguish between stimulant amphetamines, hallucinogenic amphetamines, and nonamphetamines. Data-preprocessing or the selection of variables was performed when necessary. The efficiency with which each network classifies an unknown sample was evaluated by calculating several figures of merit. The results of the comparative analysis are presented.

Keywords: Amphetamines; Artificial neural networks; Pattern recognition, Drugs of abuse.

P2-16

MICRO-FT-IR SPECTROSCOPY OF BREAST CANCER TISSUES

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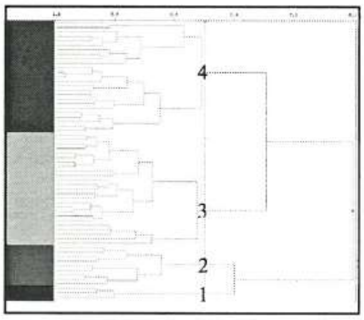
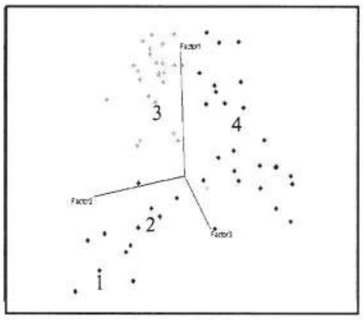
Fourier Transform Infrared Spectroscopy (FT-IR) has received great attention from various fields because it can provide information about the molecular structure and the chemical composition of biological materials. Recently, infrared spectroscopy has been considered as an early diagnostic tool for the detection of tumours in synergy with traditional methods such as histopathological analysis, ultrasound, X-rays, etc. Micro imaging FT-IR is a powerful technique applied in tissue analysis, because it allows to detect biochemical changes that can be extremely subtle and located in a small area of tissue[1,2].

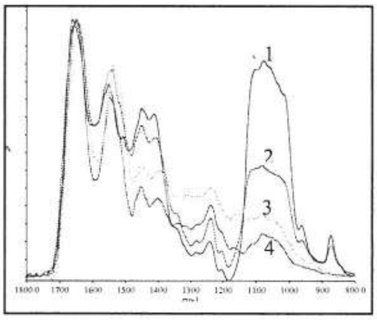
Breast cancer affects a large number of women. An early detection of this disease could expand the survival of women. FT-IR spectroscopy is a method that could achieve this goal by studying the growth of tumours. In the last years micro-FT-IR imaging of breast cells has been carried out on breast tissues and cell lines showing certain spectral features, which can distinguish different breast tumours[3,4].

We have investigated several breast cancer tissues, such as *in situ*, invasive lobular, ductal, invasive carcinoma and osteosarcoma, and performed spectral analysis of their solid state spectra. By analysing these spectra, we have found characteristic bands in the infrared regions, where the main components of these signature bands are located. For example, characteristic DNA band near 1680-1660 cm^{-1}, Amide I, II, III protein bands and phospholipid band near 1140-1170 cm^{-1}. These characteristic bands have been monitored as a function of the degree of cancer progression, which was determined for different types of cancer. Preliminary micro-FT-IR images of breast cells will be given, showing the changes that take place in these cancer cells.

The results have been obtained with chemometric methods, such as cluster analysis, principal component analysis and custom analysis. Figures 1-3 report results from cluster, PCA and spectra on a line from neoplastic (1,2) to normal zone (3,4) for an osteosarcoma tissue.







[1] M. Jackson, H.H. Mantsch, Pathology by Infrared and Raman Spectroscopy in: G.M. Chalmers, P.R. Griffiths (Ed.s), Handbook of Vibrational Spectroscopy, vol 5, Wiley, Chichester, 2002, p. 3227.
[2] C. Conti, E. Giorgini, T. Pieramici, C. Rubini, G. Tosi, FT-IR microscopy imaging on oral cavity tumours, II. J. Mol. Struct., 744-7 (2005) 187.
[3] L.Zhang, G.W. Small, A.S. Haka, L.H. Kidder, E.N. Lewis, Applied Spectroscopy, 57 (2003) 14.
[4] R. Eckel, H. Huo, HW Guan, X. Hu, Xun Che, WD Huang, Vibrat. Spectroscopy, 27 (2001) 165.

TERAHERTZ PULSED SPECTROSCOPY: APPLICATION CHALLENGES AND COMPARISON WITH FAR INFRARED FOURIER TRANSFORM SPECTROSCOPY

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The emerging field of terahertz science and technology holds immense promise in fields as diverse as medicine, security, and pharmaceuticals. The terahertz region lies in the very far infrared between the millimeter wave and mid infrared of the electromagnetic spectrum (1.0 THz corresponds to 33.3 cm^{-1} or 300 μm wavelength) and has been difficulty to access due to the requirement, until recently, to use low sensitivity room temperature pyro-electric (DLaTGS) or liquid helium-cooled bolometer detectors together with thermal plasma sources. Today, using ultrashort near-infrared pulsed lasers, it is possible to generate stable ultrashort-pulses of coherent terahertz radiation. These pulses can be used in a wide range of applications which are currently explored (1-5).

In this paper we compare the technique of terahertz pulsed spectroscopy with traditional far infrared Fourier transform spectroscopy. We compare results obtained (in one second) using a terahertz pulsed system (TPI spectra 1000) with those obtained (in sixty seconds) with the continuous wave Fourier transform interferometer. The terahertz pulsed spectrometer shows superior performance in the 2 cm^{-1} to 100 cm^{-1} region with a maximum dynamic range of 70 dB at 10 cm^{-1}.

In addition report comparative studies on standard polymeric and optical material, performed using the two systems.

[1] P. F. Taday, I. V. Bradley, D. D. Arnone and M. Pepper, *J Pharm Sci* **92**, 831 (2003).
[2] C. J. Strachan, T. Rades, D. A. Newnham, K. C. Gordon, M. Pepper and P. F. Taday, *Chem Phys Lett* **390**, 20 (2004).
[3] C. J. Strachan, P. F. Taday, D. A. Newnham, K. C. Gordon, J. A. Zeitler, M. Pepper, T. Rades, *J Pharm Sci* **94**, 837 (2005).
[4] C. Baker, W. R. Tribe, B. E. Cole, and M. C. Kemp, *P. Soc. Photo-opt. Inst.* **5616**, 61 (2004).
[5] Y. Shen, P. F. Taday, and M. C. Kemp, *P. Soc. Photo-opt. Inst.* **5619**, 83 (2004).

DEVELOPMENT OF RAMAN SPECTROSCOPIC METHODOLOGY FOR QUANTIFICATION OF CAROTENOIDS IN NORWAY SPRUCE NEEDLES

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Resonance Raman spectroscopy excited in visible range as well as FT-Raman spectroscopy with excitation line at 1064 nm belong among techniques that are commonly used for characterization of carotenoids in plants[1,2]. Especially resonance Raman scattering produces strong lines even at concentrations as low as 10^{-5} mol L^{-1}. For quantification of carotenoids in plant extract, HPLC with spectroscopic detection techniques (e.g. UV/VIS spectrometry) is used at first. It grants reliability of analytical results[3]. An advantage of Raman spectroscopy is a quick and non-destructive analysis allowing also *in vivo* measurements[4,5].

In this work a combination of measurement of FT Raman spectra of needles or needles pulps (excitation at 1064 nm) with resonance Raman spectra of needles extract (excitation at 488 nm) is used to quantify content of carotenoids.

To develop a reliable method of carotenoids determination, it has to be taken into account, that carotenoids not fixed in plant matrix are sensitive to oxygen and solar radiation. Hence, conditions for sample preparation in nitrogen atmosphere were found and a suitable measurement cell designed. An important issue is also the selection of a suitable standard as a mixture of carotenoids is extracted. *Trans*-β-carotene was commonly used in the standard addition method.

Results obtained from measurement of resonance Raman spectra of extract are compared with data from HPLC and UV/VIS spectra.

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[1] R. Withnall, B.Z. Chowdhry, J. Silver, H.G.M. Edwards, L.F.C. de Oliveira, *Spectrochim. Acta Part A* **59** (2003) 2207.
[2] H. Schulz, M. Baranska, R. Baranski, *Biopolymers* **77** (2005) 212.
[3] L. Feltl, V. Pacáková, K. Štulík, K. Volka, *Curr. Anal. Chem.* **1** (2005) 93.
[4] R. Baranski, M. Baranska, H. Schulz, *Planta* **222** (2005) 448.
[5] J. Křížová, P. Matějka, G. Budínová, K. Volka, *J. Mol. Struct.* **480-481** (1999) 547.

NEAR-INFRARED DIFFUSE REFLECTANCE SPECTROSCOPY OF SKIN WITH DIFFERENT PROBING DEPTHS FOR DIABETES SCREENING

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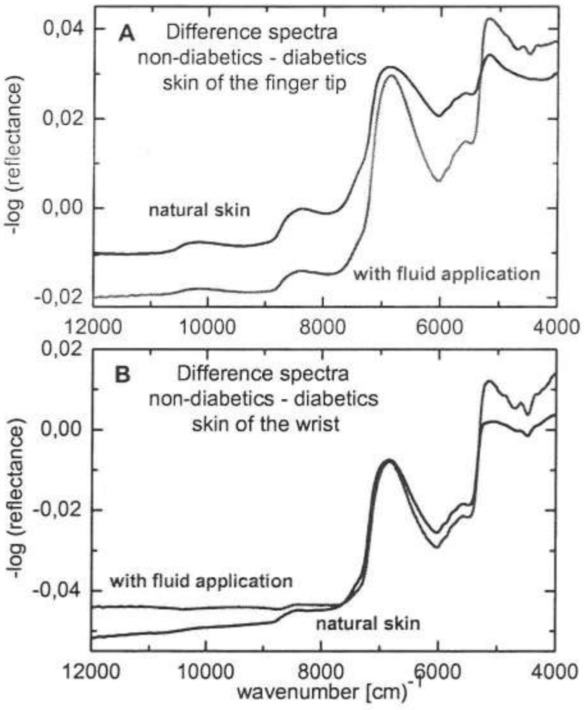

Fig. 1 Diffuse reflectance spectra of skin and differences observed for two subject categories

Near infrared spectroscopy has proved its potential for clinical chemistry and tissue pathology. Owing to its penetration depth into human skin, near infrared radiation can probe chemical and structural information non-invasively even from the subcutaneous tissue. Non-enzymatically glycated proteins in human skin and following chemical and structural skin changes were our target. Metabolic diseases such as diabetes mellitus can increase glycation, which accumulates over the years on the longest-lived proteins with the clearest evidence found in extracellular skin collagen.

We carried out measurements on 109 subjects using two different NIR-spectrometers equipped with diffuse reflection accessories by employing either a fibre-optic probe or mirror optics.[1] Spectra of different skin regions (finger and wrist) were recorded for comparison with clinical blood analysis data and further patient information, allowing a classification of the test-persons into diabetics and non-diabetics. For the mirror-optics based accessory also a fluorinated inert solvent was applied for refractive index matching and reduction of scatter from the horny layer of the skin, which allows different skin depths to be probed (see above Figure). We applied multivariate analysis techniques for supervised classification such as linear discriminant analysis (LDA) using also difference spectra from experiments with pure skin and with fluid application. Results will be compared with previous studies based on skin spectra measured by using a fibre-optic probe.[2]

[1] R. Marbach and H.M. Heise, Applied Optics 34 (1995) 610.
[2] H.M. Heise, S. Haiber, M. Licht, D.F. Ihrig et al., Proc. SPIE 6093 (2006) 250.

NEAR-INFRARED AND VISIBLE SPECTROSCOPY OF PDMS FOR CHARACTERISATION OF POLYMER OPTICAL WAVEGUIDE MATERIALS

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Solid poly(dimethylsiloxane) silicones (PDMS) have attractive characteristics as an inert, non-toxic, non-flammable and low-cost polymer showing high transparency combined with excellent tear strength. In the optical communication field, passive polymer multimode waveguides have been used for short-distance datacom optical applications, which require polymer materials of lowest intrinsic absorption losses within the spectral region of 600–900 nm [1]. Especially, Pt-catalyzed polymerization can be carried out under low-temperature curing conditions without the formation of cross-linker by-products through hydrosilylation. The two component PDMS systems were supplied by Wacker Chemie GmbH. The cladding materials were standard commercial PDMS silicones (ELASTOSIL® RT 601), whereas the core polymer is a special development by Wacker Chemie.

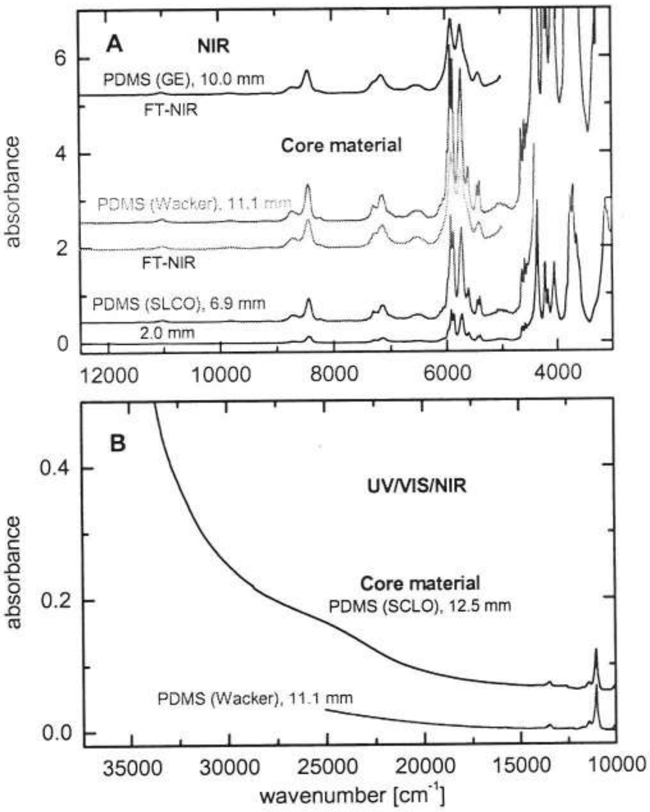

Fig. 1 NIR (A) and VIS spectra (B) of PDMS silicones used as waveguide core

A novel process for multi-mode optical waveguide device fabrication by casting polydimethylsiloxane (PDMS) has been developed at the University of Dortmund [2]. For spectral absorption band assignments, previous mid-infrared and Raman studies were taken into account. Vibrational C-H stretching overtone and combination bands dominate the near-infrared and long-wave visible spectral range. The optical characterization with absorption spectra recorded for the near-infrared and visible spectral range is given for PDMS-materials that can be used for waveguide core and cladding applications. In addition to optical propagation loss measurements, also the refractive indices of the materials are presented.

[1] N. Tanio and Y. Koike, Polymer Journal **32** (2000) 43.
[2] S. Kopetz, E. Rabe, W.J. Kang, A. Neyer, Electronics Letters **40** (2004) 668.

INTERACTION OF MELATONIN WITH NEGATIVELY CHARGED PHOSPHOLIPID MEMBRANES

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Melatonin (5-methoxy-N-acetyltryptamine), a pineal hormone derived from tryptophan, has been reported to interact with many different cells, playing a number of distinct physiological roles. Melatonin's action as a free radical scavenger and an antioxidant is well established [1,2]. Negatively charged phospholipids are present in all biological membranes in a fraction ranging from 5 to 25 molar percent. Within them, phosphatidylglycerol is abundant in the plasma membrane of microorganisms, choloroplast membranes in plants and to a lower extent in mammalian cells. Several structural and physicochemical properties of vesicles formed by charged phospholipids are strongly dependent on ionic composition of suspension medium [3]. The studies on melatonin-membrane interactions are very limited [4].

In the present work, interaction of melatonin with anionic dipalmitoyl phosphatidylglycerol (DPPG) multilamellar liposomes (MLVs) were investigated as a function of temperature and different melatonin concentration by using Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) techniques.

DSC and Fourier transform infrared spectroscopic studies show that melatonin does not perturb the phase transition profile, while a decrease in the main transition temperature (T_m) is noticed as melatonin concentrations are raised. Low concentrations of melatonin (3, 6 and 9 %) decrease the frequency of the CH_2 stretching mode, implying an ordering effect, whilst high concentrations of melatonin (15, 24 and 30 %) disorders system both in the gel and liquid crystalline phases. Furthermore, at low and high concentrations, melatonin causes opposite effect on membrane dynamics. It decreases the bandwidth of the CH_2 stretching modes at low concentrations, implying a decrease in the dynamics, while increasing it at high concentrations. In addition, it also causes significant decrease in the wavenumber for the C=O stretching and PO_2^- antisymmetric double bond stretching bands of DPPG both in the gel and liquid crystalline phases, which indicates strong hydrogen bonding.

This work was supported by State Planning Organization Fund (Project No: BAP-01-08-DPT.2003K120920-13)

[1] J.J. Garcia, R.J. Reiter, J.M. Guerrero, G. Escames, B.P. Yu, C.S. Oh, A. Munoz-Hoyos, FEBS Lett.408 (1997) 297-300.
[2] R.J. Reiter, D-X Tan, C. Osuna, E. Gitto, J. Biomed. Sci. 7 (2000) 444-458.
[3] D. Zubiri, A. Domecq, D.L. Bernik, Colloids and Surfaces B: Biointerfaces, 13 (1999) 13-28.
[4] F. Severcan, I. Sahin, N. Kazanci, BBA, 1668 (2005) 215-222

SPECTROSCOPIC STUDIES ON COOPERATIVE BINDING OF PHEOPHORBIDE-A TO POLY-L-LYSINE MATRIX

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The pheophorbide-a (Pheo) is anionic porphyrin derivative (see Fig. 1). It is widely used as a photosensitizer in photodynamical therapy of tumors because of its high photosensitizing activity in vitro and in vivo [1-2]. The cooperative binding of Pheo to model polycationic polypeptide matrix, poly-L-Lysine (pLL), in buffered (pH6.9) aqueous/ethanol solutions (volume ratio 19:1) has been investigated by means of absorption and polarized fluorescence spectroscopy. The measurements were carried out in a wide range of molar phosphate-to-dye ratios, P/D. The absorption and fluorescent properties of aggregates formed by Pheo chromophores stacking at the polycation, poly-L-Lysine, were established. Such parameters of cooperative binding as the number of binding sites per monomer unity of pLL, cooperativity parameter and the cooperative binding constant were estimated by Schwarz's method [3].

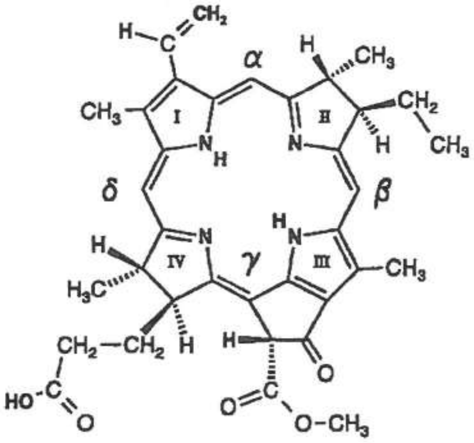

Fig.1: Molecular structure of pheophorbide-a.

This work was partially supported by Science and Technology Center in Ukraine (Project #3172).

[1] B. Roeder, J. Photochem. Photobiol. B, 5 (1990), 519 - 521.
[2] B. Roeder, Lasers Med. Sci., 5 (1990), p. 99 -106.
[3] G. Schwarz, Eur. J. Biochem., 12 (1970), p. 442 - 453.

ATR FTIR, NIR AND RAMAN SPECTROSCOPY STUDY OF THE THERMOTROPIC PHASE TRANSITION IN POLYMERS WITH AMIDE GROUPS IN MAIN AND SIDE CHAINS

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Reversible phase separation defined by a lower critical temperature in aqueous solutions of synthetic amide polymers is of great interest due to potential applications in different technological fields and biomedicine[1]. Below transition temperature T_t polymers are soluble, heating above T_t results in the phase separation. According to the chemical nature of polymers, T_t can be changed by different external influences. We have studied polymer systems undergoing inverse temperature transition near room temperature: elastin-like polypentapeptides represented by poly(GVGVP) and poly(AVGVP), with amide groups in the main chains[2], and poly(N-isopropylacrylamide) (PNIPAM) and poly(N-isopropylmethacrylamide) (PNIPMAM), with amide groups in the side chains. The aim of this study was to obtain more information about the structure of amide compounds in aqueous media by ATR FTIR, NIR and Raman spectroscopy in combination with model quantum chemical calculations.

In aqueous solutions parts of molecules of organic compounds undergo different types of interactions with the neighboring molecules of water. Hydrophobic interaction of the methyl groups causes the shift of the C-H stretching bands to the higher frequencies. Hydrophilic binding of the water molecules to amide groups by means of hydrogen bonds results in the shift of the Amide II band to higher frequencies, Amide I bands are shifted to lower frequencies due to H-bonds with water and due to coupling with H-O-H bending.

Below T_t both PNIPAM and PNIPMAM are homogeneously dissolved in aqueous solutions, however, only a part of the amide and methyl groups of studied polypentapeptides interacts with neighboring water molecules, whereas the other part of amide groups interact forming β-sheet-like structures. This is accompanied by the transition dipole coupling between the Amide I vibrations, which results in splitting of the Amide I bands. Above T_t polymers with more methyl groups, i.e. poly(AVGVP) and PNIPMAM, are more compact and resist more to the reverse dissolution. The suspensions of poly(GVGVP) and PNIPAM contain more water molecules bound to the amide groups and on backward cooling dissolve reversibly.

[1] D.W. Urry, Angew. Chem., Int. Ed. Engl. 32 (1993) 819.
[2] P. Schmidt, J. Dybal, J.C. Rodríguez-Cabello, V. Reboto, Biomacromolecules 6, (2005) 697.

EPR SPIN LABEL STUDY OF DOCOSAHEXAENOIC ACID EFFECTS ON DMPC MEMBRANES

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Effects of Docosohexaenoic acid (DHA) on dynamic and thermodynamic properties of 16 mol % cholesterol (CH) containing Dimyristoylphosphatidylcholine (DMPC) membrane dispersions were studied by Electron Paramagnetic Resonance (EPR), using 5-doxyl stearic acid (5-DSA) and 16- doxyl stearic acid (16-DSA) spin labels. Incorporation of 16 mol % DHA alone decreased maximum hyperfine splitting values at the gel phase and fluid phase. Addition of 10 wt % WO into 10 wt % CH containing DMPC decreased the order in the gel phase and in the fluid phase. These effects were observed both close to the head region and in the hydrocarbon core of the DMPC bilayer (Fig. 1). In the studied temperature range, order parameters, diffusion constants and effective tilt angles were obtained from simulations of the spectra using Microscopic Order Macroscopic Disorder (MOMD) [1] and Very Anisotropic Reorientation (VAR) models[2]. For 16-DSA, spectra were also simulated using EPRSIM [3]. Results were discussed by comparison with the results obtained for natural walnut oil, which was a mixture of unsaturated fatty acids .[4]

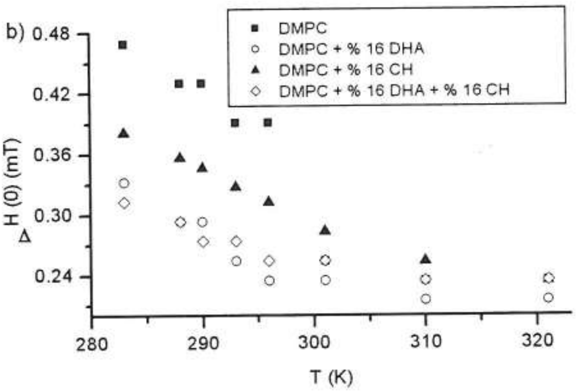

Figure 1 Peak to peak width of central peak against temperature

[1] Meirovitch E., Akbar N., Freed J. H.: J. Phys. Chem. 88, pp. 3454-3465 (1984).
[2] Mason, R. P., Polnazsek, C. F. and Freed, J. H., Comments on the interpretation of electron spin resonance spectra of spin labels undergoing very anisotropic rotational reorientation, J. Phys. Chem., 78(13), 1324-1329 (1974)
[3] Strancar, J., Sentjurc, M. and Schara, M., Fast and accurate characterization of biological membranes by EPR spectral simulations of nitroxides, Journal of Magnetic Resonance, 142, 254-265 (1999).
[4] Horasan N., Sünnetçioğlu M.M., Sungur, R., EPR Spin Label Study of walnut oil effects on phosphatidylcholine membranes, (2006), Chem.Phys. Lipids, 140,1-10.

PROTEIN LABELING WITH 18-CROWN-6: TRANSIENT ABSORPTION, MALDI-TOF AND CHROMATO-MASS SPECTROSCOPY

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The functional activity of serine proteases in organic solvents substantially differs from that in water[1,2]. Enzymatic hydrolysis (in water) is changed by a low-rate synthesis in organic solvents. Crown ethers are used to increase the rate of enzymatic reactions in organic solvent by a few orders of magnitude, although the physicochemical nature of this effect remains unknown.

Crown ethers form H-bonds rather than covalent bonds with the protein molecules. Extensive analysis of the activation of serine proteases in organic solvents in the presence of crown ethers yields assumptions regarding the binding sites of crown ethers on the surface of protein globules.

In this work, we synthesize a photosensitive crown ether (p-azido-benzo-18-crown-6) and employ four experimental techniques to study the photoinduced transformations of this substance, including the transformations in the presence of chymotrypsin.

Transient absorption spectroscopy and the analysis of the published data make it possible to determine the lifetimes and the number of components that take part in the photoinduced reaction over a time interval of 1 ns after the excitation pulse.

The results obtained with the HPLC-mass spectroscopy for the solutions of the crown ether under study in acetonitrile are used to determine chemically stable photosensitive components emerging in the solution upon irradiation with various doses of laser radiation at a wavelength of 355 nm.

The analysis of the absorption spectra of the crown ether measured simultaneously with the chromato-mass spectra at various irradiation doses enables us to determine the absorption spectra of the components of the photoinduced reaction in a wavelength range of 210-600 nm.

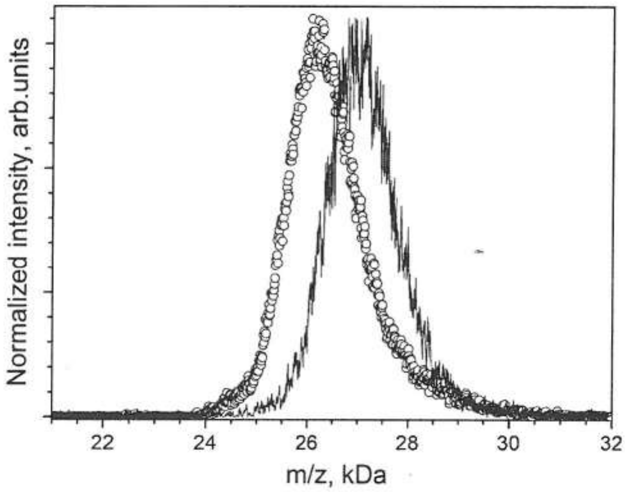

Fig. 1: MALDI-TOF mass-spectra of the chymotrypsin suspensions in acetonitrile in the presence of the crown ether at a molar ratio of 1:500: (circles) unirradiated sample and (solid line) the sample irradiated over 1 h at a wavelength of 355 nm and a laser power of 120 mW.

MALDI-TOF mass spectroscopy is used to measure the mass spectra of the irradiated and unirradiated suspensions of chymotrypsin in acetonitrile in the presence of the crown ether in the molar mass range m/z = 1-10^5 D. An increase in the enzyme mass after irradiation (Fig. 1) is interpreted as a result of the photoinduced protein labeling with the crown ether.

[1] A. Zaks, A.M. Klibanov, J. Biol. Chem. 263 (1988) 3194.
[2] A.M. Klibanov, Trends Biochem. Sci. 14 (1989) 141.

P2-26

PREVENTION OF CARCINOGENIC NITROZAMINES FORMATION IN CIGARETTE SMOKE BY IRON COMPLEXES

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The gas phase of the cigarette smoke is one of the main exogenous source of nitric oxide (NO), a short lived, highly diffusible reactive gas. There is evidence to suggest that NO capable forms nitrozamines, compounds with well established carcinogenic and mutagenic properties. Here we report that iron complexes may be used for effective trapping NO from smoke of various brands of azerbaijanian cigarettes. The ESR method was used for registration of ESR signals of di- and mononitrosyl iron complexes formed in 10^{-3}M water solution of the Fe++ with sodium thiosulphate ($Na_2S_sO_3$) and 10^{-3}M solution of the Fe++ with diethylditiocarbamate (DETC). The solution was placed into special closed tube with diameter 10-70 mm and then treated by argon gas. The quantity of NO was evaluated by the comparative studies of intensities of di- and mononitrosyl iron complexes with previously known concentration.

The estimated quantity of NO was about 120-140 μg per cigarette and consists of (i) nitric oxide, that forms paramagnetic complexes with endogenous iron and thiol ligands; (ii) oxidized nitric oxide (NO_2); (iii) nitric oxide, that involves into nitrozamines. Carried out experiments allowed us to draw two main conclusions: (i) the physiological doze of NO in cigarette smoke is more greater than that forms at the using one tablet of nitroglycerine; (ii) a little concentration iron salts and thiosulphate incorporated into cigarette filter can reduce high concentrations of nitric oxide and as a result, to prevent the carcinogenic nitrozamines formation in an organism of smoker.

STATE RESOLVED SPECTROSCOPY OF GAS-PHASE PROTONATED BIOMOLECULES.

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A new and challenging direction in spectroscopy is to provide structural information for large protonated biological molecules in the gas phase. Those species cannot be cooled in supersonic jets as they are charged. We have recently pioneered a 22-pole ion trap kept at T=6K to store and to cool large protonated biomolecules to as low as T_{vib}=10K. Such deep cooling offers vibrational resolution in UV and IR photofragmentation spectra, revealing structural and dynamical information.[1] We could follow change in dynamics of excited electronic state of tryptophan-H^+ protonated amino acid upon its gradual solvations by water. Selective IR pre-excitation of particular conformational states of water complexes of tyrosine-H^+ and of tryptophan-H^+ allows obtaining conformer specific UV spectra. This serves as a land-mark for adjustment of computational models, that finally yield 3D structure of biological molecules.

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[1] Oleg V. Boyarkin, Sébastien R. Mercier, Anthi Kamariotis, Thomas R. Rizzo: JACS communication, on-line DOI: 10.1021/ja058383u, 2006

THE POSSIBILITIES AND LIMITATIONS OF *in vivo* FT RAMAN SPECTRAL STUDY OF NORWAY SPRUCE NEEDLES UNDER SOLAR SIMULATOR

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FT Raman spectroscopy is a method that enable non-destructive analysis of Norway spruce needles performed both *in vitro* and *in vivo*[1,2]. In last few years thousands of spectra of needles collected in series of experiments were evaluated using various chemometric methods to elucidate the variability of several spectral features, e.g. the shape of background, bands of waxes, water and carotenoids. A set of preliminary experiments with irradiation of small trees and selected twigs using halogen lamp as a "solar simulator" demonstrated effects of light and dark periods on Raman bands of carotenoids and on features related to drying of needles[2].

To study these effects more precisely and correctly we equipped our laboratory with the solar simulator (Oriel, USA) and with a set of hygro-, baro-, thermo- and oxy-meters (Greisinger electronic, Germany). The simulator fitted with 300-W xenon arc lamp produces a power equivalent to ca. 2 suns. The basic set of air mass filters allow to simulate different solar spectra related to different zenith angles. The digital timer enables to adjust irradiation sequences. We monitor the temperature at the standard workplane during the various irradiation periods and consequent relaxation times. Regardless the type of air mass filter used the temperature exceeds 50°C in a few minutes of irradiation. Irradiated needles show fusion or even disappearance of stomatal waxes observed using optical microscope. FT Raman spectral changes correspond to drying of needles and to a decrease of carotenoids content without significant effect of needle wetting. The degradation of β-carotene in solution under such conditions is demonstrated using UV-vis spectrometry. Two different approaches are adopted to reduce the thermal drying and damaging of needles. One is based on the change of workplane distance from simulator output, the other on a filtration of thermal radiation using a layer of water placed between the simulator output and workplane. A decrease of temperature reached is observed; the effects on stomatal waxes, carotenoids and moisture of needles are studied using both the optical microscopy and FT Raman spectroscopy.

The results obtained show the advantages of defined irradiation conditions, but also demonstrate troubles to be solved by implementation of solar simulator to a systematic study of Norway spruce needles with a special respect to *in vivo* experiments.

Financial support from Czech Science Foundation (GA CR 203/05/0697) and from the Ministry of Education of Czech Republic (MSM 6046137307) is gratefully acknowledged.

[1] P. Matějka, L. Plešerová, G. Budínová, K. Havířová, X. Mulet, F. Skácel, K. Volka, *J. Mol. Struct.*, **565/566** (2001) 305.
[2] P. Matějka, H. Tokarová, T. Pekárek, K. Volka, *J. Mol. Struct.* **661-662** (2003) 333.

VIBRATIONAL SPECTROSCOPIC STUDY OF SULFATED SILK PROTEINS

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Silk is a natural product mainly composed by two proteins: fibroin and sericin. Fibroin is the main component of silk fiber and sericin glues the fibroin filaments in the cocoon and in textile is removed by boiling in water (degumming process). Silk can be easily functionalized, and its structure and morphology modulated to match a wide range of working requirements. In recent years, the unique chemical, mechanical, and biological properties of silk have made this natural polymer a highly attractive candidate for the development of innovative biomedical devices (*i.e.* scaffolds for tissue engineering). Recently Tamada[1-3] has reported that sulfated silk proteins show anticoagulant activity like a sulfated natural polysaccharide such as heparin and Gotoh et al.[4] have demonstrated that sulfated silk fibroins have potential as antiviral material.

Here we present an i.r. and Raman study on fibroin and sericin treated with chlorosulfonic acid in pyridine in order to elucidate the mode of linkage of sulfate groups and the amino acids involved as well as the possible conformational changes caused by sulfation. The trend of both IR and Raman spectra of sulfated silk fabrics showed that conformational changes occurred by effect of sulfation and revealed that fibroin covalently bound sulfate groups mainly through the hydroxyl groups of tyrosine and serine leading to the formation of sulfate salts. At higher sulfation rate the formation of organic covalent sulfates may be proved by the appearance of the IR band at 1385 cm^{-1}. This result points out a possible cross-linking of fibroin chains and could explain the formation of an insoluble fraction during the sulfation reaction as reported by Tamada[2]. The involvement of the amine groups of basic residues in the sulfation reaction is not easily detectable. Nevertheless, the increase in intensity of the Raman band at 1164 cm^{-1} may reasonably account for this. The same trend can be observed in the spectra of sericin. Due to the different amino acid composition and structural organization, sericin seems to react more than fibroin mainly through the hydroxyl groups of serine.

[1] Y. Tamada, J. Appl. Polym. Sci., 87 (2003) 2377.
[2] Y. Tamada, Biomaterials, 25 (2004) 377.
[3] Y. Tamada, M. Sano, K.Niwa, T. Imai and G. Yoshino, J. Biomater. Sci., Polym Edn., 15 (2004) 971.
[4] K. Gotoh, H. Izumi, T. Kanamoto, Y. Tamada and H. Nakashima, Biosci. Biotechnol. Biochem., 64 (2000) 1664.

FT-IR, NMR, VPO AND PM5 SEMIEMPIRICAL STUDIES OF PROTON CHANNEL FORMED BY METHYL ESTER OF MONENSIN A

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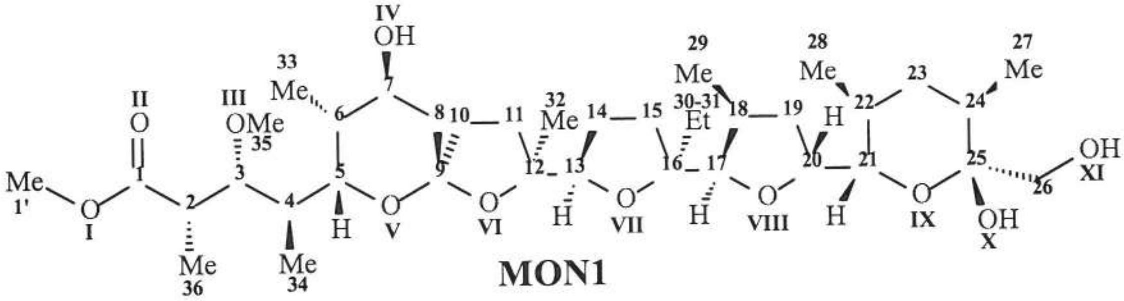
Monensin A methyl ester (MON1) was synthesised and its hydrates were studied by FT-IR, ^{1}H and ^{13}C NMR spectroscopy as well as by VPO and PM5 semiempirical methods [1].



MON1

The ability of MON1 to form hydrates is evoked by the transfer of the proton from its one hydroxyl group to the oxygen atom of a water molecule which is easily hydrated by the one or two further water molecules with the formation of (MON1+3H_2O) species. Within such pseudo-ring structures the water molecules form almost linear hydrogen bonded chain in which the excess proton shows very large proton polarizability indicated by continous absorption in the FT-IR spectra. As demonstrated by the FT-IR spectra and VPO method, along with the formation of (MON1+3H_2O) species their self-assembly process occurs and a proton channel is formed. The semiempirical calculations suggest that in the lipid bilayer such a proton channel can consist of eight (MON1+3H_2O) species.

References:

[1] Huczyński, P. Przybylski, B. Brzezinski, F. Bartl,.in preparation (2006)

SPECTROSCOPIC, ESI MS AND PM5 STUDIES OF NEW SCHIFF BASES AND HYDRAZONES OF GOSSYPOL AS WELL AS THEIR COMPLEXES WITH MONOVALENT CATIONS

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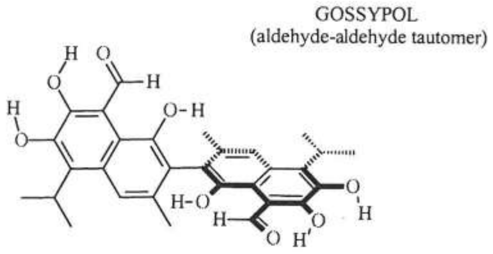
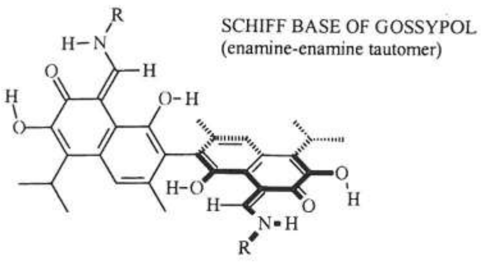
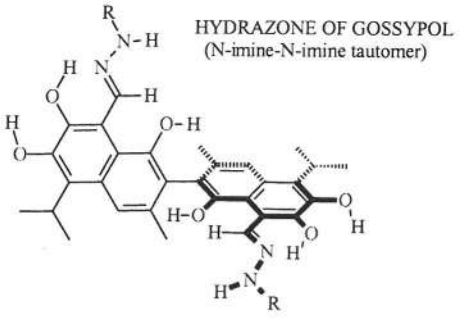
Gossypol, a yellow pigment from cottonseeds, has drawn the attention of many scientists because of its interesting physico-chemical properties as well as a number of biological and medical applications. The main obstacle in the application of gossypol in medical therapy is its relatively high toxicity evoked by the presence of two aldehyde groups in its molecule. The main aim of our study is to search for such modifications of gossypol that would be characterised not only by low toxicity but also high antibiotic activity related to the ability of complexation of monovalent cations. For the purpose of our studies gossypol was extracted from cottonseeds and further converted into the respective Schiff bases or hydrazones [1, 2].







Gossypol exists in three symmetrical tautomeric forms: aldehyde-aldehyde, lactol-lactol and ketol-ketol. Schiff bases or hydrazones of gossypol can occur only in two tautomeric forms namely the imine-imine (N-imine-N-imine for hydrazone) form and the enamine-enamine (N-enamine-N-enamine for hydrazone) one which are analogous to the aldehyde-aldehyde and ketol-ketol tautomeric forms of gossypol, respectively [1, 2]. The structures of the new Schiff bases and hydrazones of gossypol as well as their complexes were studied by spectroscopic as well as PM5 methods. The ability of complexation of monovalent cations by a new derivatives of gossypol was determined by ESI MS method.

References:

P. Przybylski, G. Bejcar, A. Huczyński, G. Schroeder, B. Brzezinski, F. Bartl, Biopolymers 2006 **in press,.**

P. Przybylski, W. Schilf, W. Lewandowska, B. Brzezinski, in preparation **(2006).**

INTERACTIONS AND TEMPERATURE TRANSITIONS OF POLYETHERS IN WATER MEDIA INVESTIGATED BY MIR, NIR AND MICRO-RAMAN SPECTROSCOPY

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The gelling properties of ethylene oxide – propylene oxide block copolymers make them very useful for applications in biotechnological and medical applications. In this study MIR, NIR and micro-Raman spectra of polyethyleneoxide, polypropyleneoxide and ethylene oxide – propylene oxide block copolymers in water media were measured at different temperatures in the range 10 – 80 °C. The found wavenumber shifts of the bands of different chemical groups of polymer chains and of water molecules served as a basis for the evaluation of interactions of polymers with the surrounding water molecules. Two types of such interactions, i.e. hydrophilic (ether group – water or amide group – water) and hydrophobic (methyl group – water molecule) are detected and confirmed by quantum chemical calculations of model molecular systems. A mechanism for the structural changes during the temperature transition is proposed.

P2-33

SPECTROSCOPIC ANALYSIS OF THE DENTAL TISSUES - HYBRID DENTAL MATERIAL INTERFACE

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The dental polymers are prospective materials for direct filling in dentistry. The aim of the study was in vitro qualitative and quantitative chemical analysis of selected compomers applications in dentine. They are composed from polymer matrix, reinforced with fluoro-alumino-silicate glass particles (FAS) [1,2]. The structures of six samples of selected polymers (PMRC) of light–curing were examined using photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and Raman scattering. Dental compomers taken into considerations were: Compoglass F (Ivoclar–Vivadent), Dyract AP (Derey Dentsply), Hytac (3M–ESPE), Glasiosite (VOCO), Freedom (SDI) and Luxat (DMG). The XPS spectra were obtained using the PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatized Al K_α X-ray radiation (1486.6 eV) [1,3]. The infrared spectra of the samples have been measured in the range of 400-4000 cm^{-1} with the use of FTS-6000 Bio-Rad spectrometer with resolution of 1 cm^{-1}. The Raman spectra were recorded using a LabRam System spectrometer, comprising an Olympus X-40 confocal microscope. All the measured polymers consist of the same basic elements: C, O, N, Al, Si, P and F. However, some extra elements were found, such as: Ba and Zn (two samples), Na (five samples), Fe and Sr (one sample), S and Ca (three samples). Content of fluorine, cariostatic element of examined materials range from 0,29 to 3,97 (at%). Ca and Sr are useful for the adhesion to the dental tissue. The XPS permitted qualitative and quantitative analysis of the dentin-hybrid dental material interface (especially changes concentration C, O, Ca, P and F). Fluorine is important, it protects against a second carious lesion and causes an anticariogenic effect, but conventional glass-ionomer cements (GIC) have a significantly better effect on fluorine release. The FTIR spectra analysis suggests that fluorides ions release from polymers and penetrate to the dental tissue structure. Infrared and Raman spectroscopy proved particularly suitable for the evaluation of the molecular structure and cristallinity of compomers and their structural changes in time. In this study we present a set of micro–FTIR and micro-Raman spectra with group frequency assignment and relative qualitative analysis of investigated polymers and polymers in dentin spectra. Moreover, micro spectroscopy with its imaging yields information of the surface of the dental samples.

[1] E. Talik, R. Babiarz, A Dziedzic, M. Tanasiewicz, Quantitative and qualitative analysis of selected dental polymers for direct filing using X–Ray Photoelectron Spectroscopy (XPS), 5th International Polymers Seminar Gliwice 2003, Vol.1, p. 241.
[2] R.G. Craig, J.G. Powers, Restorative Dental Materials, Mosby, St Louis, (2002).
[3] L. Savarino, M. Cervellati, S. Stea, J. Biomater Sci. Polym., 289 (2000).11.

A SIMPLE METHOD FOR ESTIMATING PROTEIN SECONDARY STRUCTURE FROM INFRARED SPECTRA

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Fourier transform infrared (FTIR) spectroscopy is increasingly becoming a method of choice for the experimental determination of protein secondary structure in aqueous solution. A combination of theoretical and experimental analysis have been vital for the interpretation of IR spectra of proteins, especially the assignment of the amide I band components that reflect absorbance from different types of secondary structure. Amide I bands centered around 1650-1658 cm^{-1} are generally considered to be characteristic of alpha-helices. Beta-sheets give rise to highly diagnostic bands in the region 1620-1640 cm^{-1}. The resultant protein spectra upon second-derivative or deconvolution analysis yield bands with frequencies characteristic of specific secondary structures that are essentially similar for most proteins.

In this study, the infrared spectra of 40 proteins in H_20 and D_2O solutions (18 for mainly helical proteins and 22 for mainly beta-sheet) were analyzed in the amide I region. The X-ray structure of these proteins is known. A simple method for estimating protein secondary structure from infrared spectra was developed by using the frequency of the amide I band. The variation in the frequency of this band as a function of residue length of the different secondary structures as well as the percentages of these structures was evaluated.

For the beta-sheet structure, there is a good linear correlation in H_2O for amide I frequencies. As the residue length increased, a decrease in the wavenumbers was detected. An increase in the percentage of beta-sheet structure results in a decrease in the amide I band frequency. For the alpha-helical structure, the correlation in H_2O for amide I wavenumbers was not as good, although the general trend showed that as the residue length decreases, the amide I band frequency increases. Decrease in the percentage of alpha-helical structure results in an increase in the frequency of the amide I band. Our results indicate that the data in H_2O gives a more reliable estimation of the structure than for the data in D_2O. This is due to differences in H-D exchange between proteins that results in variation in the frequency of the amide I band for samples in D_2O [1]. Overall, the findings of this study suggest that a fairly accurate estimation of protein secondary structure, and the length of such structures, can be easily determined from the frequency of the structure-sensitive amide I band in H_2O.

[1] P.I. Haris, D.C. Lee, D.Chapman, **Biochim. Biophys. Acta.** 874 (1986) 255

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P2-35

PREMALIGNANCY GRADING IN CERVICAL NEOPLASIA USING INFRARED MICROSPECTROSCOPY

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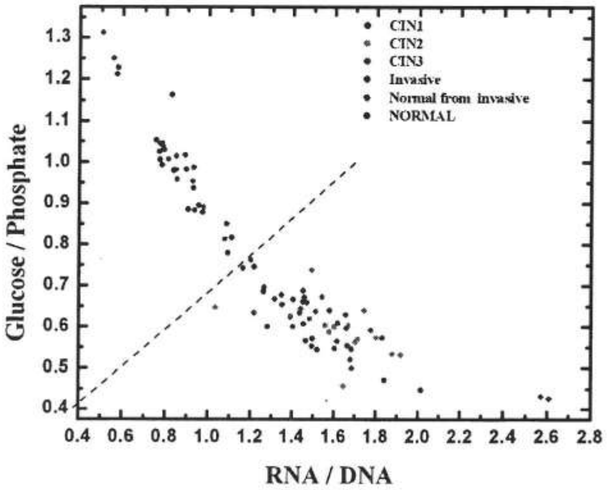
Pathological conditions alter the biochemistry of tissues. Spectroscopic techniques sensitive to these changes are often used to diagnose abnormalities in tissues and cells. **The spectroscopic methods are objective and digital in comparison with the current pathological methods.** Thus, neoplastic and cancerous cells have specific spectral patterns in the infrared region that help their identification and demarcation from normal cells/tissues[1-2]. The present study attempts to apply infrared microscopy on cervical tissues to monitor and predict changes during progression of cervical intraepithelial neoplasia (CIN) to invasive cervical cancer. The work utilized formalin fixed biopsies. The spectral data obtained from formalin fixed biopsies of CIN and cervical cancer patients were processed at selected wave numbers and analyzed to study the relative changes in nucleic acids, which are most conspicuous. **The results have been analyzed using Probabilistic Neural Networks (PNN) with four classifiers strategy. The percentage of success for normal, CIN1, CIN2, CIN3 is 90.94%, 84.28%, 89.46% and 83.26% respectively[2-3]. The results are encouraging and promise a quantitative approach for cervical pre malignancy detection and monitoring.**

Figure 1 presents a 2-D plot of ratios derived from the spectral data indicating a clear distinction between the normal and the abnormal groups based solely on these parameters from the nucleic acids region.



1. R. K. Sahu et. al., Tech in Cancer Res & Treat, Vol. 3(6), Pp 629-638, 2004.
2. S. Mark et al , J. Biomed. Optics, Vol. 9 (3), 558-67, 2004.
3. A. Podshyvalov et. al. Appl. Optics, 44 (18) 3725-34, 2005.

MICRO RAMAN STUDIES OF MCF-7 BREAST CANCER CELLS AND OF THEIR POROUS SOL-GEL DERIVED SILICA GEL SUPPORTS

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The study of diseased cells using *in vitro* cultures is one of the main steps towards understanding the intracellular disorders and developing new therapies for the corresponding disease. However, one of the limitations of most current cell biology techniques is the impossibility of working with living cells. Vibrational spectroscopic methods have been shown to be sensitive to biochemical composition. Although micro-Raman is less sensitive than FTIR microscopy, its spatial resolution of a few microns make measurements at the individual cell level possible, in relatively short times without the need of staining or fixation. For this reason, work has been undertaken to determine the possibilities of discrimination of various forms of malignant tissues using micro-Raman spectroscopy.

A second aspect is that cellular behaviour, be it *in vivo* or *in vitro*, is influenced by the chemical and topographical properties of the microenvironment around the developing cell. For this reason, as a support for the growing cells we have chosen silica gels of porosity mimicking that of typical extracellular matrix structures. In the present study particular interest has been devoted to the effect of the pH of the sol-gel media and the effect of the sterilisation by autoclave on the texture and on the biocompatibility of the final structures.

In the present work, acid and base catalysed TMOS derived silica gels have been prepared with average pore diameters of around 40 and 60 A, respectively. Raman spectra, correlated with pore volume data have been used to follow the evolution of the pore sizes both with densification and with autoclave sterilisation. Micro-Raman spectra have been recorded of MCF-7 human breast cancer cells, seeded and grown on the resulting silica gels. Spectra, with certain bands well characteristic of malignant structure being apparent, have been assigned. In addition, spectral evolutions observed for cells over a period of 60 hours have made it possible to characterize structural changes of the cells at different stages of their life-times.

LIPOIC ACID-INDUCED ALTERATIONS ON THE RAT BRAIN LIPIDS: AN FTIR SPECTROSCOPIC STUDY

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Antioxidants have a vital role in the defense and repair system of the body against the damage induced by free radicals. At the present time, there is an unfortunate increase in exposure to free radicals due to many environmental, lifestyle, and pathological situations. Consequently, the endogenous antioxidant defenses may not always be enough to cope with such additional exposure to free radicals, in turn justifying the consumption of antioxidant supplements as part of the daily intake. Therefore, in the current study, the effect of exogenously administered lipoic acid (a dose of 12 mg/kg every other day via intraperitoneal injection for seven weeks), a natural amphipathic antioxidant, on rat brain tissue was investigated via Fourier Transform Infrared spectroscopy in order to understand its interactions with biological molecules. The results suggest that lipoic acid causes an increase in the quantity of proteins, without affecting the protein secondary structure revealed by neural network predictions based on FTIR data. Moreover, lipoic acid seems to disorder the acyl chains of phospholipids as observed from the shift in the frequency of the CH_2 stretching vibrations. It also leads to a strengthening in the hydrogen bonding of the interfacial region of phospholipids as indicated by the C=O stretching band. The destabilization induced by lipoic acid might be advantageous because the interaction of antioxidants with lipid radicals is more efficient when membrane lipids are more disordered. The unaltered protein secondary structure further supports the usage of lipoic acid as an antioxidant supplement.

THE EFFECT OF MELATONIN ON LIPID ORDER AND DYNAMICS OF RAT BRAIN HOMOGENATE

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A great number of complications, such as cancer, diabetes mellitus, aging, and several neurodegenerative diseases are believed to be in part a consequence of damage inflicted by toxic free radicals. The brain is especially susceptible to free radical attack since it is rich in polyunsaturated fatty acids and consumes very high amounts of oxygen. Melatonin is a non-enzymatic amphiphilic antioxidant hormone that is widely used in medicine for protective and treatment purposes against oxidative stress. In the present work the effects of the clinically used dose of melatonin (a single intraperitoneal dose of 100 mg/kg) on rat brain homogenate was investigated as a function of temperature using Fourier Transform Infrared Spectroscopy in order to gain insight on the melatonin-membrane interaction since lipids are very vulnerable to free radical attack. The results show that the lipid to protein ratio decreases in the melatonin treated brain samples. Moreover, it is suggested that melatonin disorders and decreases the dynamics of lipids as observed from the CH_2 and CH_3 stretching modes (2852 and 2958 cm^{-1}, respectively) in the liquid-crystalline phase, which also includes the body temperature, of the brain homogenate samples. The C=O and PO_2^- stretching modes (1732 and 1230 cm^{-1}, respectively) reveal that melatonin induces a strengthening in the hydrogen bonding between the functional groups of both melatonin and the polar parts of lipids and/or water at physiological temperatures. The results will be discussed in connection with melatonin-model membrane interaction studies. Therefore, this study could provide a linkage from model to biological membranes.

IMIDAZOPHENAZINE NUCLEOSIDE ANALOGUE AS A FLUORESCENT PROBE AND STABILIZER OF ANTISENSE OLYGONUCLEOTIDE HYBRIDIZATION

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Fluorescent nucleoside analogues incorporated into antisense oligonucleotides instead of the natural nucleosides are used as effective fluorescent probes in the study of structure and dynamics of nucleic acids due to a definite fluorophore location. In the frame of this conception we studied the imidazophenazine derivative (Pzn) which can be built into oligonucleotide chain like a usual nucleoside. Besides, an intercalative capability of the dye chromophore[1] can be used for anchorage of an antisense oligonucleotide hybridization. These properties of the Pzn we have investigated upon binding to poly(rA) of $(dT)_{14}$ with the covalently attached dye (Fig.1). The investigations were carried out in buffered solutions, pH 6.9, containing 0.1 M sodium ions.

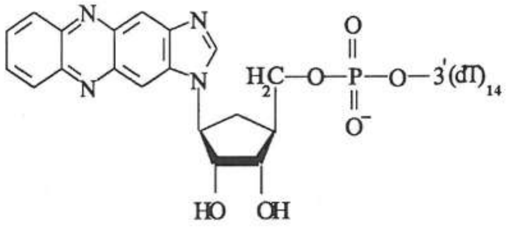

Fig. 1: Molecular structure of $(dT)_{14}$Pzn conjugate.

The double helix formed between conjugate $(dT)_{14}$Pzn and poly(rA) was studied by the method of thermal denaturation using absorption and fluorescence detection of melting transitions. Because of Pzn fluorescence quenching by the interaction with adenine bases[1], a fluorescence technique was found to be effective in the detection of the complex formation. It was shown that the attached Pzn substantially enhanced the thermal stability of poly(rA)·$(dT)_{14}$ duplex due to insertion of the dye chromophore into the adenine strand, which increased the temperature of transition midpoint by 7 °C. The thermodynamic parameters for duplex formations were derived using a simple two-state model of transitions. Values of transition enthalpy and entropy were evaluated from the concentration dependence of the melting temperature and analysis of the shape of melting curves. Molecular modeling was used to construct the geometry of the intercalation site with Pzn chromophore that turned out to be in conformity with the behavior of its fluorescence.

[1] V. Zozulya, Yu. Blagoi, G. Lober, I. Voloshin, S. Winter, V. Makitruk, A. Shalamay, Biophys. Chem. 65 (1997), 55-63.

ABSORPTION AND FLUORESCENT SPECTROSCOPIC STUDIES ON INTERACTION OF PHEOPHORBIDE DERIVATIVES WITH POLYNUCLEOTIDES

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The interactions of neutral and cationic pheophorbide-a (Pheo-a) derivatives (Fig.1) with some synthetic polynucleotides of various base compositions and secondary structures were investigated by absorption and fluorescence spectroscopy. The binding of the dyes to single-stranded poly(A) and poly(U), double-stranded poly(A)•poly(U) and poly(C)•poly(G) as well as four-stranded poly(G) were studied over a wide range of molar polymer-to-dye ratios (P/D), conducting measurements of absorbance, steady-state fluorescence intensity and emission polarization degree for the dyes. The experiments were carried out in aqueous solutions of different ionic strengths at neutral pH.

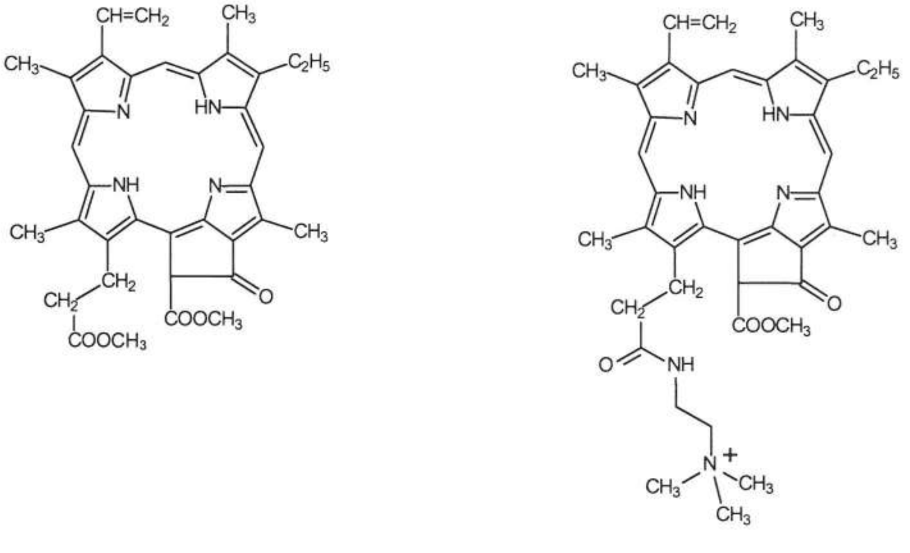

Fig. 1: Molecular structures of pheophorbide-a derivatives.

The neutral Pheo-a has essentially a less binding affinity to polynucleotides investigated in comparison with cationic one, forming only of one type of complex by means of the intercalative mechanism. On the contrary, the cationic Pheo-a shows the strong interaction and the existence of two types of complex formation. The electrostatic cooperative binding of this dye to the polyanionic chain of polynucleotides as a result of the stacking interaction of porphyrin chromophores is revealed at low P/D, which especially manifests itself in the case of single-stranded polynucleotides. At high P/D the intercalation of dye chromophores into duplex or quadruplex polymer structures predominates. Spectroscopic and thermodynamical properties as well as some structural characteristics of the complex formations were established.

This work was supported by Science and Technology Center in U1kraine, grant # 3172.

THE USE OF SPECTROSCOPIC METHODS TO THE ESTIMATION OF BIOLOGICAL TREATMENT INFLUENCE ON HUMIFICATION PROCESS OF SEWAGE SLUDGE

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The treatment plant in Sosnowiec-Zagórze was trough years the plant without the nitrification and denitrification processes. In 2005 year the plant became modernized and processes of biological treatment was introduced.

The study of the biological treatment influence on the course of humification process was conducted for sewage sludge received from each stages of the sewage purification. The extracted humic acids were investigated by means of spectroscopic and analytical methods. The concentration of free radicals and g-factor was determined with EPR, the presence of characteristic functional groups was confirmed with IR spectroscopy, aromatisation of humic acids was estimated by ^{13}C NMR method and E4/E6 parameter was determined with UV/VIS spectroscopy. The results were compared with the analogous obtained for humic acids extracted from sewage sludge before the modernization of the treatment plant [1].

It was found that processes of biological treatment have significant influence on changes of chemical elements content in the extracted humic acids. After the treatment plant modernization the obtained humic acids are nitrogen-rich (about 9%), especially after nitrification and denitrification processes. However, nitrification and denitrification processes have slight influence on the concentration of free radicals and g-factor values.

[1] J. Pajączkowska, A. Sułkowska, W.W. Sułkowski, M. Jędrzejczyk, J. Mol. Struct. 651-653 (2003) 141

Acknowledgements
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SPECTROSCOPIC STUDY OF INFLUENCE OF BIOLOGICAL TREATMENT ON HUMIFICATION PROCESS OF THE SEWAGE SLUDGE

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This work was supported by the University of Silesia BW/ICH/2006

IR SPECTROSCOPIC STUDY OF Pt-CONTAINING ZEOLITES IN THE HYDRODECHLORINATION REACTION OF C_2 CHLORINATED HYDROCARBONS

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Some of the chlorinated organic compounds are widely used commercially, because of their advantageous chemical/physical properties or having toxicity for pestiferous living substances.

However, most of them are environmental pollutants. Emitted into the atmosphere they are responsible for diminishing the ozone layer in the stratosphere. Therefore, a lot of effort is devoted in finding proper solutions to decompose these chemicals in environmentally friendly ways. Platinum on different carriers play very important role in catalytic hydrodechlorination of these compounds.

During the work leading to this contribution we have prepared Pt-containing zeolites. NaY-FAU (Union Carbide product) was the parent zeolite and ion exchange was carried out in $Pt(NH_3)_4Cl_2$ solutions. IR spectroscopic self-supporting wafer technique was employed for adsorption and catalytic measurements. The wafers were prepared from the powdered zeolites and placed into the sample holder of an *in situ* IR cell. During the pretreatment process the $Pt(NH_3)_4^{2+}$ ions were decomposed in oxygen stream, then the wafer was heated to 723 K in oxygen followed by evacuation at the same temperature for two hours. This oxidized sample was reduced in H_2 at 573 K. For hydrodechlorination experiments the pretreated zeolite wafers were loaded with the trichloroethene reactant at room temperature. Both the surface species and the gas-phase products were analysed as the reaction proceeded under various experimental conditions.

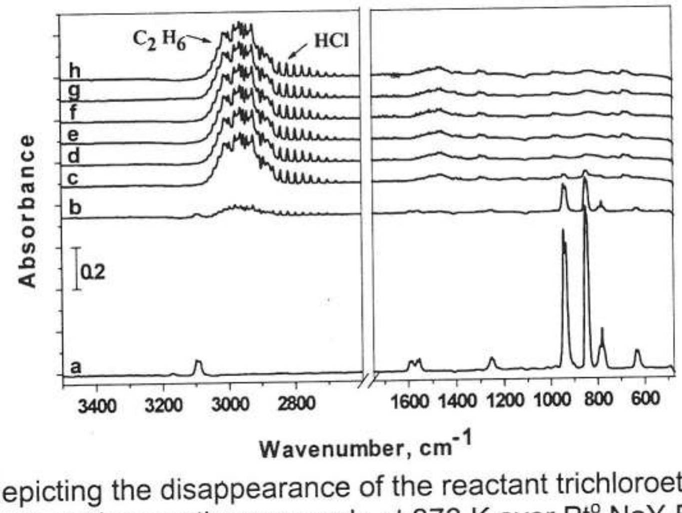

Fig. 1: IR spectra depicting the disappearance of the reactant trichloroethene (a) and the evolution of the products as the reaction proceeds at 373 K over Pt°,NaY-FAU after 0.5 (b), 1 (c), 1.5 (d), 2 (e), 2.5 (f), 3 (g) and 3.5 hours (h).

FT-IR measurements proved that the final products are ethane (C_2H_6) and HCl, and the hydrogen/reactant ratio exerts large influence on the rate of the hydrodechlorination reaction.

Acknowledgement: This work was performed with the help of grant OTKA T 042825, Hungary.

ION-PAIR INTERACTION AS PROMOTING FACTOR IN THE LIQUID-PHASE OXIDATION OF CYCLOHEXENE OR TETRALINE BY N_2O

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N_2O could be an environmentally benign oxidation agent, since upon providing the useful product(s) after oxygen transfer N_2 is only formed. A serious problem, however, that it is a sluggish reactant in liquid-phase oxidations requiring high pressure (53-120 bar) and high temperature (150-250 °C).[1] Fortunately, the oxidation can be performed under mild conditions (70 °C, 1 bar) with appreciable rate in the presence of onium salt in appropriate solvent. The presence of the onium salt was necessary and choice of solvent was found to be critical. In this work we report on results acquired during studying the interactions between the oxidant, the onium salt and the solvent by IR spectroscopy.

Solvents studied were chlorobenzene, acetonitrile, diethyl carbonate and CCl_4. The onium salt was tetrahexyl ammonium chloride. The reactants were cyclohexene or tetraline and the reactions were performed in the liquid phase at 70 °C at atmospheric pressure. For studying the possible interactions between the onium salt and N_2O in various solvents a BIORAD FT-IR spectrometer was used. Changes in the positions and band areas of N-O stretching (ν_1), the ν_2 deformation and the N-N stretching (ν_3) vibrations were monitored. Spectral evaluations were done with the WinIR package.

As far as reaction rates are concerned chlorobenzene and CCl_4 proved the best solvents. The reaction was negligible or very slow in acetonitrile and diethyl carbonate. It was observed that oxidation accelerated considerably in CCl_4 containing trace amounts of water.

In chlorobenzene the ν_3 and ν_2 vibrations and their changes could be observed. Their increased ratio of band areas ($A_{\nu3}/A_{\nu2}$) indicates ion-pair interaction between N_2O. The most reliable support for the occurrence of the ion-pair interaction of N_2O with onium salt could be was furnished in CCl_4. Here, all three fundamental peaks of N_2O were observed without any interference. In the absence of the onium salt, the absorption ratios ($A_{\nu3}/A_{\nu1}$ and $A_{\nu3}/A_{\nu2}$) were close to the values obtained in the gas phase, but in the presence of the onium salt both peak ratios were altered. Since the ν_3 peak was hardly changed and the ν_1 and ν_2 peaks decreased considerably, both ratios of band areas were increased.

The experimental results indicated that the formation of an ion pair between the onium cation and N_2O through distorting the N–O bond, thus, activating the molecule. The activated moiety reacts in the oxidation reactions of cyclohexene as well as tetraline under mild conditions.

[1] G. I. Panov, K. A. Dubkov, E. V. Starokon, V. N. Parmon, React. Kinet. Catal. Lett. 76 (2002) 401.

PRELIMINARY APPROCH FOR THE DETERMINATION OF FISH EXUDED KAIROMONE USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Chemical communication in aquatic organisms, which focuses on the interactions between organisms via info chemicals (kairomone), has been widely studied. It is a well-known phenomenon that zooplankton respond to fish predation pressure by means of kairomones exuded by the predator. This response includes various morphological and behavioral adaptations, among which Diel Vertical Migration (DVM) is a prevalent predator-avoidance strategy in the zooplankters *Daphnia*. However, the nature and origin of the fish kairomone is yet to be elucidated and hence in the current study Fourier Transform Infrared Spectroscopy (FTIR) was used in order to gain insight on the chemical structure of the kairomone with the aid of DVM of *Daphnia*. The results suggested that DVM showed seasonality, which is in accordance with the seasonal variations in the peak areas of the Amide A (3435 cm^{-1}) and Amide II (1513 cm^{-1}) bands, both of which mainly correspond to N-H stretching and bending vibrations. This observation was further supported by the bacterial biodegradation experiments' presenting that the kairomone was inactivated, which fell in line with the peak area results of the same bands. However, in both experiments the Amide IV (623 cm^{-1}) band, which mainly corresponds to O=C-N bending mode, did not show a trend similar to the one observed for the Amide A and Amide II bands. On the other hand, the Amide I band, which mainly corresponds to C=O stretching vibration, was not clearly observed in any of the spectra. All of these observations may indicate that N-H groups have a considerable contribution to the fish kairomone, while O=C-N and C=O groups do not. Moreover, the FTIR spectroscopic analysis also indicates that methyl (2963 cm^{-1}) and ester carbonyl (1730 cm^{-1}) groups do not have significant contributions to the kairomone. This study clearly indicates that FTIR spectroscopy can be a prominent tool for ecological studies in the sense that it can reduce ambiguities in the literature.

ESR (ELECTRON SPIN RESONANCE) DATING OF THE PALEOENVIRONMENT ARCHIVES DEPOSITED IN THE CAVE

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ESR (electron spin resonance) dating has been made it possible to determine the age of Quaternary secondary carbonate deposits after Ikeya dated successfully a stalactite from the Akiyoshi Cave in Japan in 1975 [1]. The paper focuses on the dating of speleothems samples collected from various sites in caves scattered in the Aladağlar Massif. Aladağlar Massif (western Taurids, Turkey) is a mountain range that is mostly made up of karstified limestone formations of Mesozoic age. Field observations suggest that the system, which is currently free from permanent snow cover, has experienced extensive glaciations during the Quaternary period. Understanding past climatic changes in this system bears special importance with regards to factors that affected the global climatic change because limited information is available on the magnitude of past glaciations in Turkey. Because the formation of speleothems in caves is associated with the climatic factors on the surface, the dating of speleothem bands could provide information on the timing of climatic changes in this area.

In this research, the speleothem rings of the samples G01 to G08 have been dated between 0ka to 8 and 30ka at lower and upper limit using the radiation-induced line at g=2.0007 and to correlate the results with geological information.

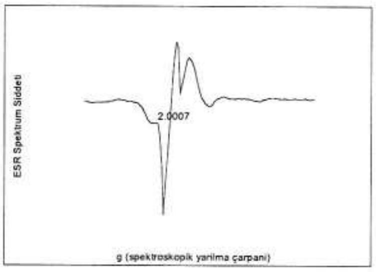

Figure: ESR spectrum of γ-irradiated G02 sample.

[1] M. Ikeya, Magnetic Resonance Review 13 (1988) 91.

ULTRAFAST TWO-DIMENSIONAL INFRARED SPECTROSCOPY AND MOLECULAR DYNAMICS OF MODEL HYDROGEN BONDED SYSTEMS

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Two-dimensional infrared (2D-IR) spectroscopy enables the investigation of molecular vibrational transitions, the analysis of static and dynamic broadening mechanisms, and the acquisition of information concerning the structure and the dynamics of molecular systems.

In this study we investigate the neat liquids formamide and formic acid, both model systems—formamide is the simplest molecule containing an amide moiety, and formic acid the simplest molecule with a carbonyl. Both systems form extended hydrogen-bonded networks in solution, which were probed by means of 2D-IR spectroscopy in the C=O stretching region, and by molecular dynamics computer simulation.

This work will compare and contrast the ultrafast vibrational dynamics of the two systems, in which the hydrogen-bond network shows very different reorganization timescales. Presented here are both broadband transient absorption experiments (demonstrating population lifetimes and anisotropy decay) and narrow-band 2D experiments (demonstrating the progression of inhomogeneous to homogeneous line broadening after vibrational excitation). Finally, we present details of the modeling both for the molecular dynamics simulations, which yield a predicted static infrared spectrum, as well as the response function-based simulations of 2D-IR spectra.

MOLECULAR PICTURE OF HYDROXIDE ANION HYDRATION IN AQUEOUS SOLUTIONS STUDIED BY FTIR ATR SPECTROSCOPY

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Attenuated Total Reflection (ATR) techniques in FTIR spectroscopy are especially suited for the study of water and aqueous solutions.[1] The ATR method has been applied recently to investigate aqueous alkali metal hydroxides in broad range of concentration.[2] In a rather outdated work focused on extremely concentrated solutions, the interpretation of so-called infrared continua from a molecular point of view was proposed.[3] Nevertheless, the convincing description of hydration mechanism of the chemically and biologically important OH^- ion is still an unresolved issue, particularly in the low concentration region and in the infinite dilution approximation.

We have measured vibrational spectra of LiOH, NaOH and KOH aqueous solutions in the concentration range 0.05-1.0 $mol \cdot kg^{-1}$. A thermostated HATR plate, equipped with a ZnSe crystal giving 6 internal reflections, has been employed. For NaOH solutions, we have recorded also temperature dependent spectra between 10-50 °C.

The interpretation of obtained results is focused on the infinite dilution limit behavior, as proposed before for HDO in aqueous electrolyte solutions.[4] Generalized 2D IR correlation spectroscopy[5] provides deeper insight into the temperature changes of vibrational spectra. Conclusions are compared with our recent study of HDO in OH^- aqueous solutions.[6]

[1] Y. Marechal, J. Chem. Phys. 95 (1991) 5565.
[2] J.-J. Max, C. Chapados, Appl. Spectrosc. 52 (1998) 963.
[3] N. B. Librovich, V. P. Sakun, N. D. Sokolov, Chem. Phys. 39 (1979) 351.
[4] J. Stangret, T. Gampe, J. Phys. Chem. B 103 (1999) 3778.
[5] I. Noda, Y. Ozaki, Two-dimensional Correlation Spectroscopy – Applications in Vibrational and Optical Spectroscopy, John Wiley & Sons, Ltd, Chichester (2004).
[6] M. Śmiechowski, J. Stangret, manuscript in preparation.

STRUCTURAL PROPERTIES OF CARBOHYDRATES AQUEOUS SOLUTIONS PROBED BY VIBRATIONAL SPECTROSCOPIC TECNIQUES ANALYSIS

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It is common knowledge that in aqueous solutions carbohydrates act as stabilizer for biological components during "water stress" dynamical processes such as drying and desiccation [1]. Moreover carbohydrates aqueous solutions constitute opportune models to understand more complexes biologic systems.

There is no consensus about the molecular mechanism responsible for conservation and stabilization of labile biomaterials. Anyway, two principal causes are invocated [2]: on one side the dynamical slowing down of the system, that leads to a partial arrest of degradation processes; on the other the capacity of carbohydrates to act as water replacers.

In this latter the water three-dimensional HB network turns out to be modified. IR and Raman spectroscopic techniques, which represent ideal probes for the observation of HB structures, have been used to clarify structural changes in water structure operated by glucose in a wide temperature and concentration range.

Our results show that the application of different spectroscopic techniques permits to distinguish the properties of bulk water from those of hydration water [3]. The aim of this work is correlating the structural properties of such a system either with the cryoprotection of biological systems and the pharmaceutical bio-preservation methods [1,4]. Our experimental findings compare very well with those obtained by MD simulation studies [5].

[1] C.J. P.G. Debenedetti, *J. Phys. Chem. B*, 103, 7308 (1999)
[2] M. Feeney, C. Brown, A. Tsai, D. Neumann, P. G. Debenedetti, *J. Phys. Chem B*, 105, 7799 (2001)
[3] M.E.Gallina, P.Sassi, M.Paolantoni, A.Morresi,R.S. Cataliotti, *J.Phys.Chem.B*, in press, (2006)
[4] T. S T. Suzuki, T. Sota, *J.Chem.Phys.*, 119, 10133 (2003)
[5] S.L. Lee, P.G. Debenedetti, *J.Chem.Phys.*, 122, 204511 (2005)

DYNAMICAL PROPERTIES OF CARBOHYDRATES AQUEOUS SOLUTIONS REVEALED BY DEPOLARIZED RAYLEIGH SCATTERING SPECTRA

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Carbohydrates are bio-relevant molecules involved in a wide variety of processes such as energy storage, molecular recognition and biological functionalities preservation in conditions of freezing or drought [1]. Their bio-protective properties are largely exploited in pharmaceutical industries for long time storage of labile bio-chemicals, especially in the vitreous form [2]. In fact, concentrated aqueous solutions are characterized by easy formation of glasses at relatively high temperatures.

A molecular-level understanding about the origin of these particular properties is still far from properly understood, such as their behaviour in aqueous solution [1].

A full comprehension of their capability to preserve biological molecules requires both dynamical and structural characterization of sugars aqueous solutions. Moreover the knowledge of dynamics of water molecules in sugar solutions will be helpful in developing a general understanding about the effects of biological compounds in water [3].

Depolarized Rayleigh scattering (DRS) spectra of glucose aqueous solutions have been recorded in a wide temperature and concentration range, in order to probe reorientational dynamics of water and sugar molecules.

The results completely agree with MD simulation data [4]. We find an appreciable slowing down of water reorientational motions; moreover our data reveal great sensitivity toward the presence of glucose and probably suggest that rotational dynamic of solute is well defined with respect to that of bulk water.

Our findings are discussed in comparison with structural properties of solutions analyzed by low frequency Raman spectra and IR and Raman OH stretching profiles [5].

[1] Molteni, M.Parrinello, *J.Am.Chem.Soc.*,120, 2168 (1998)
[2] P.G.Debenedetti, J.R.Errington, M.R.Feeney, *Abstract of Papers, 221st ACS National Meeting*, American Chemical Society (Eds), (2001)
[3] C.Talon, L.J. Smith, J.W. Brady, B.A. Lewis, J.R.D. Copley, D.L.Price, M. Saboungi, *J.Phys.Chem.B*, 108, 5120 (2004)
[4] S.L.Lee, P.G.Debenedetti, *J.Chem.Phys.*, 122, 204511 (2005)
[5] M.E.Gallina, P.Sassi, M.Paolantoni, A.Morresi,R.S. Cataliotti, *J.Phys.Chem.B*, in press, (2006)

CAN S-CONTAINING CLUSTERS SOLVATE/IONIZED HCI? ON-THE-FLY MOLECULAR DYNAMICS AND AB INITIO CALCULATIONS OF HCI on/in CH_3SH CLUSTERS

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Solid state solvation and ionization of HX (X=Cl, Br) in hydrogen bonded clusters, such as H_2O[1], CH_3OH[2], *etc.*, have been subject to many studies due to the importance of these processes in chemistry, biology and atmospheric chemistry. We present continuation of research on solvation of HCl by methanethiol clusters (CH_3SH) and CH_3SH was selected for a study complementary to that of methanol. The mixed HCl-methanethiol clusters, $(HCl)_n$-$(CH_3SH)_m$, n=1-2, m=2-4, at low temperatures have been simulated using on-the-fly Molecular Dynamics as implemented in the density functional code QUICK-STEP[3], which is part of CP2K package[4]. Some of the trajectory results have been further check with MP2-level *ab initio* calculations. Acid solvation/ionization requirements are discussed and compared with methanol clusters[2] in terms of Infrared Spectroscopy.

[1] J.P. Devlin, N. Uras, J. Sadlej, V.Buch, Nature, 417 (2002) 269.
[2] N. Uras-Aytemiz, J.P. Devlin, J. Sadlej and V. Buch, Chem. Phys. Lett. 422 (2006) 179.
[3] J. VandeVondele ,M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, R. Hutter, Comp. Phys. Comm., 167 (2005) 103.
[4] CP2K, http://cp2k.berlios.de (2000-2004).

N-H...O HYDROGEN BONDING. FT IR, NIR AND ^{1}H NMR STUDY OF N-METHYLPROPIONAMIDE - CYCLIC ETHER SYSTEMS

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The importance of hydrogen bonding in biological systems has been widely recognized, especially N-H...O hydrogen bonds. Since the N-substituted amides are suitable model systems for studies of hydrogen bonding of proteins , these compounds have been attracting the scientific attention for many years. Continuing our studies of N-substituted amides in solutions[1-3], this work was devoted to hydrogen bonding of N-methylpropionamide with tetrahydrofuran and tetrahydropyran. FT IR, NIR and ^{1}H NMR spectra have been employed at 298 K. The spectroscopic parameters as well as the equilibrium constants have been obtained and discussed.

[1] A.D. Nikolić, N.L. Kobilarov, A.N. Brzić, J. Mol. Struct., 99 (1983) 179.
[2] A.D. Nikolić, M. Tarjani-Rozsa, N.U. Perišić-Janjić, A. Petrik, D.G. Antonović, J. Mol. Struct., 219 (1990) 245.
[3] Nikolić, L. Gobor, V. Krstić, S. Petrović, J. Mol. Liq., 121 (2005) 139.

WEAK HYDROGEN BONDINGS AS STUDIED BY POLARIZED FT-IR SPECTRA OF THE OPTICALLY NONLINEAR O-METHYL-P-NITROANILINE (MNA) CRYSTAL

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The o-methyl-p-nitroaniline (MNA) crystal has been studied for a long time because of its strong nonlinear optical properties [1, 2]. Noncentrosymmetry of the crystal and nearly parallel alignment of molecules in the unit cell induce a polar axis[2]. Long range electrostatic interactions in the crystal are more pronounced than the hydrogen bonds (HB) interactions[3].

The aim of this study is to recognize the in-crystal interactions and their role towards crystal properties. We measured IR spectra of the (010) MNA crystal plates with the incident beam polarized at many angles with respect to X and Z dielectric axes. It results from the spectra that the HB framework is three dimensional. The analysis of IR spectra of deuterated samples is believed to throw more light on the studied interactions.

[1]. B.F. Levine, C.G. Bethea, C.D. Thurmond, R.T. Lynch, J.L. Bernstein, J. Appl. Phys. 50 (1979) 2535.
[2]. G.F. Lipscomb, A.F. Garito, R.S. Narang, J. Chem. Phys 75 (1981) 1509.
[3]. S.T. Howard, M.B. Hursthouse, C.W. Lehmann, P.R. Mallinson, C.S. Frampton, J. Chem. Phys. 97 (1992) 5616.

HYDROGEN BONDS BETWEEN AROMATIC AZINES AND HYDROGEN FLUORIDE. AN AB INITIO STUDY

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MP2/6-31++G** ab initio calculations have been performed to estimate the effect of the H-bond on the vibrational properties of HF due to its complexation with aromatic azines ($C_nN_{6-n}H_n$, with n= 5,4 or 3). Our calculations have revealed that greater is the number of nitrogen atoms in the aromatic ring smaller will be the HF stretching frequency downward shift as well as the increase of the H-F stretching intensity due to complexation, as can be seen to follow. For example, the H-F frequency downward shift is -899cm^{-1} in pyridine-HF, whereas its corresponding value is -597cm^{-1} in 1,3,5-triazine-HF. Their A^{C}/A^{is} infrared intensity ratios are 18.7 and 14.3, respectively.

Complex	Position of the nitrogen atom(s)	$(\nu^{C} - \nu^{is})^*$, cm^{-1}	A^{C}/A^{is}
pyridine-HF (C_5NH_5...HF)	-	-899	18.7
pyridazine-HF ($C_4N_2H_4$...HF)	*ortho-*	-770	17.1
pyrimidine-HF ($C_4N_2H_4$...HF)	*meta-*	-744	16.8
pyrazine-HF ($C_4N_2H_4$...HF)	*para-*	-768	16.6
1,3,5-triazine-HF ($C_3N_3H_3$...HF)	*meta-; meta-*	-597 (-589)	14.3
1,2,4-triazine-HF ($C_3N_3H_3$...HF)	*ortho-; para-*	-648 (-639)	14.6
1,2,5-triazine-HF ($C_3N_3H_3$...HF)	*ortho-; meta-*	-611 (-615)	14.6
1,3,4-triazine-HF ($C_3N_3H_3$...HF)	*meta-; para-*	-605 (-613)	14.1

* Obtained from equation given below; **C**= complex and **is**= isolated molecule.

It is also interesting to verify that the H-F stretching frequency downward shift follows the equation below:

$\Delta\nu^{HF\ stretch}$ = -899 + 129 (N° nitrogen atoms at *ortho* position) + 155 (N° nitrogen atoms at *meta* position) + 131 (N° nitrogen atoms at *para* position)

where –899 cm^{-1} is $\Delta\nu^{HF\ stretch}$ in pyridine-HF, 129 cm^{-1} is equals to (-770+899), 155 cm^{-1} is (-744+899) and 131 cm^{-1} is (-768+899). For example, the values of $\Delta\nu^{HF\ stretch}$ in 1,3,5-triazine-HF and 1,2,5-triazine-HF are –589 cm^{-1} and –615 cm^{-1} using this equation, respectively, whereas their corresponding values are –597 cm^{-1} and –611 cm^{-1}. Therefore, both are in excellent agreement with those obtained using the MP2 level of calculation with the 6-31++G** basis set.

IR AND RAMAN SPECTROSCOPIC STUDY OF $RbZn(HSeO_3)_2X$ (X = Cl, Br)

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As a part of our investigations on synthesis and properties of new *quasi*-quaternary hydrogenoxoselenate(IV) composite compounds [1], we have synthesized $RbZn(HSeO_3)_2X$ (X = Cl, Br). The preparation was preformed by crystallization from highly concentrated solutions of $RbSeO_3$, RbX, ZnX_2, and SeO_2 at pH 1. $RbZn(HSeO_3)_2X$ (X = Cl, Br) are isotypic, crystallizing in a new structure type in the space group P2/c, with Z = 2 and a = 647.9/652.7 pm, b = 611.0/621.7 pm, c = 1074.1/1074.3 pm and β=103.61°/103.57° for the Cl/Br compounds, respectively. Single crystal x-ray determinations show that the Zn ions have an unusual square pyramidal coordination sphere by 4 oxygen atoms and one halogen atom.

In the IR spectra, OH stretching modes of the SeOH groups are present in the region of 3000-2000 cm^{-1}, and AB bands [2,3] are formed (Fig.1). In the region of 1400-1000 cm^{-1} bands due to $\delta(OH)$ vibrations can be observed. Because all six normal vibrational modes of the trigonal pyramidal oxoselenate(IV) group are IR active in the IR spectra, bands due to the stretching modes $\nu_s(SeO)$: 920-820 cm^{-1}, $\nu_{as}(SeO)$: 820-620 cm^{-1} and the bending modes $\delta_s(SeO_2)$: 450-330 cm^{-1}, $\delta_{as}(SeO_2)$: 300-230 cm^{-1} are present.

In the Raman spectra, the bands between 820-725 cm^{-1} belong to $\nu(SeO)$ stretching vibrations, and the bands between 520 cm^{-1} and 240 cm^{-1} belong to $\delta(SeO_2)$ deformations. IR and Raman spectra were also recorded at low temperature, and the results are discussed with the respect to the crystal structure data.

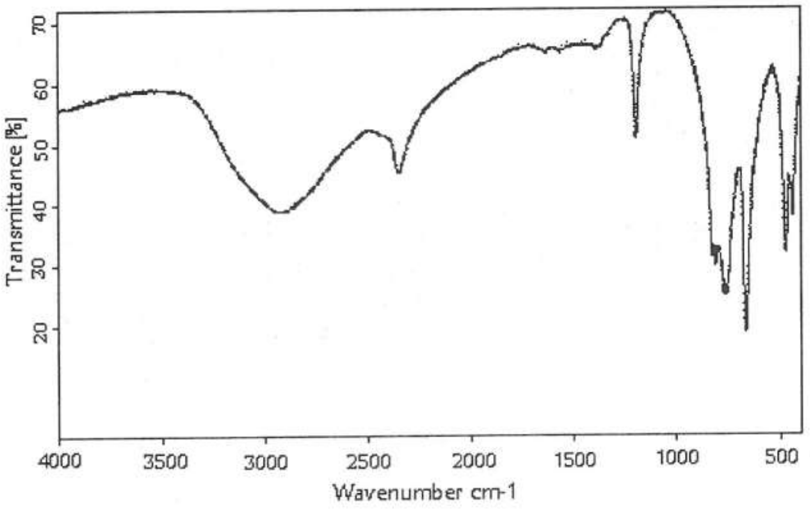

Fig. 1: IR spectrum of $RbZn(HSeO_3)_2Cl$ at 298K

[1] Y. Kang, B. Engelen, M. Wagener, Z. Kristallogr. Suppl. 22 (2005) 157.
[2] K.Boldt, B. Engelen, K. Unterderweide, Acta Crystallogr. C53 (1997) 666.
[3] K. Unterderweide, B. Engelen, K.Boldt, J. Mol. Struct. 322 (1994) 233.

P5-1

MATRIX ISOLATION FTIR SPECTRA AND THEORETICAL STUDY OF NICOTINAMIDE

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Nicotinamide (NA) is a form of Vitamin B3, essential for growth and for the production of energy. Due to its role in the improvement of beta cell function, it has been used in diabetes treatment and prevention. Potential side effects include headache, skin and gastro intestinal effects, exacerbation of gut and ulcers and allergies. It may increase serum concentrations of anticonvulsants, carbamazepine and primidone. Nicotinamide, via its major metabolite NAD (nicotinamide adenine dinucleotide), is involved in a wide range of biological processes: besides the production of energy, it also takes part in the synthesis of fatty acids, cholesterol and steroids, signal transduction and the maintenance of the integrity of the genome. Among many other applications, it is important to point out its role in pharmaceuticals formulation, dietary food, vitamins/minerals premix, nutritional ingredients and cosmetics[1-6].

In this study, NA was studied by Matrix Isolation FTIR spectroscopy and DFT(B3LYP) and MP2 calculations. For matrix isolation experiments, samples were prepared by co-deposition of NA (placed in a specially designed doubly termostatable Knudsen cell with shut-off possibility) and the inert gas, onto a cooled (9 K) CsI substrate. Irradiation of the matrices was carried out with a Hg(Xe) lamp at λ>235 nm. Theoretical calculations were performed with the GAUSSIAN 98 program, with the 6-31++G(d,p) and 6-311++G(d,p) basis sets.

The theoretical calculations predicted two conformers (see figure 1). The *(Z)*-conformer is 4.01 kJ mol^{-1} less stable than the *(E)*-conformer. In consonance with the theoretical results, the matrix isolation experiments, together with the spectra obtained after annealing the matrices, confirmed the presence of both conformers in the matrix. Assignment of the observed bands to the different conformational states was carried out on the basis of comparison with the theoretically predicted spectra, and annealing and irradiation experiments. The reactivity of NA upon irradiation has been also investigated.

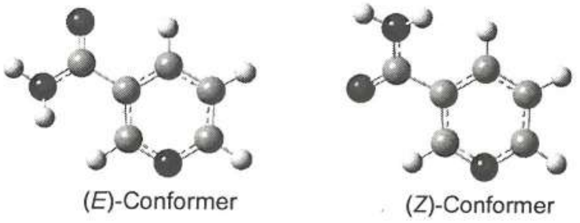
(*E*)-Conformer (*Z*)-Conformer

Fig. 1: Conformers of Nicotinamide

[1] B. Vogelsanger, R.D. Brown, P.D. Godfrey, A.P. Pierlot, J. Mol. Spectrosc, 145 (1991) 1.
[2] J. Kuthan, L. Musil, V. Jehlicka, Collect. Czech. Chem. Commun, 42 (1977) 283.
[3] P. Purcell, J. Phys. Chem, 68 (1964) 2666.
[4] P. Purcell, J.A. Singer, J. Phys. Chem, 69 (1965) 4097.
[5] R.A. Nyquist, The Interpretation of Vapor-Phase Infrared Spectra, Group Frequency Data, vol.I, Sadtler Research Laboratories, Philadelphia Pennsylvania, 1984.
[6] A. Yu, Y. Tsivadze, G.V. Tsintsadze, N.P. Gongadze, Y.Y. Kharitonov, Koord. Khim, 1 (1975) 1221.

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PHOTOCHEMISTRY OF MATRIX ISOLATED METHYL 3-METHYL 2*H*-AZIRINE-2-CARBOXYLATE STUDIED BY FT-IR AND DFT METHODS

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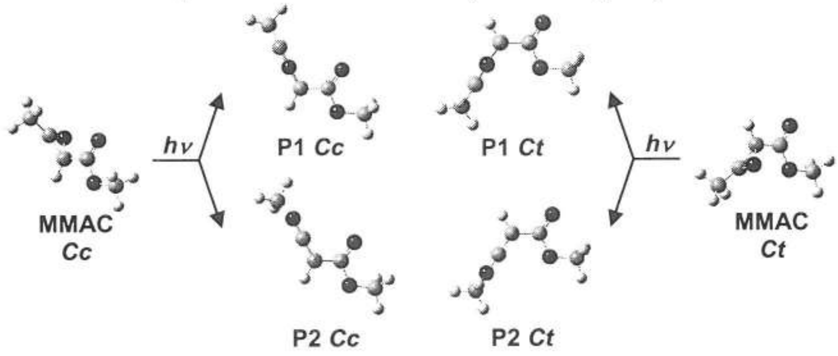
The novel aliphatic 2*H*-azirine – methyl 3-methyl-2*H*-azirine-2-carboxylate (MMAC) has been synthesized and its monomeric structure has been determined in the argon matrix at 10 K. Two conformers – *Cc* and *Ct* (the capital and lower-case letters denote the conformation in respect to C-O and C-C_α bonds, respectively) were found in the matrix, with the *Cc* form being slightly stabilized compared with the *Ct* one (see the figure).



In situ broadband UV (λ> 235 nm) excitation of the isolated compound resulted in cleavage of the C-C or C-N bond, leading to formation of nitrile ylide (P1) and ketene imine (P2) type of products, respectively (c. f., figure). The C-N cleavage, unusual for aliphatic 2*H*-azirines, was previously observed for methyl 2-chloro-3-methyl-2*H*-azirine-2-carboxylate and attributed to the simultaneous presence of two electron-withdrawing substituents (methylcarboxy group and chlorine atom), accelerating the intersystem crossing toward the triplet state and – in this way - C-N breakage [1]. Nevertheless, the study of photochemistry of MMAC allowed separating the effect of substituents, showing that the methylcarboxy group plays a crucial role in photochemical behavior of above-mentioned azirines.

[1] A. Gómez-Zavaglia, A. Kaczor, A. L. Cardoso, T. M. V. D. Pinho e Melo, R. Fausto, *J. Phys. Chem. A* (submitted).

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A COMBINED MATRIX ISOLATION AND AB INITIO STUDY OF THE BROMINE OXIDES

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Bromine oxides were generated by passing a mixture of $Ar/Br_2/O_2$ through a microwave discharge. The products were stabilized in an excess amount of argon and deposited onto a metal surface at held at 6.5 K. Infrared spectroscopy was used to analyze the species formed and isotopic exchange experiments and *ab initio* calculations were carried out to help in the assignment of the spectral bands. In addition to formerly studied species (BrO, BrBrO, and OBrO) previously not observed bromine oxides were identified. The existence of BrOBrO, $BrBrO_2$, and $BrOBrO_2$ are reported for the first time. The observed frequencies and intensity values for all the species considered are well predicted by our calculations. The chemistry involved in the production of these compounds is also discussed.

UNUSUAL PHOTOCHEMICAL C-N BOND CLEAVAGE IN THE NOVEL METHYL 2-CHLORO-3-METHYL-2H-AZIRINE-2-CARBOXYLATE

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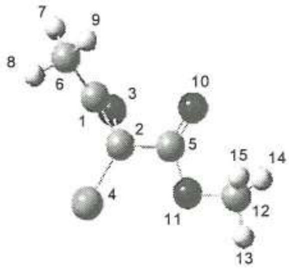
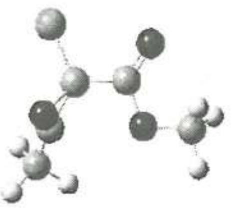
The structure, preferred conformers, vibrational spectrum and photochemical behavior of the novel azirine, methyl 2-chloro-3-methyl-2*H*-azirine-2-carboxylate (MCMAC) were investigated in low-temperature matrices and neat solid amorphous state by infrared spectroscopy and quantum-chemical calculations. Two conformers of the compound were observed in the argon, krypton and xenon matrices, in agreement with the DFT(B3LYP)/6-311++G(d,p) and MP2/6-311++G(d,p) theoretical calculations. Both conformers were found to exhibit the carboxylic ester group in the *Cis* conformation, differing in the arrangement defined by the O=C-C-Cl dihedral angle (*cis* and *trans,* for *Ct* and *Cc* forms, respectively). The *Ct* conformer was found to be the most stable conformer in the gaseous phase as well as in both argon and krypton matrices, whereas the more polar *Cc* conformer became the most stable form in the xenon matrix and in the solid amorphous phase.

Ct



Cc



In situ broadband UV ($\lambda > 235$ nm) excitation of matrix-isolated MCMAC led to azirine ring C-C and C-N bond cleavages, the latter process corresponding to the most efficient reaction channel. The photochemical cleavage of C-N bond had never been observed in case of aliphatic 2*H*-azirines. Its observation in MCMAC is attributed to the simultaneous presence in this novel azirine of two electron withdrawing substituents (methylcarboxy group and chlorine atom) connected to the azirine ring, which accelerates intersystem crossing towards triplet state from where cleavage of the C-N bond takes place.

The primary photoproducts resulting from the C-N and C-C ring-opening reactions were also found to undergo further photochemical decarbonylation or decarboxylation reactions.

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LOW-TEMPERATURE RAMAN STUDY OF WATER

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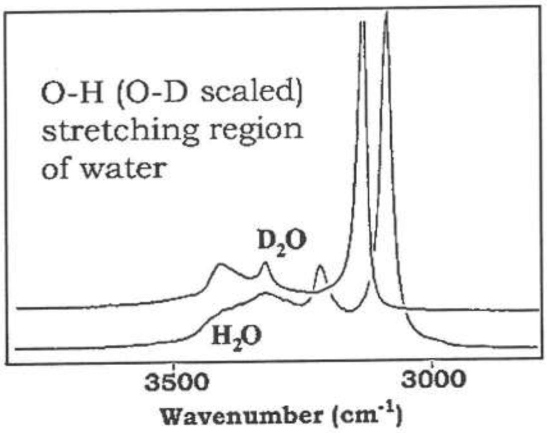
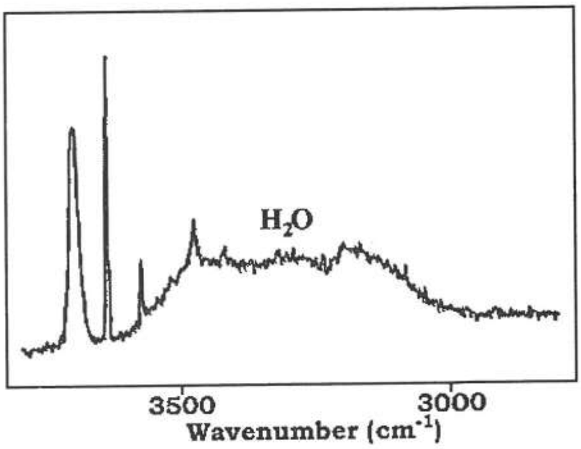
Pure water was investigated in solid state at low temperatures by Raman spectroscopy using two spray-on techniques. In the first case, we have prepared solid samples by spraying gaseous matter directly on the cold, golden finger in vacuum. Starting matter was a) double-distilled and deionized H_2O and b) commercial D_2O. The common knowledge of water structure is that ordering of water molecules in such an instant solidification strongly depends on the temperature of the substrate [1]. Below some 120 K, we confirmed a vitreous phase, but above ≈ 150 K, the matter solidified in a crystalline form [2-4]. Another spray-on technique performed here was argon matrix isolation. For that purpose, we first prepared a mixture of argon and water vapor on the vacuum line in nearly 100:1molar ratio. Then, gas mixture was solidified by spraying it on the cold finger in the same way as in the previous case of bulk water, but at temperatures 10 – 20 K.



In the high-frequency region of bulk matter we observe for both, light- and heavy-water, well known, complicated, but much better resolved spectral features. Stretching region of both spectra are plotted with the scaling factor = $\sqrt{M_{O-D} / M_{O-H}}$ (harmonic approx.). Obviously, the agreement is perfect for upper pair of bands, but for other lower bands harmonic approximation is not so good. In the low frequency region we observe a true crystalline ice band, but sometimes together with a Bose band which is characteristic for a vitreous state.

In the high-frequency region of matrix-isolated water, we have clearly observed bands of monomer species, probably dimeric bands, and broad feature characterizing *bulk water*. In the matrix- isolated heavy-water spectrum, we have noticed for the first time the presence of nitrogen molecule. Low frequency spectra of both water samples did not exhibit characteristics of crystalline structure, but Bose band was, as expected, very prominent. Our experience permits us to speculate that presence of atmospheric impurities causes disagreements between authors.



References:
[1] D. Eisenberg and W. Kauzman, The Structure and Properties of Water, Oxford University Press, London, 1969.
[2] J.-C. Li, V. M. Nield and S. M. Jackson, Chem. Phys. Letters **241** (1995) 290
[3] A. Givan, A. Loewenschuss and C. J. Nielsen, J. Phys. Chem. **B101** (1997) 8696.
[4] C. Salzmann *et al*, J. Phys. Chem. **B106** (2002) 1.

LOW TEMPERATURE RAMAN STUDY OF BIS(TRIMETHYLSILYL)ACETYLENE

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Low temperature Raman spectra of a known catalyst bis(trimethylsilyl)acetylene (BTMSAC) were recorded in temperature interval from 323 K to 10 K. Below melting point which occurs at 276 K BTMSAC crystallizes in $P2_1/c$ space group with $Z=2$. Altogether six phonons are expected below 100 cm^{-1}, together with two internal modes (linear angle bending at 40 cm^{-1}) and $Si(CH_3)_3$ torsion which is practically free in liquid, but hindered in polycrystalline state [1]. Above 100 cm^{-1} there is a degenerate linear bending mode at 127 cm^{-1}, three modes (SiC_3 sym. def. mode, CH_3 torsion A and B type [1], and CH_3 sym. torsion) at 175 cm^{-1}, three internal modes at 216 cm^{-1} (two SiC_3 deformation, and one degenerate CH_3 torsion). It is interesting to note that the triple stretching vibration occuring at 2108 cm^{-1} is asymmetric in crystalline state, the low wavenumber side of the bandwidth being considerably larger than the high wavenumber part of the asymmetrically constructed Lorentzian [2].

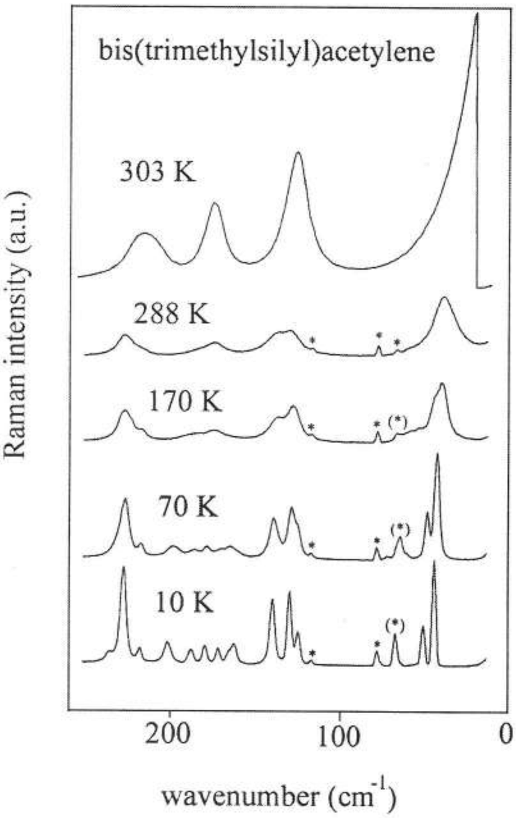

Fig. 1: Low frequency Raman spectra of BTMSAC at low temperatures.Laser plasma lines are marked with asterisks. Asterix in brackets denotes a coincidence of a plasma line and a BTMSAC band

[1] V. A. Sipachev, L. S. Khaikin, O. E. Grikina, V. S. Nikitin, M. Traetteberg: J. Mol. Struct. **523** (2000) 1-22.
[2] V. Mohaček-Grošev, K. Furić: Fizika A **14** (2005) 219-224.

UV-INDUCED RING OPENING OF 2(5*H*)-FURANONE ISOLATED IN LOW TEMPERATURE INERT MATRIX

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2(5*H*)-Furanone (or γ-Crotonolactone as usually called), is the simplest example of the butenolide ring system, which occurs in many natural products. This compound has applications in several important organic reactions as a versatile reagent used, for instance, in Michael addition reactions for synthesis of lignans and it was also been employed in three-component Michael-Aldol reactions with an aldehyde and a thiolate or carbanion.

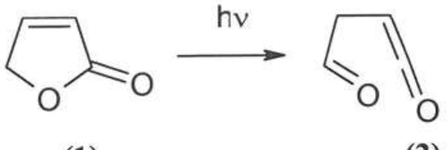
The objective of this work was the characterization of the structure of the compounds formed from the photochemical reactions of 2(5*H*)-furanone, applying the low temperature matrix-isolation technique, FTIR spectroscopy and quantum chemistry theoretical methods.

For infrared and photochemical measurements, the sample was placed in a glass tube protected against light and connected to the chamber of the cryostat via a needle valve. Before cooling down the cryostat, the compound was degassed by pumping through the vacuum chamber of the cryostat at room temperature. This approach enabled removal of possible volatile impurities, allowing an additional purification of the compound, immediately before the experiment. In order to deposit a matrix, the vapor of the sample is introduced into the cryostat chamber through the needle valve together with large excess of the host matrix gas coming from a separate line. The infrared spectra were recorded with 0.5 cm^{-1} resolution, using a Mattson (60AR Infinity Series) FTIR spectrometer equipped with a KBr beam splitter and a DTGS detector.

The matrixes were irradiated through the outer KBr window of the cryostat, with filtered or unfiltered light from a 500W Hg(Xe) lamp (Spectra-Physics, model nº 66142).

Upon irradiation of the sample (with $\lambda > 235$ nm), an intense band at 2150-2120 cm^{-1} appears, which is typical of the antisymmetric stretching vibration of ketene (-C=C=O) group[1-5], indicating that the ring-opening leading to the conjugated aldehyde-ketene isomer of 2(5*H*)-furanone (Figure 1) was produced.

The experimental spectra of both, the reactant and the photoproduct, are in a good agreement with those theoretically predicted [calculated at DFT(B3LYP)/6-311++G(d,p) level], allowing a reliable interpretation of the experimental data.



(1) (2)

Fig. 1: Schematic representation of the UV-induced photoreaction of 2(5*H*)-furanone **(1)** leading to production of the conjugated aldehyde-ketene **(2)**.

[1] S. Breda; L. Lapinski; R. Fausto; M.J. Nowak; Phys. Chem. Chem. Phys., 2003, 5, 4527-4532;
[2] S. Breda; L. Lapinski; I. Reva; R. Fausto; J. Photochem. Photobiology A, 2004, 162/1, 139-151;
[3] S. Breda; I. Reva; L. Lapinski; R. Fausto; Phys. Chem. Chem. Phys., 2004, 6, 929-936;
[4] S. S. Breda; I. Reva; L. Lapinski; R. Fausto; Chem PhysChem, 2005, 6, 602-604;
[5] S. Breda; I. Reva; L. Lapinski; M.L.S. Cristiano; L. Frija; R. Fausto; J. Phys. Chem. A, 2006, in press;

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MATRIX ISOLATION AND LOW TEMPERATURE SOLID STATE FTIR SPECTROSCOPIC STUDY OF α-FURIL

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α-Furil [C_4H_3O-C(=O)-C(=O)-C_4H_3O] (Figure 1) is a typical representative of diaromatic heterocyclic α-dicarbonyls; it is a well-known intermediate in organic synthesis and is currently used as a photosensitizer for UV photocurable inks,[1] in the preparation of photographic materials and in electronic display devices.[2-4]

In this study, α-Furil has been isolated in argon and xenon matrices and studied by FTIR spectroscopy, supported by DFT(B3LYP)/6-311++G(d,p) calculations. For matrix preparation, α-furil vapors were deposited together with a large excess of the matrix gas onto to the cold optical CsI substrate of the cryostat. After depositing the compound, annealing of the matrices was performed. The obtained spectra were fully assigned and revealed the presence in the matrices of three different conformers, all of them exhibiting *skewed* conformations around the intercarbonyl bond and the two C_4H_3O-C(=O) fragments nearly planar: the most stable conformer (form **I**; C_2 symmetry; O=C-C=O intercarbonyl dihedral equal to 153.1 degrees), the second most stable conformer (form **II**; C_1 symmetry; O=C-C=O intercarbonyl dihedral equal to 126.9 degrees) and the third conformer (form **III**; C_2 symmetry; O=C-C=O dihedral equal to 106.2 degrees). The theoretical calculations predicted the two higher energy forms being 5.85 and 6.22 kJ mol^{-1} higher in energy than the most stable form, respectively, and energy barriers for conformational interconversion higher than 40 kJ mol^{-1}. These latter are high enough to prevent observation of conformational isomerization for the matrix isolated compound. The three possible conformers of α-furil were also found to be present in CCl_4 solution, as well as in a low temperature neat amorphous phase of the compound prepared from fast condensation of its vapor onto a 10 K cooled suitable substrate. On the other hand, in consonance with the available X-ray data.[5] the IR spectra obtained for the neat low temperature crystalline state reveals that, in this phase, α-furil exists uniquely in its most stable conformational state, **I**.

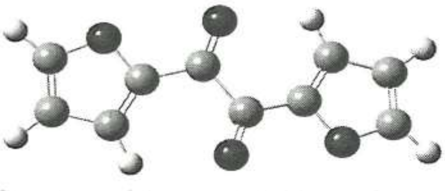

Fig. 1: Structure of the most stable conformer of α-furil, **I**.

[1] ICI LTD, Patent GB1449451, (1976).
[2] Nippon Electric Company Ltd., Japan, Patent JP58189286, (1983), Chem. Abstr. 101 (1984) 219903.
[3] T.T.J. Yu (Energy Conversion Devices Inc.) Eur. Pat. Appli. GB1477046, (1983), Chem. Abstr. 100 (1984) 129945z.
[4] G.D.,Varamasov, I.A. Bekbulatov, Sh.K. Madaliev and Y.M. Mamatov, USSR Patent SU 758753, Chem. Abstr. 101 (1984) 111964r.
[5] S.C. Biswas, S. Ray and A. Podder, Chem. Phys. Lett. 134 (1987) 541.

Acknowledgements:

The authors acknowledge the Portuguese Science Foundation (FCT – POCTI/QUI/59019/2004 and POCTI/QUI/58937/2004), FEDER, CONICET and Agencia Nacional de Promoción Científica y Tecnológica (PICT 13080) for financial support.

SYNTHESIS AND FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDY ON SOME METAL (II) HALIDE COMPLEXES OF ISONICOTINIC ACID N-OXIDE

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In this study; The FT-IR spectra of are reported for the metal (II) halide isonicotinic acid N-oxide complexes on the following stoichiometries: $Mn(INO)_2I_2$, $Zn(INO)_2I_2$, $Co_2(INO)_3X_4$ (X: Cl, Br, I), $Ni(INO)_4X_2$ (X:Br, I), $Cu(INO)_2X_2$ (X: Cl,Br), $Cd(INO)_2Cl_2$ in the 4000-400 cm^{-1} region. The vibrational assignments are given for all the observed bands. The analysis of the vibrational spectra indicates that there are some structure spectra correlations. The frequency shifts are found depend on the halogen for a given metal, and it is also found that the shifts are depend on metal for the same halogen. Certain chemical formulas were determined by the elemental analysis results.

SYNTHESIS, STRUCTURE, SPECTROSCOPIC AND ELECTROCHEMICAL PROPERTIES OF BIS(HISTAMIN SACCHARINATO)COPPER(II) COMPLEX

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Crystal structure of [Cu(II)(hsm)$_2$(sac)$_2$] (hsm is histamine and sac is saccharine) complex has been determined by X-ray diffraction analyses and its magnetic environment has been identified by electron paramagnetic resonance (EPR) technique. The title complex crystallizes in the monoclinic system, space group P 21/c with a = 7.4282(4), b = 22.5034(16), c = 8.3300(5) Å, β = 106.227(4)°, V = 1336.98(14) Å^3, and Z = 2. The structure consist of discrete [Cu(II)(hsm)$_2$(sac)$_2$] molecules in which the copper ion is centrosymmetrically coordinated by two histamine ligands forming an equatorial plane [Cu-N$_{hsm}$= 2.024(2) and Cu-N$_{hsm}$= 2.0338(18) Å]. Two N atoms from the saccharine ligands coordinate on the elongated axial positions with Cu-N$_{sac}$ being 2.609(5) Å. The significant difference between the Cu-N$_{hsm}$ bond distances in the equatorial plane and the Cu-N$_{sac}$ distances in the axial positions has also been observed in other chelated copper complexes [1-3]. This difference can easily be explained if one considers the Jhan-Teller distortion observed in most octahedral copper(II) complexes. In the crystal structure, the molecules are organized by hydrogen bonds forming a two-dimensional network.

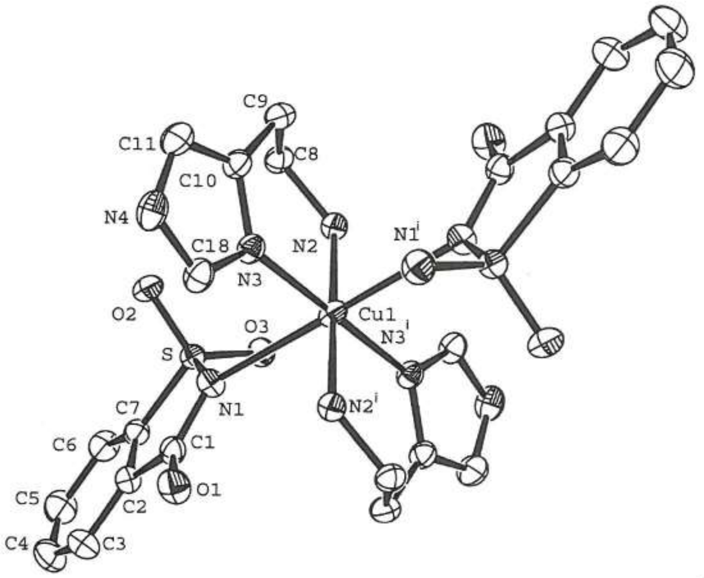

Figure 1. An OrtepIII diagram of title complex. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms have been omitted for the clarity. [Symmetry code (i): 2-x, -y, 1-z]

The title complex is also charecterized by spectroscopic (IR, UV/Vis) and cyclic voltammetric methods. The molecular orbital bond coefficients of Cu(II) ion in d^9 state is also calculated by using EPR and optical absorption parameters.

[1] G.A. Albada, I. Mutikainen, U. Turpeinen & J. Reedijk. Acta Cryst E58 (2002) m55.
[2] L. Sieron & M. B. Strzyzewska. Acta Cryst.C53 (1997) 296.
[3] A. Bulut, H. İçbudak, G. Sezer, C. Kazak. Acta Cryst C61 (2005) m228.

CONFORMATIONAL STUDY AND VIBRATIONAL SPECTRA OF 3-METHYL-4-THIOPHEN-2-YL BUT-3-EN-2-ONE (MTBEO)

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$(H_3C_4S)\text{-}CH{=}C(CH_3)(COCH_3)$ (MTBEO) is used as a starting material in many organic syntheses of heterocycles. The better understanding of its reactivity requires a knowledge about the electron distribution inside the molecule. We have used IR, Raman and NMR spectroscopy to obtain a view about its configurational and conformational equilibrium depending on the effect of environment. NMR spectroscopy confirmed that MTBEO was prepared as pure E-isomer (marked by the first letter with thienyl and acetyl groups in trans position), which is stable even in solutions with increasing polarity.

Ab initio calculations show that MTBEO can exist as four conformers (labeled by the second letter Z or E) with the carbonyl group oriented towards or from double C=C bond and with the thienyl ring oriented as *s-trans* or *s-cis* with respect to olefinic double bond (labeled by the third letter t or c).

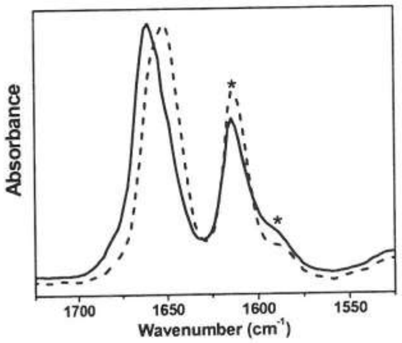

Fig.1: IR spectra of MTBEO in chloroform at 55 °C and at -20 °C (dashed line).

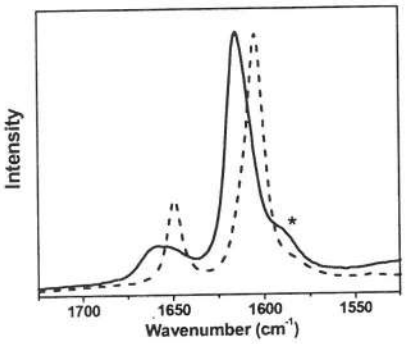

Fig.2: Raman spectra of MTBEO in chloroform and as solid (dashed line).

Table 1: MP2/6-31G** calculated ab initio relative energies of MTBEO conformers.

MTBEO	EEt	EEc	EZt	EZc
E(kJ/mol)	0.00	3.68	6.11	8.79

In the figures, asterisks denote the bands which change their relative intensity with the temperature or disappeared in solid phase. According to the calculated energies such conformational behaviour can be explained by the t or c conformation of thienyl ring with the E conformation of acetyl group.

P6-4

3,ISOMERIZATIONAL AND CONFORMATIONAL STUDY OF 3-N,N-DIMETHYLHYDRAZINO-2-ACETYL PROPENENITRILE (DMHAP) AND 3-N,N-DIMETHYLHYDRAZINO-2-METHYLSULPHONYL PROPENENITRILE (DMHSP)

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$(H_3C)_2N\text{-}NH\text{-}CH{=}C(CN)(COCH_3)$ (DMHAP) and $(H_3C)_2N\text{-}NH\text{-}CH{=}C(CN)(SO_2CH_3)$ (DMHSP) belong to the push-pull ethylenes intensively used in synthetic organic chemistry. The electron donor dimethylhydrazino group in the investigated compounds seems to have a special influence on their conformational and configurational equilibria perhaps due to the possibility to create an intramolecular hydrogen bond or an interaction of dimethylhydrazino nitrogen lone electron pair with cyano carbon.

Using ab initio MP2 calculations seven conformers of DMHAP have been found, three for Z-isomer and four for E-isomer (the first letter denotes cis and trans position of dimethylhydrazino and acetyl groups, the second Z or E and the third s or a letters denote the conformational orientation of carbonyl oxygen and dimethylhydrazino group towards or from double C=C bond, respectively). However, as shown by calculations, they significantly differ in energy. The most stable conformer is ZZa one which enables an intramolecular hydrogen bond and has been synthesized and confirmed by NMR in chloroform. ZZa can not pass to other Z-conformers. Nevertheless, in more polar DMSO only the process of isomerisation takes place and next two conformers of E-isomer with *anti* and *syn* orientation of dimethyl-hydrazino group have been confirmed.

In the case of DMHSP, there are only four possibilities from the conformational point of view because sulfonyl group can exist only in a single orientation towards the double C=C bond. Therefore we can consider for both E and Z isomers only the *anti* (a) or *syn* (s) conformational positions of dimethylhydrazino group. Analogous to DMHAP we have found by ab initio MP2 calculations that the most stable conformer is the Za one. However, in the synthetic process the pure E-isomer has been obtained. In DMSO the presence of both E-isomer conformers has been proven both by NMR and vibrational spectroscopy with Es conformer as the more stable one. Additionally, in less polar chloroform an isomerization process occurred and also Z-isomer has been detected as well. In order to explain such behavior solvent effect calculations using PCM model have been done.

Table 1: MP2/6-31G** calculated ab initio relative energies of DMHAP and DMHSP conformers.

DMHAP	ZZa	ZZs	ZEa	EZa	EZs	EEa	EEs
E(kJ/mol)	0.0	57.1	48.1	13.2	25.8	28.4	31.2
DMHSP	Za	Zs	Ea	Es			
E(kJ/mol)	0.0	27.7	6.4	9.6			

^{13}C AND ^{1}H NMR SUBSTITUENT CHEMICAL SHIFTS IN N(1)-(4-SUBSTITUTED PHENYL)-3-CYANO-4,6-DIMEHTYL-2-PYRIDONES

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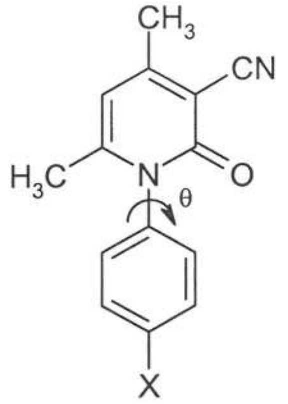
Linear free energy relationships (LFER) were applied to the ^{1}H and ^{13}C NMR chemical shifts [$\delta_{(N)}$; N = ^{13}C, ^{1}H, respectively] in the N(1)-(4-substituted phenyl)-3-cyano-4,6-dimehtyl-2-pyridones, with the aim of getting insight into the factors determining shifts in the system:



X = $N(CH_3)_2$, OH, OCH_3, CH_3, CH_3CH_2,
H, F, Cl, Br, I, NO_2, $COCH_3$, COOH

Chemical shifts were correlated using two different LFER models, based on the mono and dual substituent parameter (MSP and DSP) treatment:

Model 1. MSP equation, Simple Hammett equation, $\delta_{(N)X} = \rho\sigma_X + h$;

Model 2. DSP equation, Extended Hammett equation, $\delta_{(N)X} = \rho_I\sigma_{IX} + \rho_R\sigma_{RX} + h$;

The geometry data needed were obtained using semi-empirical MNDO-PM3 energy calculations.

Results of correlations point out a low resonance interaction of substituents on the phenyl ring with the 2-pyridone conjugated system. The mode of transmission of substituent effects in these systems, both inductive and resonance, have been discussed as well as the effect of geometry on the transmission of electronic effect through investigated molecules.

On the basis of NMR data and correlation results, considering the influences of the electronic effects of substituents on the changes of angle θ as an important factor of geometry of investigated molecules, it can be concluded that conformation of molecules is determined by the balance of resonance interactions from the N(1) substituted phenyl ring and 2-pyridone unit.

VIBRATIONAL STUDY OF THE COPPER(II)-CARCININE COMPLEXES AND TAUTOMERISM OF IMIDAZOLE SIDE CHAIN

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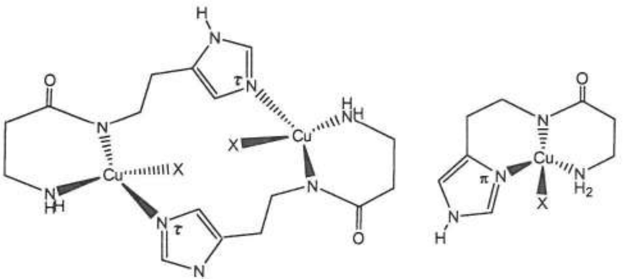
Carcinine (β-alanyl-histamine) is a natural imidazole-containing compound found in the non-protein fraction of mammalian tissues, probably involved in the carnosine-histidine-histamine metabolic pathway and in the mammalian physiologic response to stress.[1] Carcinine has a good potential to act as a natural antioxidant *in vivo* since it is able to scavenge harmful ${}^{\cdot}$OH radicals and inhibit fatty acid peroxidation. Since transition metal ions, such as Cu(II), can catalyze the formation of reactive oxygen species resulting in oxidative tissue damage, the chelation of transition metals can be one of the mechanisms by which antioxidants protect targets from oxidative stress preventing them from participating in deleterious processes.[2] Consequently, more information on the interaction of copper (II) with carcinine can shed light on the biological role of this dipeptide and aid metal-enzyme studies, since the tautomerism of the imidazole ring can play a crucial role in enzymatic mechanism.

The ability of carcinine to chelate Cu(II) ions was tested by Raman and IR spectroscopy at different pH values. Both the Raman and IR spectra present some marker bands useful for the identification of the complex structure predominating at a specific pH. In particular, Raman spectroscopy appears to be a useful tool for analyzing the tautomeric equilibrium of the imidazole ring.[3-5]

The neutral imidazole group of this dipeptide gives rise to some bands that appear at different wavenumbers, depending on whether the imidazole ring is in the N_τ-H (tautomer I) or the N_π-H (tautomer II) protonated form. Both at pH 7 and 9 the tautomer I is preferred in the free ligand, but the tautomeric preference can be completely upset after the complex formation. At neutral pH N_τ- and N_π-ligated complexes were identified (see Fig.1), whereas at basic pH the predominant species is an oligopeptide where the imidazole moiety of carcinine binds two different Cu(II) ions since N_τ and N_π nitrogens are both deprotonated.



X =Cl⁻ ; H_2O

Fig. 1: The Cu(II)-carcinine complexes mainly formed at pH 7

[1] D.N. Brotman, L.Flauncbaum, Y.E. Kang, G.F.Merrill, H. Fischer, Crit. Care Med.18 (1990) 317.
[2] D. M. Miller, G. R. Buettenerand S.D. Aust, Free Rad. Biol. Med. 8 (1990) 95.
[3] H. Tacheuchi, Biopolymers, 72 (2003) 305.
[4] A. Torreggiani, G.Fini, G.Bottura J. Mol. Struct. 565-566 (2001) 341.
[5] A.Torreggiani, A. Degli Esposti, M. Tamba, G. Marconi, G. Fini, J Raman Spectrosc. 37(2006) 291.

APPLICATION OF 2D IR CORRELATION ANALYSIS TO THE OBSERVED TEMPERATURE CHANGES IN $[(\text{cin H}_2)^{2+}(\text{CuCl}_4)^{2-}]_2\cdot3\text{H}_2\text{O}$ COMPOUND

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Far infrared (FIR) spectra have been measured for bis [cinchoninium tetrachlorocuprate(II) trihydrate compound in the temperature range of 10 – 295K. The asymmetric unit of the Cu(II) compound with cinchonine consists of two tetrahedral $(\text{CuCl}_4)^{2-}$ anions linked by hydrogen bonds to two doubly protonated cinchonine molecules $(\text{cin H}_2)^{2+}$ and also to three water molecules[1,2]. The temperature dependent FIR spectra show changes, which can be interpreted as deformation of the cooper(II) coordination sphere. These include as well distortions of tetrahedrons, which form the first coordination Cu(II) sphere, as possible formations of the bifurcated hydrogen bonds in which there are involved quinoline nitrogen atoms of both cinchonine molecules[3].

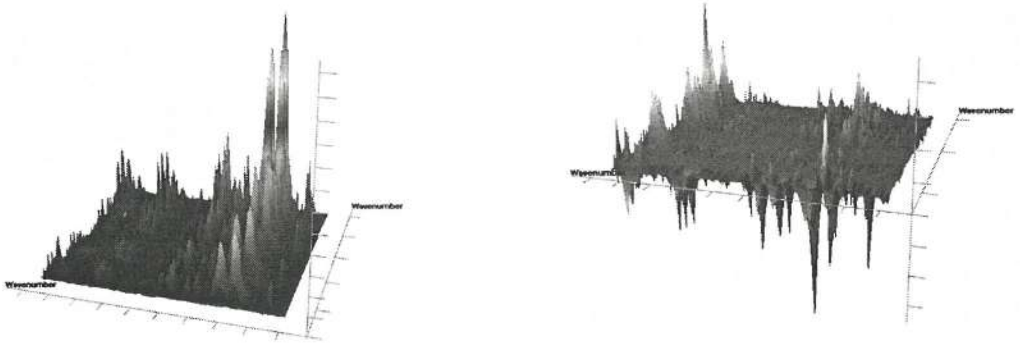

Fig. 1: Synchronous (left) and asynchronous (right) 2D correlation spectra.

In the present study there was an attempt to examine observed spectral changes in the FIR spectra using 2D correlation method. Temperature was considered as an external perturbation. Synchronous 2D correlation spectrum is presented in Fig. 1 (left side). This type of correlation points the simultaneous or coincidental changes of spectral intensities measured at two wavenumbers. The asynchronous spectrum (Fig. 1, right side) represents sequential or unsynchronized changes of spectral intensities measured at two wavenumbers, which generate the respective asynchronous cross peak. The respective correlations are discussed.

[1] K. Dyrek, J. Goslar, S.A. Hodorowicz, S.K. Hoffmann, B.J. Oleksyn, A. Wesełucha-Birczyńska, Inorg. Chem., 26 (1987) 1481.
[2] A. Weselucha-Birczyńska, B. J. Oleksyn, S.K. Hoffmann, J. Śliwiński, B. Borzęcka-Prokop, J. Goslar, W. Hilczer, Inorg. Chem., 40 (2001) 4526 – 4533.
[3] A. Weselucha-Birczyńska, B. J. Oleksyn, C. Paluszkiewicz, J. Śliwiński, J. Mol. Struci. 511-512 (1999) 301.

P6-8

VIBRATIONAL AND ELECTRONIC SPECTRAL CHARACTERISATION OF SEVERAL PHARMACOLOGICALLY IMPORTANT ARALKYL DERIVATIVES OF THE PYRIDINIUM CATION

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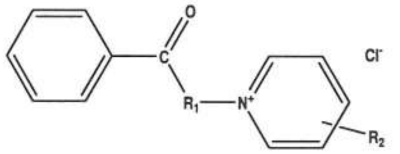
Pyridinium or bispyridinium oxime derivatives are known as potent acetylcholinesterase reactivators used for the prophylaxis and treatment of intoxications with organophosphorous compounds such as nerve agents and pesticides. Some 1-phenacylpyridinium salts have interesting antifungal and amebacidal properties while 1-benzoylethylpyridinium and 1-benzoylethylpyridinium-4-aldoxime salts act as possible protectors of human blood cholinesterase due to their capability to reversibly inhibit this enzyme.[1] The spectrophotometric studies on the coordination ability of the selected aralkyl derivatives of the pyridinium cation (Table 1) to the pentacyanoferrate(II) moiety have shown considerable differences concerning their stability and reactivity in aqueous solutions.[2,3] These findings encouraged us to perform a comparative FT IR and FT Raman spectroscopic study of the solid compounds focused on their structural features.

Table 1. The examined derivatives of pyridinium chloride



Name	R_1	R_2
1-Phenacylpyridinium chloride	$-CH_2-$	-H
1-Phenacyl-2-methylpyridinium chloride	$-CH_2-$	$-CH_3$
1-Phenacylpyridinium-4-aldoxime chloride	$-CH_2-$	-C=N-OH
1-Benzoylethylpyridinium chloride	$-CH_2CH_2-$	-H
1-Benzoylethylpyridinium-4-aldoxime chloride	$-CH_2CH_2-$	-C=N-OH

The characteristic vibrational frequencies will be discussed in correlation to their predominant keto-enol form, acido-basic properties, and in comparison with the electronic spectra of the ligands themselves and their pentacyanoferrate(II) complexes.

[1] M. Škrinjarić-Špoljar, N. Burger and J. Lovrić, J. Enz. Inhib. 14 (1999) 123.
[2] J. Lovrić, B. Foretić and N. Burger, Z. Phys. Chem. 218 (2004) 1.
[3] B. Foretić, J. Lovrić and N. Burger, J. Coord. Chem. (2005) in press.

EFFECT OF THE SUBSTITUENTS ON THE ^{13}C CHEMICAL SHIFTS OF THE AZOMETHINE CARBON ATOM OF N-(PHENYL SUBSTITUTED) SALYCYL ALDIMINES

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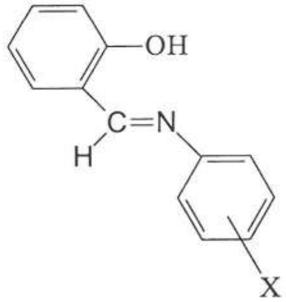
The ^{13}C NMR chemical shifts of the azomethine carbon atom of the following compounds have been determined in $CDCl_3$, at room temperature, using a Varian Gemini 200 spectrophotometer:



where X = H; *p*-Me; *p*-Br; *p*-Cl; *p*-OMe; *p*-NMe_2; *p*-COMe; *p*-NO_2; 2N; 3N.

The ^{13}C NMR chemical shifts of azomethine carbon atom were correlated with electrophilic substituent σ and σ^+ constants by Hammet equation:

$$\Delta\delta_C = \rho\sigma^+$$

Where $\Delta\delta_C$ is the relative ^{13}C chemical shifts of the azomethine carbon atom, caused by the substituent, relative to the unsubstituted compound; ρ and ρ^+ is the proportionality constant describing the sensitivity of the ^{13}C NMR chemical shifts to the substituent effects.

Results of correlations point out to a strong resonance interaction of substituents on the aniline ring with the azomethine carbon atom. The electronic effects of 2-hydroxy substituted phenyl group are compared with that of arylidenaldimines[1,2]. The mode of transmission of substituent effects is discussed in both systems.

[1] B. Ž. Jovanović; M.Mišić-Vuković, A. D. Marinković; V. Vajs, *J. Mol. Struct.*, 642 (2002) 113-118
[2] B. Ž. Jovanović; M.Mišić-Vuković, A. D. Marinković; V. Vajs, *J. Mol. Struct.*, 482-483 (1999) 375-378.

SPECTROISCOPIC STUDIES OF IONOPHORIC OCTOPUS-LIKE SI-POLYPODANDS

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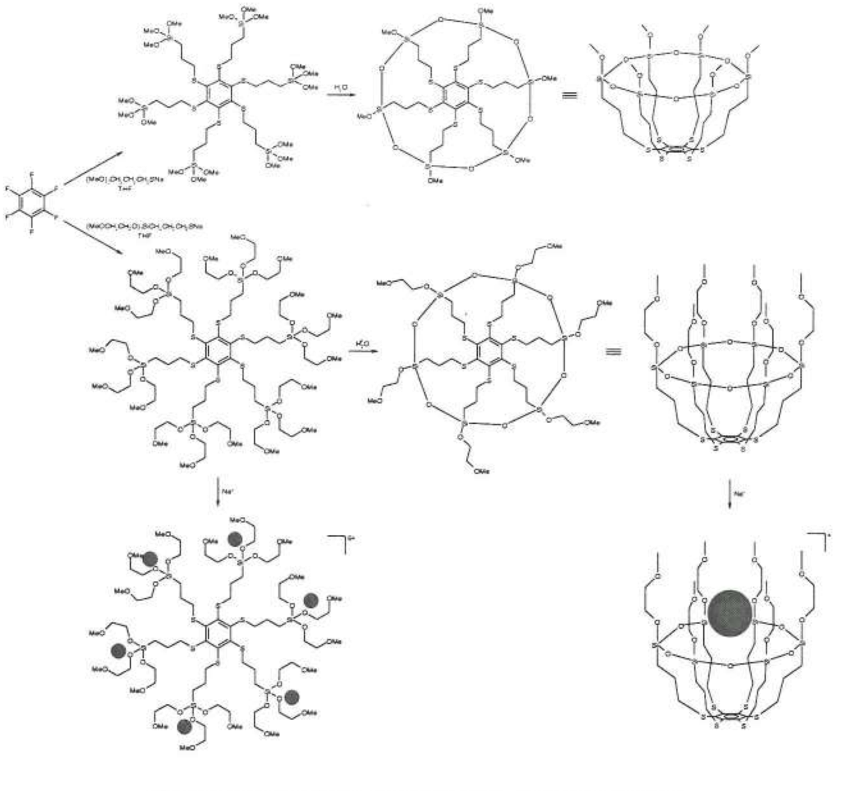
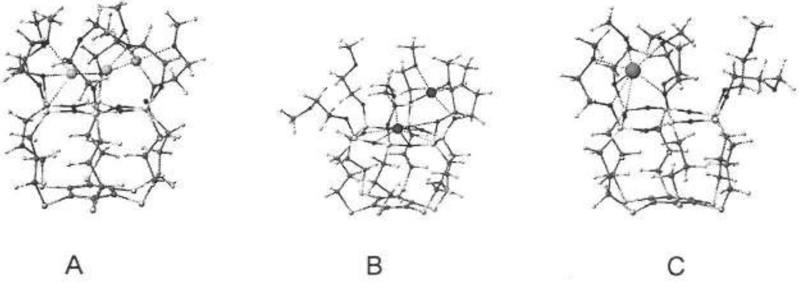
The new specific group of octopus-like Si-polypodands (Scheme 1) was obtained and studied by different spectroscopic methods (NMR, ESI-MS, FTIR). We also tried to identify the complex-forming between ionophores and some cations (Li^+, Na^+, K^+). The results were visualized by semiempirical method.



Scheme 1: Octopus-like Si-polypodands

PM5 semiempirical calculations were performed using the Mopac 2002 Program.



Scheme 2: The examples of complexes of octopus-like Si-polypodands with Li^+ (A), Na^+(B) and K^+(C) cations

PARALLEL STUDY OF THE CONVENTIONAL AND DIFFUSE-REFLECTANCE SPECTRA OF THE HYDRATES OF TWO PENTACYANONITROSYLFERRATE(II) COMPLEXES

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A parallel investigation of the diffuse-reflectance and absorbance spectra of two pentacyanonitrosylferrate(II) complexes, namely tris(bipyridine)nickel(II) pentacyanonitrosylferrate(II) tetrahydrate and tris(bipyridine)iron(II) pentacyanonitrosylferrate(II) tetrahydrate was carried out. The main purpose of this study was to reveal whether the pressed-pellets technique may cause flaws in the interpretation of the absorbance spectra of the investigated compounds either because of the possibility of ion exchange and/or the influence of the applied pressure during the sample preparation.

The diffuse-reflectance spectra was recorded either from an intimate mixture of the investigated compound and KBr or from powders obtained by grinding the previously obtained pellet used for absorption measurements. The method of dilution was used in order to prevent the occurrence of considerable specular reflection

Considerable differences between the diffuse-reflectance and absorbance spectra were detected, especially concerning the inequality in the intensities of the bands. The gain an additional insight in the reasons behind such an effect, difference spectra between the absorbance and diffuse-reflectance spectra of the corresponding compound was calculated and analyzed.

The corresponding spectra of sodium pentacyanonitrosylferrate(II) dihydrate were reinvestigated in the same manner.

RAMAN CHARACTERIZATION OF SEPARATION PROCESS OF SOLID n-ALKANE IN BINARY MIXTURES

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The micro-Raman spectroscopy, which permits very small areas of the sample to be analyzed nondestructively (down to the micron scale), has proven to be a very efficient tool for following the evaluation of the structural order of polymer molecules in time. The micro-phase separation processes are particularly interesting in systems, which feature a local quasi-crystal structure, like in mixtures of n-alkanes in a solid state. This process and orientational behavior of the n-alkanes binary mixtures in the solid state in room temperature was studied by means of the Raman scattering depolarization method. On the basis of the spectra the order parameters $<P_2>$ and $<P_4>$ were determined [1].

The phenomenon of separation process was observed for samples of different compositions and molar concentration. On the basis of Raman and FTIR spectroscopy technique it has been confirmed, that the process of self-organization depends on such factors as difference in length of n-alkanes chains, molar concentration of mixture components, as well as even or odd number of carbon atoms in the researched samples [2,3]. Moreover it has been shown that the short range order in molecular domains is relatively high.

[1] S. Jen, N.A. Clark, P.S. Perschan, E.B. Priestley, J. Chem. Phys. 66 (1977) 4635.
[2] A. Hacura, B. Kaczorowska, J. Raman Spectrosc., 36 (2005) 1029.
[3] A. Hacura, B. Kaczorowska, J. Mol. Structure, 744 (2005) 581.

VIBRATIONAL AND THERMAL STUDY OF 1H-1,2,4-TRIAZOLE HOFMANN T_d-TYPE COMPLEXES

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In this study, the M(1H-1,2,4-Triazole)$_2$M′(CN)$_4$ (M=Mn, M′=Zn, Cd or Hg; M=Cd, M′=Cd or Hg) complexes of 1H-1,2,4-Triazole have been synthesised for the first time. The FT-IR spectra of all complexes and FT Raman spectrum of Cd-1H-1,2,4-Triazole-Cd complex are reported in the 4000-400 cm^{-1} region. The vibrational modes of 1H-1,2,4-Triazole observed in the spectra of the complexes show all the characteristics of a coordinated ligand. The spectral features of the compounds studies are found to be similar to each other indicating that they have analogous structures. Vibrational data also show that our complexes belong to the classical Hofmann-T_d-type complexes.

The thermal behaviour of Hofmann-T_d-type complexes of 1H-1,2,4-Triazole was studied in dynamic nitrogen atmosphere by DTA, DTG and TG techniques. Thermal decomposition of Mn(1H-1,2,4,-Triazole)$_2$Zn(CN)$_4$ and Cd(1H-1,2,4,-Triazole)$_2$Cd(CN)$_4$ occur in the two separated stages. 1H-1,2,4-Triazole molecules are removed in the first stage, and redox decomposition of the cyano group occurs in the second stage.

SPECTROSCOPIC STUDY OF THE INFLUENCE OF LaF_3 ADMIXTURE ON THE STRUCTURE OF BOROSILICATE GLASS

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Oxyfluoride glass-ceramics based on the silicate glass-matrix and the nano-phase of LaF_3 are developed to generate up-conversion processes of luminescence [1-3]. In such materials, the low-phonon crystals of LaF_3 are desirable host for the rare-earth elements. The effect of admixture of 3 mol % of La_2F_6 on the glass-forming characteristics and structural features of glasses in the Na_2O-B_2O_3-SiO_2 system has been investigated. Glasses have been obtained for $B_2O_3/(Na_2O+3La_2F_6)$ molar ratios equal to 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 with and without La_2F_6, respectively.

The influence of LaF_3 admixture on structural change and tendency to immiscibility and crystallization of examined glasses has been observed by use of FTIR and Raman spectroscopy, XRD, SEM, and DTA/DSC. Raman spectra and DTA/DSC curves have shown that the ceramming process during heat treatment results in crystallization of LaF_3 only for some compositions of the glass. FTIR and Raman spectra reveal changes in immiscibility which are enhanced with the increase of $B_2O_3/(Na_2O+3La_2F_6)$ ratio for glasses with LaF_3 admixture.

[1] M.J. Dajneka, "Transparent oxyfluoride glass ceramics", MRS Bulletin, 23 (1998) 57.
[2] M. Środa, M. Reben, M. Kwaśny, I. Wacławska, "LaF_3 nanocrystals as a host for Er^{3+} in oxyfluoride glass", Optica Applicata, XXXV, no. 4, (2005) 15.
[3] L.L. Kukenen, I.M. Reney, D.Furniss, A.B. Seddon, "Nucleation and crystallisation behaviour of transparent erbium III doped oxyfluoride glass ceramics for active photonic devices", Physics and Chemistry of Glasses, 42 (2001) 265.

SPECTROSCOPIC STUDIES OF SOME COPPER(II) COMPLEXES WITH N-(5-ETHYL-[1,3,4]-TIADIAZOLE-2-YL)- AS LIGAND

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Sulphonamidic ligands N-substituted with heteroatomic cycles offer multiple possibilities to coordinate metallic ions [1].

Starting from N-(5-ethyl-[1,3,4]-thiadiazole-2-yl) naphthalenesulfonamide (L) as lingand, $[Cu(L)_2]$, $[Cu(L)_2(py)_2]$, $[Cu(L)_2(Cl)_2]$ complexes were synthesized and characterized by means of : elemental analysis, IR , electronic diffuse spectrometry, ESR and magnetic susceptibility measurements.

The characteristic frequency for thiadiazolic ring appears in the IR spectrum of the ligand at 1525 cm^{-1}. This band is shifted towards lower frequencies in the IR spectra of the complexes (≈ 1450 cm^{-1}) which demonstrate the involving of the nitrogen atom of thiadiazolic ring in the metal ion coordination. For the $[Cu(L)_2]$ complex the shift of the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ bands with ≈ 10 cm^{-1} to lower frequency suggests the coordination of oxygen atoms at Cu(II) ions. The valence vibration ν(S-N) appears in the higher frequency range in the complex IR spectrum, due to the deprotonation of the $N_{sulfonamide}$ nitrogen atom that compensate the positive charges of Cu(II) ion.

All the modifications in the IR spectrum of $[Cu(L)_2(py)_2]$ complex comparative to the ligand IR spectrum indicate the deprotonation of the nitrogen of sulfonamide moiety, a conjugation effect (electron displacement) between the atoms of $-NH-SO_2-$ group and the thiadiazol ring and the coordination of one $T_{hiadiazol}$ atom to the Cu(II) ion. In the IR spectrum of complex a band appears at 1085 cm^{-1} due to the pyridine coordination at metallic ions. For the $[Cu(L)_2(Cl)_2]$ complex the shift of the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ bands to the lower frequency, the shift of ν(S-N) band to the higher frequency of the spectrum are attributed to the deprotonation of $S_{ulfonamide}$ atom, witch also determines a weak conjugation effect among the three N,S,O atoms of sulfonamide moiety. The shift of the bands characteristic for the valence vibrations of the thiazole ring in the IR spectra of the complex to lower frequencies provide the involving of one of the nitrogen atoms of in the Cu(II) ion coordination.

The diffuse reflection spectra of the complexes shapes are typically for square planar local symmetry around metallic ions.

The powder ESR spectrum of the $[Cu(L)_2]$ complex at room temperature is specific for monomeric pseudotetrahedral species. The $g_{II}= 2.238$ and $g_{\perp}= 2.071$ values correspond to the CuN_2O_2 local unit. The parameters obtained from powder ESR spectrum of $[Cu\ (L)_2(Py)_2]$ complex ($g_{II}= 2.059$, $g_{\perp}= 2.255$) confirm the presence of a CuN_4 chromophore in a square planar local symmetry.

References.

1. M. Gonzales-Alvarez, G. Alzuet,J. Borras, B. Marcias, J.M. Montejo-Bernardo, S. Garcia-Grada, *J.Biol. Inorg. Chem.*, 2003, 8, 112

P6-16

SPECTROSCOPIC INVESTIGATION OF TETRANUCLEAR CLUSTERS ENCAPSULATED IN SOME POLYOXOMETALATE COMPLEXES

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During the last years, sandwich-type heteropolyoxometalates encapsulating clusters of early transition metals have received much attention both from applied and fundamental research perspectives [1].

The sandwich-type $Na_{10}[Ni_4(H_2O)_2(AsW_9O_{34})_2]\cdot 22H_2O$(**1**), $Na_{10}[Co_4(H_2O)_2(AsW_9O_{34})_2]\cdot 25H_2O$ (**2**), $Na_6[Fe_4(H_2O)_2(AsW_9O_{34})_2]\cdot 20H_2O$ (**3**), $Na_6[Cr_4(H_2O)_2(AsW_9O_{34})_2]\cdot 18H_2O$ (**4**) complexes were prepared and investigated through spectroscopic (FT-IR , UV-VIS , EPR) methods and magnetic susceptibility measurements.

The band due to the frequency stretching v(W-O_c-W) is shifted in the IR spectra of (**1**) and (**2**) with 12 cm^{-1} towards higher energies comparative to the $Na_9[AsW_9O_{34}]\cdot 11H_2O$ ligand spectrum due to the involvement of the atoms of oxygen from the As-O_i and W-O_c-W bonds at the coordination of the Ni, Co ions. The opposite shift of ν_{as}(W-O_e-W) and ν_{as}(W-O_c-W) frequencies for the bondings from the belt region shows the co-ordination of each metallic ion at oxygen atoms.

In the UV spectra was relieved the existence of the some bands that characterize the tungsten polyoxometalates structure, having maximum values situated between 32.000-40.000 cm^{-1} (v_2) due to the electronic transitions d_π-p_π-d_π from the tricentric bonds W-$O_{c,e}$-W situated at the end of some more intense bands situated between 47.000- 50.000 cm^{-1} (v_1) due to the electronic transitions p_π-d_π from the W-O_t bonds.

Three bands appear in the visible electronic spectrum in aqueous solution for the Ni complex at 8700 cm^{-1} , 14.500 cm^{-1} and 25.300 cm^{-1} and are assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions.

Powder EPR spectrum of the complexes obtained at room and T= 80 K presented: a asymmetric signal at ≈585G, a very small signal at 3500G for (**1**), a signal centered at 3250G for (**2**), a intense signal at $g \approx 4.3$ for (**3**) and an isotropic and very large signal (≈ 2495 G) centered at $g = 1.963$ for (**4**).

The temperature magnetic susceptibility measurements indicate a Curie-Weiss behavior with magnetic moments $\mu_{eff} = 6.09\mu_B$ (**1**), $\mu_{eff} = 7.88\mu_B$ (**2**), $\mu_{eff} = 9.51\mu_B$ (**3**) and $\mu_{eff} = 10.66\mu_B$ (**4**).

References

1. M. T. Pope, A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, *30*, 34.

GAMMA IRRADIATED $[(CH_3)_4N]_2S_iF_6$ SINGLE CRYSTAL INVESTIGATION BY ELECTRON PARAMAGNETIC RESONANCE TECHNIQUE

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In this study, gamma irradiation damage centers in $[(CH_3)_4N]_2S_iF_6$ single crystal has been investigated by electron paramagnetic resonance spectroscopy (EPR) at room temperature. It has been found that γ-irradiation produces the $(CH_3)_3\dot{N}^+$ radicals in this compound (Figure 1). The g factors were found to be isotropic and the hyperfine constant for H atoms was measured as 28.7 G. The hyperfine coupling constant of the N nucleus with the hole in $(CH_3)_3\dot{N}^+$ in $[(CH_3)_4N]_2S_iF_6$ was found to be anisotropic with the $a_{//} = 15$, $a_{\perp} = 23$ G. Each methyl groups rotate around the their C_{3v} – axis and they also rotate around the C_{3v} – axis of $(CH_3)_3\dot{N}^+$ radical. These results were compared with the earlier studies [1-4] in $(CH_3)_3\dot{N}^+$ radical and discussed.

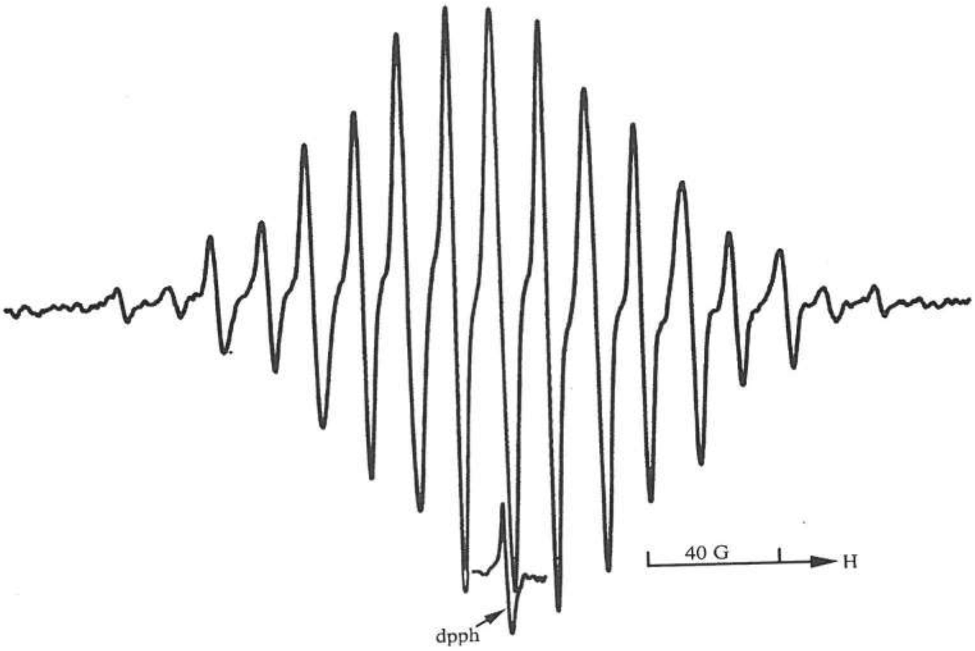

Figure 1: The EPR spectrum of γ-irradiated $[(CH_3)_4N]_2SiF_6$ single crystal at room temperature. The magnetic field is along the b-axis.

[1] Köksal, F., Kartal, İ., Rad. Phys. and Chem. 53, 501-504, 1998
[2] Köksal F, Yerli Y., Journal of Physics and Chemistry of Solids, 64(8), 1349-1352, 2003
[3] Yu, J.T., Liu, K.T. and Jeng, Y.H., Solid State Commun. 89, 6, 543-547, 1994
[4] Tench, A. J., J. Chem. Phys., 38, 593, 1963

P6-18

EFFECT OF THE SUBSTITUENTS ON THE ^{13}C CHEMICAL SHIFTS OF THE CARBON ATOMS OF 5-SUBSTITUTED OROTIC ACIDS

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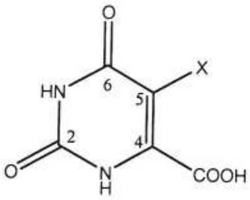
The chemistry of orotic acid and its derivatives has been intensively investigated for many years, because of their marked therapeutic properties; orotic acid is a precursor of all biologically important pyrimidines. In recent years there is an increased interest in the coordination chemistry of orotic acid. The synthesis of corresponding metal complexes has been studied, for therapeutic purposes, and also for the use in materials chemistry, because of orotic acid exceptionally interesting acceptor-donor properties[1, 2].

A series of eleven 5-substituted orotic acids have been synthesized of the formula:



Where X are H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, Cl, Br, I, NH_2, NO_2 and OH.

The ^{13}C NMR chemical shifts of carbon atoms of the investigated compounds have been recorded in DMSO-d6 solution using a Varian Gemini 200 spectrophotometer.

^{13}C substituted chemical shifts (SCS) for the investigated acids were applied with the principle of liner free energy relationships (LFER) using the Hammett or DSP equation in the form:

$$SCS = \rho\sigma + h \qquad (1)$$
$$SCS = \rho_I\sigma_I + \rho_R\sigma_R + h \qquad (2)$$

where SCS are the substituent chemical shifts (^{13}C NMR chemical shifts of the corresponding carbon atom, caused by a substituent relative to the unsubstituted compound), ρ, ρ_I and ρ_R are the proportionality constants reflecting the sensitivity of the ^{13}C NMR chemical shifts to substituent effects, σ, σ_I and σ_R are the corresponding substituent constants, and *h* is the intercept.

The mode of transmission of the substituent effects, both inductive and resonance was discussed.

[1] Z. Machon, R. Jasz Told-Howorko, Pol. J. Pharamacol. Pharm.,28 (1976)61.
[2] E. J. Behram, J. Chem. Research (S)., (2003) 702.

DFT CALCULATIONS AND VIBRATIONAL (FT-IR, FT-RAMAN) SPECTRA ON A URACILYL-PYRIDINIUM SALT

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Nature produces a large variety of conjugated molecules that have to be represented by dipolar canonical formulae. They are named mesomeric betaines. Many of them have been identified as alkaloids, and in some cases they can serve as modified nucleobases[1]. The study of modified nucleobases and related model compounds has became an important topic in modern bioorganic chemistry, since it provides us molecular properties which can be useful to design new chemical drugs against degenerative diseases.

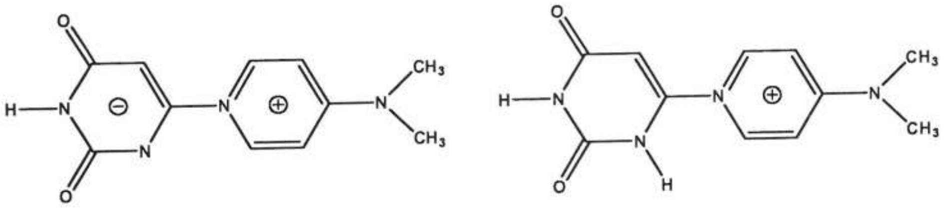

Figure 1. Chemical structures of the uracilyl-pyridinium betaine and its N-protonated derivative.

In this work we report a structural and spectroscopical study of the pyridinium-uracil cation depicted in Fig. 1. The optimized geometry of this molecule was calculated from quantum chemistry density functional theory (DFT-B3PW91) at the 6-31G** level. It shows a twisted conformation with a torsion angle between aromatic rings of 52.3 deg. The shortest carbon-nitrogen distance, 1.336 Å, was predicted for the $(CH_3)_2N$-C(pyridinium) bond, which indicates a strong double-bond character. The net charge of the cation was largely shared between the pyridinium and the uracil rings, namely +0.592 and +0.339 a.u. respectively. A force field calculation on the optimized structure was performed. Vibrational wavenumbers, infrared and Raman intensities and normal mode descriptions were predicted. Calculated wavenumbers and intensities were compared with the FT-IR and FT-Raman spectra of this salt, thus supporting for a general assignment of the recorded spectra.

[1] A. Schmidt, Adv. Heterocycl. Chem. 85 (2003) 67.

MINERALS FROM MACEDONIA. XVIII. VIBRATIONAL SPECTRA OF SOME SOROSILICATES

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The vibrational spectroscopy is used in order to identify and characterize three sorosilicate minerals originating from the localities in the Republic of Macedonia: epidote, $Ca_2Al_2(Fe^{3+},Al)(SiO_4)(Si_2O_7)O(OH)$, hemimorphite, $Zn_4(Si_2O_7)(OH)_2{\cdot}H_2O$ and ilvaite, $CaFe^{2+}{}_2Fe^{3+}(Si_2O_7)O(OH)$. The chemical composition of these minerals is not necessarily fixed, especially for epidote-clinozoisite mineral series: $Ca_2Al_2(Fe^{3+},Al)(SiO_4)(Si_2O_7)O(OH)$ –$Ca_2Al_2Al(SiO_4)(Si_2O_7)O(OH)$, where the content of Fe^{3+} and Al could substantially vary. In this context, it was shown that the intensity and especially the frequency of the IR band in the ν(OH) region could serve as a tool for reliable determination of the Fe^{3+} and/or Al^{3+} in epidote. The similarity between the sorosilicate infrared spectra in the 1300-370 cm^{-1} region is based on their common structural characteristics. The bands in this region are tentatively assigned being mostly prescribed to the vibrations of the Si_2O_7 units (and SiO_4 tetrahedra in epidote). On the other hand, the similarities between their Raman spectra are less expressed, especially in the case of ilvaite spectrum. The results of the study are compared with the corresponding literature data for the analogous mineral species originating all over the world.

MINERALS FROM MACEDONIA.
XIX. VIBRATIONAL SPECTRA OF SOME SHEET SILICATE MINERALS

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The results of the identification of the six sheet silicates originating from the Republic of Macedonia: chrysotile, $Mg_3Si_2O_5(OH)_4$; antigorite, $(Mg,Fe^{2+})_3Si_2O_5(OH)_4$; talc $Mg_3Si_4O_{10}(OH)_2$; clinochlore, $(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$; cymrite $BaAl_2Si_2O_8{\cdot}H_2O$ and montmorillonite $(Na,Ca)_{0..33}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$, using vibrational (infrared and Raman) spectroscopy are presented. The above mentioned minerals show IR spectral similarities in the region bellow 1200 cm^{-1}, mainly due to their common structural characteristics being mostly expressed in the case of isomorphous chrysotile and antigorite. In the highest wavenumber region of chlorite, three medium bands are observed which arise from the presence of three crystallographically different OH groups in its structure. In the infrared spectra of cymrite and montmorillonite, a sharp peak at 1630 cm^{-1} is noticed (absent in spectra of other minerals) discriminating between hydroxide and water-containing minerals. The similarities between the Raman spectra 1200-100 cm^{-1}) are less expressed confirming that these spectra are more sensitive to compositional changes as well as to structural disorder. Identification was based on the comparison of the results of our study with the literature date for the corresponding mineral species originating from other localities all over the world.

FT-IR SPECTROSCOPIC STUDY OF THE HOFMANN-Td-TYPE ANILINE CLATHRATES

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Hofmann-Td-type clathrates, M(dahxn)Cd$(CN)_4$.nG (dahxn=1,6-diaminohexane, M=Ni, Co or Cd, G=Aniline), were synthesized and their structure was determined by an elemental analysis and FT-IR spectroscopy. The infrared spectra of 1.6-Diaminohexane, its cadmium tetracyanide clathrates with Ni(II), Co(II) and Cd(II) and guest molecule aniline have been investigated within the range 4000-400 cm^{-1}. The spectral data suggest that these compounds are similar in structure to those of the Hofmann-Td-type clathrates.

FT-IR SPECTROSCOPIC STUDY OF ADSORPTION OF ETHYLENEDIAMINE ON SEPIOLITE AND BENTONITE

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The adsorption of ethylenediamine on sepiolite and bentonite was investigated using FT-IR spectroscopy and X-ray diffraction (XRD). The intercalation of ethylenediamine within sepiolite and bentonite has been shown by X-ray diffraction to increase the interlayer spacing. FT-IR spectroscopic results indicate that sorbed ethylenediamine molecules by sepiolite and bentonite are coordinated directly or indirectly through water bridges.

NOVEL MATERIAL FOR SECOND HARMONIC GENERATION - 3-AMINO-1,2,4-TRIAZOLINIUM(1+) HYDROGEN L-TARTRATE

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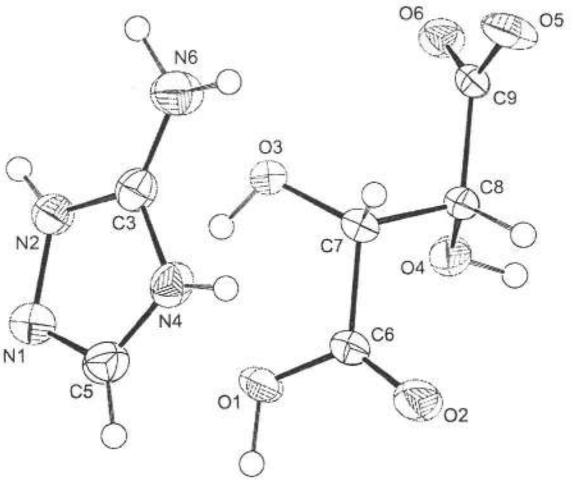

3-amino-1,2,4-triazolinium(1+) hydrogen L-tartrate (**3at-L-tart**) was prepared within our project focused on preparation of new non-linear optical materials. **3at-L-tart** was prepared by a slow evaporation of aqueous solution of equimolar mixture of 3-amino-1,2,4-triazole and L-tartaric acid.

Title organic salt crystallizes in the monoclinic system with non-centrosymmetric space group $P2_1$ and lattice parameters: a = 7.7130(2) Å, b = 6.7690(2) Å, c = 9.2170(3) Å, β= 95.726(2) °, (R = 0.0255 for 5922 observed reflections). The crystal structure consists of hydrogen L-tartrate 3D network, in which the anions are interconnected by O-H...O hydrogen bonds with the lengths of 2.53 - 2.63 Å. The vacancies in the net structure are filled by 3-amino-1,2,4-triazolinium(1+) cations fixed by two types of bifurcated hydrogen bonds forming five- and six-membered rings.

3at-L-tart was also characterised by the methods of vibrational spectroscopy (FTIR and FT Raman). The interpretation of the vibrational spectra is based on „ab initio" calculations. The calculations were performed applying the Hartree-Fock (HF), Density Functional Theory (B3LYP) and Møller Plesset perturbation (MP2) methods with the 6-31G and 6-311G basis sets (according to literature[1,2]). The calculations and visualisations of the results were carried out with Gaussian 98W[3] and GaussViewW[4] program package.

Quantitative SHG measurements of powdered **3at-L-tart** were performed relatively to KDP (KH_2PO_4) using solid state Ti-sapphire laser (800 nm). The efficiency of SHG response at 400 nm was 28 % compared to KDP.

1. M. H. Palmer, D. Charisten, J. Mol. Struct. 705 (2004) 177-187
2. F. Billes, H. Endrédi, G. Keresztury, J. Mol. Struct. (TEOCHEM) 530 (2000) 183-200
3. Gaussian 98W, Revision A.11, M. J. Frisch et al., Gaussian, Inc., Pittsburgh PA (2001)
4. GaussViewW, version 2.1, Gaussian, Inc., Pittsburgh PA (2001)

This study was supported by the Grant Agency of Charles University in Prague - grant No. 337/2005/B-CH/PřF.

SYNTHESIS, STRUCTURE, SPECTROSCOPIC AND CYCLIC VOLTAMMETRY PROPERTIES OF (2-AMINO-4-METHYLPYRIMIDINE)-(PYRIDINE-2,6-DICARBOXYLATO)COPPER(II) MONOHYDRATE COMPLEX

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The (2-amino-4-methylpyrimidine)(pyridine-2,6-dicarboxylato)copper(II) monohydrate complex was synthesized and characterized by spectroscopic (IR, UV/vis, EPR) and electrochemical methods. X-ray structural analysis of the title complex revealed that the copper ion has two coordination spheres. In the first coordination sphere the copper ion forms distorted square-planar geometry with trans-N_2O_2 donor set, and also the metal ion is weakly bonded to the amino-nitrogen in the layer over and to the carboxylic oxygen in the layer underneath in the second coordination sphere. The second coordination environment on the copper ion is rather elongated octahedron.

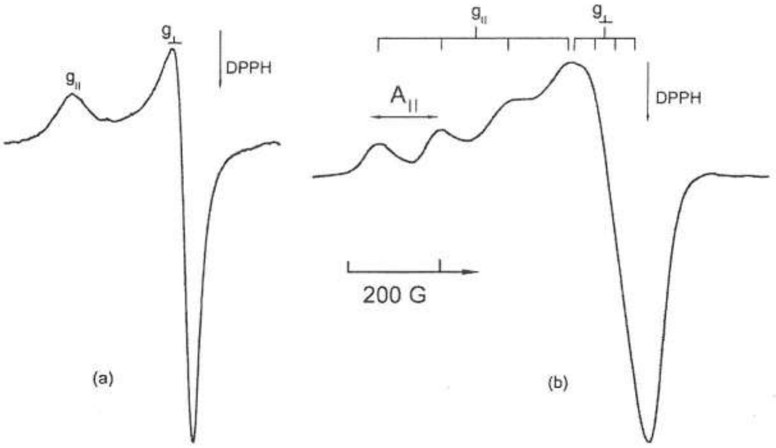

Fig . 1 EPR spectrum of title complex a) powder, b) in DMF solution

Table 1. Principle $g_{//}$, $g_{\perp}$ and hyperfine values (A) of title complex

	Temperature (K)	$g_{//}$	$g_{\perp}$	$A_{//}$	$A_{\perp}$
powder	293 and 113	2.247	2.261	-	-
DMF solution	113	2.247	2.052	138 G	44 G

The powder EPR spectra of Cu(II) complex at room and liquid nitrogen temperature were recorded (Fig. 1). As can be seen from the Fig.1a that there is only one $g_{//}$ and one $g_{\perp}$ components were obtained due to exchange interaction. This is the reason that makes the hyperfine lines smaller. In the EPR spectrum of the Cu(II) complex in DMF solution at liquid nitrogen temperature, four parallel together with and broadened perpendicular components have been observed (Fig.1b). The calculated *g* and *A* parameters have indicated that the paramagnetic centre is axially symmetric. The molecular orbital bond coefficients of the Cu(II) ion in d^9 state is also calculated by using EPR and optical absorption parameters.

P6-26

EPR STUDY OF GAMMA IRRADIATED $NA_2S_2O_3.5H_2O$ SINGLE CRYSTALS

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EPR study of gamma irradiated sodium thiosulphate pentahydrate single crystals has been carried out at room temperature. It crystallizes in monoclinic system with the unit cell parameters, a=5.94 $\overset{0}{\mathrm{A}}$, b=21.57 $\overset{0}{\mathrm{A}}$, c=7.53 $\overset{0}{\mathrm{A}}$ and $\beta = 103.58^0$, Z=4[1]. The observed lines in the EPR spectra have been attributed to the species of S_2O^-, SO_2^-, $S_2O_2^-$, SO_3^- and $S_2O_3^-$. Each radical has shown two magnetically distinct sites in monoclinic lattice. The angular variation of EPR spectra has also shown that both S_2O^- and $S_2O_2^-$ radicals have two groups and each of that has two distinct sites. The principal values of g for each site have been calculated[2] and given in Table 1.

Table 1. The principal g values of the S_2O^- and $S_2O_2^-$ radicals

Radicals	g_{xx}	g_{yy}	g_{zz}
S_2O^- (I) Site 1	2.0185	2.0365	2.0088
S_2O^- (I) Site 2	2.0165	2.0390	2.0085
S_2O^- (II) Site 1	2.0112	2.0308	2.0058
S_2O^- (II) Site 2	2.0111	2.0307	2.0060
$S_2O_2^-$ (I) Site 1	2.0189	2.0409	2.0055
$S_2O_2^-$ (I) Site 2	2.0191	2.0413	2.0047
$S_2O_2^-$ (II) Site 1	2.0233	2.0406	2.0017
$S_2O_2^-$ (II) Site 2	2.0203	2.0435	2.0021

[1] P. G. Taylor and C. A. Beevers, Acta Cryst. 5 (1952) 341.
[2] Atherton N. M., *Electron Spin Resonance Theory and Applications,* John-Wiley and Sons, New York.(1973).

SYNTHESIS, STRUCTURAL AND CONFORMATIONAL STUDY OF SOME AMIDES DERIVED FROM 3-METHYL-3-AZABICYCLO[3.2.1]OCTAN-8α(β)-AMINES

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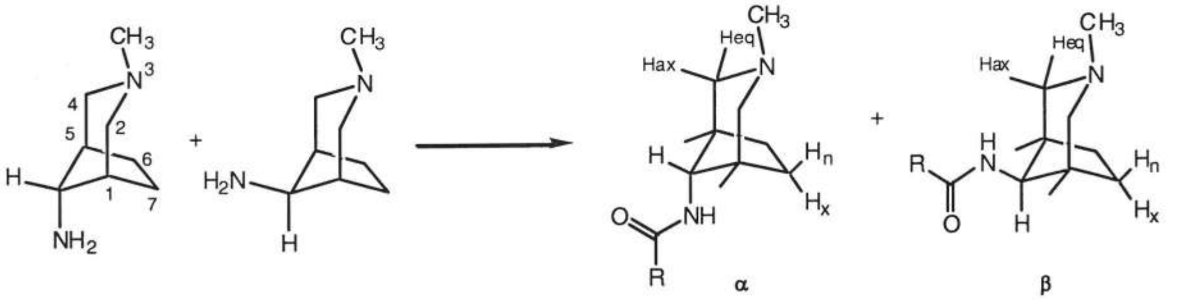
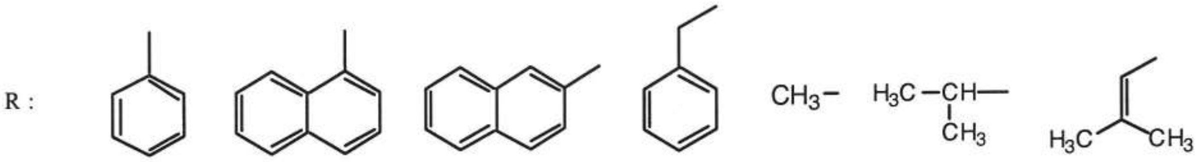
As a part of a research program related to the synthesis and structural study of potential pharmacologically interesting compounds we have focused our attention on the preparation of some amides derived from 3-methyl-3-azabicyclo[3.2.1]octan-8-α(β)amines.





1 2 3 4 5 6 7

A detailed study by IR (in solid state and in solution), and by ^{1}H and ^{13}C NMR (in $CDCl_3$ solution) has been done to determine the preferred conformations.

The assignments of proton and carbon resonances for both α and β epimers have been made on the basis of NOE, TOCSY, gDQCOSY, gHSQC and DEPT experiments.

All compounds adopt in $CDCl_3$ solution a chair envelope conformation with the N-CH_3 group in equatorial position with respect to the piperidine ring. The most relevant difference concerning the conformations of the α and β epimers is the flattening of the piperidine ring. In the α epimers ^3J H2(4)eq-H1(5) [~ 4 Hz] is greater than ^3J H2(4)ax-H1(5) [< 2Hz] and consequently, the dihedral angle H2(4)eq-C–C-H1(5) is smaller than H2(4)ax-C–C-H1(5) according to the Karplus relationship. This is consistent with a non-flattened chair conformation for the piperidine ring. On the contrary, in the β epimers ^3J H2(4)ax-H1(5) [3.5 Hz] is greater than ^3J H2(4)eq-H1(5) [<2 Hz]; therefore they adopt a flattened chair, probably to relieve the 1,3-diaxial interactions between the amido group and H2(4)ax. Finally, NOE experiments and the νN-H frequencies suggest that the amides **1-7** are predominantly in a *trans* conformation.

OXIDATION PROCESSES OF ANTIOXIDANTS BASED ON N,N'-SUBSTITUTED p-PHENYLENEDIAMINES – IN SITU EPR, UV-VIS AND IR SPECTROELECTROCHEMICAL STUDIES

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Complex spectroscopic (EPR, UV-VIS, IR) studies of aromatic secondary amines N,N'-diphenyl-1,4-phenylenediamine (DPPD), N-phenyl-N'-isopropyl-p-phenylene diamine (IPPD), N-phenyl-N'-(α-methylbenzyl)-p-phenylenediamine (SPPD) and N-phenyl-N'-(1,3-dimethyl-butyl)-p-phenylenediamine (6PPD), which represent the most important group of antioxidants used in the rubber industry[1], are presented. All the compounds showed two reversible redox couples and the splitting of the redox peaks indicates different interaction between redox sites depending on the substitution of the –NH– moiety. Spin delocalisation in cation radicals of DPPD, SPPD, IPPD and 6PPD generated both electrochemically and by chemical oxidation with peroxyl radicals in acetonitrile is limited to –NH– moiety and its near neighborhood[2]. The dominating splittings in their EPR spectra comes from two equivalent nitrogens and equivalent protons from –NH– group and neighboring aliphatic –CH– groups. Very similar UV-VIS spectra of monocation radicals and dications for DPPD, SPPD, IPPD and 6PPD were observed by applying anodic oxidation as well as oxidation by tert-butyl hydroperoxide both in air and inert atmosphere. Electrochemical and spectroelectrochemical results for all the compounds under study indicate the mixed-valence state within the class II/III transition state[3]. By the oxidation of all the above mentioned compounds with solid PbO_2 no EPR spectra were observed and UV-VIS and IR studies indicate rapid formation of the final dehydrogenated oxidation product. Samples with N-bonded aliphatic carbon in the molecule (e.g. IPPD) heated in air undergo consecutive chemical reactions leading to the formation of –N=C– group in the molecule[4].

[1] F. Cataldo, Eur. Polym. J. 38 (2002) 885.
[2] B. Grossmann, J. Heinze, T. Moll, C. Palivan, S. Ivan, G. Gescheidt, J. Phys. Chem. B 108 (2004) 4669.
[3] T. Nishiumi, Y. Nomura, M. Higuchi, K. Yamamoto, Chem. Phys. Lett. 378 (2003) 18.
[4] J. Polovková, I. Kortišová, A. Gatial, M. Breza, Polym. Degrad. Stab., In press.

AMINO ACIDS AND THEIR Cu COMPLEXES COVALENTLY GRAFTED ONTO A POLYSTYRENE RESIN – A VIBRATIONAL SPECTROSCOPIC STUDY

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Many enzymes contain one or more metal ions in their active centres[1]. The ions are surrounded by amino acids and they form highly active and selective catalysts. Since both factors, especially selectivity is a key issue in catalysis, an obvious approach may be mimicking the active sites of the enzymes, and, at the same time increasing the durability of the resulting catalytic material[2]. For functional modelling metal–amino acid complexes should be prepared and for increasing their heat and solvent tolerance they should be immobilised onto a solid support. One way of immobilisation is covalently anchoring the ligands onto a suitably functionalised support and then preparing the actual complex by adding the metal ions and excess amino acids to the modified polymer. In this contribution we report the syntheses of covalently grafted Cu–amino acid complexes onto a swellable chlorinated polystyrene support. The syntheses were performed stepwise as described above. First, the amino acids were covalently attached to the support, then, the complex was prepared. The steps of the syntheses were followed by FT-IR spectroscopy.

In order to exert control on covalent anchoring, C-protected tyrosine (L-tyrosine methyl ester – H-Tyr-OMe) or N-protected histidine (*tert*-butoxycarbonyl-L-histidine – BOC-His-OH) was used. The host material was a chlorinated polystyrene resin [poly(styrene-co-vinylbenzyl chloride-co-divinyl-benzene]. Simple organic reactions (N-alkylation or esterification) were used for covalent anchoring. The modified polymer samples were soaked in $Cu(NO_3)_2$, then, in surplus amino acid solutions. The synthetic steps were followed by IR spectroscopy (Matheson Genesis I spectrophotometer, WinIR software package).

FT-IR spectra attest that covalent anchoring of the amino acids was successful. Comparison of the spectra of the resin, the amino acid containing resin samples and the samples after treatment with copper solution and excess amino acids revealed that complexes were formed and they were covalently attached to the polymer support indeed. Structural models for the anchored complexes could also be given (HyperChem molecular modelling package[3]).

[1] B.G. Malström, L.E. Andreasson, B. Reinhammer, in: Enzymes, Academic Press, New York, pp. 533-538 (1975).
[2] I. Szilágyi, I. Labádi, K. Hernadi, I. Pálinkó, I. Fekete, L. Korecz, A. Rockenbauer, T. Kiss, New J. Chem. 29 (2005) 740.
[3] HyperChem 7.0, Hypercube Inc., Gainesville, FL, USA (2001).

CONFORMATIONAL BEHAVIOUR OF ACETAMIDE DERIVATIVES STUDIED BY NMR SPECTROSCOPIC AND COMPUTATIONAL METHODS

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Acetamide derivatives may serve as simple peptide models. Rotation around their N-C bond is restricted because of its partial double bond character. The lone pair of nitrogen provides the electrons for this partial double bond, thus, its availability for any other purposes such as, e.g., acid-base reaction is limited. Limited it is, however, it is certainly not impossible[1]. If, for instance, a phenyl group is attached to the nitrogen atom it may compete for the lone electron pair successfully enough to lower the double bond character of the peptide bond and restrict the free rotation of the phenyl group. The effect may be further increased if the other hydrogen on the amide nitrogen is substituted for an alkoxymethyl group. The substitution pattern on the nitrogen of the acetamide derivative is certainly expected to influence the conformational behaviour of the molecules.

During the work leading to this contribution a range of acetamide molecules was prepared[2] containing phenyl or alkyl groups directly attached to nitrogen of the amide bond. In many compounds the other hydrogen was substituted as well, with alkoxymethyl group of various kinds. The conformational behaviour of these molecules was studied experimentally (NMR spectroscopic methods) as well as computationally (semiempirical and HF *ab initio* methods) using the conformational search and the NMR modelling modules of the HyperChem package[3]. Other related acetamide analogues were also studied but only computationally.

Experimentally as well as computationally it was found that having synperiplanar (Z-like) arrangement eased on substituting hydrogens on the nitrogen atom. Normally, this type of structure is of low probability. The alkyl substituents enjoyed more rotational freedom than the phenyl derivatives. 2,6-Disubstituion further decreased rotational possibilities – two clearly distinguishable isomers could be identified. Substituting the other hydrogen on the amide nitrogen only slightly affected the conformational mobilities of the molecules.

[1] J.P. Chupp, J.F. Olin, J. Org. Chem. 32 (1967) 2297.
[2] I. Ledneczki, P.M. Agócs, Á. Molnár, Synlett (2003) 2255.
[3] HyperChem 7.0, Hypercube Inc., Gainesville Fl, USA (2001).

IMPACT OF WATER MOLECULE ON STABILITY OF APST

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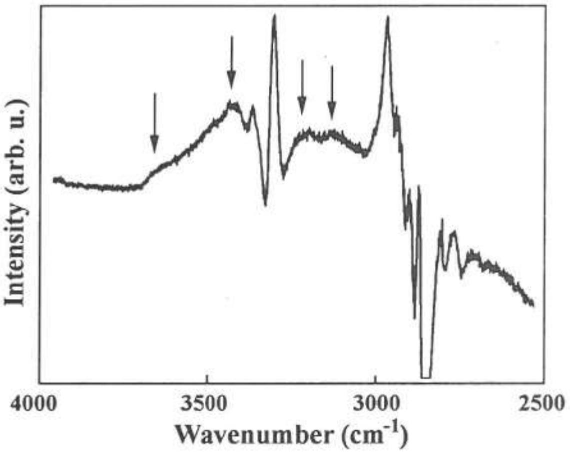
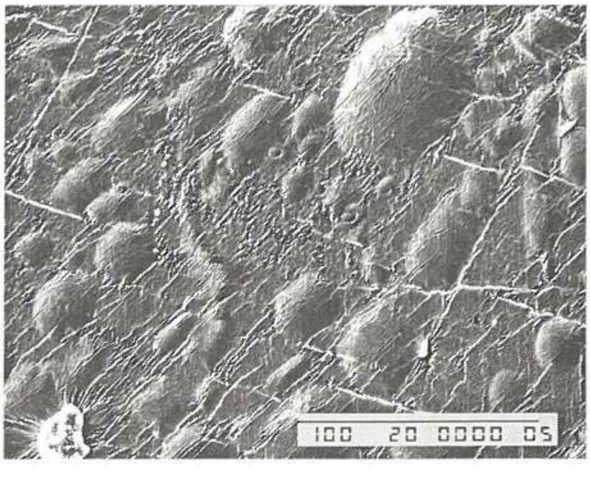
Aminopropylsilanetriol (APST) $NH_2CH_2CH_2CH_2Si(OH)_3$ is a new organosilane compound, simple to use, with good properties in contacting with various optical fibers, semiconducting substrates and nano-particles [1,2]. The polymerization process of this coupling agent was not explained to the point of satisfaction even for pure APST polymer as well as for APST-metal, APST-glass and APST-plastic contacts, in spite of many efforts over the last decade. Until now most of the authors agree in claiming that mechanical properties of pure matter and in contacts with other materials are significantly affected by temperature/humidity conditions of the environment. In our previous work we were focused on light, temperature and substrate dependence [3,4] of the polymerization process, but here the attention is paid more to the presence of water molecule.



We obtained the best samples by slow water evaporation at room temperature, in the dark, on the polyethylene substrate. Raman difference spectrum performed in this experiment (before - after the drying at 60 °C for 60 h) exhibited some line shifts, broadenings, and loss of water contents (indicated by vertical arrow). To our opinion, two lower frequency bands could be assigned to the bulk water, but the upper two indicate monomers and other, simpler water units.

First speculations based on Raman difference spectrum were confirmed using scanning electron microscopy in spite of its weakness against water containing samples. For samples that were prepared at 60 °C, growing and breathing blobs were observed. Final precious weight measurements corroborated the decision of the important role of water molecule in the stabilization of APST structure that was derived from RDS results.



References:
[1] I. Shimizu *et al*, Vibr. Spectrosc. **14** (1997) 113
[2] T. Ogasawara *et al*, Colloid Surf. A-Physicochem. Eng. Asp. **180** (2001) 317
[3] V. Volovšek *et al*, Book of Abstracts, EUCMOS XXVII, Krakow, Ed. M. Handke *et al*
[4] V. Volovšek *et al*, Jour. Phys: Conf. Ser. **28** (2006) 135

NUCLEAR MAGNETIC DIPOLE MOMENTS FROM NMR SPECTRA

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There are currently no nuclear models that can accurately predict the large variation in the nuclear magnetic dipole moments for different nuclides, and the values of the moments are thus determined experimentally. The magnitude of the nuclear moments is crucial for many spectroscopic methods where the values of nuclear magnetic dipole moments are treated as physical constants. Some of the most accurate reference values of nuclear magnetic moments were derived from NMR spectra [1]. However, in the procedure applied to extract the moments of bare nuclei from the NMR spectra of molecules the shielding of nuclei by electrons has been treated in a very crude manner. Using more accurate shielding constants (σ) and resonance frequencies (ν) of isolated molecules we have determined new values of the moments for ^{13}C, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{31}P and ^{33}S [2].

The standard technique of establishing a nuclear magnetic dipole moment (μ) from NMR spectrum is based on the equation

$$\mu_Y = \frac{\nu_Y}{\nu_X}\frac{(1-\sigma_X)}{(1-\sigma_Y)}\mu_X$$

relating the properties of two nuclei, X and Y, in the same external magnetic field. Thus, the unknown magnetic moment μ_Y can be determined once the frequency ratio for two nuclei ν_Y/ν_X is measured, the absolute shielding constants σ_X and σ_Y are known and the value of the other magnetic moment, μ_X, is known. To avoid unnecessary errors in the experiment, the measurement is usually performed for two nuclei in the same molecule. The most suitable nucleus X to be used as the reference is ^1H - for this nucleus the magnetic moment is presently known with high accuracy [3]. Resonance frequencies and shielding constants are obtained in our gas phase NMR experiments. For the ^{29}Si and ^{73}Ge nuclei we have used the recent ab initio shielding constants determined for XH_4 molecules in ref. [4]. The absolute shielding for the NMR standards – X in liquid $X(CH_3)_4$ - has been next established using the chemical shifts between gaseous XH_4 and liquid $X(CH_3)_4$.

We have systematically analyzed all the results and demonstrated that it is a very efficient and unique way of checking the consistency of the interrelation between magnetic dipole moments, NMR frequencies and absolute shielding constants of different nuclei in different molecules. Our analysis has shown that for the studied nuclei the largest inconsistencies were caused by insufficiently accurate literature values of the nuclear magnetic dipole moments if the literature data were used. Once reliable nuclear moments are determined, the same approach can be applied to examine the accuracy of the other properties, for example computed absolute shielding constants or measured NMR frequencies. We have shown that the new values of the nuclear magnetic moments, in contrast to the old ones, are consistent with NMR absolute shielding constants in every case. A similar analysis can be performed for all the isotopes with non-zero magnetic moment.

[1] P. Raghavan, Atomic Data and Nuclear Data Tables 42 (1989) 189.
[2] A. Antušek, K. Jackowski, M. Jaszuński, W. Makulski and M. Wilczek, Chem. Phys. Lett. 411 (2005) 111.
[3] P.J. Mohr, B.N. Taylor, Rev. Mod. Phys. 77 (2005) 1.
[4] M. Jaszunski and K. Ruud, Mol. Phys. in print.

RAMAN AND FAR-INFRARED SPECTRA OF THE LOW FREQUENCY REGION IN HOFMANN TYPE CLATHRATES

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A series of Hofmann type clathrates with a general formula: $M(NH_3)_2M'(CN)_4{\cdot}2G$, where $M \in \{Ni, Mn, Cd\}$, $M' \in \{Ni, Pd,\}$, while G is benzene or thiophene, were prepared and their Raman and far-infrared spectra were recorded.

In the previous studies, our main interest was focused on the various aspects of the problem of host-guest interactions in Hofmann type clathrates. Thus, all the observed changes in the vibrational (mid-infrared, far-infrared and Raman) spectra referred to host-guest interactions originating from weak hydrogen bonding between the ammonia hydrogen atoms from the host lattice and the π electron cloud of the aromatic guest molecules.

Of particular interest to the present study is the interpretation of the vibrational spectra of the host lattice in the low frequency region. This work contains the results of the assignment of the far infrared and Raman bands (below 650 cm^{-1}) due to the host lattice in Hofmann type clathrates. In this course, we used the method of comparison with the far-infrared and Raman spectra of the series of Hofmann type clathrates and their "empty" clathrates in which NH_3 or $(CN)_4$ groups from the host lattice are coordinated to the same metal, M or M', consequently. For this purpose, we recorded a series of Raman and far-infrared spectra of (a) $M(NH_3)_2Ni(CN)_4{\cdot}2G$ where G is benzene or thiophene and (b) $M(NH_3)_2Pd(CN)_4{\cdot}2G$, where again G is benzene or thiophene. In this way, by *(i)* changing the guest molecules in the same host lattice, and by *(ii)* changing M' and M metals in the host lattice with the same guest molecules, we were able to "locate" most of the fundamental modes due to the host lattice in Hofmann type clathrates. The main bands in the vibrational spectra in the low frequency region were assigned to the stretching and deformational vibrations: ν(Ni-C)/ν(Pd-C), δ(NiCN)/ δ(PdCN), δ(CNiC)/ δ(CPdC), ν(M-N) and δ(NMN) originating from the host lattice: $M(NH_3)_2Ni(CN)_4$ or $M(NH_3)_2Pd(CN)_4$.

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VIBRATIONAL SPECTRA, INTERMOLECULAR INTERACTIONS AND STRUCTURES OF 2-, 3-, AND 4- BIPHENYLMETHANOLS

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The structural dynamic models of free 2-, 3- and 4-biphenylmethanols (BPM) molecules and of their H-complexes (cyclic tetramers, dimers and trimers) have been built using Gaussian'03 software with B3LYP/6-31G(d) method.

According to the modeling results the 2BPM molecules tetramer is composed of two non-equivalent pairs of molecules and belongs to C_i point group. The lengths of the O-H...O bridges in this H-complex are 2,726Å and 2,700Å correspondingly. The dihedral angle between phenyl rings is decreasing from 55° (in free 2BPM molecule A conformer) to 46-49° in the first pair of the 2BPM tetramer, and from 76° (in free 2BPM molecule B conformer) to 67-70° in the second pair. The orientation of methanol group relatively of the closest phenyl ring is increasing from 20° (in A conformer) to 86-87° in the first pair of molecules in 2BPM tetramer and decreasing from 105° (in B conformer) to 9-10° in the second pair. O-H valence bond length increases from 0,969Å to 0,994Å and 0,993Å in 2BPM tetramer correspondingly. The results of the 2BPM tetramer structure modeling are in good agreement with X-ray structure analysis data [1]. Frequency of its vibration in free 2BPM molecule is decreasing and splitting into four components at the formation of the 2BPM tetramer. In the free molecule the frequency of valence vibration of the O-H bond is 3763 cm^{-1} and in the hydrogen bridge of 2BPM tetramer its components are 3233, 3315, 3360, and 3385 cm^{-1}.

At the 2BPM dimer formation the O-H valence bond length is increasing from 0.969Å (in free molecule) to 0.971Å in H-complex. The length of the hydrogen bridge is 2,838 Å. The dihedral angles between phenyl rings are 62-65° and 47-51° in first and second molecule in H-complex correspondingly. The orientations of methanol group relatively of the closest phenyl ring are 8,6° and 87,5° in first and second molecule in H-complex correspondingly. The frequency of O-H valence vibration in dimer H-complex is 3608 cm^{-1}.

The formation of 2BPM trimer is unlikely because of the minimum of the potential energy is very flat and the calculated structure could not be realized on our opinion because of steric difficulties.

Analysis of the measured IR absorption spectra of 2BPM in crystal and glassy state [2] and 2-, 3- and 4BPM polycrystalline samples absorption spectra on KBr disc [3] points to the H-bond formation. Because of the fact, that these spectra are identical in the region 3200-3400 cm^{-1}, the structures of their H-complexes must be identical too. In solid crystal state most likely the formation of tetramers of 2-, 3- and 4BPM molecules. In glassy state of 2BPM the dimers can to form too, but the formation of trimers and chain associates is unlikely.

1. James B. Foresman and AEleen Frisch Exploring Chemistry with electronic structure methods. Second Edition, Gaussian Inc., Pittsburgh, PA, **1996**, 302 p.
2. L.M. Babkov, J. Baran N. A. Davydova, A. Pietraszko, K. E. Uspenskiy. J. Mol. Struct., **2005**, 744-747C, 433-438.
3. SDBSWeb : http://www.aist.go.jp/RIODB/SDBS/ (National Institute of Advanced Industrial Science and Technology, 29.03.2006)

IR SPECTRA OF HETEROGENIC BICOMPONENT SYSTEMS ON THE BASE OF TITANIUM DIOXIDE NANOCRYSTALLINE PARTICLES AND NEAR SURFACE LAYERS STRUCTURE MODELS

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Vibrational spectra of heterogenic bicomponent systems in solid crystal phase have been measured at room temperature. These heterogenic bicomponent systems are titanium dioxide-benzophenone (TiO_2-BP) and titanium dioxide - 4-pentyl-4'-cyanobiphenyl (TiO_2-5CB). The analysis of the spectra points to the hydrogen bond formation in the samples with participation of water molecules adsorbed by the surface of TiO_2 particles.

To make clear the structure peculiarities of near surface layers, the modeling of the structure and vibrational spectra of BP, 5CB, H_2O and H-complexes BP-HOH, ≡Ti-OH.....BP, HOH.....5CB, ≡Ti-OH.....5CB, based on the density functional theory method B3LYP/6-31+G(d) using Gaussian'03 software [1] have been carried out.

According to the modeling results at the complex formation the length of C=O bond in BP is increasing from 1,228 Å to 1,236 Å, the frequency of its vibration is decreasing from 1718 cm^{-1} to 1688 cm^{-1}. The dihedral angle between phenyl rings planes is increasing from 64° to 66°. The length of the O-H...O hydrogen bridge in ≡Ti-OH.....BP H-complex is 2,774Å (O-H bond length is 0,987 Å). O-H bond vibration frequency 360 cm^{-1} decreasing at the complex formation and its value becomes 3454 cm^{-1}. The frequency of hydrogen bond deformational vibration is 83 cm^{-1} and frequency of its stretching vibration is 103 cm^{-1} respectively.

The length of C≡N valence bond in 5CB is decreasing a little (from 1,164 Å to 1,162 Å), the frequency of its stretching vibration is increasing from 2331 cm^{-1} to 2343 cm^{-1}, the dihedral angle between phenyl rings is not changed and its value was 38° the N...H-O hydrogen bridge length is 2,904 Å (O-H bond length 0,981 Å). Frequency of the O-H stretching is decreasing by 235 cm^{-1} and its value is 3581 cm^{-1}. Frequency of N...H stretching vibration is 77 cm^{-1}.

The estimation of the energy in H-complexes using empirical formula [2] gives the following results: in BP-TiO_2 system it is 7,0 kcal/mole and in 5CB- TiO_2 it is 3,6 kcal/mole.

Because of the results, mentioned above, the H-bond is the basic mechanism of intermolecular interactions in near surface layer. When it forms, the spectra of BP and 5CB free molecules are transforming. This transformation appears in the regions of C=O and C≡N stretching vibrations and particularly in O-H stretching vibrations of hydroxyl group region. In BP-TiO_2 mixture H-bond stimulates of the layers formation in which adsorbed BP molecules have certain orientation.

1. James B. Foresman and AEleen Frisch Exploring Chemistry with electronic structure methods. Second Edition, Gaussian Inc., Pittsburgh, PA, **1996**, 302 p.
2. A. V. Iogansen. IK spektroskopiya i opredelenie energii vodorodnoi svyazi / Vodorodnaya svyaz, Moscow, "Nauka", **1981**, pp. 112-155. (in Russian).

CONFORMATIONAL AND VIBRATIONAL ANALYSIS OF GAMMA-AMINOPROPYLTRIETHOXYSILANE

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Gamma-aminopropyltriethoxysilane (APTES) has wide application as a surface functionalizing material. The structure of deposited silane layers on the substrates depends on the molecular conformations of APTES. Therefore, a comprehensive conformational and vibrational analysis has been carried out on APTES by density functional theory (DFT) using Becke's three-parameter exchange functional in combination with the Lee-Young-Parr correlation functional (B3-LYP) and standard 6-311+G(d,p) basis set. In order to reveal all possible conformations, a detailed potential energy scan (PES) in SiCCC dihedral angle has been performed. The scan was done by minimizing the potential energy in all geometrical parameters changing SiCCC torsion angle every 3.6° for a 360° rotation around CC bond. The obtained theoretical data suggest that there are seven stabile conformations. The lowest energy conformer has *trans* structure at torsion SiCCC angle near 180°. There are several *gauche* conformers with torsion angle around 70° with various orientations of ethoxy chains. The calculated energy of *trans* conformer corresponding to the global minimum was found to be 600 cm^{-1} below the energy of most stable *gauche* conformer. The maximal energy difference between local minima corresponding to *gauche* conformers is about 60 cm^{-1}.

The infrared (500 to 4000 cm^{-1}) spectra and Raman (100 to 3500 cm^{-1}) spectra of liquid APTES with qualitative polarization measurements have been recorded. A complete vibrational assignment for APTES conformers is supported by the normal coordinate analysis, calculated IR intensities as well as Raman activities. The force constants matrix transformed into local symmetry coordinates was scaled with scaling factors transferred from aminopropylsilanetriol [1]. On the basis of the results, the vibrational spectra of APTES have been analyzed. The data indicate that *trans* and *gauche* forms co-exist in the liquid APTES [2].

[1] L. Bistričić, V. Volovšek, V. Dananić, I. Movre Šapić, Spectrochimica Acta Part A (in press)
[2] L. Bistričić, V. Volovšek, V. Dananić, M. Leskovac, Journal of Physics: Conference Series 28 (2006) 131.

MAGNESIUM, CALCIUM, COPPER AND ZINC BENZOATES – THE VIBRATIONAL STRUCTURE AND ANTIMICROBIAL ACTIVITY*

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Sodium benzoate is used in pharmaceuticals and food for preservation purposes and for therapeutic regimens in patients instead of benzoic acid for its significantly better water solubility. We have tested new Mg(II), Ca(II), Cu(II) and Zn(II) benzoates and their antimicrobial properties. The dependency between molecular structure and microbiological activity of selected benzoates was studied [1,2].

FT-IR spectra of studied benzoates were registered, and selected spectral bands were assigned to appropriate bonds of molecule. This assignment was used to compare electronic charge distribution in carboxylic anion and aromatic ring of the studied compounds. On the other hand, turbidimetry measurements, reflecting growth of bacteria *Escherichia coli*, *Bacillus subtilis* and yeasts *Hansenula anomala* and *Saccharomyces cerevisiae* after incubation in optimal growth conditions as well as with addition of appropriate portion of studied benzoates, showed antimicrobial activity of the studied compounds against the mentioned micro-organisms. Sodium benzoate was used as reference material. The level of activity differs and depends on the tested compound, type of micro-organism, and time of incubation. A significant correlation between spectral data and the degree of the influence of a given compound on the growth of *E. coli* was observed while using selected wavenumbers in PLS (partially least square) technique to correlate molecular structure and antimicrobial activity of the studied compounds.

[1] P. Koczoń, J. Piekut, M. Borawska, W. Lewandowski, J. Mol Struct. 651-653 (2003) 651.
[2] P. Koczoń, J. Piekut, M. Borawska, W. Świsłocka, W. Lewandowski, Anal. Bioanal. Chem. 384 (2005) 302.

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VIBRATIONAL SPECTROSCOPIC STUDIES OF METAL(II) HALIDE 1,2-BIS (4-PYRIDYL) ETHANE MOLECULE

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Infrared spectra (4000–400 cm^{-1}) are reported for metal 1,2-bis (4-pyridyl) ethane complexes of the following stoichiometries: M(bpa)X_2 [M=Cd, Zn; X=Cl; bpa=1,2-bis(4-pyridyl) ethane], Vibrational assignments are given for all the observed bands. The analysis of the vibrational spectra indicates that there are some structure–spectra correlations. For a given series of isomorphous complexes the sum of the difference between the values of the vibrational modes of uncoordinated bpa and coordinated to metal ion bpa was found to increase in the order of the second ionization potentials of metals. In addition, quantum chemical calculation was used in order to calculate the optimized geometries and harmonic vibrational wavenumbers of the coordination compound and its isolated ligand[1-2].

Keywords: Infrared spectra, 1,2-bis(4-pyridyl) ethane (bpa), metal complexes

[1] T. Iwamoto in J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Eds), Inclusion Compounds Vol. 1, Academic Press, London 1984, Chapter 2, p. 29.
[2]S.Akyüz, J.E.D. Davies, K. T. Holmes, J. Mol. Struct. 42 (1997) 59.
[3] Ş.Yurdakul, S.Akyüz, J.E.D.Davies, Spectrosc. Lettt. 29 (1996) 175

MOLECULAR STRUCTURE AND VIBRATIONAL SPECTRA OF ZINC COMPLEX OF PHTHALAZINE BY QUANTUM CHEMICAL CALCULATIONS

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In this work, structural and spectroscopic analysis of the Zinc complex of phthalazine were made by using semiemprical calculations. Geometric parameter and Infrared spectra were compared with single crystal x-ray diffraction data of the complex. Geometric parameters and the vibrations due to complexation of the molecule are changed with respect to the free phthalazine in line with their coordination to the metal atom. Previous proposed structure for the complex derived from the infrared spectra are consistent with the x-ray diffraction data and theoretical calculations [1-3].

Keywords: Infrared spectra; phthalazine, metal complexes

[1]M.A.V.R.Da Silva, M.A.R.Matos and V.M.F.Morais, J.Chem. Soc. Faraday Trans.Vol 91(1995) 1907.
[2] Ö.Çelik,S.Ide,M.Kurt, Ş.Yurdakul, Acta Crystallogr. Sect.E: Struct.Rep. 60 (2004) M1134-M1136 Part 6.
[3] Ö.Çelik,S.Ide,M.Kurt, Ş.Yurdakul, Acta Crystallogr. Sect.E: Struct.Rep. 60 (2004) M424-M425 Part 4.

EFFECT OF THE SUBSTITUENTS ON THE ^{13}C CHEMICAL SHIFTS OF THE AZOMETHINE CARBON ATOM OF SUBSTITUTED N-[1-(4-PYRIDINYL)ETHYLIDENE]-ANILINES

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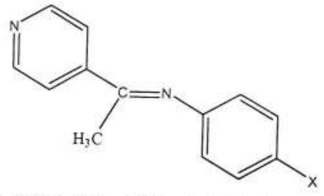
It has been established that substituted N-[1-(4-pyridinyl)ethylidene]-anilines are important intermediates for the synthesis of pharmacologically active triazoles and triazolines[1,2], and some derivatives are anticonvulsant drugs[3]. In that context it is very interesting to study effect of substituent effect on the geometry of such compounds.

A series of investigated compounds have been synthesized of the formula



where substituents X are: H (1); 4-$N(CH_3)_2$ (2); 4-OH (3); 4-OCH_3 (4); 4-CH_3 (5); 4-F (6); 4-Cl (7); 4-Br (8); 4-$COOCH_3$ (9); 4-$COCH_3$(10).

The ^{13}C NMR chemical shifts of the azomethine carbon atom of the investigated compounds have been recorded in DMSO-d_6 solution using a tetramethylsilane (TMS) as internal reference standard using a Varian Gemini 200 spectrophotometer. All the spectra were recorded at ambient temperature. For quantitative assessment of the substituent effects on the ^{13}C NMR chemical shifts, we have postulated a Hammett equation of the type:

$$\Delta\delta_C = \rho\sigma,$$

or $$\Delta\delta_C = \rho_I\sigma_I + \rho_R\sigma_R,$$

where $\Delta\delta_C$ is the relative ^{13}C chemical shifts of the azomethine carbon atom, caused by the substituent (relative to the unsubstituted compound 1); ρ is the proportionality constant reflecting the sensitivity of the ^{13}C NMR chemical shifts to the substituent effects, and σ_I and σ_R are corresponding substituent constants.

Results of correlations point out to a moderate resonance interaction of substituents on the aniline ring with azomethine carbon atom of the investigated series. The demand for electron of azomethine carbon atom in the investigated systems is being compared. The mode of transmission of substituent effects in these systems, both inductive and resonance, have been discussed as well as the effect of geometry on the transmission of electronic effect through investigated molecules.

[1] P. K. Kabada, J. Heterocyclic Chem. 12 (1975) 143
[2] B. Schnell, J.Heterocyclic Chem., 36(2) (1999) 541
[3] P. K. Kabada, U.S. 5648369 (1997)

P6-41

SPECTROSCOPIC STUDIES OF SOME COPPER (II) COMPLEXES WITH AMINO ACIDS

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The copper amino acids complexes in aqueous solution: $[Cu(L_1)_2]$ .1/2 H_2O (L_1=methionine), $[Cu(L_2)_2]$ .1/2 H_2O (L_2=phenylalanine) and $[Cu(L_3)_2]$ .1/2 H_2O (L_3= triptophan) were synthesized and analyzed by means of: thermogravimetric differential analysis, atomic absorption, IR, UV-VIS and EPR spectroscopy

The thermogravimetric differential analysis results are similar for all the complexes, the mass lost occurred in one or more steps owing to the crystallization water elimination, until the complex is destroyed and the copper oxide is formed.

For $Cu(L_1)_2$ only one endothermic effect took place at 130 ^{0}C with 47% (51 mg) mass lost, for $Cu(L_2)_2$ at 120 ^{0}C with 51 % (183.6 mg) mass lost and for $Cu(L_3)_2$ at 120^0 C with 12 % (32 mg) mass lost and 220^0 C with 19% (50.35 mg).

Atomic absorption spectroscopy results showed the copper ion presence in the complex in nearby proportion with the theory, which demonstrates that complete reactions took place.

Comparing the ligand and the corresponding complex IR spectra there was established that the –NH– stretching vibration is decreasing at complex formation and we could establish a strong covalent character of metal-nitrogen bond in the amino acids complexes [1]. The synthesized complexes present shifting toward lower frequencies of asymmetric vibrations of NH and carboxyl, which shows their complexation with copper.

Powder EPR spectra at room temperature are typically for monomeric species with square-planar local symmetry around the metallic ion, the principal values of the **g** tensor are: g_{II}= 2.187, $g_\perp$= 2.125 for $Cu(L_1)_2$, g_{II}= 2.201, $g_\perp$= 2.215 for $Cu(L_2)_2$ and g_{II} = 2.18, $g_\perp$=2.108 for $Cu(L_3)_2$. The EPR spectra of the Cu(II)-amino acid complexes in DMF solution display the copper hyperfine structure ($g_0 \approx 2.122$, $A_0 \approx 82$ G).

References

1. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 5th ed. John Wiley: New York, 1997

^{13}C AND ^{1}H NUCLEAR MAGNETIC SHIELDING AND SPIN-SPIN COUPLING CONSTANS OF ^{13}C-ENRICHED IODOMETHANE AND BROMOMETHANE IN GASEOUS MIXTURES WITH SF_6 AND CO_2

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Intermolecular interactions modify NMR chemical shifts and spin-spin coupling constants. The intermolecular effects can be determined if the NMR parameters for an isolated molecule are known. Gas-phase NMR spectroscopy offers such methods which allow one to measure the shielding and spin-spin coupling constants at the zero-density limit where the NMR parameters are free from intermolecular contributions. In our laboratory we can monitor micrograms of gaseous chemical compounds and it permits the determination of NMR parameters free from intermolecular effects for many chemical compounds which are even liquid at room temperature [1]. In such a case the molecules studied must be isotopically enriched e.g. $^{13}CH_3I$ and $^{13}CH_3Br$. Recently we have found that the $^{1}J_{CF}$ spin-spin coupling constant of CD_3F is significantly density-dependent [2]. It is fairly unusual because the majority of spin-spin coupling is independent of density in the gas phase. This study shows that the $^{1}J_{CH}$ coupling constants of CH_3I and CH_3Br are also density-dependent. We have determined the appropriate J_o and J_1 parameters using sulfur hexafluoride (SF_6) and xenon (Xe) as the gaseous solvents [3,4]. At the same time the ^{1}H and ^{13}C shielding parameters (σ_o and σ_1) have been also measured. Our present results show that the role of a heavy atom (iodine or bromine in this case) is very important and has large influence on the NMR parameters of iodomethane and bromomethane molecules. It is consistent with the theoretical studies [5,6] which prove that relativistic effects in the ^{13}C shielding of a $^{13}CH_3I$ molecule are significant and their largest part of about 20-40 ppm is due to the spin-orbit contribution, for a $^{13}CH_3Br$ molecule this change of ^{13}C shielding is slightly smaller. There are also relativistic effects changing molecular orbitals when the mass of electrons of a heavy atom is increased and the velocity of electrons is approaching the velocity of light. The latter effects have smaller but also observable influence on the magnitude of ^{13}C nuclear magnetic shielding [7]. These laborious investigations of heavy-atom effects in ^{13}C shielding demand a good experimental standard for further studies. Our present work gives such a standard - the ^{13}C and ^{1}H nuclear magnetic shielding of isolated $^{13}CH_3I$ and $^{13}CH_3Br$ molecules. It also reveals more examples of the density-dependent spin-spin couplings ($^{1}J(CH)$) in the gas phase.

[1] M. Wilczek, W. Koźmiński and K. Jackowski, Chem. Phys. Lett. **358** (2002) 263.
[2] K. Jackowski, M. Kubiszewski and W. Makulski, J. Mol. Struct. **614** (2002) 267.
[3] K. Jackowski, Int. J. Mol. Sci. **4** (2003) 135.
[4] M. Wilczek, M. Kubiszewski and K. Jackowski, J. Mol. Struct. 704 (2004) 311.
[5] J. Vaara, K. Ruud, O. Vahtras, H. Ågren and J. Jokisaari, J. Chem. Phys. 109 (1998) 1212.
[6] S.K. Wolf and T. Ziegler, J. Chem. Phys. 109 (1998) 895.
[7] J.I. Melo, M.C. Ruiz de Azua, C.G. Giribet, G.A. Aucar and R.H. Romero, J. Chem. Phys. 118 (2003) 471.

VIBRATIONAL SPECTRA OF A NON LINEAR OPTICAL CHROMOPHORES BASED ON C_3-SYMMETRIC 1,3,5-TRISALKYNYLBENZENES

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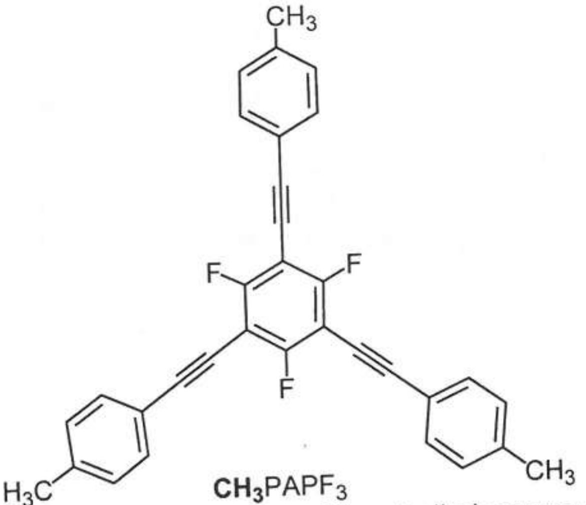
Second-order nonlinear optical (NLO) materials have attracted much interest because of their potential applications in optoelectronic technology. In particular organic molecules are very suitable in this field owing to their fast electronic responses to external stimuli, ease and flexibility of chemical design. In this context, two-dimensional (2D) octopolar molecules are shown to exhibit similar second-order NLO features as their one-dimensional (1D) D-π-A dipolar homologues, further overcoming their intrinsic limitations. A common way to design NLO-active octopolar molecules is to synthesize non-centrosymmetrically substituted trigonal systems. Acetylenic systems constitute among octopolar NLO chromophores with the highest second-order polarizabilities known so far.



CH_3 $PAPF_3$

Fig. 1. Chemical structure of the studied compound

In this communication, a detailed study of the vibrational spectra of **CH_3**$PAPF_3$ (see Figure) is proposed. These vibrational properties are related with its molecular and electronic structure, and an evaluation of the charge transfer (CT) interaction between the peripheral arms and the core is addressed. This CT feature is shown to be the responsible for the non-optical activity of these molecules.

VIBRATIONAL SPECTRA OF OLIGOTHIENYL-VINYLENES WITH DONOR-π-DONOR AND DONOR-π-ACCEPTOR SUBSTITUTION PATTERNS

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The remarkable electronic and molecular properties of oligothiophenes (i.e., the low aromaticity of thiophene favours extended π-electron conjugation) have attracted the interest of many groups pursuing the modulation of these features. Their relevant non lineal optical responses have been exploited in a series of applications in which the π-carbonated skeleton is functionalized to obtain improved conjugational properties, or to induce an intramolecular charge transfer when donor/acceptor groups are properly attached to the termini α, ω-positions. These two strategies are used here. First, the oligothiophene backbone is spaced with vinylene groups, and then substituted with donor(ferrocene)/donor(ferrocene) and donor(ferrocene)/acceptor(dicyanovinyl) groups (Figure 1).

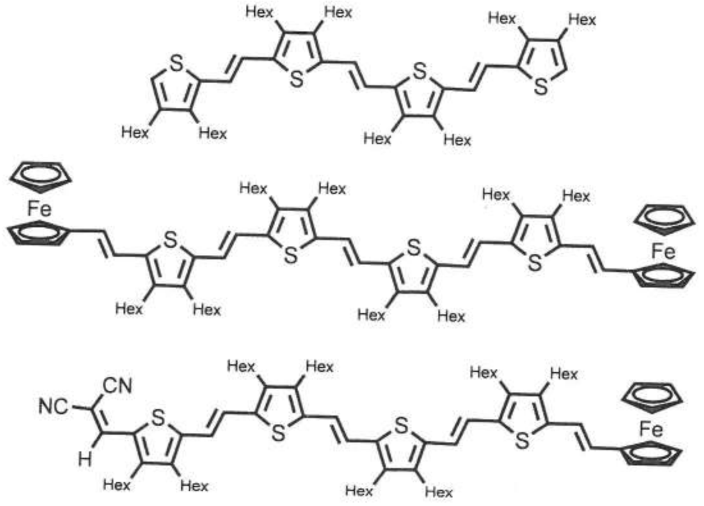

Fig. 1. Chemical structures of the studied compounds

In this communication, their IR/Raman spectra are described focusing the analysis on the dependence of the vibrational bands with the substitution pattern. The effects of symmetric and asymmetric charge polarization of the ground electronic state and charge transfer in excited states are explored. DFT theoretical calculations are used to interpret and support the experiments.

FT-IR AND NMR INVESTIGATION OF 2-(1-CYCLOHEXENYL)ETHYLAMINE: A COMBINED EXPERIMENTAL AND THEORETICAL STUDY

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FT-IR and ^{1}H, ^{13}C spectra of 2-(1-cyclohexenyl)ethylamine (2-Che) are reported for the first time. The vibrational frequencies and ^{1}H, ^{13}C NMR chemical shifts of 2-Che ($C_8H_{15}N$) are calculated by means of the Hartree-Fock (HF) , Becke-Lee-Yang-Parr (BLYP) and Becke-3-Lee-Yang-Parr (B3LYP) density functional methods with 6-31G(d) and 6-31G(d,p) basis sets, respectively. The comparison between experimental and theoretical results indicate that density functional B3LYP method is superior to the scaled HF and BLYP approach for vibrational frequencies and predicting NMR properties.

Key words: 2-(1-cyclohexenyl)ethylamine, IR spectra, NMR spectra, HF, DFT.

FTIR / RAMAN STUDY OF THE CONCENTRATION DEPENDENCE OF THE ν(C=O) BAND OF *N,N*-DIMETHYLFORMAMIDE

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From the longstanding discussion of the solvation process of *N,N*-dimethylformamide (DMF) in aprotic solvents, a discrepancy in the interpretation of the spectral data is evident. The first interpretation was that DMF molecules build structurally well defined aggregates in liquid state. Much of the infrared[1], NMR[2] and, more recently, Raman[3,4] spectroscopic works were supported by this interpretation. Asymmetric shape of the isotropic Raman carbonyl stretching band was considered in terms of well defined DMF-DMF aggregate formation[3,4]. However, the second interpretation was based on an assumption that in liquid state one can not consider any intermolecular interactions between DMF molecules which give rise to well structured complexes. From that point of view, asymmetric shape of isotropic Raman carbonyl stretching band was interpreted in terms of concentration fluctuations within the interaction volume of DMF molecule[5] and in terms of the hydrodynamic and electronic dispersion force dependence of the Raman band shape[6].

In the present study we attempt to resolve the above described discrepancy. We report results obtained from experimental infrared and Raman spectra of the DMF solutions in the whole concentration range, from very dilute solutions to pure liquid DMF. Combination of the obtained data enables us to monitor dynamic and interaction processes in liquid state in terms of orientational dipole-dipole interactions.

In both DMF/CCl_4 and DMF/CH_2Cl_2 systems, infrared ν(C=O) band is symmetric in the whole concentration range, being predominantly of Lorentzian character. It is observed that in DMF/CCl_4 system resonant transfer of vibrational energy (RET) is predominant factor of band broadening, while effect of local field (LFE) is of negligible importance here. However, in DMF/CH_2Cl_2 system importance of LFE to band broadening increases. while RET contribution rapidly decreases, becoming comparable in magnitude with LFE. Infrared ν(C=O) band for infinite dilution is also broader in CH_2Cl_2 than in CCl_4, which is another reflection of the relative importance of solvent influence to band width in the DMF/CH_2Cl_2 system.

Both corresponding anisotropic and isotropic Raman bands are also of predominant Lorentzian character in both systems. However, they differ in their behaviour. Anisotropic ν(C=O) band is symmetric in the whole concentration range for both systems, while isotropic band is symmetric for dissolved solutions, but, upon increasing DMF concentration, it becomes asymmetric, being steeper on its lower wavenumber side, as observed previously[3]. Noncoincidence splitting increases with DMF concentration, behaving in accordance with Logan's model for DMF/CCl_4 system, and with McHale-Mirone's model for DMF/CH_2Cl_2 system.

According to these, in DMF/CCl_4 system, considerable changes occur in microscopic liquid structure due to dipole-dipole interactions between DMF molecules. On the other hand, local ordering of DMF/CH_2Cl_2 system is not largely affected by DMF concentration, and the concentration dependence of noncoincidence effect is in agreement with macroscopic McHale-Mirone's model. These findings are in agreement with above-mentioned second interpretation, *i.e.* that in liquid state, no well-structured aggregates of DMF molecules are present.

[1] G. Fini, P. Mirone, *J. Chem. Soc. Faraday Trans. 2* **70** 1776 (1974)
[2] M. Rabinovitz, A. Pines, *J. Chem. Soc. (B)* 1110 (1968)
[3] I. S. Perelygin, *Russ. J. Phys. Chem.* **65** 1064 (1991)
[4] F. H. Tukhvatullin, V. E. Pogorelov, U. N. Tashkenbaev, A. Jumaboev, H. Hushvaktov, M. Seit-Enon, S. A. Osmanov, *J. Raman. Spectrosc.* **34** 813 (2003)
[5] V. M. Shelley, A. Talintyre, J. Yarwood, R. Buchner, *Faraday Discuss. Chem. Soc.* **85** 211 (1988)
[6] A. Purkayastha, K. Kumar, *J. Raman Spectrosc.* **19** 249 (1988)

COMPUTATION OF CHEMICAL SHIFT TENSOR AND SYNTHESIS OF METHANESULFONAMIDE, N-(2-AMINOETHYL)

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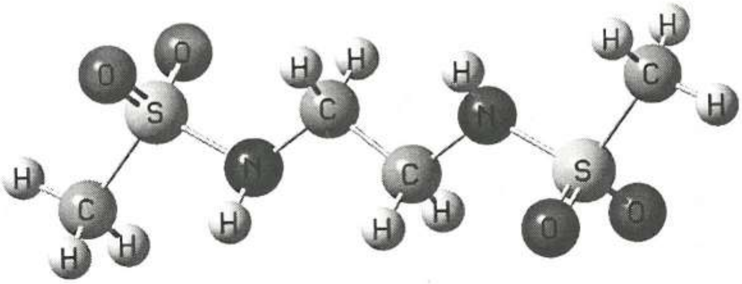
Sulfonamides are well-known class of potent chemiotherapeutic agents including an antitumor effect. The methanesulfonamide residue has also appeared as a suitable pharmacophoric equivalent to replace fuctional groups in drug design.

In thes study, metanesulfonamide, N-(2-aminoethyl) *(msen)* was synthesized for the first time with chemical equation given below.

2 CH_3SO_2Cl + ${}_2HN.CH_2.CH_2.NH_2$ → $CH_3.SO_2.NH.CH_2.CH_2.NH.SO_2.CH_3$ + 2 HCl

Identification of the structure of *msen* compound was determined by using elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR and LC-MS spectroscopic techniques.



Density functional theory (DFT) combined with **G**auge-**I**ndipendent **A**tomic **O**rbital (GIAO) and Continuous Set of Gauge Transformations (CSGT) methods were applied to calculate the chemical shielding of carbon, hydrogen and nitrogen atoms in the gas phase of *msen*.DFT-B3LYP/6-31++G(2d,2p) and DFT-B3PW91/ 6-31++G(2d,2p) basis sets and Gaussian 03 programme were used for the calculations. GIAO method was given better result than CSGT method.

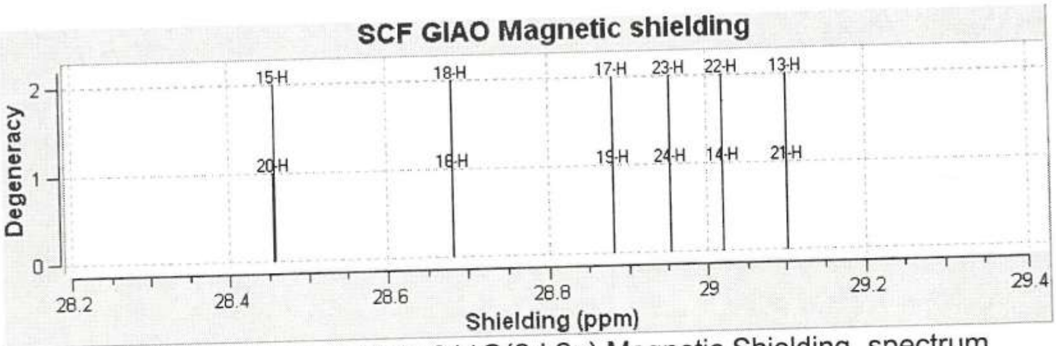


Fig.1 ^{13}C – GIAO B3LYP/6-311G(2d,2p) Magnetic Shielding spectrum

CONFORMATION ANALYSIS AND SYNTHESIS OF METHANESULFONIC ACID, 1-METHYLHYDRAZIDE; STUDY OF THEIR ANTIMICROBIAL EFFECT

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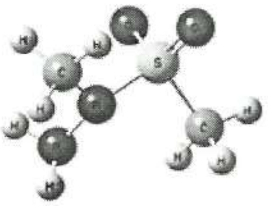
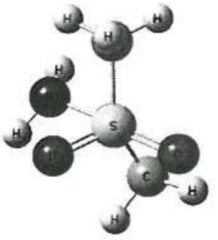
Sulfonamides and their hydrazide are widely used as antibacterial agents in pharmaceutical industry and antitumor agent in chemoterapy. In addition, sulfonamide moiety appears to be a cruical functionality to interact with many kinds of cellular protein targets.

In this study, metanesulfonic acid, 1-methylhydrazide *(msmh)* was synthesized for the first time. Identification of the structure of *msmh* was determined by using elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR and LC-MS spectroscopic techniques.

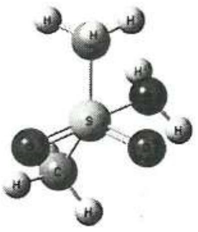


After testing antibacterial activity, **msmh** compound showed moderate activity against *Staphylococcus aureus, Escherichia coli, Yersinia enterocolitica.*

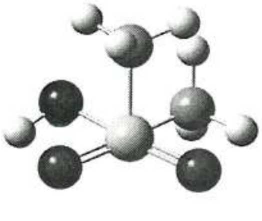
Conformation analysis of **msmh** was studied with Density Functional Method with B3LYP/6-311G(d,p) basis set using Gaussian 03 programme. Newman projections of most stable conformers (1) and (2) and their enantiomers (1') and (2') are given below.



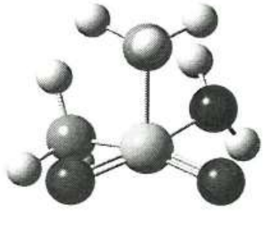
1



1'



2



2'

In the most stable conformer, pyramidal group $MeSO_2$ and $N(CH_3)NH_2$ group is staggered with repect to the S-N axis.

FT-IR SPECTROSCOPIC STUDY OF M(1,3-DIAMİNOPROPANE)Ni(CN)$_4$. 1,4-DIOXANE CLATHRATES (M = Cd, Co, Ni)

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It is well-known that infrared spectroscopy is one of the most powerful tools for investigation of the host-guest interactions in Hofmann-type clathrates which have cage structure and inclusion behaviours. In our work the ligand 1,3-diaminopropane with the divalent transition metal ions Cd(II), Co(II) and Ni(II) were prepared and characterized using by elemental analysis, thermal analysis, X-ray diffraction patterns and FT-IR spectra. The complexes formed have the formula $ML_2Ni(CN)_4$. 1,4-Dioxane where M = Cd(II), Co(II) and Ni(II), L = ligand where 1,3-diaminoprapane which acts in bidentate. The FT-IR spectra of the complexes Co(1,3-diaminopropane) Ni(CN)$_4$ and Co(1,3-diaminopropane) Ni(CN)$_4$.1,4-Dioxane are assigned in wavenumber range 4000-400 cm^{-1} at room temperature and are given in Fig. 1.

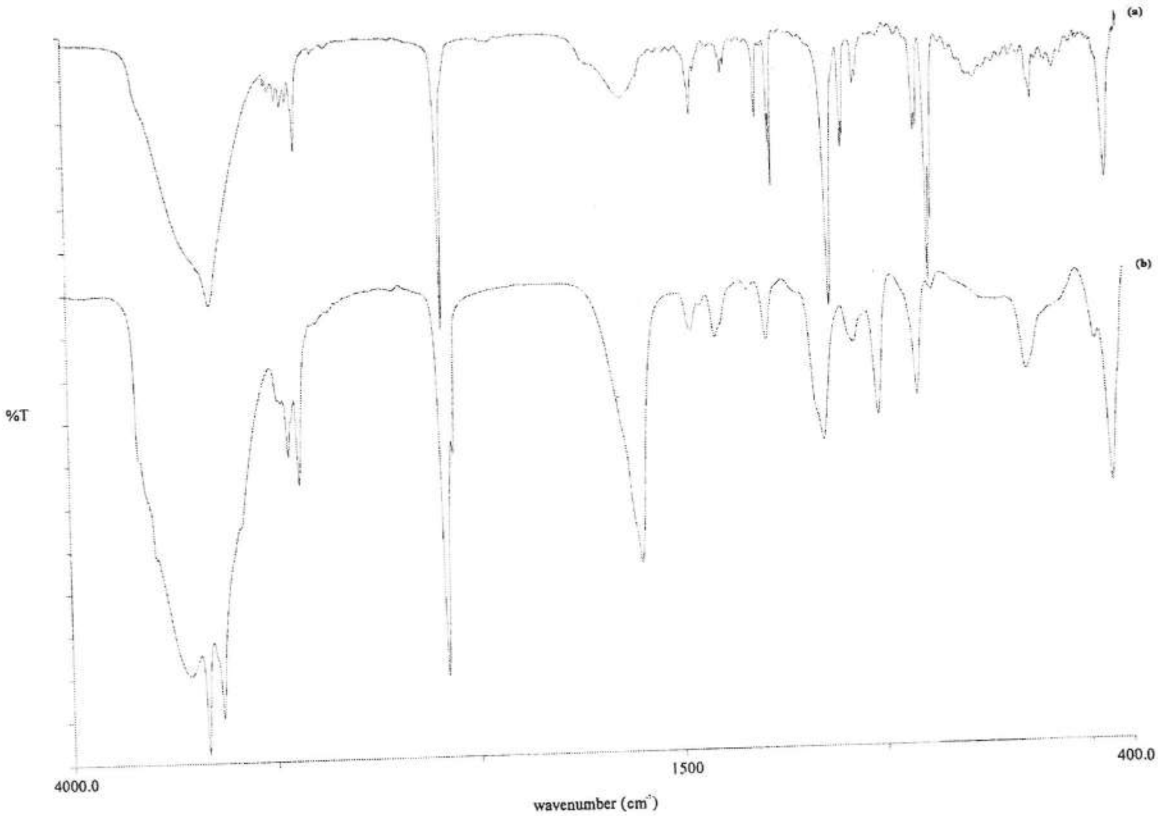

Fig. 1. a) IR spectrum of Co(1,3-diaminopropane) Ni(CN)$_4$.1,4- Dioxane clathrate and **b)** "Empty" clathrate

[1] T. Iwamoto, J. Incls. Phenom. 24 (1966) 61
[2] M.T. Güllüoğlu, Ş.Yurdakul, Vibr. Spectr., 25 (2001) 205

LINEAR FREE ENERGY RELATIONSHIPS OF THE ^{13}C NMR CHEMICAL SHIFTS OF 5-(3- AND 4-SUBSTITUTED ARYLAZO)-4,6-DIMETHYL-3-CYANO-2-PYRIDONE/2-HYDROXYPIRIDINE TAUTOMERS

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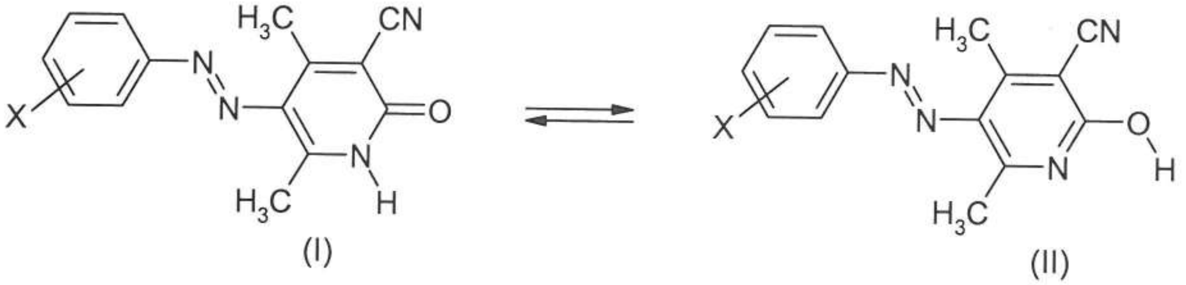
The arylazo pyridone dyes present very important class of colorants. The physico-chemical properties of these dyes are closely related to their tautomerism. The equilibrium between the two tautomers is influenced by the structure of the compounds.

In this work seventeen 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones (Fig. 1) were synthesized and ^{13}C NMR chemical shifts of investigated compounds have been recorded in DMSO-d_6 solution using a tetramethylsilane as internal reference standard using a Varian Gemini 200 spectrophotometer. All the spectra were recorded at ambient temperature. It is shown that there is 2-pyridone/2-hydroxypiridine tautomerism in these dyes.



X = 4-OCH_3, 3-OCH_3, 4-CH_3, 3-CH_3, 4-C_2H_5, 3-C_2H_5, H, 4-Cl, 3-Cl, 4-Br, 3-Br, 4-I, 4-$COCH_3$, 4-CN, 3-CN, 4-NO_2 and 3-NO_2

Fig. 1. The equilibrium between 2-pyridone form (I) and 2-hydroxypiridine form (II) of 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones

For quantitative assessment of the substituent effects on the ^{13}C NMR chemical shifts, we postulated a simple Hammett equation of the type: $\delta_{(C2)X} = \rho\sigma_X + h$, and an extended Hammett equation in the form: $\delta_{(C2)X} = \rho_I\sigma_{IX} + \rho_R\sigma_{RX} + h$, in order to separate inductive and resonance effect of the substituents in the benzene ring and to observe their individual influence at ^{13}C NMR chemical shifts of C2 carbon in the pyridone/pyridine ring. The mode of transmission of substituent effects in 2-pyridone and 2-hydroxypyridine tautomers, have been discussed as well as the effect of geometry on the transmission of electronic effect through investigated molecules. The geometry data needed were obtained using semi-empirical MNDO-PM3 energy calculations.

SELECTED MONOVALENT CATION COMPLEXES WITH LASALOCID ESTERS STUDIED BY FT-IR, NMR, ESI MS AND SEMIEMPIRICAL METHODS

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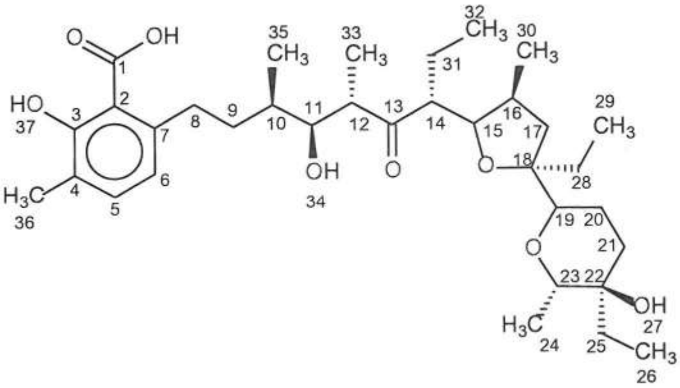

Lasalocid acid

Formation of complexes between some newly synthesized lasalocid esters and the cations (Li^+, Na^+, K^+, Rb^+ and Cs^+) has been studied by FT-IR, NMR, ESI mass spectrometry and the PM5 semiempirical method [1-3]. The ESI-MS spectra indicate that these esters form stable 1:1 or 1:2 complexes with all cations studied. The FT-IR spectra of complexes in acetonitrile solution have provided evidence of equilibrium between keto and enol forms, with the predominance of the keto form. No effect of the kind of cations on this keto - enol equilibrium has been found. The results of the PM5 semiempirical calculations show that the keto form is more favourable than the enol form. Under ESI conditions the formation of stable fragment complexes with the involvement of oxaalkyl chains has been observed, demonstrating the importance of these chains in the complexation process.

References:
[1] R. Pankiewicz, G. Schroeder, B. Gierczyk, B. Brzezinski, F. Bartl *Biopolymers(Biospectroscopy)* 65 (2002) 95
[2] R. Pankiewicz, G. Schroeder, P. Przybylski, B. Brzezinski, F. Bartl *J. Mol. Struct.* 688 (2004) 171
[3] R. Pankiewicz, G. Schroeder, B. Brzezinski, F. Bartl *J. Mol. Struct.* 749 (2005) 128

STRUCTURAL CHARACTERIZATION OF ALKALI METAL 3 - NITROOBENZOATES

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Nitroaromatic compounds are widely distributed in the environment because of their extensive use in the manufacturing of pharmaceuticals, pesticides, azo-dyes and explosives. The changes in physical, chemical and biological properties of them decided about their effect on the biological systems. One of the aims of our works is searching for the correlation between electronic charge distribution and microbial activity of studied molecules[1-3].

In this paper the influence of lithium, sodium, potassium, rubidium and cesium on the electronic system of the 3 – nitrobenzoic acid was studied. The vibrational (FT – IR, FT – Raman) and NMR (^{1}H and ^{13}C) spectra for 3 – nitrobenzoic acid and its alkali metal salts were recorded. Characteristic shifts of band wavenumbers and changes in band intensities along the metal series were observed. The changes of chemical shifts of protons (^{1}H NMR) and carbons (^{13}C NMR) in the series of studied alkali metal 3 – nitrobenzoates were observed too.

Optimized geometrical structures of studied compounds were calculated by B3PW91 method using 6-311++G** and 6-311++G basis sets. Geometric aromaticity indices, dipole moments and energies were also calculated. The theoretical wavenumbers and intensities of IR and Raman spectra were obtained. The calculated parameters were compared to experimental characteristic of studied compounds.

[1] P. Koczoń, J. Piekut, M. Borawska, R. Świsłocka, W. Lewandowski, Anal. Bioanal. Chem. 384 (2006) 302
[2] P. Koczoń, J. Piekut, M. Borawska, R. Świsłocka, W. Lewandowski, Spectrochim. Acta Part A 61 (2005) 1917
[3] P. Koczoń, J. Piekut, M. Borawska, W. Lewandowski, J. Mol. Struct. 655 (2003) 89.

P6-53

MOLECULAR STRUCTURE OF ALKALI METAL 4-NITROBENZOATES

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One of the aims of our works is the investigation of specific effect of various metals on the electronic system of some benzoic acid derivatives[1-4].

In this paper the influence of lithium, sodium, potassium, rubidium and cesium on the electronic system of the 4-nitrobenzoic acid was studied. The vibrational (FT-IR, FT-Raman) and NMR (^1H and ^{13}C) spectra for 4-nitrobenzoic acid salts of alkali metals were recorded. The assignment of vibrational spectra was done. Characteristic shifts of band wavenumbers and change in band intensities along the metal series were observed. Good correlations between the wavenumbers of the vibrational bands in the IR and Raman spectra for 4-nitrobenzoates and ionic potential, electronegativity, atomic mass and affinity of metals were found.

The chemical shifts of protons and carbons (^1H, ^{13}C NMR) in the series of studied alkali metal 4-nitrobenzoates were observed too.

Optimized geometrical structures of studied compounds were calculated by HF, B3PW91, B3LYP methods using 6-311++G** basis set. The theoretical IR, Raman and NMR spectra were obtained. The theoretical vibrational spectra were interpreted by means of potential energy distributions (PEDs) using VEDA 3 program. The calculated parameters were compared to experimental characteristic of studied compounds.

[1] R. Świsłocka, M. Samsonowicz, E.Regulska, W. Lewandowski, J.Mol. Struct., *in press*
[2] W. Lewandowski, M. Kalinowska, H. Lewandowska, J Inorg Biochem 2005, 99, 1407
[3] R. Świsłocka, E. Regulska, M. Samsonowicz, T. Hrynaszkiewicz, W. Lewandowski, Spectrochim. Acta A 2005, 61, 2966
[4] P. Koczoń, T. Hrynaszkiewicz, R. Świsłocka, M. Samsonowicz, W. Lewandowski, Vib. Spectrosc. 2003, 33, 215

VIBRATIONAL SPECTROSCOPIC STUDY OF TWO DIMENSIONAL POLYMER COMPOUNDS OF PYRAZINAMIDE

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Pyrazinamide (pyrazine carboxamide) is a well known anti tubercle bacillus drug. The parent molecule and its some complexes are widely used due to their antituberculotic activity. In this study the Raman and far-IR spectra of the two dimensional coordination polymer compounds, $M(PZA)_2Ni(CN)_4$ {where M = Mn, Zn or Cd; PZA = pyrazinamide} and mid-IR spectrum of $Zn(PZA)_2Ni(CN)_4$ were reported for the first time. The spectral features suggest that the compounds are similar in structure to the Hofmann type two dimensional coordination polymer compounds, formed with $Ni(CN)_4^{-2}$ ions bridged by $M(PZA)_2^{+2}$ cations. Far-IR spectroscopic study allowed us to make correction in the bonding mode of PZA. PZA molecules are found to involve coordination through one of the pyrazine ring nitrogen atoms. Vibrational bands originated from both PZA and $Ni(CN)_4$ group were assigned. The assignment of the $\nu(MN)$ and $\delta(NMN)$ modes originated from the $M(PZA)_2^{+2}$ groups was made by taking the advantage of studying a series of isostructural compounds. The aim of this study is to investigate, particularly the metal ligand bond vibrations. The results were compared with those obtained for corresponding spectra of Hofmann type clathrates.

Acknowledgments

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STRUCTURAL AND VIBRATIONAL STUDY OF 6-HYDROXYPICOLINIC ACID

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The 6-Hydroxypicolinic acid is characterized by enol-ketonic tautomerism. It possesses multiple coordination sites, the carbonyl oxygen, the tertiary nitrogen and the carboxylate oxygen atoms. It can act as a hydrogen-bond acceptor and also as hydrogen-bond donors. Therefore, the molecule is preferentially good ligand for the synthesis of metal complexes allows [1]. In this study, we report X-ray and vibrational spectroscopic studies of 6-hydroxypicolonic acid. The crystals of investigated molecule belong to P $2_1/c$ of the monoclinic system, a=11.714 Å b=3.7088Å c=18.223Å and β=123.71°. X-ray diffraction data show that the molecule is in the ketonic form (Fig.1). Comprehensive studies of the molecular structures and vibrational frequencies and infrared intensities of the molecule have been performed by using Hartree-Fock, density functional B3LYP and second-order Moller–Plesset MP2 methods with the 6-31G basis set. The calculated geometrical parameters of investigated molecule in gas phase were compared with the experimental X-ray data. The assignment of the experimental spectra has been carried out. The experimental IR data show that the molecule could possibly be in the keto rather than in the enol form.

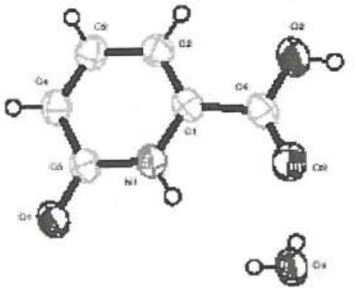

Fig.1: ORTEP plot of the 6-Hydroxypicolinic acid

[1] C.Yan Sun, X.Jun Zheng, and Lin-Pei Jin Z. Anorg. Allg. Chem., 630 **(2004)** 1342

VIBRATIONAL SPECTRA AND MOLECULAR STRUCTURES A NEW SERIES OF 1H-INDOLE-2,3-DIONE-3-THIOSEMICARBOZONES

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Isatin (1*H*-indole-2,3-dione), an endogenous inhibitor of monoamine oxidase (MAO), has several physiological properties for stress and anxiety. Isatin-β- thiosemicarbazone (1*H*-indole-2,3-dione-3-thiosemicarbazone) is well known for its chemoprophylactic activity against certain poxvirus infections. The investigation of the biological properties led us to design other derivatives by introducing appropriate functional groups in the thiosemicarbazone molecule.

Molecular parameters (bond lengths and bond angles, dipole moments, HOMO-LUMO energies, polarizability) and vibrational IR spectra (harmonic wavenumbers, intensities) of isatin-β- thiosemicarbazone derivatives (5-Fluoro-1H-indole-2,3-dione-3-(N-benzylthiosemi carbazone, 5-Fluoro-1H-indole-2,3-dione-3-[N-(4-chlorophenyl) thiosemicarbazone], 5-Fluoro-1H-indole-2,3-dione-3-(N-cyclohexylthiosemicarbazone) have been predicted by ab initio and DFT methods.

Infrared spectra (4000-400 cm^{-1}) of molecules in the solid phase were recorded. All the observed vibrational bands were assigned with the aid of predicted spectra.

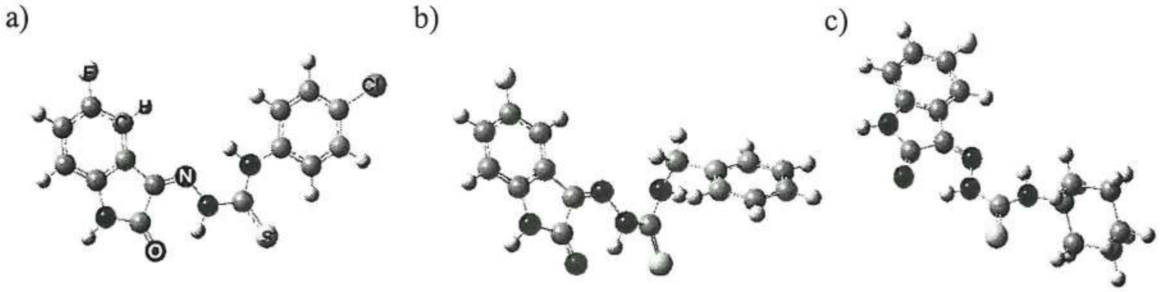

Fig.1: Optimized geometry of a) 5-Fluoro-1H-indole-2,3-dione-3-[N-(4-chlorophenyl)thiosemicarbazone]
b) 5-Fluoro-1H-indole-2,3-dione-3-(N-benzylthiosemicarbazone)
c) 5-Fluoro-1H-indole-2,3-dione-3-(N-cyclohexylthiosemicarbazone)

Acknowledgements
The authors gratefully acknowledge Professor Nilgun Karalı for providing 1H-Indole-2,3-Dione-3-Thiosemicarbozones.

DFT STUDIES AND VIBRATIONAL SPECTRA OF 2-ACETYLPYRIDINE

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The geometry, frequency and intensity of the vibrational bands of 2-acetylpyridine were obtained by the density functinal theory (DFT) calculations with the B3LYP, BLYP and B3PWW91 functionals and 6-311G* basis set.

The vibrational spectral data obtained from the solid phase FT-IR spectra of 2-acetylpridine are assigned modes based on the results of the theoretical calculations. The observed spectra are found to be in good agreement with the calculations.

POSSIBLE SPECTROSCOPIC MANIFESTATION OF THE AGIBA (ANGULAR GROUP INDUCED BOND ALTERATION) EFFECT IN TOLUENE

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During more than one and a half century aromaticity serves as one of the most important concepts in organic chemistry. The most obvious consequence of this concept is the common confidence that in aromatic compounds, bond lengths do not alternate and are between typical to the single and double ones. However, in 1994, performing *crystal structure investigations* of substituted pyridines and their salts, Krygowski and co-workers have discovered a very surprising effect [1]: It appears that some substituents can induce bond alternation in aromatic rings.

In this presentation we discuss possible *spectroscopic manifestations* of the AGIBA effect. In Fig. 3, isotropic Raman spectrum of the liquid toluene is presented demonstrating that instead of being single, the line corresponding to the ring vibration is clearly split by 0.7 cm^{-1}. The energy difference between two unidentified (cis- and trans- AGIBA?) isomers estimated in temperature dependent Raman studies appears equal to 6.68 kJ/mol (Fig. 4). Similar splittings are noticed in the spectra of other methyl substituted benzenes.

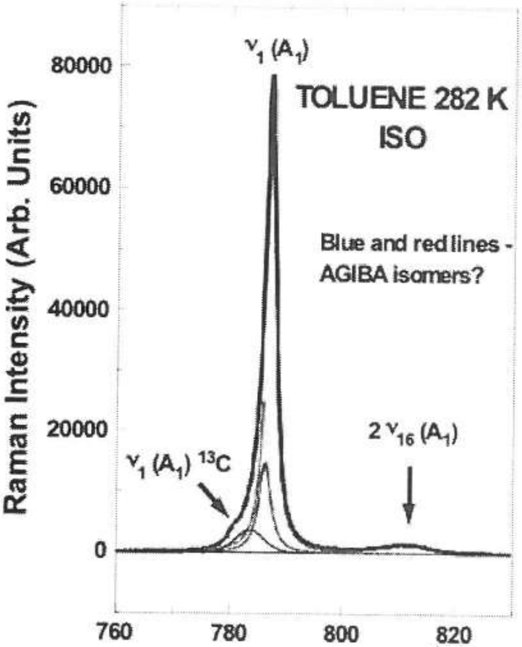
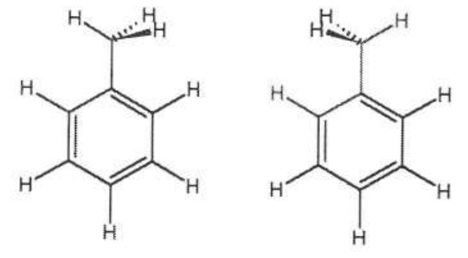


Fig. 3



cis AGIBA isomer trans AGIBA isomer

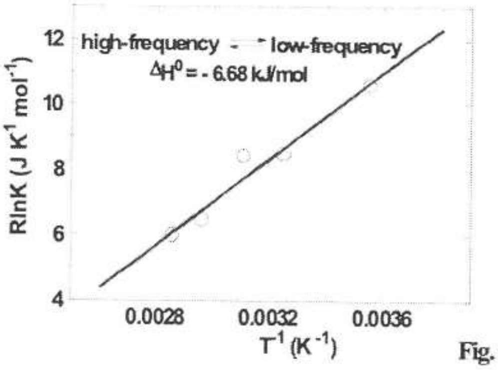


Fig. 4

[1] T. M. Krygowski et al., *Tetrahedron* **50** (1994) 13155.

SPECTROSCOPIC STUDY OF N-SUBSTITUTED CAPROAMIDES IN SOLUTIONS

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As a part of an extensive study on structural characteristics of various N-substitued amides[1-3], FT-IR, NIR, ^{1}H NMR and mass spectra of N-subtituted caproamides have been obtained and interpreted. The synthesis of N-substituted caproamides of general formula $RNHCO(CH_2)_4CH_3$ were performed according to the common Schotten-Baumann reaction of acylation of amines with caproyl chloride. R represents: ethyl, n-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, cyclopentyl, cycloheptyl, phenyl, 4-methylphenyl, 4-methoxyphenyl, 4-N-dimethylaminophenyl, 4-nitrophenyl, 4-acetylphenyl, 4-chlorophenyl, 4-bromophenyl, 4-iodophenyl, 4-fluorophenyl, 4-biphenyl, 4-phthalimidoyl, 3-iodophenyl, 3,5-di-methoxy-2-pyrimidinyl.

FT IR spectra in the region of the $\nu(N-H)$ band have been recorded for the above series of N-substituted caproamides in solutions. The spectroscopic parameters have been discussed and interpreted in terms of the chracteristics of the N-substituent.

Due to the hindered rotation around the nitrogen-carbonyl bond in amides, cis/trans rotational isomerism is studied.

[1] A. D. Nikolić, N.L. Kobilarov, A. N. Brzić, J. Mol. Struct. 99 (1983) 179.
[2] S.D. Petrović, N.D. Stojanović, D.G. Antonović, D.Ž. Mijin A.D. Nikolić, J. Mol. Struct. 410-411 (1997) 35-38.
[3] L. Gobor, S. Petrović, A. Nikolić, D. Antonović, D. Molnar-Gabor, J. Mol. Struct. 482-483, (1999) 343.

FT-IR AND RAMAN SPECTROSCOPIC STUDY OF 4-AMINOPYRIMIDINE TETRACYANONICKELATE COMPLEXES

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Pyrimidine is the parent heterocycle of very important group of compounds that have been extensively studied due to their occurrence in living systems. Pyrimidine ring system provides a potential binding site for metals and so any information on their coordinating properties are important for understanding the role of metal ions in biological system. Aminopyrimidines are of great biological importance.

In this study 4-aminopyrimidine tetracyanonickelate, $M(4APM)_2Ni(CN)_4$ {where M = Mn, Co, Ni, Zn or Cd; 4APM = 4-aminopyrimidine}, coordination polymer compounds are prepared for the first time and their FT-IR (400-4000 cm^{-1}) and FT-Raman (50-4000 cm^{-1}) spectra are reported. The FT-IR spectrum of $Mn(4\text{-}APM)_2Ni(CN)_4$ is given in Fig.1. The spectral features suggest that the compounds are similar in structure to the Hofmann type two dimensional coordination polymer compounds, formed with $Ni(CN)_4^{-2}$ ions bridged by $M(4APM)_2^{+2}$ cations. 4APM is coordinated to M(II) through the pyrimidine ring nitrogen atom; the amino group is not involved in the complex formation. Vibrational bands originated from both 4APM and $Ni(CN)_4$ group were assigned. Coordination effect on 4APM vibrational wavenumbers is analysed.

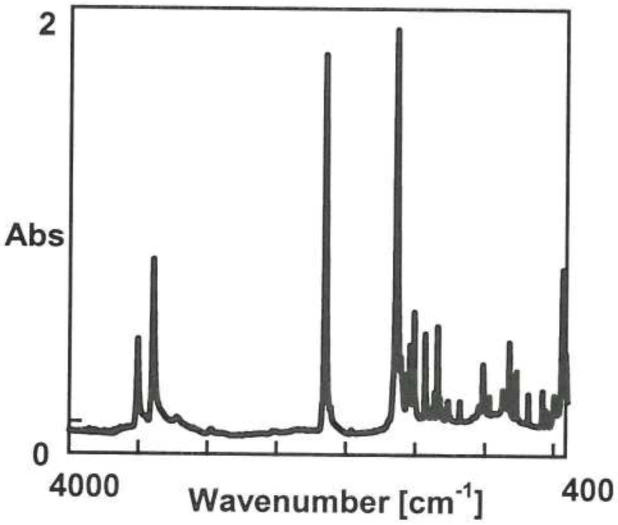

Fig 1. FT-IR spectrum of $Mn(4\text{-}APM)_2Ni(CN)_4$

STRUCTURE ELUCIDATION OF A NEW REARRANGED ABIETANE DITERPENE USING SPECTRAL AND SEMI-EMPIRICAL/DFT CALCULATION METHODS

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NMR spectroscopy is the most important and informative method in structure elucidation of the organic compounds. As a continuation of our structure elucidation studies on natural compounds from *Salvia* species, a new rearranged abietane diterpene was isolated from an endemic *Salvia* (Sage) species, *Salvia eriophora*, and its structure[1] (eriophoroxide) was elucidated based on namely 1D- and 2D-NMR and MS spectroscopic techniques. The NMR data was highly sufficient in determining its abietane structure, however, for determination of most stable structure considering the stereochemistry at C-1, molecular modeling studies were employed through semi-empirical AM1 and DFT based B3LYP structure methods, and results have exhibited almost equal possibility for both α and β stereochemistry of C-1 proton.

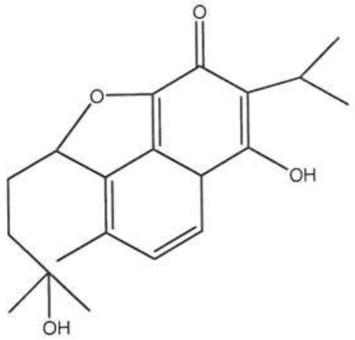

Fig. 1: Eriophoroxide

[1] A. Frisch, M.J. Frisch, Gaussian 98 User's Reference, 2nd Edition, Gaussian Inc.:Pittsburg-U.S.A. 1994, 25-196.
[2] J.B. Foresman, A.E. Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd Edition, Gaussian Inc.: Pittsburg-U.S.A. 1996, 39-90.

FOURIER TRANSFORM INFRARED SPECTRA OF $NiNH_4PO_4 \cdot 6H_2O$

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The Fourier transform infrared spectra of the struvite analogue, nickel ammonium phosphate hexahydrate, $NiNH_4PO_4 \cdot 6H_2O$ and of its partially deuterated analogues were recorded from room temperature (RT) down to the boiling temperature of liquid nitrogen (LNT).

The crystal structure of $NiNH_4PO_4 \cdot 6H_2O$ was solved by X-ray diffraction [1,2]. According to the crystallographic results, it crystallizes in the orthorhombic space group $Pmn2_1$ with $Z = 2$. It was found that Ni^{2+}, PO_4^{3-} and two (out of four) types of water molecules occupy special positions with C_s symmetry, while the other two types lay on general positions. The crystallographic data do not suggest disorder in the ammonium group. The water molecules donate some of the shortest hydrogen bonds ever found in crystalline hydrates [3] and are very similar to that of struvite, $MgNH_4PO_4 \cdot 6H_2O$ [4].

The existence of strong hydrogen bonds between water molecules is supported by the appearance of a broad band from 3800 to 2100 cm^{-1} in the stretching region of the infrared spectrum. In the LNT difference spectrum of a sample with low deuterium content (≈2-3 % D), at least ten bands appear in the OD and ND stretching mode region of isotopically isolated HDO molecules and NH_3D^+ ions between 2600 and 1900 cm^{-1}. In the RT spectrum of such a sample, two bands are observed in the region of the ND bending vibrations of isotopically isolated NH_3D^+ ions at around 1290 cm^{-1} and 1250 cm^{-1}, whereas four bands can be seen in the corresponding LNT spectrum. All this implies the existence of some kind of disorder of the ammonium ion, at least at subambient temperatures.

In the region of $\nu_3(PO_4)$ modes one strong and broad band is found, while in the region of the $\nu_4(PO_4)$ bending vibration and of the external modes of the water molecules, several bands can be seen. On the basis of a careful analysis of the RT and LNT spectra of the protiated compound, as well as those of its partially deuterated analogues, we assigned the band at 574 cm^{-1} to the $\nu_4(PO_4)$ modes and the remaining ones as due to librational and translational modes of the water molecules.

References

[1] A. Goni, J.L. Pizarro, L.M. Lezama, G. E. Barberis, M.I. Arriortua, T. Rojo, J. Mater. Chem, 6 (1996) 421.
[2] R. Blachnik, Th. Wiest, A. Dulmer, H. Reuter, Z. Kristallogr., 212 (1997) 20
[3] G. Chiari and G. Ferraris, Acta Crystallogr., B**38** (1982) 2331.
[4] G. Ferraris, H. Fuess and W. Joswig, Acta Crystallogr., B**42** (1986) 253.

DFT STUDY OF VIBRATIONAL DYNAMICS AND STRUCTURE OF AMINOPROPYLSILOXANE POLYMER

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Aminopropylsiloxane is an organosilane coupling agent whose capacity of adsorption on different materials is frequently used for functionalisation of surfaces like optical fibers, nanoparticals, semiconductors or metals. These molecules can form various kinds of bonds with the surface of substrate changing thus their mechanical, optical or electrical properties. The nature of these bonds depends greatly on the conformation of the polymerized structure.

In this work we investigated IR and Raman spectra of aminopropylsiloxane polymerized on PVC substrate at room temperature. Complete assignment of the vibrational spectra was carried out using density functional theory calculations with Becke's three-parameter exchange functional in combination with the Lee-Young-Parr correlation functional (B3-LYP) and standard 6-311+G(d,p) basis set. The vibrational spectra were calculated for two different conformations of silicooxygen rings: ladder like structure and cubic structure (Fig.1).

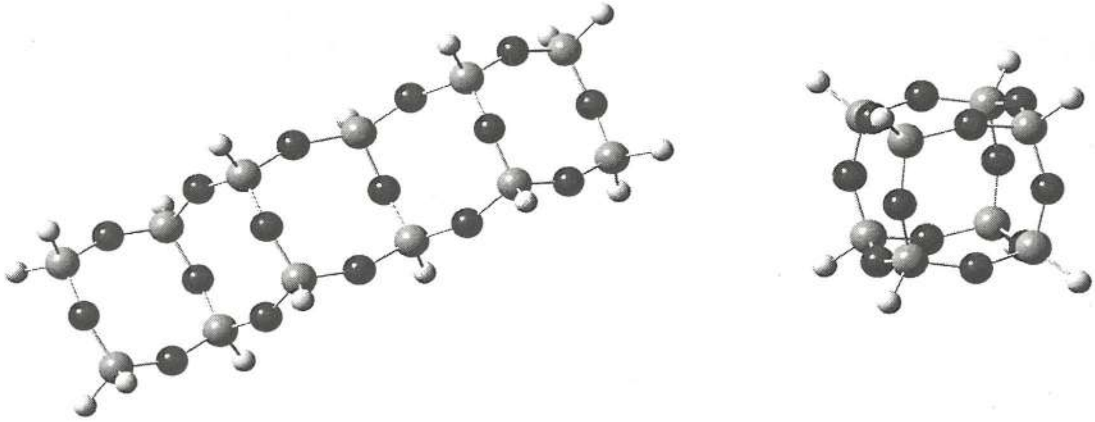

Fig. 1: Ladder and cubic siloxane structures

Comparative analysis of calculated and measured spectra reveals that ladder structure has been formed at the surface of PVC support.

P6-64

SPECTROSCOPIC (IR, RAMAN, UV, ^{1}H AND ^{13}C NMR) AND MICROBIOLOGICAL STUDIES OF Fe(III), Ni(II), Cu(II), Zn(II) AND Ag(I) PICOLINATES

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The FT-IR, Raman spectra of picolinic acid as well as Fe(III), Zn(II), Cu(II), Ni(II) and Ag(I) picolinates were registered, assigned and compared. Some regularities in the spectra of studied picolinates within the regions: 1650-1340 cm^{-1} [$\nu(CC)_{ar}$, $\nu_{as}(COO^{-})$, $\nu_{s}(COO^{-})$]; 1300-1020 cm^{-1} [β(CH)]; 780-620 cm^{-1} [γ(CH), α(CCC)] were found. ^{1}H and ^{13}C NMR spectra for picolinic acid, Zn(II) and Ag(I) picolinates were recorded and studied as well. Moreover the UV spectra of picolinic and picolinates were registered and compared. The influence of Ag(I), Zn(II), Ni(II), Cu(II) and Fe(III) on the electronic system of picolinic acid was investigated. The microbiological activity of picolinates against two species of bacteria: *Escherichia coli, Bacillus subtilis* as well as two species of yeasts: *Saccharomyces cerevisiae* and *Hansenula anomala* was also studied. The dependency between molecular structure and microbiological activity was studied [1-3].

[1] P. Koczoń, J. Piekut, M. Borawska, W. Lewandowski, J. Mol Struct. 651-653 (2003) 651.

[2] W. Lewandowski, M. Kalinowska, H. Lewandowska, J. Inorg. Biochem. 99 (2005) 1407.

[3] P. Koczoń, J. Piekut, M. Borawska, W. Świsłocka, W. Lewandowski, Anal. Bioanal. Chem. 384 (2005) 302.

[4] P. Koczoń, J. Piekut, M. Borawska, R. Świsłocka, W. Lewandowski, Spectrochim. Acta Part A 61 (2005) 1917.

^{1}H, ^{13}C and ^{17}O NUCLEAR MAGNETIC SHIELDINGS OF METHANOL AND ITS DEUTERATED ISOTOPOMER FROM THE GAS PHASE MEASUREMENTS

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A small amount of methanol isotopic mixtures (CH_3OH + CH_3OD) in fluoromethane and trifluoromethane as gaseous buffers were studied using ^{1}H, ^{13}C and ^{17}O NMR spectra. Strictly linear density dependence was observed when the pressure of each buffer was changed. After extrapolation of the results to the zero-density limit it was possible to determine the appropriate shielding constants free from intermolecular interactions, σ_o(H), σ_o(C) and σ_o(O) at 300K. They were recalculated to the absolute nuclear magnetic shielding scales. Additionally, high-resolution ^{1}H, ^{13}C and ^{17}O NMR spectra of pure liquid methanol isotopomers were also recorded and NMR chemical shifts were measured. Reliable gas-to-liquid shifts and the magnitudes of isotope effects on nuclear shielding constants caused by H/D substitution are reported. It is shown that the new experimental NMR parameters are suitable for comparison with the results of quantum-chemical calculations [1-4].

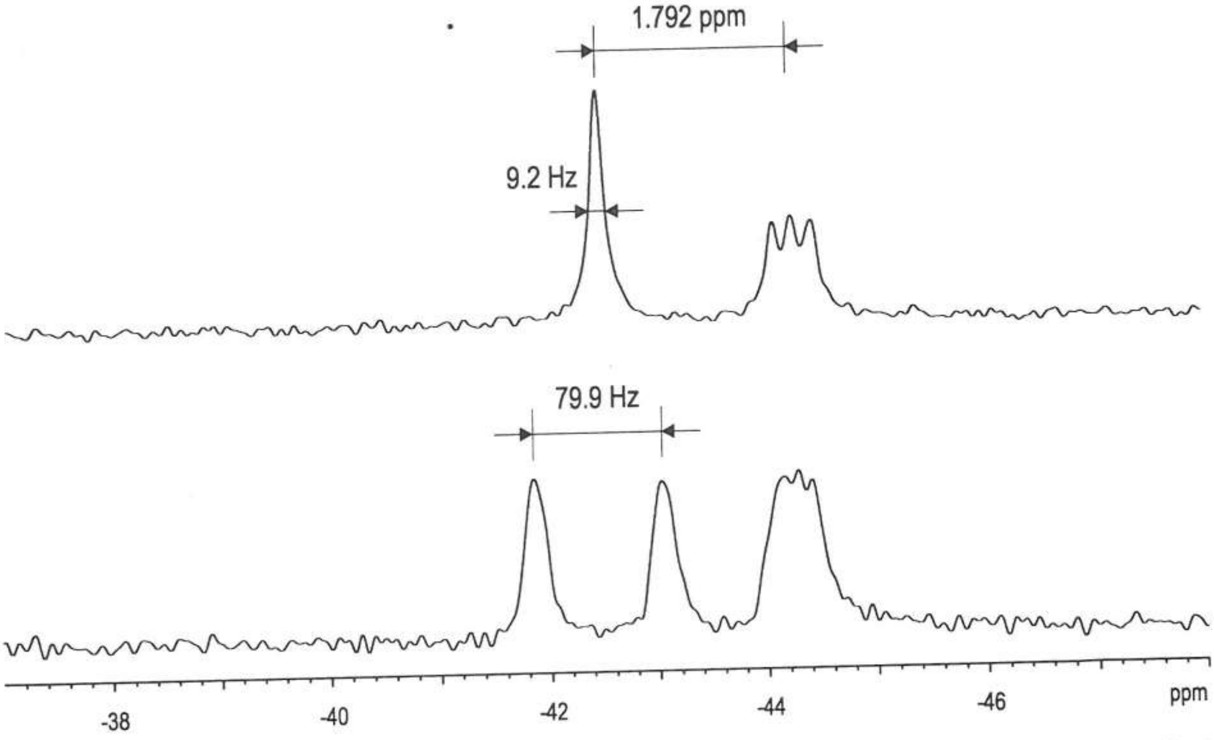

Fig.1. The 67.8648 MHz ^{17}O NMR spectrum of $CH_3{}^{17}OH/D$ mixture in gaseous CH_3F at density 1.426 mol/L and temperature 300K. The upper spectrum is recorded as decoupled from protons; isotope effect on oxygen chemical shift connected with H/D substitution is clearly visible. The lower spectrum is recorded as a coupled one and shows the $^{1}J(^{17}O,^{1}H)$ coupling constant of a hydroxyl group.

[1] K.Ruud, P.Astrand and P.Taylor, J.Am.Chem.Soc.123 (2001) 4826.
[2] A.Dransfeld, Chem.Phys. 298 (2004) 47.
[3] C.Adamo and V.Barone, Chem.Phys.Lett. 298 (1998) 113.
[4] A.A.Auer, J.Gauss and J.F.Stanton, J.Chem.Phys. 118 (2003) 1047.

ANALYSIS OF THE RAMAN FREQUENCIES CLOSE TO THE λ-PHASE TRANSITION IN NH_4Cl

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This study gives our analysis of the Raman frequencies for the lattice modes of ν_5 TO (174 cm^{-1}), ν_5 TO(144 cm^{-1}) and ν_7 TA (93 cm^{-1}), and an internal mode of ν_2 (1708 cm^{-1}) as functions of temperature in NH_4Cl close to its λ-phase transition (T_λ=241.2 K, P=0). This analysis is performed using a power-law formula with the critical exponent β for the order parameter according to the soft mode-hard mode coupling model.

Our β value is very close to zero for all the modes studied in NH_4Cl close to its λ-phase transition. This indicates that the soft mode-hard mode coupling theory predicts a logarithmic divergence of the Raman frequencies of those modes considered here, as the temperature increases toward the λ transition temperature T_λ in NH_4Cl.

FT-IR SPECTROSCOPIC STUDY OF M(SUCCINIC ACID)Ni(CN)$_4$.(1,4-DIOXANE) CLATHRATES (M = Ni, Co and Mn)

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In this study, clathrate of Succinic acid-tetracyanonickel given by the formula M(Succinic Acid)Ni(CN)$_4$.(1,4-Dioxane) (M = Ni, Co and Mn) is obtained for the first time through chemical methods. The similarities of the observed spectra indicate that the obtained clathrate of Succinic acid-tetracyanonickel is new example of the Hofmann-type clathrates.

Key words: Inclusion Compounds; Succinic Acid (SA); Infrared Spectroscopy (IR); Tetraciyanonickelate, Hofmann-type Clathrate

SPECTROSCOPIC STUDIES ON THE FORMATION KINETICS OF SnO_2 NANOPARTICLES SYNTHESIZED IN A PLANETARY BALL MILL

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SnO_2 nanoparticles are intensely studied nowadays because of their advantageous sensing properties. Sensors aimed at detecting e.g. ethanol, LPG, CNG and CO have been realized by several groups. SnO_2 nanoparticles can be prepared by a broad variety of synthesis techniques including hydrothermal treatment[1], thermal decomposition[2] and the sol-gel process[3]. It is also possible to prepare the nanoparticles by mechanochemical synthesis when performing the following reaction in a high impact planetary ball mill:

$$SnCl_2 + Na_2CO_3 + ½\,O_2 \rightarrow SnO_2 + 2\,NaCl + CO_2$$

This reaction offers good contol over the morphology and the size distribution of the resulting nanoparticles and therefore, it is currently investigated in our group. In particular, we are interested in uncovering the details of the kinetics of tin-oxide formation by continuously monitoring the temperature and pressure in the milling jar during reaction, and analyzing the structure of the products (Figure 1) by mid-IR, far-IR, Raman and XPS spectroscopy as well as electron microscopy. In this contribution, we report on the effect of milling time on the vibrational spectroscopic properties of the products. These results help us interpret the pressure vs. time curves recorded during the mechanochemical reaction.

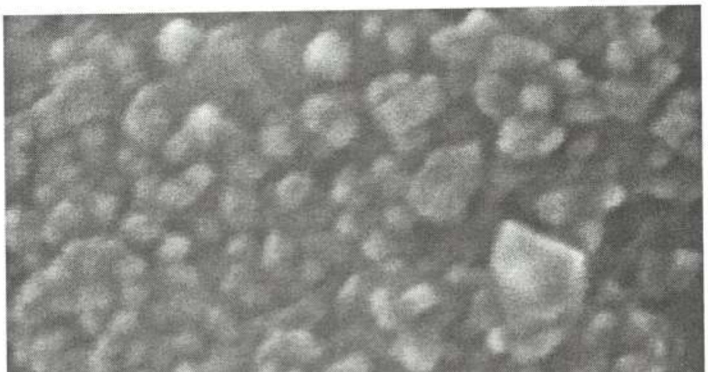

Figure 1. Characteristic high resolution SEM image of SnO_2 nanoparticles synthesized in a planetary ball mill and calcined at 600 °C for 2 hours in O_2 flow.

[1] J.R. Zhang and L. Gao, J. Inorg. Mat. 19 (2004) 1177.
[2] M. Epifani, J. Arbiol, R. Diaz, M.J. Peralvarez, P. Siciliano and J.R. Morante, Chem. Mater. 17 (2005) 6468.
[3] S.R. Wang, J. Huang, Y.Q. Zhao, S.P. Wang, S.H. Wu, S.M. Zhang and W.P. Huang, Mat. Lett. 60 (2006) 1706.

SPIN-ORBIT SPLITTING OF THE VALENCE BAND IN SEMICONDUCTING THIN FILMS OF VARIABLE-SIZED ZnSe AND CdSe QUANTUM DOTS FOLLOWED BY OPTICAL SPECTROSCOPY

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Thin films of semiconducting ZnSe and CdSe quantum dots were synthesized by chemical deposition techniques[1,2]. Optical properties of as-deposited and thermally annealed films were investigated by UV-VIS spectroscopy. Special emphasis was put on the evolution of band structure parameters upon average crystal size increase induced upon annealing treatment. Using the parabolic approximation for the dispersion relation, within the framework of the Fermi's golden rule for band-to-band electronic transitions, the band gap energies corresponding to the $\Gamma_8^v \to \Gamma_6^c$ transitions in synthesized thin films of sphalerite-type ZnSe and CdSe quantum dots were calculated. Evolution of these quantities with crystal size increase was rationalized in terms of the effective mass approximation model for the three-dimensional confinement effects. Also, from the constructed semiconductor absorption functions, the energies corresponding to $\Gamma_7^v \to \Gamma_6^c$ transitions (appearing at energies E_g + Δ_{SO}) were calculated. While these transition energies basically follow the same trends with crystal size increase as the minimal band gap energies, the spin-orbit splitting between the Γ_8^v and Γ_7^v valence band components is practically insensitive to QD size variations. This behavior was attributed to the fact that the low-lying 1*S* hole states arising from valence band Γ_7 and Γ_8 components are relatively pure (*i.e.* do not mix with higher angular momentum states) in the case of small nanocrystallites. Both of these states shift together to higher (in absolute value) energies via the *isotropic* hole mass (not the light or heavy hole mass). Therefore, despite the detected overall band gap blue shift (manifested as a shift in optical transition energies), the splitting between the two transitions remains unchanged with crystal size variations. Several other points, such as the crystal size dependence of the exciton oscillator strengths in the case of the studied nanocrystalline semiconductors, were studied as well.

[1] B. Pejova, A. Tanuševski, I. Grozdanov, J. Solid State Chem. 177 (2004) 4785.
[2] B. Pejova, A. Tanuševski, I. Grozdanov, J. Solid State Chem. 172 (2003) 381.

WOLLASTONITE-BASED CERAMIC OBTAINED BY THERMAL TREATMENT OF ACTIVE FILLERS-CONTAINING POLYSILOXANE PRECURSORS

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The aim of this work was to investigate new ceramic materials for bone implant applications. The ceramic materials were obtained by thermal treatment of active fillers-containing polysiloxane precursors. Ceramics active fillers, namely $Ca(OH)_2$ and silica nanopowders were used.

The phase composition of ceramic samples obtained by thermal transformation of active fillers-containing polysiloxanes was analysed by means of FTIR spectroscopy and XRD analysis. The microstructure of the obtained material was studied by scanning electron microscopy (SEM) with EDS point analysis. The bioactivity test in "in vitro" conditions was determined by immersing of ceramic samples in simulated body fluid (SBF). The surface of ceramic samples after immersion in simulated body fluids were analysed by means of SEM with EDS point analysis.

It was found that thermal treatment of active fillers-containing polysiloxane precursors leads to formation of wollastonite-containing ceramic nanomaterials. Such ceramic materials demonstrate bioactivity in "in vitro" conditions. It can be concluded that the ceramic materials seem to be useful as bone substitute.

OPTICAL AND STRUCTURAL PROPERTIES OF SOL-GEL MADE Nb_2O_5 –Ta_2O_5 MIXTURES

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There are several investigations on niobium pentoxide and tantalum pentoxide as an element of electrochromic devices. Tantalum pentoxide was also shown as a good candidate on constructing interference filters.

In this work, mixtures of these films at various percentages were investigated to look at their optical and structural properties. The films are prepared with sol-gel spin coating method and heat treated at 550°C.

Refractive index and extinction coefficient of the films were obtained by using a software program which makes use of the transmittance and reflectance data of an NKD spectrophotometer.

The spectral range used was in between 300 nm and 1000 nm. Optical band gap values were extracted from the extinction coefficient data.

Structural characterizations of the films were obtained using scanning probe microscope and x-ray diffractometer.

THE INFLUENCE OF THERMAL TREATMENT ON THE PHASE DEVELOPMENT OF ZrO_2-NiO PRECURSORS

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Structural and microstructural changes during thermal treatment of the amorphous precursors of the ZrO_2-NiO system were examined by differential thermal analysis, X-ray powder diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy, field emission scanning electron microscopy and energy dispersive X-ray spectrometry. The amorphous precursors of the ZrO_2-NiO system on the ZrO_2-rich side of the concentration range were prepared by co-precipitation from aqueous solutions of the corresponding salts. The crystallization temperature of the amorphous precursors increased with an increase in the NiO content, from 405°C (0 mol% NiO) to 600°C (30 mol% NiO). The results of phase analysis indicated that maximum solubility of Ni^{2+} ions in the ZrO_2 lattice occurred in the metastable products obtained after crystallization of the amorphous precursors. A precise determination of unit-cell parameters using the whole-powder-pattern refinements shows that the unit-cell parameters of the t-ZrO_2 solid solution decrease with an increase of Ni^{2+} ions up to ~5 mol%. Further increase of nickel content has no influence on the lattice parameters but increase the stability of metastable t-ZrO_2-type products. The obtained results indicate presence of very strong surface interactions between nickel oxide and zirconia.

Keywords: ZrO_2-NiO, XRD, Raman spectroscopy, FE-SEM, FT-IR spectroscopy, DTA

EFFECT OF AGING ON SOL-GEL MADE ZnO FILMS PREPARED AT TWO DIFFERENT SOL CONCENTRATIONS

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Zinc oxide (ZnO) thin films were prepared by the sol-gel spin coating method using two different sol concentrations. The films were heat treated for 1h and 16h, and afterwards aged up to 175 days. Optical properties of the films were determined by an NKD spectrophotometer and their structural properties were investigated by an X-ray diffractometer and atomic force microscopy. The results showed that optical properties of the diluted solution changed with respect to aging while the concentrated solution showed no change.

P7-7

SPECTROSCOPIC STUDY AND AFM IMAGING OF SOLID LIPID NANOPARTICLES OF ORGANIC COMPOUNDS IN GEL MATRICES

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Many therapeutically active molecules are non-soluble in aqueous systems, or chemically and biologically fragile, so they need to be encapsulated in a drug carrying system. These systems protect the loaded drug against degradation and the active molecule can be effectively delivered in biological media. The development of such systems include micelles, liposomes, micro- and polimeric nanoparticles and solid lipid nanoparticles (SLNs). The SLNs represent one of the most promising classes of colloidal carriers for bioactive organic molecules. Their advantages on other carrier systems include high temporal and thermal stability, high loading capacity, ease of preparation, low production costs, large scale industrial production since they can be prepared from natural sources.[1]

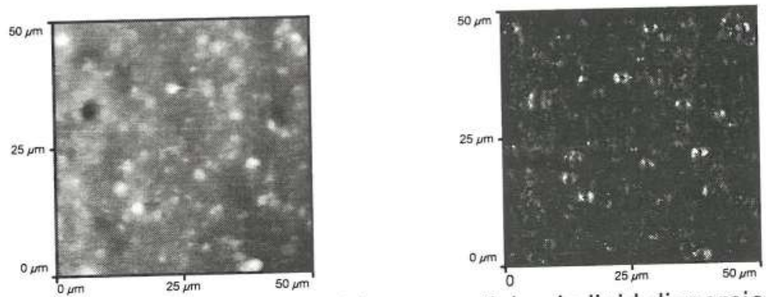

Fig. 1: Dibenzalacetone lipid nanoparticles in lipid dispersion:
AFM images topographic mode (left) and force modulation mode (right)

SLNs were obtained by the ultrasound method, using phosphatidyl choline and glyceryl triestearate as surfactants. Contact mode AFM has been used to characterize SLNs including organic compounds, which are contained in lipid dispersions. The simultaneous use of modulated force and topography imaging allows a clear interpretation of the observed images,[2] showing the presence of nanoparticles in the gels sub-surface. Spectroscopic methods as Raman, SNOM, XPS and NMR were used to elucidate the SLN composition and structure. Complete results will be reported in the communication.

[1] R.B. Gupta, U.B. Kompella, Nanoparticle Technology for Drug Delivery, Taylor and Francis CRC Press, USA (2006).
[2] P. Shahgaldian, L. Quattrocchi, J. Gualbert, A.W. Colleman, P. Goreloff, Eur. J. Pharm. & Biopharm. 55 (2003) 107.

OPTICAL AND STRUCTURAL PROPERTIES OF CeO_2-Ta_2O_5 THIN FILMS

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Transparent metal oxide thin films are of growing interest for constructing interference filters and electrochromic devices. CeO_2 and Ta_2O_5 thin films are good candidates for these purposes. In this study, the sol-gel spin coating method has been used to make CeO_2 and Ta_2O_5 thin films. These films have been mixed together in several ratios to observe changes in their optical and structural properties. Refractive indices and extinction coefficients of the films were obtained from NKD spectrophotometer data in the spectral range of 300-1000 nm. Optical energy band gaps were calculated from extinction coefficient data. The structure of the films was characterized by an X-Ray Diffractometer (XRD) and Atomic Force Microscopy (AFM).

[1] E. Masetti, F. Varsano, F. Decker, A. Krasilnikova, Electrochimica Acta, 46 (2001) 2085
[2] F. E. Ghodsi, F. Z. Tepehan and G. G. Tepehan, Solar Energy Materials and Solar Cells, 68, Issues 3-4 (2001) 355
[3] Amita Verma, Amish G. Joshi, A.K. Bakhshi, S.M. Shivaprasad and S.A. Agnihotry
Applied Surface Science, In Press, Corrected Proof, (2005)

MÖSSBAUER, FT-IR AND FE SEM INVESTIGATION OF IRON OXIDES PRECIPITATED FROM $FeSO_4$ SOLUTIONS

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Iron oxides (group name for oxyhydroxides and oxides) have found important applications as pigments, catalysts, gas sensors, magnetic materials etc. Chemical, microstructural and physical properties of iron oxides heavily depend on the route of their synthesis[1-3]. Iron oxides can be synthesised by slow or forced hydrolysis of iron(III) salts, crystallisation from "amorphous" iron(III)-hydroxide gel or the oxygenation of Fe(II)-hydroxide, hydrolysis in microemulsion, the sol-gel procedure or a thermal decomposition of various iron(III)- and iron(II)-salts. In the present work we report the results of Mössbauer, Fourier transform infrared (FT-IR) and field emission scanning electron microscopic (FE SEM) investigation of the precipitation of iron oxides from the $FeSO_4$ salt solution. The hydrolysis of urea at 90°C was used for the generation of OH^- ions. The formation of specific oxyhydroxide or oxide phase(s) depended on the concentrations of $FeSO_4$ and urea, as well as on the rate of oxygenation. In dependence on the experimental conditions different iron oxide phases, such as goethite, lepidocrocite, hematite and magnetite were found in the precipitates. Only substoichiometric magnetite $Fe_{3-x}O_4$ was detected. Significant differences in the Mössbauer spectra of goethite were noticed. Some Mössbauer spectra could be fitted only if the distribution of hyperfine magnetic fields was taken into account. The results of Mössbauer and FT-IR measurements were correlated with the results of FE SEM inspection of the size and geometrical shape of the iron oxide particles.

[1] S. Musić, S. Popović, M. Gotić, Croat. Chem. Acta 60 (1987) 661.
[2] S. Musić, S. Popović, M. Gotić, J. Mater. Sci. 25 (1990) 3186.
[3] M. Gotić, S. Popović, N. Ljubešić, S. Musić, J. Mater Sci. 29 (1994) 2474.

TRANSFORMATION OF LOW CRYSTALLINE FERRIHYDRITE TO α-Fe_2O_3 IN THE SOLID STATE

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Ferrihydrite is a naturally occuring mineral of Fe^{3+} ions with poorly defined crystallinity and varying chemical composition. It can be found in sediments and soils, or as the product of acid mine drainage. Ferrihydrite was also found as corrosion product of steel. In the laboratory it can be prepared by adding alkali to a solution of Fe(III)-salt, however, this simple method of ferrihydrite synthesis is very sensitive to the parameters of the precipitation process (concentration and type of Fe(III)-salt, pH, temperature, ageing of the precipitate), and consequently, ferrihydrite of varying crystallinity may be produced. Generally, ferrihydrite is commonly considered to have two different forms, one with only two very broad bands in the X-ray diffraction (XRD) pattern (so-called *two-XRD-line* ferrihydrite with an extremely low degree of crystallinity) and the other one with six, less broadened reflections (so-called *six-XRD-line* ferrihydrite). The present work focuses on the synthesis of a 2-line ferrihydrite species and its thermal decomposition up to 325°C in air in order to monitor in more detail the temperature region of the phase transformation ferrihydrite - hematite. The obtained products were characterized by XRD, FT-IR and ^{57}Fe Mössbauer spectroscopies. XRD showed that α-Fe_2O_3 did not appear up to 220°C. The IR band at 330 cm^{-1} for the sample obtained after heating at 245°C indicated that at this temperature some α-Fe_2O_3 has crystallized, whereas the FT-IR spectrum of the sample obtained after heating at 325°C fully corresponds to that of α-Fe_2O_3. The Mössbauer spectrum recorded at room temperature (RT) of the sample prepared at 220°C showed a broadened quadrupole doublet, whereas hyperfine-field distributions are observed at 78 and 12 K, presumably due to non-uniform chemical environments for the Fe^{3+} and/or to the shape and size distributions of the α-Fe_2O_3 clusters. The RT Mössbauer spectrum of the sample heated at 245°C showed a superposition of a quadrupole doublet and a distributed sextet, the latter believed to be due to poorly crystalline α-Fe_2O_3. At 78 K, two sextets were resolved. The sharper one, with a hyperfine field H_{hf} = 52.7 T and quadrupole shift $2\varepsilon_Q = -0.12$ mm s^{-1}, and fractional area of RA=0.22, is due to hematite, which possibly shows the coexistence of antiferromagnetic and weakly ferromagnetic spin states. The much broader magnetic component is assigned to ferrihydrite. At 12 K, hematite has H_{hf} = 53.5 T and $2\varepsilon_Q = -0.03$ mm s^{-1}. The ferrihydrite sextet is still considerably broadened. Mössbauer spectra at RT and 78 K recorded for the sample obtained upon heating at 325 °C correspond only to α-Fe_2O_3 fraction. For the sample obtained by heating at 245°C, a Mössbauer spectrum was recorded at 4.2 K in an applied field of 6 T. The ferrihydrite component clearly splits into a high- and low-field contribution. The heating of 2-line ferrihydrite caused a certain crystalline ordering and in the next stage the transformation to α-Fe_2O_3.

SILICON NANOCRYSTALS BY THERMAL ANNEALING OF SILICON REACH OXIDE PREPARED BY THE LPCVD METHOD

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The silicon reach oxide (SiO_x) thin films are prepared on quartz and silicon crystalline substrates by low pressure chemical vapor deposition (LPCVD) method at the temperatures 700-900 °C. The oxygen concentration x are controlled by the ratio of the partial pressures of SiH_4 and N_2O gases in the reaction chamber. In order to induce the phase separation quartz and crystalline silicon nanostructures the samples are annealed at the temperatures 900-1100 °C. The structural and optical properties of the samples are investigated by Raman and infrared spectroscopy UV/Visible absorption spectroscopy and scanning, transmission electron and atomic force microscopies (SEM, TEM and AFM).

The Raman spectra of the deposited layers shows the characteristic bands of SiO_x structure that consists of the broad peaks at 160 and 460 cm^{-1} which corresponds to the TO and TA phonon-like bands. In IR spectra the position of the band at ~1100 cm^{-1} was used in determination the oxygen content x. With increasing of the annealing temperature the broadened band of TO(Γ) confined phonons of silicon at the wavenumbers between 500 and 520 cm^{-1} and the low frequency symmetrical and quadrupolar modes of silicon nanocrystals appears in the Raman spectra. The model of phonon confinement of optical modes and the calculation of spherical acoustical modes are applied to in order to deduce the mean size and distribution with of silicon nanocrystals[1]. The results are correlated with the morphology and size distributions obtained by SEM, TEM and AFM techniques.

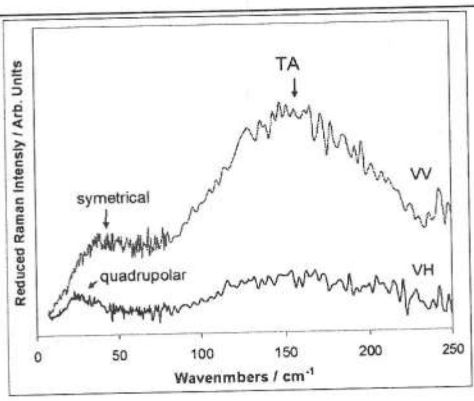

Fig. 1: The low frequency Raman modes of silicon nanocrystals for the sample annealed at 900 °C.

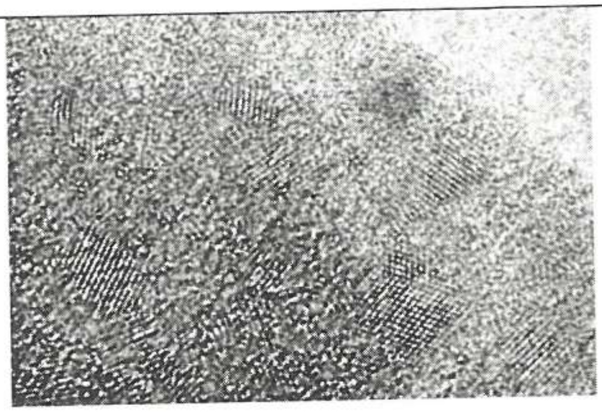

Fig. 2: TEM image of silicon nanocrystals in silicon reach oxide annealed at 900 °C.

[1] M. Ivanda, A. Hohl, M. Montagna, G. Mariotto, M. Ferrari, Z. Crnjak Orel, A. Turković, and K. Furić, **Raman Scattering Of Acoustical Modes Of Silicon Nanoparticles Embedded In Silica Matrix,** J. Raman Spectroscopy **37**, 161-165 (2006)

CHEMICAL AND MICROSTRUCTURAL PROPERTIES OF NANOCRYSTALLINE AL-OXIDES OBTAINED BY THE SOL-GEL PROCESSING

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Sol-gel processing shows some advantages to the conventional ceramic processing, such as a fine scale mixing, elimination of milling operation, a lower densification temperature and improved microstructural properties. This method has been used in the production of very fine powders, thin films, various coatings, fibers, fine abrasive grains, optical glasses etc. Fine particles of boehmite have been extensively investigated since they are precursors for many advanced ceramics. In present work we are focused on the formation of boehmite by sol-gel processing. Al-*sec*-butoxide was hydrolysed varying chemical composition of the solvent and additive, temperature, reaction time and pH. As a result of these changes, the crystallinity of boehmite varied from almost amorphous up to relative well-crystalline. In some cases we found other phases, such as bayerite, gibbsite and nordstrandite. In such cases X-ray powder diffraction (XRD) patterns were quantitatively analysed by Rietveld method. This method was also used to analyse the contributions of crystallite size and lattice strains on the broadening of diffraction lines. The effects of boehmite crystallinity and the size of particles on the corresponding Fourier transform infrared (FT-IR) spectra were also investigated. The size and geometrical shape of the precipitated particles were monitored by thermal field emission scanning electron microscopy (FE SEM) as a function of the synthesis conditions.

STRUCTURE AND OPTICAL PROPERTIES OF POROUS SILICON PREPARED ON THIN EPITAXIAL SILICON LAYER ON SILICON SUBSTRATES

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The porous silicon samples were prepared by electrochemical etching[1] of 10 μm tick p-type (111) silicon epitaxial layer grown on a thin 80 nm SiO_2 layer on silicon substrates, by varying the concentration of 48% HF in ethanol solution. Within the epitaxial layer micro- and nano-pores of different sizes in dependence on HF concentration were obtained. The structural and optical properties of prepared samples were investigated by Raman and infrared spectroscopy and scanning electron microscopy (SEM).

SEM images showed high density of micrometer sized pores whose morphology and density depend on the HF concentration. Nanometer sized silicon structures were observed by the phonon confinement effects of TO, TA phonon bands in the Raman spectra[2]. The broadening of c-Si vibrational band at 520 cm^{-1}, that indicates the phonon confinement, increased with the decrease of the HF concentration. At the same time the TA-like phonon vibrational band at 150 cm^{-1}, that characterizes the short range confinement, also appeared in the same samples.

All samples showed photoluminescence (PL) peak in the visible spectral range. The change in the intensity and position of the PL peak showed strong sensitivity to the influence of different environment conditions; air, vacuum, acetone, methanol and the pressure of applied gases of oxygen, hydrogen and nitrogen. The measurements of electrical resistivity of the porous thin layers also showed the sensitivity to the above mentioned environment conditions.

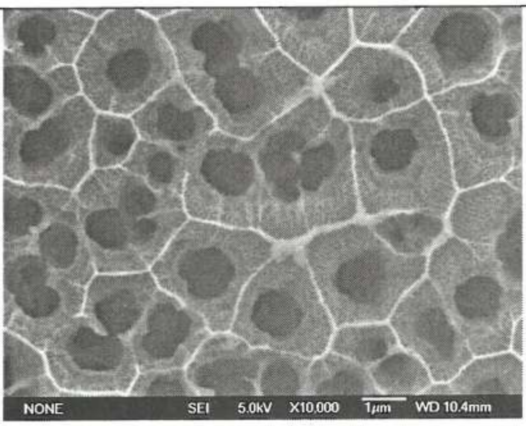

Fig. 1: SEM image of porous epitaxial layer etched in 1:1 HF-ethanol solution

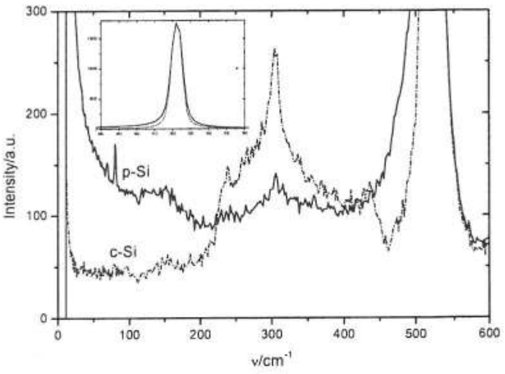

Fig.2: Raman spectra shows broadening of TO and appearance of TA phonon bands

[1] R. L. Smith, S. D. Collins, J. Appl. Phys. 71 (1992) R1.
[2] P. Y. Yu and M. Cardona, Fundamentals of Semiconductors, Springer, Berlin, 1999.

SPECTROSCOPIC INVESTIGATIONS OF POST-DOPING OF POROUS SILICA GELS WITH CdS NANOPARTICLES

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Semiconducting nanocrystal-based systems are called upon to be used for a large variety of applications including photovoltaic technology, electronics and optically-active components for telecommunications. Many of the properties depend strongly on the size of these nanoparticles, thus lying somewhere between those of bulk materials and those of molecules. The quantum confinement of the charge carriers within the nanoparticles or quantum dots (QD) leads to the appearance of discrete exciton levels, and as a result the occurrence of optical nonlinearities much greater than for bulk crystals of the same composition. Hence, these systems are regarded as potential non-linear elements for all-optical devices. For this kind of application, the QD are usually inserted in a matrix, often a glass. Silica materials are ideal as matrices because of their excellent mechanical, thermal and optical properties, as well as the fact that these systems are compatible with current optical fibers.

Because of the sensitivity of the QD to high temperatures, the best way of inserting them in a matrix is by post-doping a porous material. In the present work, silica matrices were prepared using a sol-gel process which yields porous materials with variable and closely reproducible pore sizes. Tetramethyl orthosilicate (TMOS) was selected as the suitable precursor. In order to systemize the control of the nanostructure of the derived materials, the densification state and the porous texture of the resultant gels were followed using Raman spectroscopy and nitrogen adsorption-desorption measurements.

The selected gels were introduced into solutions of CdS precursors. The systems obtained were characterized by Raman spectroscopy which is a suitable tool to check the presence of CdS nanoparticles in the silica matrix even at low concentrations. The driving idea of the present work was to study the influence of the nature of the cadmium and sulfur precursors on the porosity of the resulting matrix, as well as on the quantity and size distribution of the CdS QD. For this investigation, Raman and photoluminescence spectroscopic data were correlated with results of nitrogen adsorption-desorption measurements. It is found that the precursor has a strong influence on the size distribution of the resulting QD.

EVOLUTION OF Si-O-Si STRETCHING MODE OF SiO_2 AT THE OBLIQUE INCIDENCE USING FTIR DURING THE FORMATION OF Ge AND Si NANOCRYSTALS BY ION IMPLANTATION AND SPUTTERING

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Fourier Transform Infrared Spectroscopy (FTIR) has been employed to monitor and understand structural variations in SiO_2 during the formation of Si and Ge nanocrystal by sputtering and ion implantation as a function of processing parameters. FTIR measurement has been carried out at an angle of incidence 40°. The Si-O-Si stretching mode has been deconvoluted to show the evolution of SiO_2 and/or SiO_x films during the annealing process. The integrated area, full width half maximum (FWHM) and the shifts in the peak positions have been correlated with the change of the film stoichiometry and nanocrystal formation. It was shown that the recovery process in the SiO_2 matrix is quite different in Si and Ge implanted samples and Si and Ge sputtered samples. The deformation resulted by Ge atoms in the matrix can be recovered by annealing the implanted samples at lower temperatures than that by Si atoms. For the samples prepared by sputtering, the recovery of the matrix was shown to be similar to implanted samples except that the recovery rate is smaller. It was shown that the formation kinetics of Ge and Si nanocrystals can be studied by this technique as the nanocrystal formation is directly correlated with the matrix recovery.

SPECTROSCOPIC AND AFM STUDIES OF DNA:SWNT HYBRIDS

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The outstanding mechanical and electrical properties, chemical stability of carbon nanotubes open the door for the development of new bionanotechnolgy. The first step that should be done in this direction is realization of biocompatibility of the carbon nanotubes. This problem can be resolved by a surface functionalization of nanotubes. To preserve the unique physical properties of single-walled carbon nanotubes (SWNTs), noncovalent functionalization is usually used [1]. Water solulable polymers are good candidates for this purpose, and DNA is the best from them [2,3] because this polymer itself, in addition to execution of biocompatibility of the carbon nanotubes, possesses a recognition function that can simplify elaboration of biological sensors.

In this report results of a study on hybrids consisted of SWNTs and ultrasonically fragmented double-stranded (fds-) DNA and single-stranded (ss-) DNA are presented. Aqueous suspensions of fds- or ss-DNA:SWNTs have been investigated by near IR luminescence, Raman, IR- and UV- absorption spectroscopy. According to gel-electrophoresis, the lengths of the polymer fragments after a 30 min sonication (44 kHz, 1W) were 500-100 base pairs. The comparative analysis of the IR and UV spectra taken on native, ss and fds-DNA points to the presence of both ds- and ss-regions in the fragments. It is assumed that the formation of fds-DNA:SWNTs hybrids starts due to the interaction between untwisted ss-regions of DNA and a nanotube: the strands wrap on a tube and thus create an "anchor" for the whole polymer. The interaction of the fds-DNA with the nanotube surface thermostabilizes the ds-structure of the polymer.

AFM investigation shown that ss-DNA fragments wrapped around the tube form a few layers of the polymer on the nanotube surface, with a thickness of each layer about 0.5 nm. Fragmented double-stranded DNA wraps around the nanotube too but also has compacted structures attached to the tubes. Compacted structures are built up due to bound short fragments of ds-DNA. Different fragments attach one to another due to the hybridization of two complementary end parts of fds-DNA, based on the DNA sequence-specific pairing interaction.

The linear dependence of the DNA melting temperature on the logarithm of the Na^+ concentration for solutions with and without SWNTs was determined. For the fds-DNA:SWNTs solution the slope of this dependence decreases. These dependences were used to estimate the negative charges density on the polymer. It turns out that the DNA interaction with the SWNT decreases charges density that leads to stabilization of the double helix. The phenomenon observed can be attributed to the positive image charge induced by the negative charges of the phosphates groups of DNA on the surface of metallic nanotubes.

ACKNOWLEDGMENTS

This work was supported partly by Science and Technology Center in Ukraine (grant 3172) and Ministry of Education and Science of Ukraine (grant M228-2004).

[1] M.J. O'Connell, P. Boul, L.M. Ericson, C. Huffman, Y.H. Wang, E. Haroz, R.H. Hauge, R.B. Weisman, R.E. Smalley. Chem Phys Lett 342 (2001) 265

[2] M. Zheng, A. Jagota, E. Semke, B. Diner, R. Mclean, S. Lustig, R. Richardson and N.Tassi, Nature Materials 2 (2003) 338

[3] V.A. Karachevtsev, A.Yu. Glamazda, U. Dettlaff-Weglikowska, V.S. Leontiev, P.V. Mateichenko, S. Roth, A.M. Rao, Carbon 44 (2006) 1292

SPECTROSCOPIC STUDIES ON SELF-SUPPORTING MULTI-WALL CARBON NANOTUBE BASED COMPOSITE FILMS FOR SENSOR APPLICATIONS

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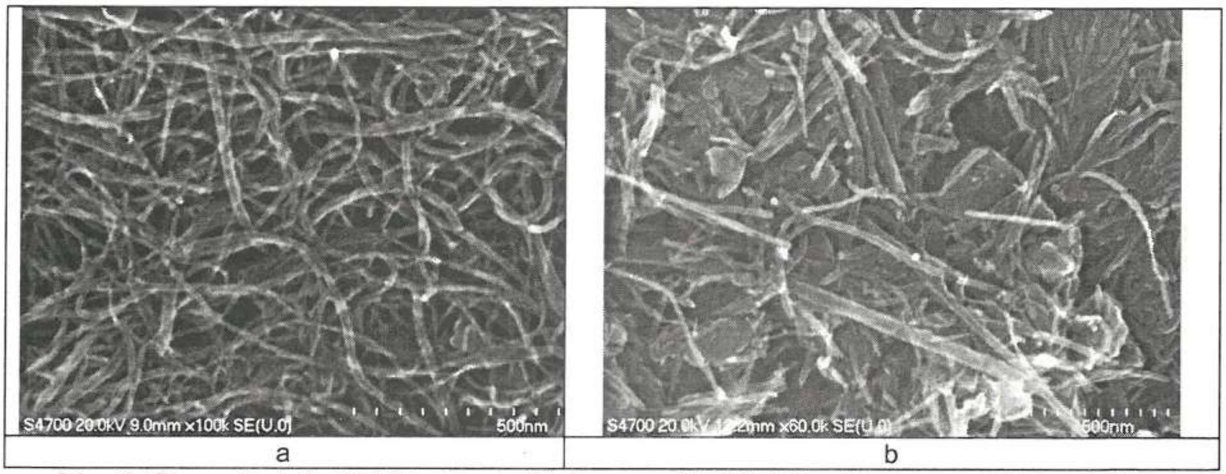
Sensorics is a rapidly expanding field of carbon nanotube application research. Besides the well-known single-wall carbon nanotubes, multi-wall carbon nanotubes (MWCNTs) can also be utilized as gas sensors[1]. The selectivity of carbon nanotube sensors can be improved either by decorating the nanotubes with functional groups and utilizing the selective adsorption of the target molecules on these centers or by developing a nanocomposite architecture consisting of inorganic nanoparticles dispersed in an unfunctionalized MWCNT matrix[2]. In this latter case, the MWCNT matrix can be prepared by the inexpensive filtration method (buckypaper) and the improved sensor performance is thought to originate from the special characteristics of the MWCNT–nanoparticle–target molecule triple interface. Nanoparticles exhibiting sensor behavior on their own are especially well-suited for this purpose.

In this contribution we report on our observations on the structure and sensor performance of self-supporting MWCNT based nanocomposite films containing V_2O_5, $BaTiO_3$, SnO_2, Cu_2O and Pt nanoparticles (Figure 1). The morphology of the composites is studied by electron microscopy whereas the structure of the active MWCNT-nanoparticle interface is probed by IR, Raman and XPS spectroscopy. Our results offer new insight into the sensing mechanism of the studied nanocomposite films.



a b

Fig. 1: Characteristic SEM images of (a) a pure MWCNT buckypaper matrix and (b) a MWCNT–V_2O_5 nanorod (10 w%) nanocomposite film offering improved sensing properties.

[1] O.K. Varghese, P.D. Kichambre, D. Gong, K.G. Ong, E.C. Dickey and C.A. Grimes, Sens. & Act. B-Chem. 81 (2001) 32.
[2] N. Sinha, J.Z. Ma and J.T.W. Yeow, J. Nanosci. Nanotech. 6 (2006) 573.

THE FT-IR AND RAMAN SPECTROSCOPIC STUDIES OF β-$FeSi_2$ GROWTH ON Si(100) AND Si(111) SUBSTRATES

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The β-$FeSi_2$ thin films have been prepared by unbalanced magnetron sputtering on Si(100) and Si(111) substrates. The substrates were sputter etched by neutral molecular source before coating process. This process causes defects and dislocations which provide iron to be diffused into silicon much faster. The silicon substrates were investigated by Fourier-transform infrared (FT-IR) spectroscopy. The Infrared transmittance spectra show the variation in spectrum of silicon band after the etching process. Crystalline structures of the β-$FeSi_2$ films were determinated by X-ray diffraction (XRD) analysis and Raman spectroscopy. We observed two strong spectral peaks due to the symmetric and anti-symmetric vibrations in the molecular structure. We investigated the effects of deposition time on polycrystalline β-$FeSi_2$ using Raman spectroscopy.

CHARCTERIZATION OF MODIFIED ZIRCONIA COATINGS BY FTIR SPECTROSCOPY

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Metal alloys are widely used in medicine, e.g.. for bridges and other prosthetic constructions in dentistry. The nature of their surface can directly influence cellular response, ultimately affecting the rate and quality of new tissue formation. Titanium and its alloys used as implants are usually covered with various kinds of layers in order to improve their properties[1]. It is known that the sol-gel is a method which allows to form coatings on metal and it has several advantages[2-3]. The bioinert ceramic materials, for example alumina and zirconia, have attractive properties, such as strength and fracture for medical applications[4]. The aim of this work has been to examine zirconia coatings modified by various admixtures (calcium, silica, hydroxyapatite) obtained by sol-gel method on titanium and its alloys. Additionally their biological activity in synthetic body fluids has been investigated.. The changes in phase composition of the coatings have been determined using FTIR reflection technique. Scanning electron microscopy with X-ray microanalysis has been used as the complementary measurement.

[1] I. Ozcan, H. Uysal „*Effects of silicon coating on bond strength of two different titanium ceramic to titanium*" Dental Materials 21 (2005) 773.

[2] A. Stoch, W. Jastrzębski, E. Długoń, W. Lejda, B. Trybalska, G.J. Stoch, A. Adamczyk "*Sol-gel hydroxyapatite coatings on titanium and its alloy Ti6Al4V*" Journal of Molecular Structure" 744-747 (2005) 633.

[3] C. Paluszkiewicz, A. Stoch „*FTIR microscopic imaging of metal-ceramic joints*" Vibrational Spectroscopy 35 (2004)183.

[4] A. Rapacz-Kmita., A. Ślósarczyk, Z. Paszkiewicz, C. Paluszkiewwicz "*Phase stability of HAp-ZrO$_2$ composites for bone replacement*" Journal of Molecular Structure, 704 (2004) 333.

THE STRUCTURAL PROPERTIES OF CeO_2 THIN FILMS GROWN ON Si(100) AND GLASS SUBSTRATES BY PULSED e-BEAM

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The cerium dioxide (CeO_2) thin films were grown on glass and Si(100) substrates by pulsed e-beam evaporation method at room temperature. Prior to coating process the structural of bulk CeO_2 were determined by micro-Raman spectroscopy. The structure of CeO_2 thin films were investigated by X-Ray Diffraction (XRD) analysis, Fourier-transform infrared (FT-IR) and Raman spectroscopy. Surface properties of CeO_2 films were found to be strongly dependent on the surface conditions of the substrates.

ADSORPTION AND INTERACTION OF 5-FLUOROURACIL WITH MONTMORILLONITE AND SAPONITE BY FT-IR SPECTROSCOPY

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5-fluorouracil (5-FU) is one of the oldest chemotherapy drugs, and has been around and in use for decades. It is an active medicine against many cancers and effectively blocks the replication of DNA viruses. Montmorillonite and saponite are belong to smectite group of clays and are composed of aluminosilicate layers stacked one above the other. It is well known that smectites can accommodate various types of compounds in its interlayer space to give an intercalation type of inclusion compounds. In a previous study [1] 5-FU has been confirmed to intercalate into the layers of montmorillonite. In this study the adsorption and interaction of 5-fluorouracil by montmorillonite and saponite have been investigated using FT-IR spectrometry. The aim of this study is to investigate the interaction of 5FU with smectite group of clays. Adsorption capacity of the clays studied for 5-fluorouracil is compared.

The anharmonic vibrational spectra of the free 5-FU and 5-FU interacting with $Al(OH)_3$ have also been calculated at the DFT/B3LYP level with 6-31++G(d,p) basis set, in order to investigate how coordination to Lewis acidic centers effects the vibrational wavenumbers of 5-FU.

Acknowledgement
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Reference

[1] F.H. Lin, Y.H. Lee, C.H. Jian, J. Wong, M. Shieh, C. Wang, Biomaterials, 23 (2002)1981.

NEW EXPERIMENTAL METHOD FOR IR SPECTROSCOPIC INVESTIGATION OF REACTIONS TAKING PLACE ON SUPPORTED METAL SURFACES

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It is well known in the heterogeneous catalysis that the chemical transformations occur on the metal surface, and both the activity and selectivity of supported noble metal catalysts are influenced by several factors, such as the concentration of noble metal clusters, the number of corners, edges and terraces on the metal particles[1]. The IR spectroscopy gives indispensable information on the elementary steps of heterogeneous transformations, however rather high concentration of catalytically active metal particles are required to obtain high quality spectra. When the concentration of catalytic metal particles is low, the bands in the registered spectra have low intensities hindering most of the information. In this paper we report on a new method, which allows us to follow the reactions taking place on the surface of supported metal catalysts.

Platinum nanoparticles were prepared as described elsewhere[2]. Samples containing 0.1 w% Pt nanoparticles supported on SBA-15[3] were synthesized by different methods. IR measurements were carried out in an *in situ* IR cell using self supported wafers. The adsorption and transformation of cyclohexene over the catalyst were carried out loading cyclohexene or cyclohexene/hydrogen mixture and the spectra both of the gas phase and the adsorbed phase were monitored in time.

During the adsorption of cyclohexene, 1,3- and 1,4-cyclohexadiene and benzene on SBA-15 silicate support in the absence of platinum nanoparticles no changes were observed in the spectra even at high temperature showing that the SBA-15 is inactive in the transformation of these compounds.

Upon introduction cyclohexene, 1,3- cyclohexadiene, 1,4- cyclohexadiene or benzene into the cell containing Pt/SBA-15 wafer at ambient temperature either in the presence or in the absence of hydrogen, new bands appeared attributed to the adsorbed species and simultaneously the OH band of the silicate was shifted to lower wavelength. Upon heating these systems different changes were observed both in the gas phase and in the adsorbed phase.

The advantage of such a combined IR spectroscopic measurement is the parallel investigation of the catalyst surface and the gas phase. From this it follows, that one has much greater chance to observe even small differences in the nature of surface species, opening new surface reaction pathways, accumulation one of the surface intermediate or other changes remaining locked for the analysis only the gas phase or investigation of surface transformation separately and not simultaneously.

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[1] G.C. Bond, Heterogenous Catalysis: Principles and Applications, Oxford University Press, (1987); G.A. Somorjai, Catal. Lett. 9 (1991) , 311

[2] A. Miyazaki, I. Balint, Y. Nakano, J. Nanoparticle Research, 5 (2003) 69; W. Tu, H. Liu, Y. Tang, J. Mol. Catal. A: Chem., 159 (2000) 115

[3] M.S. Morey, S. O'Brien, S. Schwarz, G.D. Stucky, Chem. Mater. 12 (2000) 898

AN INFRARED STUDY ON LANGMUIR-BLODGETT FILMS OF 12,13-BIS(HYDROXYIMINO)-11,14-DIAZATETRACOSANE

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In the present study, Fourier Transform Infrared (FTIR), Grazing Angle Infrared (GAIR) and Horizontal Attenuated Total Reflectance (HATR) techniques were used to characterize Langmuir-Blodgett (LB) films of 12,13-bis(hydroxyimino)-11,14-diazatetracosane (DTC)[1] deposited on an aluminium plated substrate. The LB films of DTC were prepared successfully by transferring onto the solid substrate. The molecular structure of LB films was investigated by comparing the GAIR and HTAR spectra. The results suggest that the alkyl chains in DTC are nearly in all-trans conformational state and the alkyl chain tilt, which is the angle between the axis which bisects the C-C bonds and the surface normal, are quite large[2,3]. The splitting of the bands due to the methylene scissoring mode indicates that in LB films of DTC alkyl chains are packed in either an orthorhombic or a monoclinic structure with an orthorhombic subcell containing two mutually orthogonal molecules[3].

[1] I. Gürol, V. Ahsen, Synth. React. Inorg. Met. Org. Chem. 31 (1) (2001) 127.
[2] C. Topacli, A. Topacli, B. Teşneli, T. Richardson, İ. Gürol and V. Ahsen, Journal of Molecular Structure, 752 (1-3) (2005) 192.
[3] C. Topacli, A. Topacli, B. Teşneli, T. Richardson, G. Gümüş and V. Ahsen, Vibrational Spectroscopy, 40 (1) (2006) 20.

SPONTANEOUS COATING OF SOME METAL SURFACES WITH POLYMERIC MESHES AND A NOVEL TECHNIQUE FOR ONLINE MONITORING OF THE POLYMERIZATION KINETICS

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Polymers and metals come into contact in many areas of modern technology. The properties of polymer molecules adsorbed onto metal surfaces are of major importance in applications such as adhesion, wetting, corrosion protection, electrochemistry, biocompatibility, colloid stabilization, microelectronics and many other areas. Those applications include technological domains as the aeronautical and space industries, electronics, packaging and automobile manufacture etc. But the techniques used for performing strong coatings are mostly very sophisticated and expensive. In our study, we discovered some kind of monomers which start to polymerize spontaneously around some metal surfaces (like *steel*, *copper*, *silver*) and cover it as a three dimensional mesh when some cross-linker added into the polymer solution. The metals can be coated in different thickness as a function of the coating time. The compactness or strictness changes with the concentration of the pre-polymer solution. The trace amount of fluorescence molecules (probes) added to the pre-polymerization solution binds to the polymer strands, and thus the number of the free probe molecules in the solution decreases during the course of the coating. This technique enables us to monitor the amount of the polymer deposited on the metal surface in real time by measuring the fluorescence intensity of the free probes. In addition to the technological importance of coating the metals with a polymer mesh, the *coated mass-time* curve, shown in the Figure 1 as an example, can be used for online monitoring of the monomer conversion, and thus observing the polymerization kinetics.

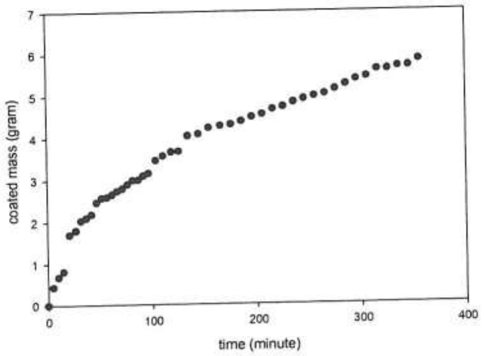

Fig. 1: The coated mass-time curve

[1] Çifter F. "Metallerin Jellerle Kaplanması" Bitirme Tezi, İ.T.Ü.(2003-2004 Bahar Yarıyılı)
[2] Y. Yılmaz, *Phys. Rev. E*, **66**, 05801(2002).
[3] D. Kaya, Ö. Pekcan and Y. Yılmaz, *Phys. Rev. E*, **69**, 016117 (2004)
[4] Y. Yılmaz, A. Alemdar, *Applied Clay Science*, **30**, 154 (2005).
[5] Cole, D. G. "Metal-Polymer İnteraction in a Polymer/Metal Nanocomposite" PRL, 78, 26 (1997)
[6]Kim Dong Ha, Won Ho Jo, "Effect of Substituent of Polymethacrylate on the Interfacial Characteristics between Polymethacrylates and Copper" Macromol. Chem. Phys. 202, 3065-3071 (2001)

P8-8

REVERSIBLE FILM FORMATION FROM PNIPAM MICROGEL PARTICLES BELOW, TG.

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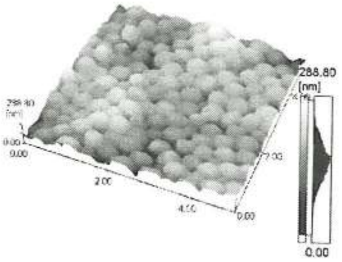
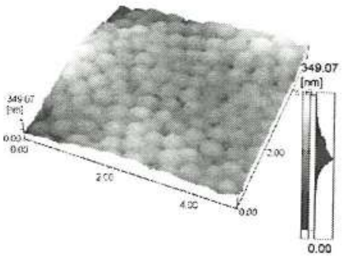
Reversible film formation process from nano-sized Poly (N-isopropylacrylamide) (PNIPAM) microgel particles were studied during heating-cooling cycles at various rates. Photon transmission technique was employed and transmitted photon intensity I_{tr} was monitored during heating-cooling cycles. The increase and decrease in I_{tr} during heating and cooling was explained with the void closure and void reconstruction processes[1-2], and the corresponding activation energies were measured. It was observed that PNIPAM microgels required less energy during reconstruction of voids than their closure.

(a)



(b)



References

1- P. R. Sperry, B.S. Snyder, M.L. O'Dowd and P.M. Lesko, Langmuir, 10, 2619(1994).
2- J. K. Mackenzie and R. Shutlewort, Proc. Phys. Soc. 62, 838(1949).

TEMPERATURE DEPENDENT VIBRATIONAL SPECTROSCOPIC STUDY OF MONTMORILLONITE FROM THE REPUBLIC OF MACEDONIA: I. INTERACTION OF 2-AMINOPYRIMIDINE WITH MONTMORILLONITE

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Montmorillonite belongs to smectite (or montmorillonite-saponite) group of clay minerals. It is composed of aluminosilicate layers stacked one above the other. Each layer has small net negative charge because of isomorphous substitution of ions in the framework. The charge is compensated by interlayer hydrated cations, which are known as exchangeable cations. It is well known that montmorillonite can accommodate various types of compounds in its interlayer space to give an intercalation type of inclusion compounds.

Pyrimidine and pyrimidine derivatives play an important role in biological systems. 2-amino pyrimidine is closely related to isocytosine and isothiocytocine Thus it is find to be interesting to investigate sorption properties of 2-amino pyrimidine by clays using vibrational spectrometry.

In this study, a natural clay from the Republic of Macedonia obtained from Kriva Palanka (near the town of Kumanovo) was used. The XRD analysis indicated that clay sample is montmorillonite and contain dolamite and quartz as impurities. The temperature dependent mid and far-IR spectra of the natural and 2-aminopyrimidine treated clay were recorded in the range from 20 to -273°C by a variable temperature unit. Room temperature FT-Raman spectrum of 2-aminopyrimidine treated clay was also recorded.

Significant changes in the OH stretching, bending and silicate Si-O stretching region of the IR spectra of the natural clay sample have been obtained with the decrease in temperature. The intercalation of 2-aminopyrimidine within clay has been shown by X-ray diffraction to increase the interlayer spacing. IR and Raman spectroscopy indicates that sorbed 2-aminopyrimidine by montmorillonite are mostly coordinated to exchangeable cations directly or indirectly through water bridges. Amino nitrogen is not involved in coordination.

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MICRO-RAMAN STUDIES OF THE "GEL" LAYER ON LEACHED LEAD-SILICATE GLASSES

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In the domain of patrimony, numerous are the glaze coatings on ceramics or glasses which contain notable, though variable, quantities of lead. Lead oxide is, in fact, a powerful fluxing agent which not only helps to simplify the protocols of baking, but also helps to enhance the brightness of the colors obtained in the final material. As early as 1000 BC, the use of lead glazes was a well-known technique. For this reason, one can find innumerable items in museum collections world-wide, which have suffered from the effects of being buried for varying periods of time and under varying conditions of aggressivity. Many of these items, though extremely damaged, are of still of great value, and hence in need of preservation.

While much work has been devoted to the study of leaching processes for alkaline and calco-alkaline glasses, very little has been done with lead-rich systems. Lead, whose role (former or modifier) in a glass matrix depends on its concentration, is of great importance for the evolution of a glass during leaching processes, be it for patrimony table crystal or for waste glasses.

In the present study we have used commercial high-lead content materials (66% PbO and 25% PbO). The attacks were made using both nitric and acetic acids. In order to assure the formation of a relatively thick leached layer, slightly extreme conditions were used: pH 2, a leaching temperature of 90°C, and static and non- renewed conditions. The leaching times were thus quite short, running only up to two months.

Structural evolutions of the glasses, both on the surface and in depth, as a function of leaching time were characterised using micro-Raman spectroscopy. In particular, changes in the plombo-silicate matrix were evidenced by following variations of the Q1, Q2, Q3, Q4 and the silanol bands.

SPECTROSCOPIC STUDIES OF AGEING AND SORPTION ABILITY OF PRECIPITATED MANGANESE-III OXIDES

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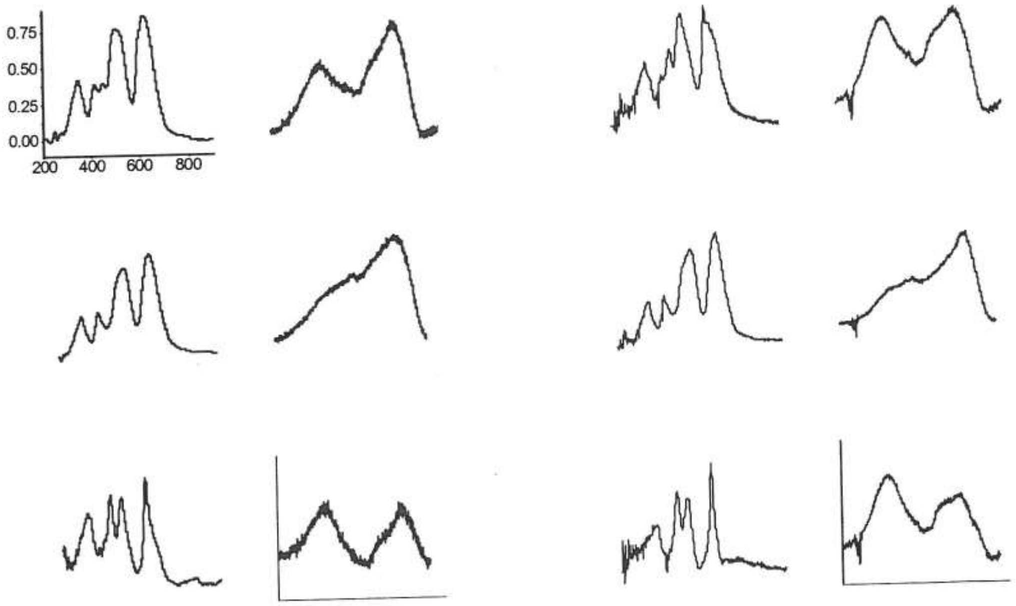
IR spectroscopy is considered one of the most powerful methods of identifying various manganese oxides[1] widely used in analytical practice.[2,3] In this study we apply IR methods for characterization of manganese oxides obtained by reaction of manganese-II salts with hydrogen peroxide. Precipitates obtained in the course of this reaction are amorphous, and their analysis by means of, say, x-ray diffraction methods is impossible.

It is found that fresh precipitates contain haussmanite (Mn_2O_3) and manganite (MnOOH). On ageing, haussmanite undergoes oxidation forming manganite. As an example, two sets of spectra are demonstrated. The fresh sample contains 75 % of haussmanite and 25 % of manganite, and the aged sample contains equal amounts of haussmanite and manganite. Furthermore, on ageing, a new band at ~3300 cm^{-1} appears corresponding to sorption centers on the surface of manganite.



[1] R. M. Potter, G. R. Rossman, *Amer. Mineralogist*, **64** (1979) 1199.
[2] S. V. Gevorkian, L. N. Egorova, V. A. Kutniy, and Yu. V. Sobolevskiy, *Mineral. Sborn.* (Russ.) **43** (1989) 29.
[3] N. D. Ivanova, S. A. Kirillov, and A. B. Mishchenko, *Electrochim. Acta*, **38** (1993) 2305.

LUMINESCENCE OF PRISTINE AND PHOTOPOLYMERIZED FULLERENE FILMS AT 300 AND 5K

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The effect of fullerene films photopolymerization on their luminescence properties was studied. C_{60} films (thickness 0.5 μm) on Si substrates were produced by thermal evaporation from a graphite Knudsen cell. The photopolymerized fullerene films were prepared by a simultaneous thin film deposition and UV-Visible irradiation method[1]. Photopolymerized C_{60} films were obtained by irradiating with a 1000 W Hg lamp during the films deposition in the vacuum chamber. Raman spectroscopy was used to evaluate the polymerization degree of the films produced. The intensity of the $A_g(2)$ "pentagonal pinch" mode at 1468 cm^{-1} in the Raman spectra of pristine C_{60} was used as a sensitive indicator of the presence of polymerized fullerene phase in the sample. In the spectral range 600-1100 nm the luminescence spectra of non-polymerized and polymerized fullerene films were investigated at 300 K and 5 (Fig.1). In comparison with the spectrum of pristine C_{60} film at 300 K, at 5 K it became more structured, and a new band at 695 nm appears the intensity of which decreases under polymerization. For polymerized films the structured luminescence spectrum washed out. The sum of eight separate curves described by the Gaussian function was fitted to the experimental spectrum. The shift of luminescence bands to the red region and an increase of the luminescence intensity were revealed after films polymerization. This phenomenon became apparent significantly in the spectra at 5K. The nature of the emission centers in fullerene is discussed.

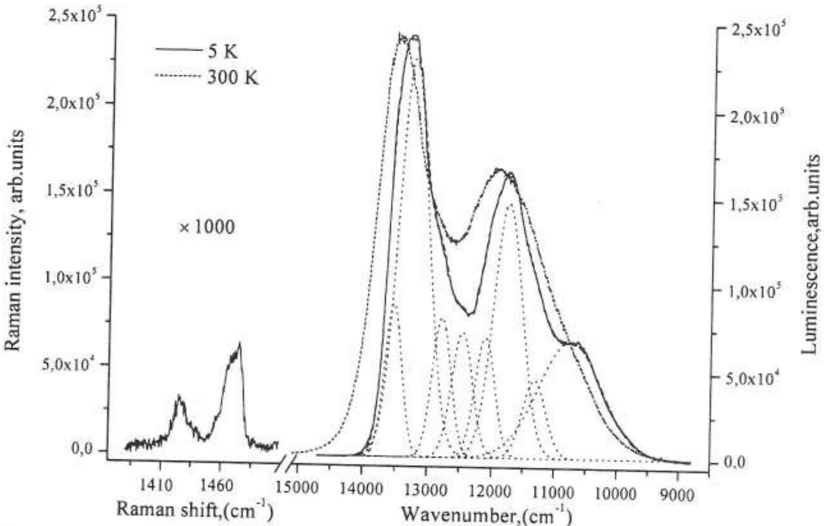

Fig.1 Luminescence spectra (right) and Raman spectrum (left) of polymerized fullerene film on Si substrate, observed at 300 K and 5 K. Spectra were obtained with excitation at 488 nm (Ar^+ laser). Low temperature emission spectrum was fitted by sum of 8 Gaussians (dotted curves).

[1] V. Karachevtsev, P. Mateichenko, N. Nedbailo, A. Peschanskii, A. Plokhotnichenko, O.Vovk, E. Zubarev, A. Rao, Carbon 42 (2004)209.

ACKNOWLEDGMENTS

This work was supported partly by the Ministry of Education and Science of Ukraine (Grant M228-2004) and NATO Reintegration Grant (NUKR.RIG.981328) for Dr. Vlada Pashynska.

P9-1

INFLUENCE OF INCORPORATION OF LIPOPHILIC PHOTOSENSITIZERS INTO LIPOSOMES ON TRIPLET STATES LIFETIMES AND SINGLET OXYGEN PRODUCTION

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Liposomes are generally considered to be suitable carriers of photosensitizers for photodynamic therapy. They are also simplified model of cell membrane. In this contribution excitation energy transfer from lipophilic photosensitizers incorporated into the liposomes to singlet oxygen was investigated. Lipophilic photosensitizers used in photodynamic therapy, such as haematoporphyrin derivatives, protoporphyrin IX, and tetraphenylporphyrin were studied. Aqueous solutions of L-α-phosphatidylcholine large unilamelar vesicles of 100 nm diameter prepared by extrusion were used.

Excitation energy transfer from photosensitizers to singlet oxygen in the liposomes was examined in wide range of photosensitizers concentrations in liposomes by direct detection of the weak near-infrared phosphorescence of photosensitizers (around 840 nm) and singlet oxygen (about 1275 nm) with parallel time and spectral resolution.

The higher complexity of the liposomal systems is reflected in the fact that neither the phosphorescence kinetics of the photosensitizers, nor that of singlet oxygen follows monoexponential decay. The obtained concentration dependencies of corresponding rate-constants are discussed and explained in the frame of a proposed model for photosensitizer – oxygen – lipids interactions based on different distribution of photosensitizers in the liposomal membranes.

ACKNOWLEDGMENTS

This work was supported by project MSM0021620835 from the Ministry of Education of the Czech Republic and by Charles University grant GAUK 235/2005 B FYZ.

TIME RESOLVED TWO-DIMENSIONAL IR SPECTROSCOPY OF A PUSH-PULL DYE MOLECULE: PHENOL BLUE

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Dimethylindoaniline (phenol blue) is a typical push-pull dye molecule, whose sovatochromism is due to the equilibrium between two ground state resonant structures (neutral and separated charges, respectively). Two-dimensional time resolved infrared spectroscopy is employed to investigate the vibrational coupling between CO and CN stretching vibrations, strongly dependent on the electronic structure. The spectra are measured in solvents of different polarity; they provide direct information on i) the vibration-vibration and electron-vibration couplings; ii) the inhomogeneous character of the vibrational transitions in polar solvents; iii) on the relaxation time of the solvent cage. The results are compared with the predictions of the proposed theoretical models.

SINGLET OXYGEN PRODUCTION BY BACTERIOCHLOPHYLL-*c* DIMERS

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Bacteriochlorophyll-*c* (BChl-*c*) is a photosynthetic pigment found in unique light harvesting complexes (LHC) of green photosynthetic bacteria, the chlorosomes. The chlorosomes are the only LHCs, where the pigment organization stems solely from interactions between pigments. In LHCs of all other photosynthetic organisms, the pigment arrangement is maintained by their binding to protein matrices.

Self-assembled BChl-*c* dimers can be prepared in aqueous buffers. Chlorophyll-like molecules in monomeric form are known as efficient generators of singlet oxygen [1, 2]. Singlet oxygen photogeneration by BChl-*c*, -*d* and -*e* monomers in organic solvents was studied in [2, 3]. The photogeneration of singlet oxygen by BChl-*d* and -*e* aggregates, both in chlorosomes and artificially prepared, is described in [3, 4]. In both papers it was shown that the aggregates do not sensitize singlet oxygen due to their short excited state lifetime and consequently low triplet state yield. On the other hand, triplet state kinetics and its quenching by means of singlet oxygen in BChl-*c* dimers is not known yet.

In this contribution, we present time resolved measurements of infrared phosphorescence of BChl-*c* dimers as well as of singlet oxygen. The high sensitive set-up for time and spectral resolved measurements of weak infrared luminescence, which proved to be well suited for detection of singlet oxygen production in photosynthetic systems [5] was used.

Acknowledgement:
This work was supported by project MSM0021620835 from the Ministry of Education of the Czech Republic and by Charles University grant GAUK 235/2005 B FYZ.

References:
[1] Kupper, H., Dedic, R., Svoboda, A., Hala, J., and Kroneck, P. M. H. *Biochim. Biophys. Acta-Gen. Subj.* **1572** (2002) 107–113.
[2] Krasnovsky, A. A., Cheng, P., Blankenship, R. E., Moore, T. A., and Gust, D. *Photochem. Photobiol.* **57** (1993) 324–330.
[3] Arellano, J. B., Melo, T. B., Borrego, C. M., and Naqvi, K. R. *Photochem. Photobiol.* **76** (2002) 373–380.
[4] Krasnovsky, A. A., Lopez, J., Cheng, P., Liddell, P. A., Blankenship, R. E., Moore, T. A., and Gust, D. *Photosynth. Res.* **40** (1994) 191–198.
[5] Dedic, R., Svoboda, A., Psencik, J., Lupinkova, L., Komenda, J., and Hala, J. *J. Lumines.* **102** (2003) 313–317.

SYNTHESIS, EXPERIMENTAL AND THEORETICAL STRUCTURAL AND VIBRATIONAL STUDY OF 2- (2- FURYL)-4, 5- DIHYDROIMIDAZOLE

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In this work we reported the synthesis, and the IR, Raman and RMN spectra of 2-(2- furyl)-4, 5-Dihydroimidazole. The crystalline structure was determined by X-Ray diffraction and it was found that the crystals of the above titled species belong to the orthorhombic system as well as to the Pcab space group. The theoretical molecular structure and vibrational properties were obtained using the Density Functional Theory (DFT) method, with the B3LYP functional and the 6-31 G* and 6-311++G** basis sets, as implemented into GAUSSIAN 03.

A comparative analysis of the different used theoretical methods in supporting the assignment of the spectral bands to the fundamental normal modes of the molecule was performed. The 6-311++G** basis set produced the best results after to accomplish a scaling of the theoretical force constants by using the SQM method by Pulay et al (1). Both the data relatives to its vibrational spectrum and those coming from the theoretical calculations of its molecular geometric parameters in the isolated molecule approach showed the possible existence of two stable conformers for the of 2- (2- furyl)-4, 5-Dihydroimidazole in gas phase. The geometries of both were optimised by means of the mentioned method

References:

(1) P. Pulay, G Fogarasi, G. Pongor, J. E. Boggs, A. Vargha; J. Am. Chem. Soc., **105**, (1983), 7037.

GAS-PHASE STRUCTURE OF TRIFLUOROMETHYL TRIFLUOROMETHANESULFONATE, $CF_3SO_2OCF_3$: CONFORMATIONAL AND VIBRATIONAL PROPERTIES

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$CF_3SO_2OCF_3$ was synthesized by reaction of CF_3SO_2OH with $(CF_3SO_2)_2$ according to the method reported by Hassani et al.[1]. The gas-phase structure was determined using electron diffraction techniques, supported by HF, MP2 and DFT (B3LYP) calculations of the structure and force field. The experimental and theoretical results showed agreement in the description of $CF_3SO_2OCF_3$ as a single conformer with *gauche* orientation of the two CF_3 groups and with a dihedral angle CSOC of 128.6(16)° by GED, compared to 110.8° by theory. Such a *gauche* conformation seems to be a common structural characteristic of covalent sulfonates [2,3].

Infrared and Raman spectra were obtained for the compound, in which bands assignable to 27 out of the expected 30 normal modes of vibration were observed. These experimental data, along with the theoretically calculated force constants, were used to define a Scaled Quantum Mechanical [4] force field for the target molecule, which allowed reproduction of the measured frequencies with a final root-mean-square deviation of 6.0 cm^{-1} after a reliable assignment of the vibrational spectrum.

[1] M.O. Hassani, A. Germain, D. Brunel and A. Commeyras, Tetrahedron Lett., 1981**, 22**, 65.

[2] M. E. Tuttolomondo, L. E. Fernández, A. Navarro, E. L. Varetti and A. Ben Altabef, Spectrochim. Acta, 2004, **60**, 611.

[3] F. Trautner, A. Ben Altabef, L. E. Fernández, E. L. Varetti, H. Oberhammer, Inorg. Chem., 1999, **38,** 3051.

[4] P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, and A. Vargha, J. Am. Chem. Soc., 1983, **105**, 7037.

CALCULATION OF $^1J(C,H)$ COUPLING CONSTANTS IN 1,3-DIOXANES, 1,3-OXATHIANES AND 1,3-DITHIANES

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The conformational equilibria of a number of methyl substituted 1,3-dioxanes **1**, 1,3-oxathianes **2** and 1,3-dithianes **3** were calculated at the HF/6-311G** and B3LYP/6-311G** DFT level of theory using GAUSSIAN03 program package. Beside the *chair* conformers also the energetically adjacent *twist* conformers were considered and the positions of the corresponding conformational equilibria were estimated. On basis of the global energy minima of the conformers, participation in the conformational equilibria, the $^1J_{C,Hax,equ}$ coupling constants were calculated using the Amsterdam Density Functional package (ADF). Comparison of calculated data with the experimental values obtained from ^1H coupled ^{13}C NMR spectra show conformational and configurational influences on $^1J(C,H)$ coupling constants. The PERLIN effect, the influence of the solvent and the ability of this NMR parameter to assign the present conformational equilibria is critically considered.

COMPUTER SIMULATION OF MULTIPLE PULSE NMR SPECTROSCOPY

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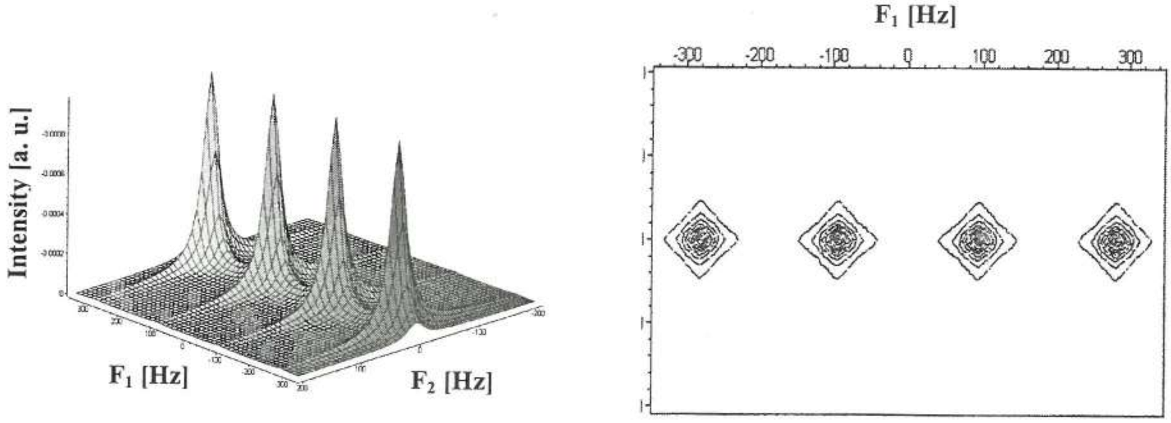
A simulation program in the framework of Maple procedures to analyze one-and two-dimensional muitiple pulse NMR experiments using product operator theory is reported. In our work, the simulation program has been designed to be quite general by the definion of new data type such as the expansion of product operators for weakly coupled IS (I=1/2, S=3/2) spin systems. The application of this simulation program to the analytical descriptions of the 2D J-Resolved NMR experiment has been verified for trimethyltinchloride [$(CH)_3SnCl$] molecule as weakly coupled IS (I = 1/2 = ^{119}Sn, S = 3/2 = ^{35}Cl) spin systems by using product operator formalism. Figure 1 shows the simulated spectrum of weakly coupled ^{119}Sn{^{35}Cl} 2D J-resolved NMR experiment by using this generalized simulation program.



a)

b)

Fig. 1: The simulated spectrum of 2D J-resolved NMR experiment for an IS (I=^{119}Sn=1/2, S=^{35}Cl=3/2) spin system ($\delta_{Sn} = 0Hz$, $J_{Sn\text{-}Cl}$=375 Hz, $T2_{[Sn]}$=0.01 s) a) Stacked plot, b) Contour plot plot

[1] A. Heck, Introduction to Maple, Second ed., Springer-Verlag, New York, (1997).
[2] Kanters. R.P.F., Char, B.W., Addisob. A.W., J.Magn.Reson., A101, (1993) 23
[3] A. Gençten, Ö. Tezel, S. Bahçeli, Chem. Phys. Lett., 351, (2002)109

VIBRATIONAL STRUCTURE OF FREE and HYDROGEN BONDED COMPLEXES OF ISONIAZID : FT-IR, FT-RAMAN and DFT CALCULATIONS

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Isoniazid (isonicotinic acid hydrazide [INH]) is an antimicrobial that has been used as a first-line agent for prophylaxis and treatment of tuberculosis since 1952. In this work we report combined experimental and theoretical study on molecular vibrations of INH. Density functional (DFT) method was used to determine the geometric and vibrational characteristics of INH with the B3LYP/6-31++G(d,p) basis set. Anharmonic corrections to the wavenumbers were done and the results led to a good overall agreement with the observed wavenumbers. A complete assignment of the fundamentals was proposed based on the total energy distribution (TED) calculation. The calculated harmonic wavenumbers were also scaled by a single scaling factor (0.97) and the calculated anharmonic wavenumbers were shown to be superior to the scaled wavenumbers in being much closer to the observed wavenumbers in amount.

To investigate the hydrogen bonding interactions of INH, hydrogen bonded complexes of the molecule (H_2O-INH) were studied, again using DFT method with B3LYP/6-31++G(d,p) basis set both at harmonic and anharmonic levels. To see the solvent effect on the free INH molecule, another calculation was done using DFT/B3LYP/6-31++G(d,p) in connection with PCM (Polarizable Continuum Model - water chosen as the solvent). The FT-IR and FT-Raman spectra of aqueous solution of INH were recorded and the observed spectrum was compared to the results of PCM added calculations.

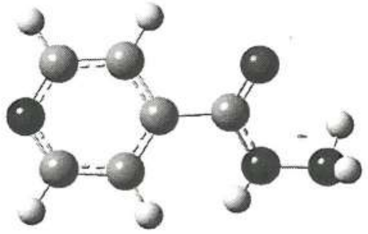

Fig. 1: Molecular model of Isoniazid

P10-6

THEORETICAL AND EXPERIMENTAL STUDIES ON METHYL α-D-GLUCOPYRANOSIDE DERIVATIVES

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Esterification of saccharides is a ubiquitous cellular regulatory mechanism [1]. Sugar derivatives are of great therapeutic interest as antiviral, anti-cancer and anti-HIV agents, as well as components of vaccines [2]. Recently, the presence of glycine and phosphate in bacterial lipopolysaccharides (LPS) has been reported. The glycine is located in the sugar unit, mainly D-gluco- or D-galactopyranosyl, usually phosphorylated at primary hydroxyl group. Determination of the structure of these compounds is difficult, because ester group can migrate and a mixture of isomers is formed. The aim of our research is to predict the structure of synthesized sugar derivatives, using theoretical computational methods and to compare the obtained results with spectroscopic data.

The synthesis of such compound was performed using the direct phosphorylation methyl α-D-glucopyranoside with diphenyl phosphoryl chloride and esterification with protected amino acid group (BOC-glycine). In next step one phenyl group and BOC group were selective removed from methyl [3-(*N*-BOC-glicynyl)-α-D-glucopyranosid-1-yl]-6-diphenylphosphate (Fig. 1).

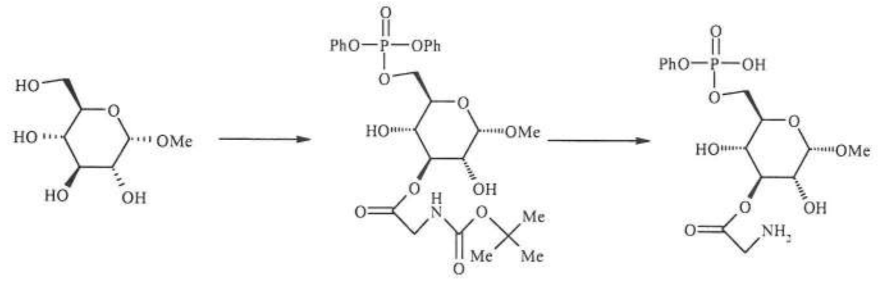

Fig. 1: Synthesis of methyl (3-glicynyl-α-D-glucopyranosid-1-yl)-6-phenylphosphate.

Taking into account the possible linkage sites of the phosphoric acid and glycine radicals, the 12 structures and their zwitterionic forms have been regarded. For all these structures the geometries were optimized performing density functional theory (DFT) calculations at the B3LYP level with the Gaussian 03 software package. To confirm theoretical results, the NMR and Raman measurements were carried out and obtained experimental ^{1}H, ^{13}C, and ^{31}P chemical shifts and Raman spectra are compared with calculated spectroscopic characteristics.

[1] F.W. Westheimer, Science 235 (1987) 1173.
[2] K. Danker, A. Fischer, W. Reutter in C-H. Wong (Ed.), Carbohydrate-based Drug Discovery, Wiley-VCH Gmbh, Weinheim 2003, p. 875 and references therein.

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THE THEORETICAL ANALYSIS OF DERIVATION OF THE DENSITY MATRIX AND METHOD OF SOLUTION FOR A THREE LEVEL ATOM INTERACTING WITH TWO OPTICAL RADIATION FIELDS

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In this study, the density matrix is investigated for a three level atom interacting with two optical radiation fields. Some analytical method of solutions to the coupled equations of density matrix derivation is also realized [1-2].

Key Words : Quantum matrices, density matrix, theoretical analysis

Acknowledgement

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References

[1] S. Sengupta, A. Chakrabarti Unusual Modes and Photonic gaps in a Vicsek waveguide network (2005)
[2] X. Ren, G. Guo, J. Li, G. Guo, Entanglement of the Hermite-Gaussian modes states of photons (2005)

THEORETICAL NMR AND UV SPECTRA OF SOME CROWN ETHERS: A TDDFT STUDY

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Crown ethers are known for their ability as a chemical separation agent which can bind selectively to the cations of Group 1. The dominant factor in the selectivity is the geometrical fit between the cation and the cavity in the ligand that accomodates it. A series of crown ethers synthesized previously[1] were studied theoretically in terms of their selectivities against Group I cations. Density Functional Theory (DFT) method was used to determine the minimum energy structures of several crown ether complexes by using B3LYP functional at 6-31g(d) level. Then, theoretical UV spectra were obtained by Time-Dependent DFT (TDDFT) and compared to the experimental ones. H-NMR frequncies were also calculated and compared to the real NMR spectra of the molecules. Calculations were repeated for the structures comprised of a single alkali metal cation, Li^+, Na^+, K^+. An example to the molecules in this study is shown in Fig.1. UV spectral informations were used to obtain a correlation between the theoretical calculations of the complexes with and without ion and the ion selectivities measured experimentally from the steady state emission fluorescence spectra of free and cationic solutions of chromenone crown ethers in acetonitrile.

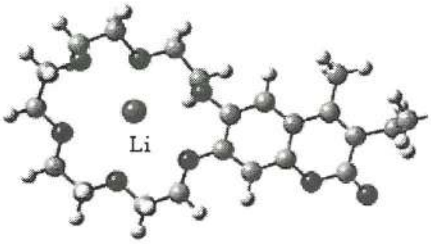

Fig. 1: Optimized geometry of Li^+ bearing structure of 20-Ethyl-21-methyl 2,3,5,6,8,9,11, 12,14,15-nonahydro-18*H*-[1,4,7,10,13,16]hexaoxacyclo- octadecino[2,3-*g*]chromen-18-one

[1] Tiftikci E., Erk C., J.of Heterocyclic Chem., 41(6), pp.867-871, 2004.

THEORETICAL STUDY OF THE MOLECULAR CONFORMATION OF TRIETHYLBROMOSILANE AND APPLICATION TO THE STUDY OF ITS IR AND RAMAN SPECTRA

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Up to six conformations of the triethylbromosilane molecule (shown in Fig. 1) has demonstrated to be real minima of its potential energy surface, one of C_3 symmetry, two of C_s symmetry, and three of C_1 symmetry.

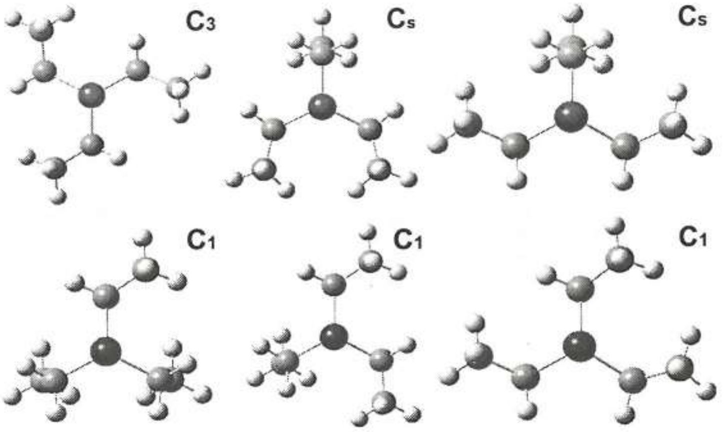

Fig. 1 Different molecular conformations defined for the triethylbromosilane molecule.

Each conformer's structure was optimised at DFT/B3LYP and ab-initio/MP2 level using the 6-31G*, DZP+diff and aug-cc-pVDZ basis sets.

These optimised structures have been taken as starting point for the later analysis of the experimental features observed in its vibrational spectra. The IR spectra (of the liquid and gas phase) and the Raman spectra (of the liquid phase) of the triethylbromosilane molecule were newly recorded and several splittings were observed in certain vibrational bands of the IR and Raman spectra of the liquid phase that could only be explained if we consider the presence of different conformers in the sample.

The correct vibrational assignment is supported by theoretical calculations at B3LYP level, combined with the standard split 6-31G* and the Huzinaga's type basis set called DZP+diff, and the use of the SQM methodology.

THEORETICAL STUDIES OF MOLECULAR STRUCTURE AND VIBRATIONAL SPECTRA OF FREE AND HYDROGEN BONDED COMPLEXES OF SULFANILAMIDE

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Sulfanilamides were widely used as effective chemotherapeutic agents for the prevention and cure of bacterial infections in humans. Moreover, sulfa drugs are synthetic antimicrobial agents that contain the sulfonamide group. In bacteria, sulfa drugs act as competitive inhibitors of para-Aminobenzoic acid (PABA), a substrate of the enzyme dihydropteroate synthetase. This reaction is necessary in these organisms for the synthesis of folic acid.

In this work, the vibrational spectra of free sulfanilamide and hydrogen bonded complexes between sulfanilamide and water were calculated. In the ground states, the geometry optimisation and frequency calculations of sulfanilamide and sulfanilamide-H_2O complex were performed using HF and DFT/B3LYP levels of theory, employing 6-31G++(d,p) basis set. A complete assignment of the fundamentals was proposed based on the total energy distribution (TED) calculation. The calculated wavenumbers were scaled by using two different scale factors and then compared to the experimental IR and Raman wavenumbers.

P10-11

LINEAR, NONLINEAR OPTICAL PROPERTIES AND CONFORMATIONAL ANALYSIS OF 3-PHENYLTHIOPHENE AND ITS FLUORO DERIVATIVES A THEORETICAL STUDY

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The energies, dipole moments (μ), HOMO-LUMO energy differences (ΔE), polarizability (α) and hyperpolarizability (β) values of 3- phenylthiophene (PT) and its fluoro-substitued derivatives (3-(2-fluorophenyl)thiophene (2-FPT), 3-(3-fluorophenyl)thiophene (3-FPT) and 3-(4-fluorophenyl)thiophene (4-FPT)) are investigated by GAUSSIAN 98W program package in the gas-phase as a function of the torsional angle. For each molecule, geometrical parameters were obtained using ab initio [Hartree-Fock (HF/6-31++G**, 6-311++G**) and second-order Møller-Plesset (MP2/6-31++G**)] and Density Functional Theory (DFT/B3LYP/6-31++G**, 6-311++G**) levels of theory. The effect of the position of fluorine substituent on structural parameters, on dipole moments and on torsional potentials is examined. The frontier molecular orbital calculations clearly show the inverse relationship of HOMO-LUMO energy differences with their polarizabilities (Fig.1). The $\lambda_{\max}$ values are calculated from the HOMO-LUMO energy differences.

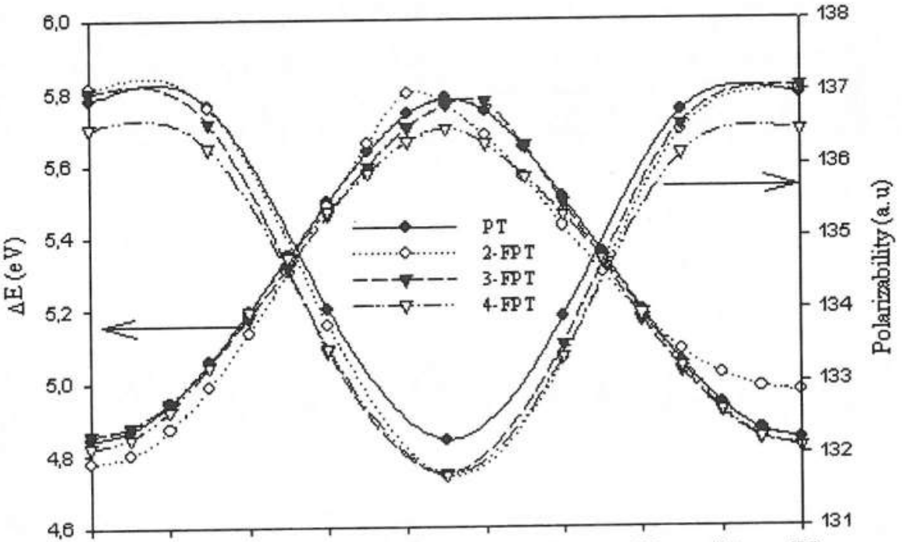

Fig. 1: The dependence of HOMO-LUMO energy difference and polarizability curves obtain, B3LYP/ 6-31++G** calculations, on the torsion angle for PT, 2-FPT, 3-FPT and 4-FPT

TORSIONAL BARRIERS AND NONLINEAR OPTICAL (NLO) PROPERTIES OF PHENYLTRIAZINES

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The torsional behaviour and nonlinear optical properties of biphenyl like molecules has been subject of many experimental and theoretical studies[1-8] because of their potential scientific and technological importance. In this study, the torsional barriers and nonlinear optical properties (nlo) for all phenyltriazine molecules were calculated by using Hartree-Fock (HF) theory and density functional theory via B3LYP hybrid approaches with the 6-31++G(d, p) basis set. The calculated properties are electronic energy, dipole moment, HOMO-LUMO energies, polarizability (α), anisotropy of polarizability ($\Delta\alpha$) and first hyperpolarizability (β) at equilibrium geometry and their torsional dependence, angle between phenyl and triazine ring, from 0° to 180°.

[1] J.W. Emsley, D. S. Stephenson, J. C. Lindon, L. Lunazzi and S. Pulga, J. Chem. Soc. (Perkin II), 14 (1975) 1541.
[2] F. Lelj, N. Russo, and G. Chidichimo, Chem. Phys. Lett., 69 (1980) 530.
[3] C.W. Cumper, R. F.A. Ginman and A.I. Vogel, J. Chem. Soc., (1962) 4518.
[4] M. A. V. Riberio da Silva, M. A. R. Matos, C. A. Rio, V. M. F. Morais, J. Wang, G. Niclos, J. S. Chickos, J. Phys. Chem. A ,104 (2000)1774.
[5] V. Barone, L. Commisso, F. Lelj, N. Russo,Tetrahedron, 41(1985)1915
[6] S. T. Howard, I.A. Fallis, D.J. Willock , Mol. Phys., 97 (1999) 913.
[7] M. Rumi and G. Zerbi, Chem. Phys., 242 (1999) 123.
[8] H. Alyar, M. Bahat, E. Kasap, Z. Kantarcı, Czech. J. Phys., 56 (2006), in press.

PRODUCT OPERATOR THEORY OF 2D MAXY–HMQC NMR SPECTROSCOPY FOR CD_n GROUPS

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Two–dimensional liquid–state NMR experiments containing selective pulse angles allow enhancing more information than conventional ones in complex molecules such as 2D DEPT–HMQC[1], 2D MAXY–HMQC[2]. In 2D MAXY–HMQC NMR experiment, both multiplicity information of MAXY[3] and chemical shift information of HMQC[4] are observed in two–dimension. Product operator formalism is widely used for analytical description of these experiments for weakly coupled spin systems[5-8]. In this study, analytical description of 2D MAXY–HMQC NMR experiment is demonstrated using product operator formalism for $IS_n(I=\frac{1}{2}, S=1; n=1, 2, 3)$ spin systems. Analytical calculations are performed by a program written in Mathematica. Density matrix operators at the end of the experiment are obtained as σ_{12} for IS, IS_2 and IS_3 spin systems. Then, obtained $\mathrm{Tr}\left[S_y\sigma_{12}\right]$ values representing the FID signals of the experiment are given in a generalized and normalized form as following:

$$\mathrm{Tr}\left[S_y\sigma_{12}\right](IS_n) = \frac{1}{3^{n-1}}\left(1-2C_{2\theta}\right)^{n-1} S_\theta C_I C_S$$

By using these results, theoretical discussion and experimental suggestions for the sub–spectral editing of CD, CD_2 and CD_3 groups are presented for this experiment.

[1] H. Kessler, P. Schmieder and M. Kurz, J Magn. Reson. **85** (1989) 400.
[2] M. Liu, X-A Mao, C. Ye, J. K. Nicholson and J. C. Lindon, J Magn. Reson. **129** (1997) 67.
[3] M. Liu, R. D. Farrant, J. K. Nichalson and J. C. Lindon, J Magn. Reson. Series A **112** (1995) 208.
[4] P. K. Mandal and A. Majumdar, Conc. Magn. Reson. **20A** (2004) 1.
[5] N. Chandrakumar and S. Subramanian, Modern Techniques in High Resolution FT NMR. New York. Springer 1987.
[6] O. W. Sϕrensen, G. W. Eich, M. H. Levitt, G. Bodenhausen and R. R. Ernst, Prog. NMR Spec. **16** (1983) 163.
[7] İ. Şaka, Ö. Tezel and A. Gençten, Z. Naturforsch, **58a** (2003) 139.
[8] F. J. M. Van de Ven and C. W. Hilbers, J. Magn. Reson. **54** (1983) 512.

DFT STUDY ON VIBRATIONAL SPECTROSCOPY MARKERS OF CONFORMATIONS OF THE CYSTEINE MOLECULE IN THE GAS PHASE

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Cysteine, $NH_2CH(CH_2SH)COOH$, named after the Greek *kustis* meaning bladder, is a naturally occurring hydrophobic amino acid which has a thiol group and is found in most proteins in small quantities. Thanks to its nucleophilic tiol group, with pKa=8.5, in the intracellular milieu it acts as a nucleophilic catalyst easily tuned by its environment. When it is exposed to air it oxidizes to form cystine, which is two cysteine molecules joined by a disulfide bond. Thus, in the extracellular environment, cysteines play a valuable role by crosslinking proteins and by increasing the molecular stability and by supporting the protein secondary structure.

The cysteine molecule is conformationally labile due to possibility for free rotation about the single bonds between the non-hydrogen atoms. In 1995, Gronert and O'Hair considered 324 conformers at the semiempirical level and found 42 of them stable at the ab initio MP2/6-31+G*//HF/6-31G* level [1]. Since that time, the cysteine conformers have been repedetly investigated [2], however, unlike for some other aminoacids [3, 4], the gas phase or matrix isolation IR spectra of cysteine remain unknown. Cysteine crystalizes in either the orthorombic or monoclinic space groups with the molecule as its zwitterionic tautomer [5]. Also in solution, the zwitterion form is the most populated form of cysteine [6].

In this study, we found 51 cysteine conformers stable at the B3LYP and MP2/aug-cc-pVDZ levels. For the most stable eight ($TA^-(R)G^+G^-$, $TA^-(D)TG^+$, $CG^+(L)TG^-$, $TA^-(R)TG^+$, $CG^+(L)G^+G^-$, $TA^-(R)TG^-$, $CG^+(L)G^+G^+$, and $TA^-(R)G^+A^+$) we repeated the calculations by using the aug-cc-pVTZ basis set. It is important that the energetic order of the conformers do change upon both: thermochemical correction for the normal conditions and method change from DFT to MP2. It is also important that not all of them were previously found. For the eight most stable conformers the IR, Raman, and VCD spectra were calculated and interpreted by means of the potential energy distribution analysis (PED). In the PED interpretation refused mixing of the steching, bending, and torsion modes, as well as tried to describe movement of heavy atoms separately from local modes of hydrogens. We tried also to preserve a common set of local coordinations for all set of conformers, however, it was hardly possible. The conformers are geometrically so different, that they vibrate almost as eight different molecules. The IR, Raman, and VCD markers for all the important cysteine conformers are selected and discussed. In such a way, a platform for interpretation of the experimental cysteine vibrational spectra is prepared. Interpretation of the low-temperature IR matrix spectra is in progress.

[1] S. Gronert, R. A. J. O'Hair, J. Am. Chem. Soc., 1995, 117, 2071-2081.
[2] R. Linder, M. Nispel, T. Häber, K. Kleinermanns, Chem. Phys. Lett., 2005, 409, 260.
[3] M. Pecul, Chem. Phys. Lett., 2006, 418, 1.
[3] A. Kaczor, I. D. Reva, L. M. Proniewicz, R. Fausto, J. Phys. Chem. A, 2006, 110, 2360.
[4] S. A. Moggach, S. J. Clark, S. Parsons, Acta. Cryst., Acta Cryst., 2005, E61, o2739.
[5] E. Grunwald, K. C. Chang, P. L. Sklpper, V. K. Anderson, J. Phys. Chem., 1976, 80, 1425.

DFT STUDY OF VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF D-LACTIC ACID–WATER COMPLEXES

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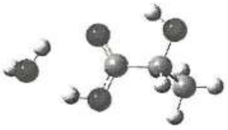
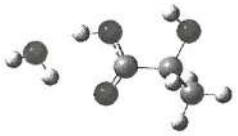
In this study [1] we have presented the results of DFT(B3LYP)/aug-cc-pVDZ calculations of vibrational optical activity spectra for 1 : 1 complexes of chiral D-lactic acid with a water molecule. The main conclusions can be summarized as follows:

1. The calculations predicted the conformer (I) stabilized by a C–OH_A...O=C intramolecular H-bond to be the most stable form. The second stable form (II), higher in energy by ca. 9.2 kJ mol^{-1}, is also stabilized by the intramolecular C–OH_A...OH_C H-bond. Subsequently, more conformers were found, but they were ruled out of further considerations.

2. For each of the conformers I and II, interacting with a water molecule, four stable minima have been found and studied. The complexes with a cyclic intermolecular H-bond between the carboxylic group of the acid and water (Ia and IIa) proved most stable, playing both a proton donor and proton acceptor role. The binding energies of the two most stable complexes do not differ substantially, with values of -38.9 and -40.0 kJ mol^{-1}, for Ia and IIa, respectively. The Gibbs free energy of the Ia complex is ca. 7.5 kJ mol^{-1} lower than that of the IIa complex, and thus the former is predicted to be much more populated in a mixture of these two complexes.



Ia



II a

VA spectroscopy discriminates between lactic acid conformers Ia and IIa, on the basis of frequency shifts for ν(OH_A), ν(C*H), and ν(C=O) where the OH_A hydroxyl group is a proton donor to an intramolecular H-bond. The calculated VCD spectra change when the interacting molecules of D-lactic acid...water assume different configurations. First, after forming a complex with the D-lactic acid molecule, the VCD modes of the achiral water molecule acquire significant rotational strengths, whose signs change in parallel with the geometry of the complex. Second, several VCD bands enable unequivocal differentiation between conformer structures, which may give new insight into the interpretation of vibrational spectra of complex mixtures. As well as for VCD bands such as ν($OH_{W,hb}$) and ν(OHC), which highlight the differences between patterns in the VA and VCD spectra and in this way help interpretation, there are modes like, for example, β$(CH+OH)_1$ and β(OC=O) which change their signs upon a change in the complex structure. Third, the stretching vibration ν(C=O) VCD band has a small rotational strength for a monomeric form of D-lactic acid, whereas it turns quite intense when the carbonyl group is engaged in an intramolecular H-bond. In conclusion, the VCD spectra of intramolecularly interacting molecules can be used as a powerful tool for the structural investigation of intermolecular interactions of chiral molecules, and can yield information complementary to data obtained from other molecular spectroscopy techniques.

[1] J. Sadlej, J. Cz. Dobrowolski, J. E. Rode, M. H. Jamróz, Phys. Chem. Chem. Phys., 2006, 8, 101–113.

P10-16

CONFORMERS AND VIBRATIONAL CIRCULAR DICHROISM (VCD) SPECTRUM: STUDY OF R-(+)-LIMONENE

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Vibrational Circular Dichroism (VCD) is a modern and very useful technique for determining absolute configurations as well as possible conformations of chiral molecules. In order to achieve a suitable interpretation of the VCD spectra of such a type of molecules, previous detailed studies of their structures and vibrational spectra are required.

In this work, the complete study of the VCD spectrum in the middle IR range (1400-900 cm^{-1}, Fig. 1) of the terpene R-(+)-Limonene, in terms of its axial and equatorial conformers, is presented.

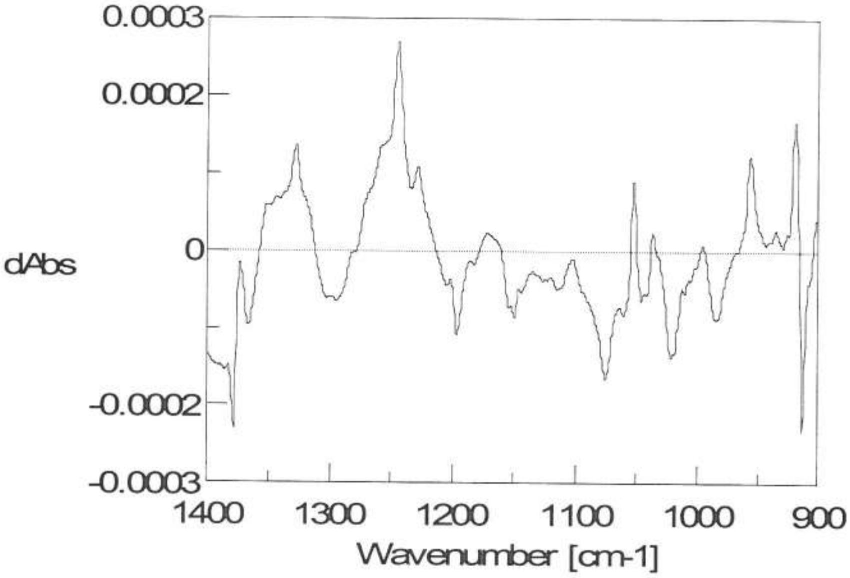

Figure 1. VCD spectrum of R-(+)-Limonene in the 1400-900 cm^{-1} range

Previously, a theoretical study of the molecular structure at DFT/B3LYP/cc- pVDZ level and, for the first time, a complete assignment of its vibrational spectra using the SQM methodology at the same level, was carried out. This study allowed us to improve earlier interpretations[1-3] of the VCD spectrum of R-(+)-Limonene.

[1] P. L. Polavarapu, M. Diem, L. Nafie, *J. Am. Chem. Soc* 102 (17) (1980) 5449-5453.
[2] R. D. Singh, T. A. Keiderling, *J. Am. Chem. Soc.*, 103 (9) (1981) 2387-2394.
[3] E. D. Lipp, L. Nafie, Appl. Spectrosc. 38 (6) (1984) 774-778.

A THEORETICAL VIBRATIONAL SPECTROSCOPIC INVESTIGATION ON FREE 2- AND 3- ETHYL AMINO BENZOATE MOLECULES

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The stable conformers of free 2- and 3- ethyl amino benzoate molecules in electronically ground state were searched by subsequent single point energy calculations carried out at the semi-empirical PM3 theory level, and thereby, the most stable conformers of the two molecules corresponding to the global minima on their potential energy surfaces were defined. The equilibrium geometrical parameters for the most stable conformers were achieved by the geometry optimizations carried out using B3LYP hybrid DFT method and basis sets of different size and type. The harmonic vibrational modes of the molecules and their corresponding frequencies and IR intensities were calculated using again the same method and basis sets. In the light of these calculated spectral data, a successful assignment of the fundamental bands observed in the recorded IR spectra of the two molecules was given. To fit the calculated harmonic frequencies to the experimental frequencies two different scaling procedures, called "Scaled Quantum Mechanics Force Field (SQM FF) methodology" and "Scaling frequencies with dual empirical scale factors", were proceeded independently.

A THEORETICAL IR SPECTROSCOPIC STUDY BASED ON DFT CALCULATIONS FOR FREE MN-15S_2O_3 MALEONITRILE-DITHIACROWN ETHER COMPOUND

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In the light of the electronic structure calculations based on the density functional theory (DFT), a successful assignment of the fundamental bands observed in the recorded IR spectrum of free mn-15S_2O_3 dithiacrown ether compound was given. To fit the harmonic frequencies calculated at the B3LYP/6-31G(d) theory level to the corresponding experimental bands observed in the 400-3000cm^{-1} spectral region, two different scaling procedures, called "Scaled Quantum Mechanics Force Field (SQM FF) methodology" and "Scaling frequencies with dual empirical scale factors", were proceeded independently. Potential energy distribution (PED) calculations were carried out to define the internal coordinate contributions to each normal mode. The effects of one CH_2-O-CH_2 dentate fragment substitution into the macrocyclic ring onto group vibrations and experimental IR fundamental bands associated with them were discussed in detail through a comparison of the corresponding experimental and theoretical IR spectral data of mn-12S_2O_2 and mn-15S_2O_3 molecules

VIBRATIONAL SPECTRA AND THEORETICAL STUDIES ON THE NOVEL ADENOSINE DERIVATIVE

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The influence of substituents on the chemical compound nature can be determined and explained by spectroscopic and quantum-chemical tools. Any substituents, which can complex metal ions, develop a new way of chemical system modification through interaction with metal ions present in solution. Ionophores with substituents based on crown ethers form a new group of compounds with selective biological activity in a presence of metal ions. From this point of view, we present our results on physicochemical features of adenosine modified by attaching crown ether moiety.

Vibrational spectra (FT-IR, FT-Raman and SERS) of adenosine bearing benzo-15-crown ether moiety [N^6-4'-(benzo-15-crown-5)-adenosine, Fig. 1] have been recorded in solid phase (IR, Raman) and in aqueous solution on the silver colloid (SERS). To interpret all the mentioned set of experimental data, the harmonic force fields of the isolated molecule have been calculated after fully geometry optimization at the density functional theory level [B3LYP/6-31G(d)][1]. Some discrepancies have however been found on the comparison between the experimental and theoretical results. They are mainly related to inter- and intramolecular H-bonding occurring in the solid state in which the labile hydrogen atoms are mainly involved. The assignment of the observed vibrational modes has been extensively discussed on the basis of the theoretical results for N^6-4'-(benzo-15-crown-5)-adenosine as well as its basic units, e.g. adenosine and benzo-15-crown ether. On the other hand, the analysis of SERS spectrum indicates that the adenosine and benzene fragment interacts with the silver surface. Adenine lays flat while benzene adopts almost a vertical position in respect to the metal layer. Moreover, charge distribution and aromaticity have been calculated by using GAPT (Generalized Atomic Polar Tensor) and HOMA (Harmonic Oscillator Model of Aromaticity) methods[2], respectively.

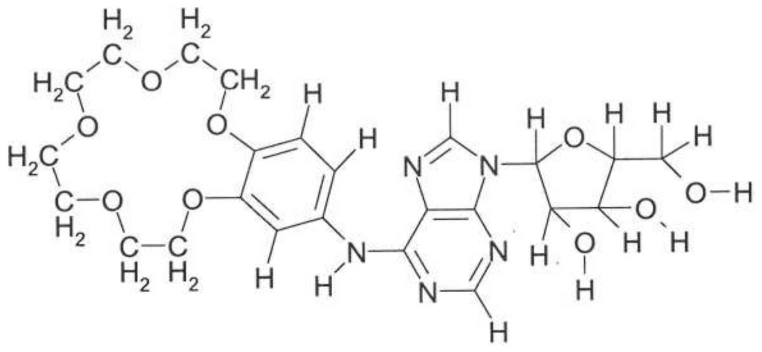

Fig. 1: N^6-4'-(benzo-15-crown-5)-adenosine.

[1] C. Lee, W. Yang, R.G. Parr. Phys. Rev. B37 (1988) 785; A.D. Becke. J. Chem. Phys., 98 (1993) 5648.
[2] J. Cioslowski, J. Amer. Chem. Soc., 111 (1989) 8333; T.M. Krygowski, J. Chem. Inf. Comput. Sci., 33 (1993) 70.

DFT MODELING OF VIBRATIONAL SPECTRA AND AROMATICITY OF THE OXADIAZOLES DERIVATIVES

K. Malek[1], **K. Gebski**[1], **M. Swiatlowska-Szczygiel**[1], **M. Skrabalak**[1], **M. Szczerba**[1], **G. Schroeder**[2], **L.M. Proniewicz**[1,3]

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The oxadiazole compounds, especially aromatically substituted 1,3,4-isomers, are extensively studied because of their interesting electro-optical[1], electronic[2] and biological activities[3]. The wide use of these compounds in medicine, agriculture and industry has stimulated investigations of their chemical properties. Although IR and Raman spectra of the unsubstituted and some disubstituted derivatives have already been published[4], there has been no systematic study of the vibrational structure – activity relationship. Moreover, the detailed assignment of the observed transitions has been carried out rather qualitatively than quantitatively.

In the present work, we report the experimental and calculated IR and Raman spectra for the series of 2-aryl- and 2,5-diaryl-1,3,4-oxadiazoles (Fig. 1) in the spectral region of 400-4000 cm^{-1}. Use of the high-quality DFT method (B3LYP) and basis set [6-311++G(d,p)] led to very good reproduction of the experimental data. Furthermore, calculations of Raman intensities (from Raman scattering activity) and potential energy distribution of normal modes (PED) have been performed for a detailed description of the vibrational spectra. In the analysis of results, we focus also on elucidation of the substituent effect on the chemical nature of the oxadiazole ring.

The presence of π-π stacking in the crystalline state of the title compounds leaned us towards study of their aromatic character also. Among many methods of aromaticity determination, we used the HOMA scheme[5]. In this part of our research, we investigate heteroaromaticity of the oxadiazole ring and its alteration upon various substitution.

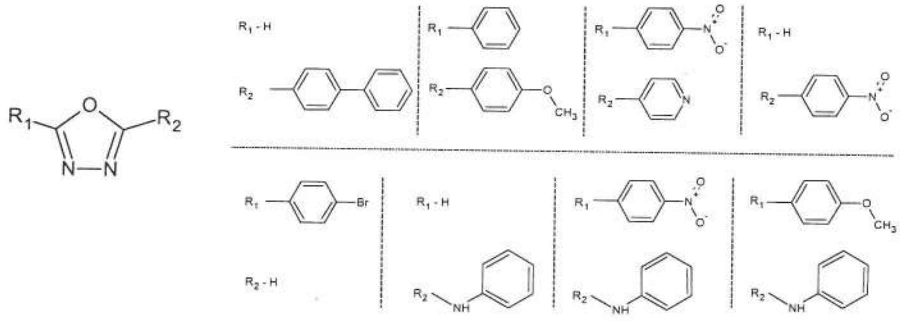

Fig. 1: The 1,3,4-oxadiazoles studied.

[1] B. Schultz, M. Bruma, L. Brehmer, Adv. Mater, 8 (1997) 601.
[2] R. Giebler, et al., Langmuir, 15 (1999) 1291.
[3] H.L. Yale, K.J. Losee, J. Med. Chem., 9 (1996) 478.
[4] A.A. El-Azhary, et al., Spectrochim. Acta, 52A (1996) 33; I. Orgzall, et al., J. Phys. Chem. Solids, 60 (1999) 1949;
[5] T.M. Krygowski, J. Chem. Inf. Comput. Sci., 33 (1993) 70.

ADVANCED DIELECTRIC PERMITTIVITY MODEL OF ANISOTROPIC SINGLE CRYSTALS Zn_3P_2 AND $ZnGeP_2$ IN INFRARED REGION

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Binary and ternary anisotropic diphosphide single crystals are promising for application in non-linear optics, nano-technics, constructing photoelectrical analyzers of polarized radiation, optoelectronic devices, etc.

Advanced model of dielectric permittivity of diphosphide single crystals ZnP_2 and CdP_2 were presented in [1,2]. None of present research papers describes model of dielectric permittivity of Zn_3P_2 and $ZnGeP_2$ in infrared. The aim of this research is obtaining of permittivity model, optical parameters of Zn_3P_2 and $ZnGeP_2$ crystals in infrared region.

Raman and FIR reflection spectra for a set of Zn_3P_2 and $ZnGeP_2$ single crystals samples were measured using polarized radiation: reflection spectra in the range $80 \div 550$ cm^{-1} and Raman spectra in $80 \div 550$ cm^{-1}. Set of infrared- and Raman-active vibrations show itself in infrared reflection and Raman spectra of Zn_3P_2 and $ZnGeP_2$. In present study for the first time the Raman and reflection spectra were used for the first time to obtain mutual coordinated advanced model of dielectric permittivity of Zn_3P_2 and $ZnGeP_2$ in infrared region. Two theoretical forms of model of dielectric permittivity (additive and factorized [3]) were used in order to describe experimental reflection spectra of Zn_3P_2 and $ZnGeP_2$. Contribution of free charge carriers in dielectric permittivity of Zn_3P_2 and $ZnGeP_2$ was included in this model and based on original experimental data. Taking in account plasmon subsystem for the first time allowed us to reach the best coincidence between experimental and theoretical data. Parameters of model of dielectric permittivity were obtained by fitting of the calculated reflection spectra to measured ones. We showed that this model of dielectric permittivity with phonon and plasmon contribution describes reflection spectra of Zn_3P_2 and $ZnGeP_2$ in the best way. Dispersion of complex refractive index, ranges of negative dielectric permittivity of Zn_3P_2 and $ZnGeP_2$ were obtained.

Thus, in the present study we investigated Zn_3P_2 and $ZnGeP_2$ single crystals by IR reflectance and Raman spectroscopy method. Advanced multi-oscillator model of dielectric permittivity for Zn_3P_2 and $ZnGeP_2$ crystals based on original experimental data was obtained.

This research was carried out in frames of CELTAM program.

[1] E.F. Venger, Yu. A. Pasechnik, K.V. Shportko, Journal of Molecular Structure, 744-747, 947 (2005).

[2] J. Baran, Yu. A. Pasechnik, K.V. Shportko, M. Trzebiatowska-Gusowska, E.F. Venger Proc. VIII International Conference on Molecular Spectroscopy. Ladek Zdroj (Poland), 80, (2005).

[3] J.L. Ribeiro. Eur. Phys. J. B 36, 21–26 (2003).

P10-22

INVESTIGATION OF THE FT-IR SPECTRA OF SOME PARTIALLY DEUTERATED AMMIN COMPLEXES

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In order to obtain information on the bands due to vibrations of different types of isotopomeres of ammonia, the FT-IR spectra of a series partially deuterated nickel hexaammin complexes, $[Ni(NH)_6]_6Cl_2$ and some bicomplexes with a general formula $[M'(NH_3)_2][Ni(CN)_4]$, where M' = Ni or Cd were studied. The spectra were recorded in the region between 400 and 4000 cm^{-1}, at room temperature and at liquid nitrogen boiling temperature. The assignments of the absorption bands were made. Due to the exchange of hydrogen by deuterium in ammonia, four types of isotopic species (NH_3, NH_2D, NHD_2, ND_3) are present in the structure of the investigated complexes. Since chemical isolation of the mixed isotopic parent is not possible, the vibrations of all four isotopic species were studied. The corresponding bands due to vibration of all isotopic species of coordinated ammonia were assigned. Along with the experimental studies, also quantum chemical studies of several model systems mimicking the title complexed were carried out – the $Ni(NH_3)^{2+}$ and $Cd(NH_3)^{2+}$. The B3LYP and mPW1PW91 density functional levels of theory were employed, with the 6-31++G(*d,p*) basis sets on all atoms except Cd, for which various effective core potentials were used. Theoretical studies included full geometry optimizations of the mentioned species, followed by subsequent harmonic vibrational analyses of all possible isotopomers. The shifting of the band due to different types of $(NH,D)_3$ groups to low frequencies is in good agreement with the theoretical predictions, but it is different for different types of isotopic species.

QUANTUM CHEMICAL STUDY OF THE PROTON TRANSFER POTENTIAL IN DIHYDROXYHYDROGENMALONATE ANION

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The dixydroxyhydrogenmalonate anion was investigated with quantum chemical methods. The studies included analysis of the potential energy hypersurface of the title ion, subsequent harmonic vibrational analyses of the stationary located points and analysis of the possibility for intramolecular proton transfer.

Several levels of theory were employed for these purposes. Besides the HF and MP2/6-31++G(*d*,*p*) levels, several density-functional theory-based methods were used, such as B3LYP, mPW1PW91 and the HCTH/6-31++G(*d*,*p*). The proton transfer potential was calculated by a pointwise procedure on the basis of IRC methodology and the DRP approach. The Schrödinger equation for a proton moving in the computed double-well potential was solved variationally, *i.e.* by diagonalization of the Hamiltonian matrix.

From the computed energy levels, conclusions about the dynamical aspects of the proton-transfer process were derived, and the rate constant for this process was estimated at the employed levels of theory.

VIBRATIONAL SPECTROSCOPY AS A TOOL FOR EXPLORING THE ACIDITY OF LEWIS SITES ON METAL OXIDE SURFACES. A CLUSTER MODEL QUANTUM CHEMICAL STUDY OF PYRIDINE ADSORBED ON FLUORINATED γ-ALUMINA SURFACES

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The influence of fluorination of γ-alumina surfaces on the acidity of the exposed Lewis acid sites was studied by quantum chemical methods. Experimental studies of the Lewis sites acidity often rely on vibrational spectroscopic investigations of adsorption of small molecular systems on microcrystalline surfaces. The most frequently used test molecule for such purposes is pyridine. In order to provide a more in-depth theoretical insight into the processes of adsorption of pyridine on fluorinated γ-alumina surfaces, and also to support the interpretation of experimental data, a quantum chemical study of the adsorption of this molecule on partially fluorinated γ-alumina surfaces was performed at HF/6-31++G(*d,p*) and B3LYP/6-31++G(*d,p*) levels of theory. Simulations of adsorption phenomena were based on finite-cluster representation of partially fluorinated microcrystalline γ-Al_2O_3 surface. The non-polar (100) and (110) planes of partially fluorinated surface were exposed[1]. Besides the standard potential energy hypersurfaces (PESs) of the considered γ-$Al_2F_xO_y$-pyridine clusters, also the counterpoise-corrected ones were explored at both levels of theory. The computed counterpoise-corrected interaction energies were compared to the values obtained for the corresponding γ-Al_2O_3-pyridine clusters[1]. Conclusions about the magnitude and direction of the charge-transfer interaction in the studied clusters were derived on the basis of NBO analysis, including the second-order perturbation theory analysis of the Fock matrix (or its Kohn-Sham analog). The character of pyridine-γ-$Al_2F_xO_y$ interaction was rationalized on the basis of Bader's theory of atoms in molecules (AIM). Special attention was paid to the spectroscopic manifestations of pyridine adsorption on the studied fluorinated surfaces. In particular, the calculated harmonic vibrational frequency shifts of pyridine ν_8 and ν_{19} internal mode components upon adsorption on partially fluorinated clusters at both levels of theory were compared to the corresponding values in the case of adsorption on non-fluorinated analogues[1]. The purely electrostatic influence of the surface on these intramolecular modes of pyridine was studied by the charge-field perturbation approach, *i.e.* by representing the surface by a suitably chosen set of point charges.

[1] Lj. Pejov, T. Skapin, Chem. Phys. Lett. 400 (2004) 453.

P10-25

FTIR SPECTROSCOPIC AND THEORETICAL STUDIES ON MATRIX ISOLATED THIOACETIC ACID

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The tautomeric $CH_3C(=O)SH \rightleftharpoons CH_3C(=S)OH$ equilibrium in thioacetic acid was studied by DFT/B3LYP calculations, with the 6-31++G** basis set. The compound was also isolated in an argon matrix and the spectra of the monomeric forms assigned.

cis-thione *trans*-thione *cis*-thiol *trans*-thiol

The calculations predicted the *cis*-thiolacetic tautomer as the most stable form, in agreement with the spectroscopic observations. The calculations also provided a general overview of the change in properties like atomic charges, dipole moments, barriers to methyl group internal rotation (Figure 1) and ionization potentials with replacement of the carbonyl by the thiocarbonyl group.

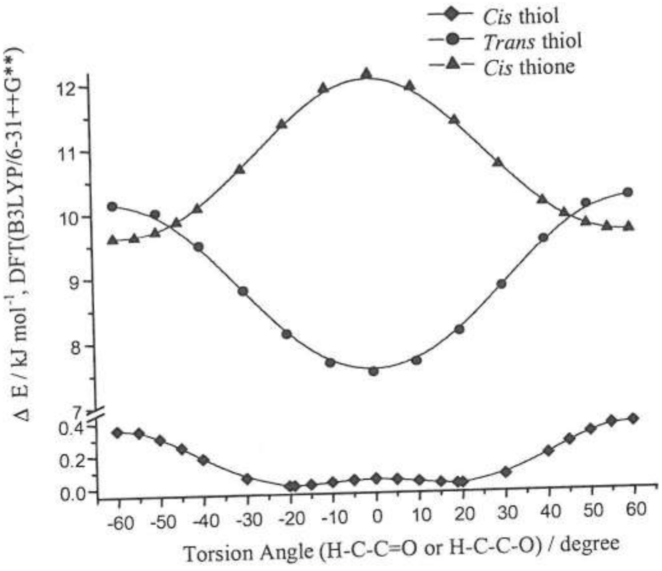

Figure 1. DFT/B3LYP/6-31++G** calculated energies ΔE (kJ mol^{-1}) as a function of the methyl group rotation for *cis* and *trans*-thiol and *cis*-thione tautomers of thioacetic acid.

P10-26

SPECTROSCOPIC AND THEORETICAL DETERMINATION OF ACID DISSOCIATION CONSTANTS OF SOME BENZOTHIAZOLE SCHIFF BASES

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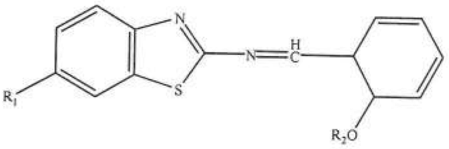
Schiff Bases have been used extensively as ligands in the field of coordination chemistry[1]. Proton transfer reactions in Schiff bases have been studied extensively both experimentally and theoretically in the last three decades[2-3]. The acid dissociation constants have been used in various areas of research, such as stereochemical and conformational structure determinations[4-5]. Following our work on benzothiazole Schiff bases, we are now reporting on the acid dissociation constants of some biological active benzothiazole Schiff bases.

The acid dissociation constants(pK_a) or four biologically active benzothiazole Schiff bases were determined using a UV-vis spectroscospic technique at 25±0.1 °C and theoretical acidity constants (pKa) measurements(investigate) .

Theoretical acidity constants (pKa) measurements procedure which was used in determining can be summarized as follows;

$$B + AH^+ \rightleftharpoons BH^+ + A$$

The aqueous phase acidity constants were determined by using AM1, PM3, PM5 and MNDO semi-empirically calculated physical parameters.



R_1= H R_2= H
R_1= H R_2= CH_3
R_1= CH_3 R_2= H
R_1=CH_3 R_2= CH_3

Scheme 1: Possible protonation Pattern for Studied Molecules 1-4

[1] Callgaris, M.; Randaccio, L. Comprehensive Coordination Chemistry; Wilkinson, G., Ed.; Pergamon: London, 1987; Vol. 2, p 715.
[2] Nagaoka, S.; Itoh, A.; Mukai, K.; Nagashima, U. Investigation of triplet states of benzothiazole and 2-(2'- hyroxyphenyl)benzoxazole by transient absorbtion spectroscopy and ab initio calculations. J. Phys. Chem. 1993, 97, 11385.
[3] Yamagochi, S.; Hamaguchi, H. Chem. Phys.Lett.1994, 227,225.
[4] Brown, H. C; Mc Daniel, O.H.; Haflinger, O. Determination of Organic Structure by Physical Methots; Academic Pres: New York, 1985.
[5]Chilton, J.; Stenlake. J.B. Dissociation constats of some compounds related to lysergic acid. II. Ergometrine, ergometrinine and alkanol-amides of 3-dimethylaminopropionic acid, 1-methylhexahydronicotinic acid and arecaidine j.Pharm. Pharmacol. 1962, 14, 367.

HIGH-RESOLUTION INFRARED STUDY OF GASEOUS OXAZOLE AND COMPARISON WITH THEORETICAL STUDIES

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The five-membered heterocyclic molecules are important constituents in both pharmaceutical and natural products. In recent years the parent compounds have attracted considerable attention for high-resolution (HR) infrared experimental studies as well as *ab initio* theoretical studies, and we have made a major contribution to that study, with analyses of isoxazole [1], isothiazole [2], 1,2,5-thiadiazole [3] and other related compounds. Owing to the spectral resolution available in contemporary infrared Fourier transform spectrometers, the rotational fine structure of their fundamental bands can be fully resolved in many cases, which makes a detailed spectroscopic analysis possible.

We are currently studying oxazole, C_3H_3NO and thiazole C_3H_3NS; these are unsaturated five-membered rings with oxygen (or sulphur) and nitrogen atoms in the 1,3-positions. The infrared spectra have previously been determined under low-resolution, and tentatively assigned, but these are the first HR studies. The Fourier transform gas-phase infrared spectrum of the molecules has been recorded at room temperature with a resolution of ca. 0.003 cm^{-1} in the wavenumber region 600-1400 cm^{-1}. In the present study, we concentrate on oxazole. Ten fundamental bands in this region have been analysed by the Watson Hamiltonian model to yield ground state rotational and quartic centrifugal distortion constants as well as upper state spectroscopic constants.

Reassignment of the highest c-type band υ_{14} as the weak top observed at 858.19 cm^{-1} is confirmed by observed local resonance in the neighboring υ_{15} band. This is in good agreement with the theoretical anharmonic υ_{14} band center predicted at 868.22 cm^{-1}. Around 900 cm^{-1}, υ_{12} and υ_{13} are observed at 909.29 and 899.34 cm^{-1}, also in good agreement with the predicted centers of 914.56 and 904.08 cm^{-1}. These close lying bands show strong resonance interactions.

Rotational constants, harmonic and anharmonic frequencies have been calculated using a cc-pVTZ basis, at the MP2 and B3LYP methodology levels, and compared with the experimental data.

[1] F. Hegelund, R. W. Larsen, F. M. Nicolaisen, M. H. Palmer, J. Molec. Spectroscopy, **229** (2005) 244-256.
[2] F. Hegelund, R. Wugt Larsen, R.A. Aitken, M. H. Palmer, J. Molec. Structure, **780-781** (2006), 45-56.
[3] F. Hegelund, R Wugt Larsen, R. A. Aitken, M. H. Palmer, J. Molec. Spectroscopy, **233** (2005), 256-268

MOLECULAR STRUCTURE AND VIBRATIONAL SPECTRA OF PIPERIDINE AND 4-METHYLPIPERIDINE BY DENSITY FUNCTIONAL THEORY AND AB-INITIO HARTREE-FOCK CALCULATIONS

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The molecular geometry and vibrational frequencies of piperidine and 4-methylpiperidine in the ground state have been calculated using the Hartree-Fock and Density Functional methods (B3LYP and BLYP) with 6-31 G(d) as the basis set. The optimized geometric bond lengths that have been obtained by DFT (B3YLP) show the best agreement with the experimental values. The comparison of the observed fundamental vibrational frequencies of piperidine and 4-methylpiperidine, and the calculated results using the density functional B3LYP, BLYP and Hartree-Fock methods indicates that B3LYP is superior to the scaled BLYP, Hartree-Fock approach for the molecular vibrational problems.

Other conformations that differ from the chair (boat, envelope, or twist boat) were not be considered because of their high energy [1]. Thus; the chair conformers of both molecules are the most stable. The chair conformers of both molecules belong to the C_s point group.

Quantum chemical density functional calculations were carried out with GAUSSIAN 98 [2] and Gaussview molecular visualization programs [3].

[1] L. Carballeira, I. Pe'rez-Juste, Journal of Computational Chemistry 19 (1998) 961-976
[2] M.J. Frisch, et all, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh PA, 1998.
[3] A. Frisch, et all, Gaussview Users Manual, Gaussian Inc., Pittsburg, 2000

THE EXPERIMENTAL AND THEORETICAL INFRARED SPECTROSCOPIC STUDY OF 1-METHYL-1-(2-OXOFURANO[4,5-G]2H-CHROMEN-7YL)ETHYL BENZOATE

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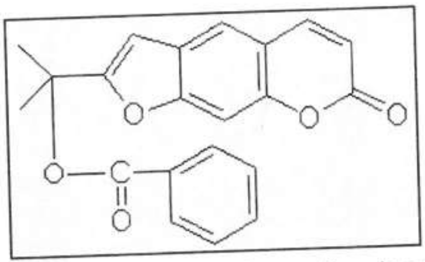
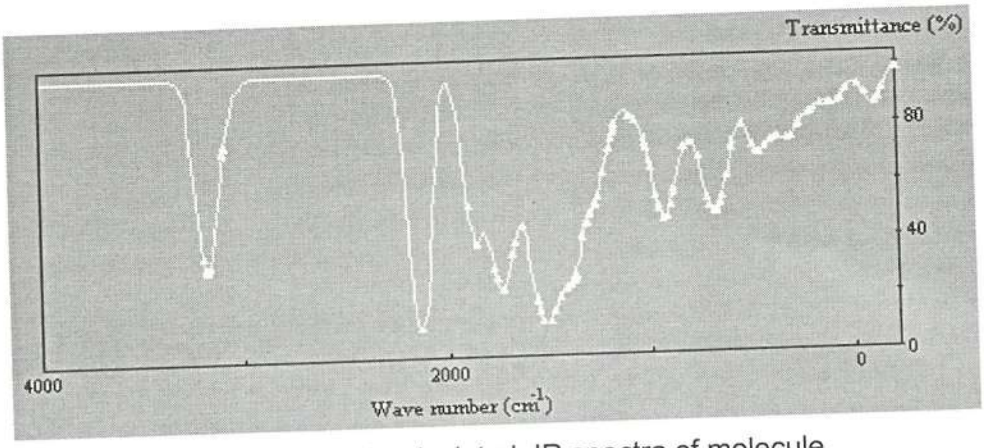
The vibrational frequencies of the 1-methyl-1-(2-oxofurano[4,5g]2H-chromen-7yl)ethyl benzoate have been computed using the semi empirical methods (AM1, PM3, PM5 and MNDOd) compared with the experimental values. The vibrational frequencies were calculated using Cache 6.1.12 and Gaussian03 program package. We calculated theoretical regression analysis and compared with and experimental data. The theoretical calculations IR spectral values were found in agreement with experimental values.



Scheme1. The structure of molecule



Scheme 1. AM1 calculated IR spectra of molecule

Acknowledgement

We are grateful to ESOGU, for financial support as a Research Project No: 200519010 and C. Sibel Kılıç who isolated compound.

VIBRATIONAL SPECTROSCOPY AND THEORETICAL STUDIES 0N 2- AND 3-ACETYL PYRIDINE

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Combined experimental and theoretical studies on molecular and vibrational structure of 2- and 3-acetyl pyridine were reported. In order to get new insights into molecular structure and properties of the molecules vibrational wavenumbers of acetyl pyridine-water complexes were also calculated. For computational purposes, HF and DFT/ B3LYP, in conjunction with 6-31G++(d,p) basic set were used. The complete vibrational assignment for acetyl pyridine molecules has been made on the basis of the calculated total energy distribution (TED) by using Scaled Quantum Mechanics (SQM) method. The general agreements between the observed and calculated frequencies are shown.

QUANTUM-CHEMICAL COMPUTATIONAL METHODS AS AN EFFECTIVE TOOL FOR ANALYSIS OF FTIR SPECTRA OF CELLULOSE AND ITS DEGRADATED DERIVATIVES

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Cellulose is the most important and abandoned polymer ever discovered in nature. However, as well as ubiquitous, as unpredictable in its chemical reactions can it be.

Nowadays one of the fields of interest of researchers is the problem of cellulose degradation in paper due to acid hydrolysis and oxidation [1,2]. The model of degradation was proposed in our previous work [3]. It assumes the degradation as an autocatalytic process of the parallel and consequent hydrolytic and oxidative reactions with a great impact of water molecules. The model was based mainly on *in situ* FTIR experiments performed at different conditions.

To confirm the above-mentioned model, quantum-chemical calculations were performed. The purpose of calculations was to compare theoretical and experimental infrared spectra, in order to assign some key bands. Calculations were based on the observation that the IR spectra of cellooligomers with just a few glucopyranose rings are almost undistinguished from IR spectrum of cellulose [4]. Calculations were performed from cellobiose to cellooctose using of the high-quality DFT method (B3LYP) in different basis sets. Finally, computation based on cellopentose with use of 6-31G basis set gave satisfactory results in reasonable time (Fig.1) and was chosen for calculations of IR spectrum of cellulose and its presumable derivatives. Formation of aldehydes, ketons, enols, as well as carboxylic acids and the molecules with open terminus rings was modelled. The impact of molecules of water on the cellopentose was also taken in consideration. Moreover, some steps to modelling of interaction between neighbouring cellooligomers were taken and what follows, calculations of the impact of intermolecular hydrogen bonding were performed.

The results obtained allowed us to create a database of theoretical IR spectra of a few dozen of cellooligomers both unchanged and modified. This database served as an indirect verification of the model of cellulose degradation, achieved with the method independent from spectroscopic techniques. The results obtained underlined the great agreement and cohesion of the postulate model of mix-controlled mechanism of degradation of cellulose.

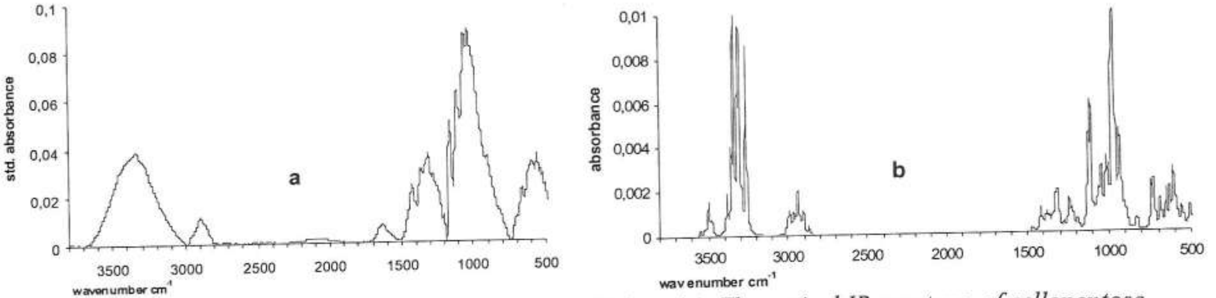

Fig.1 Experimental FTIR spectrum of untreated cellulose (a). Theoretical IR spectrum of cellopentose, calculated with B3LYP method using 6-31G basis set.

[1] X. Zou, T. Uesaka, N. Gurnagul. Cellulose 1996;3:243-267.
[2] S. Margutti, G. Conio, P. Calvini, E. Pedemonte. Restaurator 2001;22(2):67-83.
[3] J. Lojewska, P. Miskowiec, T. Lojewski, L.M. Proniewicz. Polym. Degrad. Stabil. 2005; 88, 512-520
[4] A.J. Michell, H.G. Higgins,CSIRO Forestry and Forest Products, Melbourne, Australia, 2002

VIBRATIONAL ANALYSIS AND QUANTUM CHEMICAL CALCULATIONS OF 2,2'-BIPYRIDINE ZINC(II) HALIDE COMPLEXES

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In this study the molecular structure and vibrational spectra of Zinc(2,2'-bipyridine)X_2 (X= Cl and Br) complexes (see Fig 1) were studied in their ground states by computational vibrational study and scaled quantum mechanical (SQM) analysis. The geometry optimization, vibrational wavenumber and intensity calculations of free and coordinated 2,2'-bipyridine were carried out with the Gaussian03 program package by using Hartree-Fock (HF) and Density Functional Theory (DFT) with B3LYP functional and 6-31G (d,p) basis set. The total energy distributions (TED) of the vibrational modes have been calculated by using Scaled Quantum Mechanical (SQM) analysis. Fundamentals were characterised by their total energy distributions. The aim of this study is to investigate the coordination effects on 2,2'-bipyridine vibrational wavenumbers. The frequency shifts were also found to depend on the halogen.

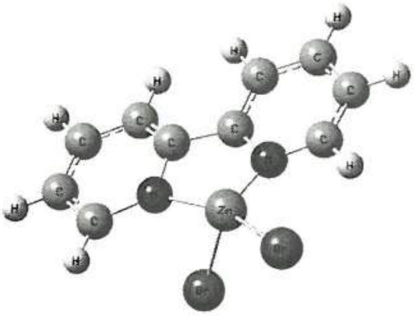

Fig. 1. Molecular model of Zinc(2,2'-bipyridine)X_2 (X= Cl and Br) complexes.

ALKYLATION OF THE TOLUENE METHYL GROUP OVER A SUPERBASIC CATALYST. A DFT STUDY ON MECHANISM AND IR MONITORING

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Side chain alkylation of alkylaromatics is a process of industrial importance. For example, alkylation with ethylene of the cumene side chain to obtain t-amylobenzene proceeds in 408 ^{0}C over $K/KOH/g\text{-}Al_2O_3$ superbasic catalyst. The industrialized process exhibits both high selectivity and high cumene conversion [1, 2]. Recently Kijeński et al. studied alkylation of alkyl groups of alkylaromatics over superbasic catalysts and showed that the aromatic ring alkylation, which is potentially a competitive process, did not occur [3]. So far, the authors have assumed, after Pines et al. [4], the three-stage reaction mechanism:

$$\text{Ph-CH}_3 + \text{BNa} = \text{Ph-CH}_2\text{Na} + \text{BH} \quad (1)$$

$$\text{Ph-CH}_2\text{Na} + \text{H}_2\text{C=CH}_2 = \text{Ph-CH}_2\text{CH}_2\text{CH}_2\text{Na} \quad (2)$$

$$\text{Ph-CH}_2\text{CH}_2\text{CH}_2\text{Na} + \text{Ph-CH}_3 = \text{Ph-CH}_2\text{CH}_2\text{CH}_3 + \text{Ph-CH}_2\text{Na} \quad (3)$$

where B stands for a base.

In this study we modeled the toluene methyl group alkylation with ethylene over the Na_2 molecule as the idealized superbase. The modeling was performed at the B3LYP/6-311++G** level. We found that the proces has five main stages, the initial and the final one is adsorprion of reactant (toluene) and desorption of the product (propylbenzene) from the superbasic catalyst (Na_2). However, the middle three reactions (1-3) are crutial. The activation barrier of the metalation (1) is equal to ca. 36 kcal/mol (in terms of ΔG), and the product is only 2 kcal/mol less stable than the reactant. Next, ethylene attacks the Ph-CH_2Na molecule (2) and the barrier of the reaction towards Ph-$CH_2CH_2CH_2$Na is ca. 30 kcal/mol. The product of the reaction (2) is less stable than the reactants by ca. 9 kcal/mol. However, the most likely the stage (3) proceeds in different way than that supposed by Pines et al., i.e., it is not a proton exchange between toluene and Ph- $CH_2CH_2CH_2$Na. Instead, the proton located at the superbase (after toluene metalation) returns to the alkyl chain, yet in a different place. Such a process needs ca. 54 kcal/mol to overcome the barrier. The product, propylbenzene, is more stabilized than the reactants by ca. 21 kcal/mol.

In the previous study the process was monitored by the ESR method [3]. Here, we predict that the reactions may proceed through the intermediates and TSs in their singlet states, as well. Based on the IR spectra calculated for all the individua studied we propose an easy way of monitoring of the alkylation process by observation of the IR bands that can be assigned to the stretching CH vibrations of both alifatic and aromatic moieties.

[1] W. F. Hoelderich, New reactions in various fields and production of specialty chemicals, in: Proceedings of the 10th International Congress on Catalysis, Stud. Surf. Sci. Catal. 75 (1993) 127-163.

[2] K. Tanabe, H. Hattori, T. Yamaguchi, T. Tanaka (Eds.), Acid-Base Catalysis, VCH, Weinheim, 1989.

[3] J. Kijeński, P. Radomski, E. Fedoryńska, Alkylation of Alkyl Aromatic Hydrocarbons over Metal Oxide-Alkali Metal Superbasic Catalysts, *J. Catal.*, 203(2001)407-425.

[4] H. Pines, J. A. Vesely, V. N. Ipatieff, Migration of Double Bonds in Olefinic and Diolefinic Hydrocarbons Catalyzed by Sodium. Dehydrogenation of *d*-Limonene to *p*-Cymene, *J. Am. Chem. Soc.*, 77(1954)347-348.

Ar-MATRIX IR SPECTRA OF 2-PROPANOL AND ITS OD, D_7, AND D_8 ISOTOPOMERS

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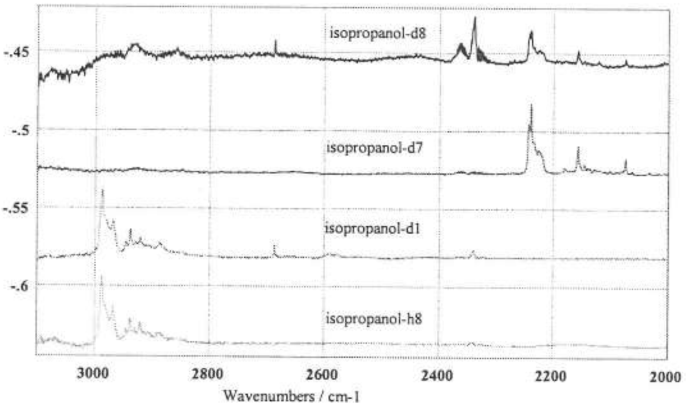
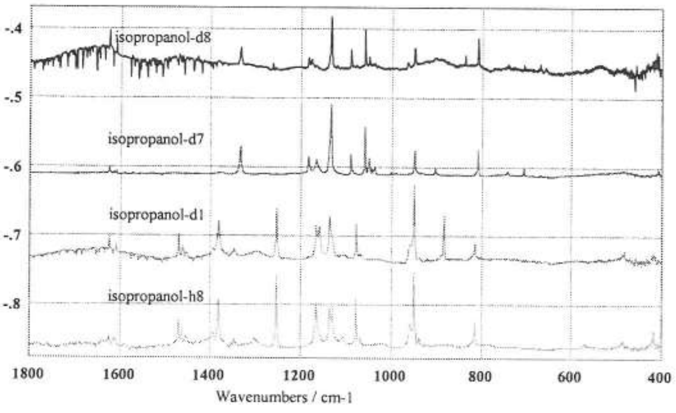
Ar-matrix IR spectra of $(CH_3)CHOH$, $(CH_3)CHOD$, $(CD_3)CDOH$, and $(CD_3)CDOD$ molecules were measured and interpreted by means of DFT calculations followed by the potential energy distribution (PED) analysis.





To interpret the experimental Ar-matrix IR spectra, seven conformers of 2-propanol were subjected to B3LYP/aug-cc-pVTZ calculations, for each of the isotopomers. Two conformers, out of these, were predicted to have all positive harmonic frequencies, and almost identical stabilities, the energy gap being just 0.1 kcal/mol (B3LYP) or 0.2 kcal/mol (MP2/cc-pVTZ). The lowest energy conformer, which has no symmetry elements, differs from the other stable species (C_s symmetry) by the HCOH dihedral angle: -63.5 deg. for the former and 180 deg. for the latter. Out of the remaining five geometries, two correspond to first-order transition states separating the energy minima, while the other three are higher-order stationary points. Interpretation of certain regions of infrared spectra, where a Fermi resonance was supposed to occur, required the calculation of anharmonic vibrational frequencies. These were performed at the B3LYP/cc-pVTZ level.

VIBRATIONAL FREQUENCIES AND STRUCTURAL DETERMINATION OF 2,2' BIQUINOLINE

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We present a detailed analysis of the structure and infrared spectra of 2,2'-biquinoline. The vibrational frequencies of the 2,2'-biquinoline molecule have been analyzed using standard quantum chemical techniques. Frequencies have been calculated at the HF, and DFT (BLYP, B3LYP, and B3PW91) levels of theory using the standard 6-311G* as the basis set.

The assignments of the observed bands corresponding to 2,2'-biquinoline were made on the basis of such calculations and the comparison with related molecules [1-2].

1. S. C. Wait and J. C. Mc Nerney, J. Mol. Spectr., 34 (1970) 56
2. Ş. Yurdakul, S. Akyüz, J. E. D. Davies, J. Mol. Struct.,174 (1988) 435

CRITICAL BEHAVIOUR OF THE SPECIFIC HEAT CALCULATED USING THE RAMAN FREQUENCIES OF THE LATTICE AND INTERNAL MODES NEAR THE λ-PHASE TRANSITION IN NH_4Br

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We calculate here the specific heat of NH_4Br using our Raman frequency shifts for the lattice mode of ν_7TA(56 cm^{-1}) and the internal mode of ν_2 (1684 cm^{-1}) near its λ-phase transition (T_λ=234 K, P=0).By analyzing our Raman frequency shifts, values of α=0.19 ($T<T_\lambda$ and $T>T_\lambda$) for the lattice mode, and α=0.45 ($T<T_\lambda$) and α=0.57 ($T>T_\lambda$) for the internal mode, are used as the values of the critical exponent for the specific heat to predict its critical behaviour based on an Ising model near the λ-phase transition in NH_4Br.

The specific heat which we calculate here using our frequencies of both Raman modes agrees well with the observed specific heat C_P near the λ-phase transition in NH_4Br. Some discrepancy occurring in the specific heat above T_λ due to the lattice mode is explained within the framework of an Ising pseudospin-phonon coupled model for NH_4Br.

ASSIGNMENT OF THE VIBRATIONAL SPECTRUM OF TRIMETHYLPYRAZINE

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Infrared and Raman spectra of trimethylpyrazine have been recorded and assigned following the scaled quantum chemical force field (SQMFF) methodology by Pulay[1-2]. Basically, this method allows us to fit the calculated frequencies to experimental ones by using scale factors that can be transferred between structurally related molecules[3]. In this way, we are able to obtain an a priori estimation of the fundamental vibrational frequencies, which is of great help in resolving some of the doubts typically arising in the vibrational analysis of molecules with a large number of atoms and little symmetry. In this case, three methyl substituents are present in the aromatic ring of pyrazine and therefore, the number of fundamentals is notably increased with respect to the non-methylated molecule. This makes the assignment of some vibrational bands difficult since they appear at very close frequencies. To overcome these difficulties the ab initio force field has been refined with the scale factors directly transferred from 2-methylpyrazine[4]. The scaled frequencies agree quite well with the experimental ones and all Raman and infrared bands have been assigned. Figure 1 shows the assignment of the strong bands in the Raman spectrum recorded from 100 cm^{-1} up to 1700 cm^{-1}.

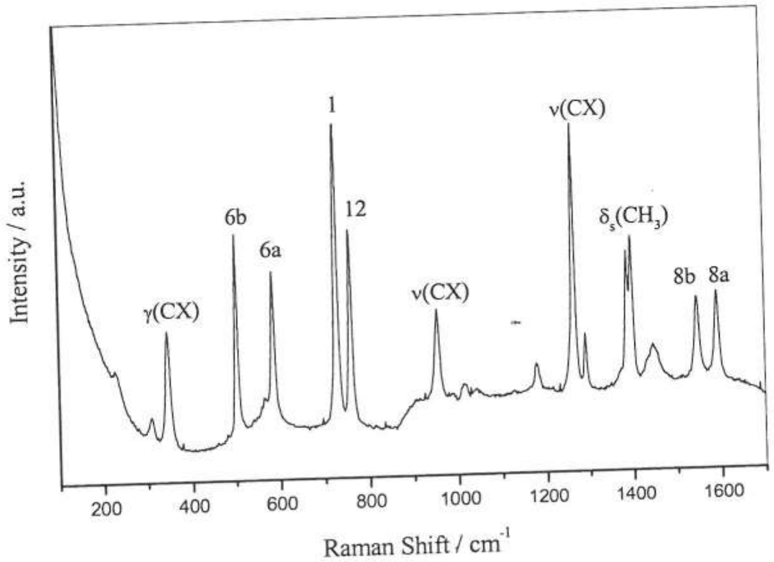

Fig.1: Raman spectrum of 1M aqueous solution of trimethylpyrazine.

[1] P. Pulay, G. Fogarasi, J.E. Boggs, J. Chem. Phys. 74 (1981) 3999.
[2] P. Pulay, G. Fogarasi, F. Pang, J.E. Boggs, J. Am. Chem. Soc. 101 (1979) 2550.
[3] J.F. Arenas, I. López-Tocón, J.C. Otero, J.I. Marcos, J. Phys. Chem. 99 (1995) 11392.
[4] J.F. Arenas, I. López-Tocón, J.C. Otero, J.I. Marcos, Vibr. Spectrosc. 19 (1999) 213.

ANHARMONICITY OF ISOTOPICALLY ISOLATED OH/OD OSCILLATORS IN SERIES OF METAL CHLORIDES HYDRATES. MODEL CALCULATIONS BASED ON EXPERIMENTAL DATA

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Anharmonicity constants and the harmonic eigenvalues of the decoupled OH and OD oscillators in series of metal chlorides hydrates were calculated on the basis of the experimentally obtained frequencies of isotopically isolated OH and OD species. Several theoretical models were used for that purpose: the model of Berglund *et al*[1], Sceats and Rice[2] and Engstrom *et al*[3]. A good correlation between the anharmonicity constants (as well as the ν(OH)/ν(OD) isotopic ratios) with the stretching frequencies of the isotopically isolated OH and OD oscillators was noticed. On the basis of anharmonicity constants and isotopic ratios as criteria for the anharmonicity of the OH (OD) vibrations it was concluded that, with very few exceptions, the vibrational anaharmonicity increases upon increase of the strength of the hydrogen bond in which the particular oscillator is involved. The exceptions from the trend are explained in terms of local electrostatic field differences and force constant changes due to the coordination to the metal ion. The derived regression equations were used to predict the anharmonicity constants of the ν(OD) modes in other members of the series. Approximating the hydrogen bonded complexes with a three-particle model, the parameters characterising the coupling of the ν(OH)[ν(OD)] modes with the low-frequency ν(O...O) ones were estimated. The calculated vibrational anharmonicity parameters were also used to predict the positions of the overtones of OH and OD stretching vibrations in the studied compounds.

[1] B. Berglund, J. Lindgren, J. Tegenfeldt, J Mol. Struct. 43 (1978) 169.
[2] M.G. Sceats, S.A. Rice, J. Chem. Phys. 71 (1979) 973.
[3] H. Engstrom, J.B. Bates, L.A. Boatner, J. Chem. Phys. 73 (1980) 1073.

SPECTROSCOPIC (FT-IR, FT-RAMAN, UV AND ^{1}H, ^{13}C NMR) AND THEORETICAL STUDIES OF ALKALI METAL CINNAMATES

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The effect of alkali metals (Li→Na→K→Rb→Cs) on the electronic structure of cinnamic acid (phenylacrylic acid) was studied. In this research many miscellaneous analytical methods, which complement one another, were used: infrared (FT-IR), Raman (FT-Raman), electronic absorption spectroscopy (UV), nuclear magnetic resonance (^{1}H, ^{13}C NMR) and quantum mechanical calculations. The spectroscopic studies lead to conclusions concerning the distribution of electronic charge in molecule, the delocalization energy of π-electrons and the reactivity of metal complexes[1,2].

The change of metal along with the series: Li→Na→K→Rb→Cs caused: (1) the change of electronic charge distribution in cinnamate anion what is seen via the occurrence of the systematic shifts of several bands in the experimental and theoretical IR and Raman spectra of cinnamates, (2) systematic chemical shifts for protons ^{1}H and ^{13}C nuclei, (3) hipsochromic shifts in UV spectra of salts as compared to ligand.

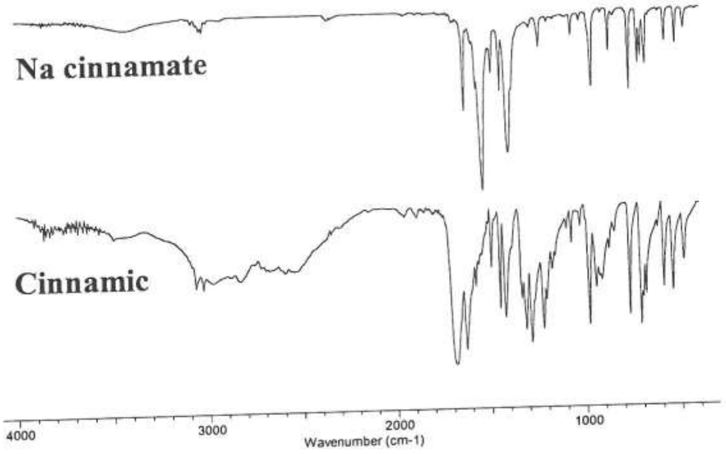

Fig. 1: The FT-IR spectra of cinnamic acid and sodium cinnamate

[1] W. Lewandowski, M. Kalinowska, H. Lewandowska, J. Inorg. Biochem. 99 (2005) 1407.
[2] W. Lewandowski, M. Kalinowska. H. Lewandowska, Inorg. Chim. Acta. 358 (2005) 2155.

VIBRATIONAL ANALYSIS OF 4-AMINOPHENYLACETIC ACID

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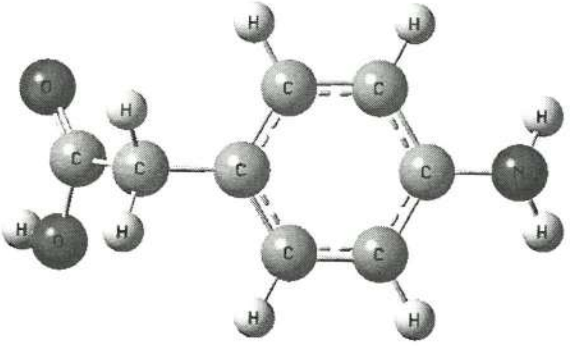
The experimental and theoretical study on the structures and vibrations of 4-aminophenylacetic acid are presented. The optimisation of the molecule gives non-planar structure as the most stable conformer. Harmonic and anharmonic vibrations of 4-aminophenylacetic acid are investigated by density fuctional theory calculations with 6-31G++(d,p) basis set. The assignment is performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated by using Scaled Quantum Mechanics.

The spectroscopic and theoretical results are compared to the corresponding properties for some similar molecules. The anharmonic vibrational wavenumber calculations of the molecule provided a good agreement between the observed and calculated wavenumbers without performing a scaling procedure.



MOLECULAR STRUCTURE AND VIBRATIONAL SPECTRA OF 4,4′-TRIMETHYLENEDIPIPERIDINE BY DENSITY FUNCTIONAL THEORY AND AB-INITIO HARTREE-FOCK CALCULATIONS

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The aim of this study is to calculate optimal molecular geometry, vibrational wavenumbers and modes of free 4, 4′-Trimethylenedipiperidine **(TMDP)**. Up to our knowledge no ab initio and DFT calculations have been performed on TMDP molecule.

The molecular geometry and vibrational frequencies of TMDP in the ground state have been calculated by using the Hartree-Fock and Density Functional Theory (B3LYP and BLYP) with 6-31 G(d) as the basis set. We optimized the structure of TMDP on HF, BLYP and B3LYP level under C_s symmetry. The molecule of TMDP consists of 41 atoms, so it has 117 normal vibrational modes. On the basis of C_s symmetry the 117 fundamental vibrations of TMDP can be distributed $60A' + 57A''$.

The comparison of the observed fundamental vibrational frequencies of TMDP with the calculated results using the Density Functional Theory (B3LYP and BLYP) and Hartree-Fock methods indicates that B3LYP is superior to the scaled Hartree-Fock approach for the molecular vibrational problems.

Quantum chemical calculations were carried out with GAUSSIAN 98 [1] and Gaussview molecular visualization programs [2].

[1] M.J. Frisch, et all, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh PA, 1998.
[2] A. Frisch, A.B. Nielsen, A.J. Holder, Gaussview Users Manual, Gaussian Inc., Pittsburg, 2000

LAST
MINUTE
ABSTRACTS

LASER INDUCED TRANS-CIS TRANSFORMATION OF P-NITROPHENYL ESTER OF TRANS-4-NITROCINNAMIC ACID

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Any enzyme represents a molecular motor, whose functioning id structure-dependent. It is expedient to study the protein dynamics related to its functioning in real time. This problem can be solve using the pump-probe technique provided that the enzymatic reaction is induced with a (short) laser pulse.

Varfolomeev et al. demonstrated that, for the alpha-chymotrypsin-catalyzed reaction, the reaction rates corresponding to the cis and trans isomers of p-nitrophenyl ester of cis-4-nitrocinnamic acid (cis-NPNC and trans-NPNC, respectively) differ by four orders of magnitude ($k_{cis}/k_{trans} \sim 10^{-4}$)[1]. It is also known that the characteristic time of the cis-NPNC binding with the enzyme and, hence, the acylenzyme formation is about 10^5 s. UV irradiation leads to the trans-cis transformations. However, the details of this process, the characteristics of the transients, and the optimal irradiation parameters remain unknown. Therefore, a detailed analysis of the light-induced trans-cis transformation of NPNC is needed for the experimental study of the laser-induced enzymatic reaction.

We study the rates and efficiencies of the trans-NPNC reversible transformation into the cis conformation induced by the laser irradiation. We measure the NPNC absorption spectra at various irradiation doses and excitation wavelengths. Figure 1 demonstrates variations in the absorption spectrum with a variation in the absorbed energy for the NPNC solution in acetonitrile irradiated with the Nd:YAG third-harmonic pulses (λ=355 nm). It is seen that the intensity of the band peaked at 300 nm decreases, whereas the intensity of band peaked at 260 increases indicating the laser-induced cis-trans transformation. The components are characterized and their masses are controlled using NMR, MALDI-TOFF и HPLC.

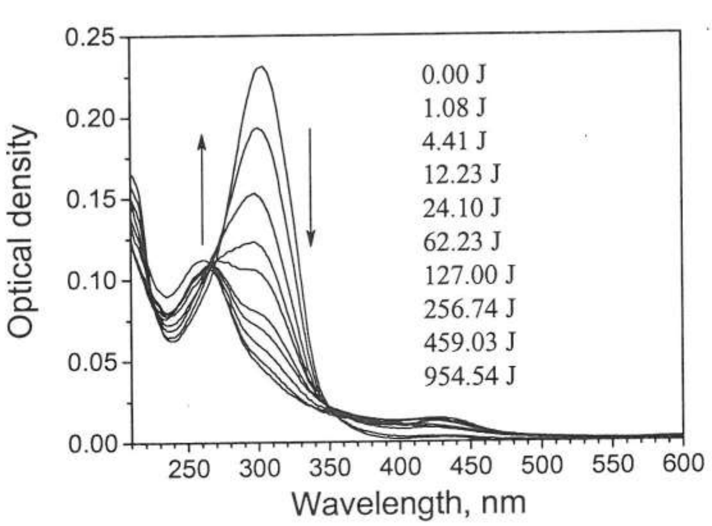

Fig. 1: NPNC absorption spectra at various irradiation doses.

[1] I.V.Berezin, S.D.Varfolomeyev, K. Martinek, FEBS Letters, 8 (1970), 4
[2] S.D. Varfolomeyev, A.M. Klibanov, K. Martinek, I.V. Berezin, FEBS Letters, 15 (1971), 2

SPECTROSCOPIC CHARACTERIZATION OF PH INDICATORS BY QM/MM METHODOLOGY

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The optical properties of organic materials have been subject to extensive studies aimed not only to the understanding of their intrinsic origin but also to the possible use of these systems in electronic and photonic applications. Important molecular systems, like pH indicators, have not only its linear optical properties modified by the acid concentration of its environment, but also its nonlinear coefficients change with the pH of the surrounding medium. Methyl red ($C_{19}H_{15}N_3O_2$) [MR] and Methyl Orange ($C_{14}H_{14}N_3O_6S^-$) are well-known pH indicators that can exist in different conformations [1].

The aims of this work are to investigate theoretically and experimentally the optical properties of ph indicators and the synthesis of new supramolecular composites based on the incorporation of this dye in an aluminum polyphosphate gel network.

The theoretical methodology was based on sequential Monte Carlo/quantum mechanics (MC/QM) methodology. This procedure differs from the conventional QM/MM method in that solute and solvent molecules are treated by quantum mechanics. The classical MC part is used to generate the statistical structure of the liquid. This procedure has been successfully applied to study the solvent effects on the electronic spectrum of several systems [2]. The system consisted of one pH indicator molecule plus 1000 solvent molecules. The simulation consisted of a thermalization stage of 10^7 MC steps.

In this present study we selected a total of 100 configurations, for each solvation shell, with less than 15% of statistical correlation. With the 100 QM calculations were made for each of the first, second and outer solvation shells. The electronic spectra were then calculated using the INDO/CIS approach. The MC statistical mechanics simulations were performed using the DICE program [3,4]. Figure 1 shows several of the statistically uncorrelated solvation shell of MR + 11 water molecules. We find that the pi → pi* transition suffers a red shift upon solvation. The solvation shifts founded are thus converged values both with respect to the number of molecules explicitly included as well as the number of configurations used for the statistical averages. We could conclude that the sequential use of the Sequential QM/MM calculations allows the advantageous use of the statistical information before the QM calculations.

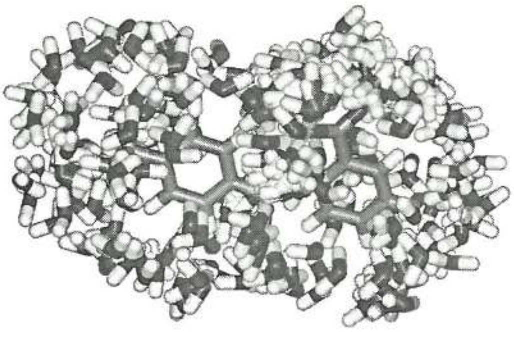

Fig. 1. Several uncorrelated supermolecules (MR basic + 11 water) generated by the simulation corresponding to the first solvatation shell.

[1] J. Del Nero, R.E. de Araujo, A.S.L. Gomes, C.P. de Melo, J. Chem. Phys. 122 (2005) 104506.
[2] W.R. Rocha, K.J. De Almeida, K. Coutinho, S. Canuto, *Chem. Phys. Lett.* **171** (2001) 345.
[3] K. Coutinho, S. Canuto, *Adv. Quantum Chem.* **28** (1997) 89.
[4] K. Coutinho, S. Canuto, DICE Program, University of São Paulo (2003).

P10-43

AN EFFICIENT SEQUENTIAL MONTE CARLO / QUANTUM MECHANICS INVESTIGATION OF THE ABSORPTION SPECTRUM OF A FURAN-2,3-DIONE DERIVATIVE

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In this work we investigate the absorption spectrum of the 9-oxa-2,3-4'-methoxy benzo bicyclo [4,3,0] non-1(6)-ene-7,8-dione (MBBD) on liquid environment. Using Monte Carlo (MC) simulations we build the liquid structure composed by 1 MBBD + 600 acetonitriles. The molecular interactions are described by Lennard-Jones plus Coulomb potential and are used periodic contour conditions associated to the image methods. Furthermore, the average electronic properties are determined with quantum chemistry calculations performed on structures generate by MC simulations. As in previous works[1-2], good results are found with less than 80 quantum calculations performed on structures composed just by 1 MBBD + several hydratation layers.

Figure 1(left) shows the radial distribution function between the center-of-mass of MR and the center-of-mass of water, G_{cm-cm} (*r*). As it can be seen, there is a hydrogen bond peak that starts at around 1.9 Å and has a minimum at 3.9 Å. Spherical integration of this peak gives a coordination number of 26.

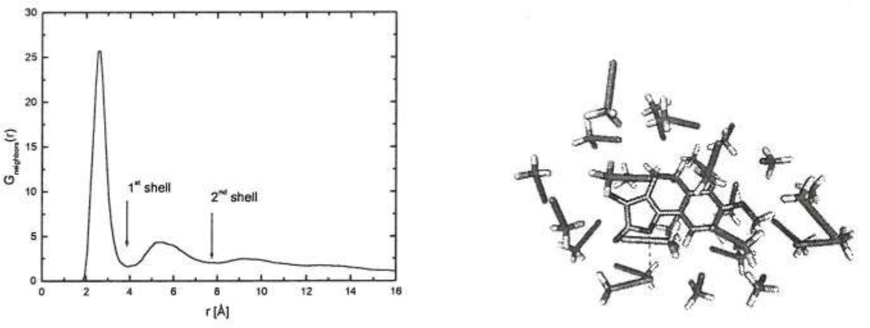

Figure 1. (left) The pairwise radial distribution function between the center-of-mass of MBBD and the center-of-mass of acetonitrile; (right) MBBD surrounded by 26 acetonitrile molecules of the 1st solvatation shell.

Quantum-mechanical calculations using the intermediate neglect of differential overlap with singly excited configuration interaction (INDO/CIS) are then performed in the supermolecular clusters corresponding to the hydrogen bond shell and the first (1 MBBD+26 acetonitriles) and second solvation shells. The largest cluster includes one MBBD and 95 acetonitriles molecules.

We have found a strong band centered at 401.2 nm [400.6 nm] for 1st [2nd] shell. Still in this region is possible to see the $\pi \rightarrow \pi^*$ excitation at 377.6 nm [375.1 nm]. Namely, we obtain converged results for 301.2 [297.6 nm] and 265.54 nm [259.9 nm]. When compared with the gaseous phase, the solvent effect on this compound is characterized by a considerable red shift. For $\pi \rightarrow \pi^*$ transition, this deviation is of the order 0.215 eV. However, ours observations are in good agreement with experimental predictions[3] of 396 and 360 nm to the lowest energies and finally, 290 and 256 nm to the highest transitions. This work is a proof that the sequential MC/QM treatment is a powerful methodology to describe systems in liquid phase.

[1] K. Coutinho, S. Canuto, International Journal of Quantum Chemistry, 77 (2000) 192.
[2] S. Urahata, S. Canuto, International Journal of Quantum Chemistry, 80 (2000) 1062.
[3] S. Ait-Iyazidi, M. Ckaki, M. Hnach, J.P. Aycard, C. Cazeau-Dubroca Spectrochimica Acta Part A: 53 (1997) 605.

LARGE SCALE QUANTUM MECHANICAL CALCULATIONS ON THE VIBRATIONAL LEVEL STRUCTURE IN BENZENE. THE FERMI RESONANCES

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In this article we present a continuation of our work on the reliable determination of the harmonic force constants $F_{i,k}$ for benzene (in symmetrized Whiffen's coordinates), as well as some higher order (anharmonic) force constants $F_{i,j,k}$, $F_{i,j,k,l}$, that are of determining importance for the benzene isotopomer invariant potential energy surface (PES). The refined set of harmonic and anharmonic force constants allows for the improved agreement of the experimentally measured benzene vibrational energy levels with those calculated using our large scale, full-dimensional, nonperturbative and fully symmetrized vibrational calculation procedure. Particular attention is given to the well known Fermi resonance vibrational level structure in benzene.