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UNIVERSITÄT DÜSSELDORF

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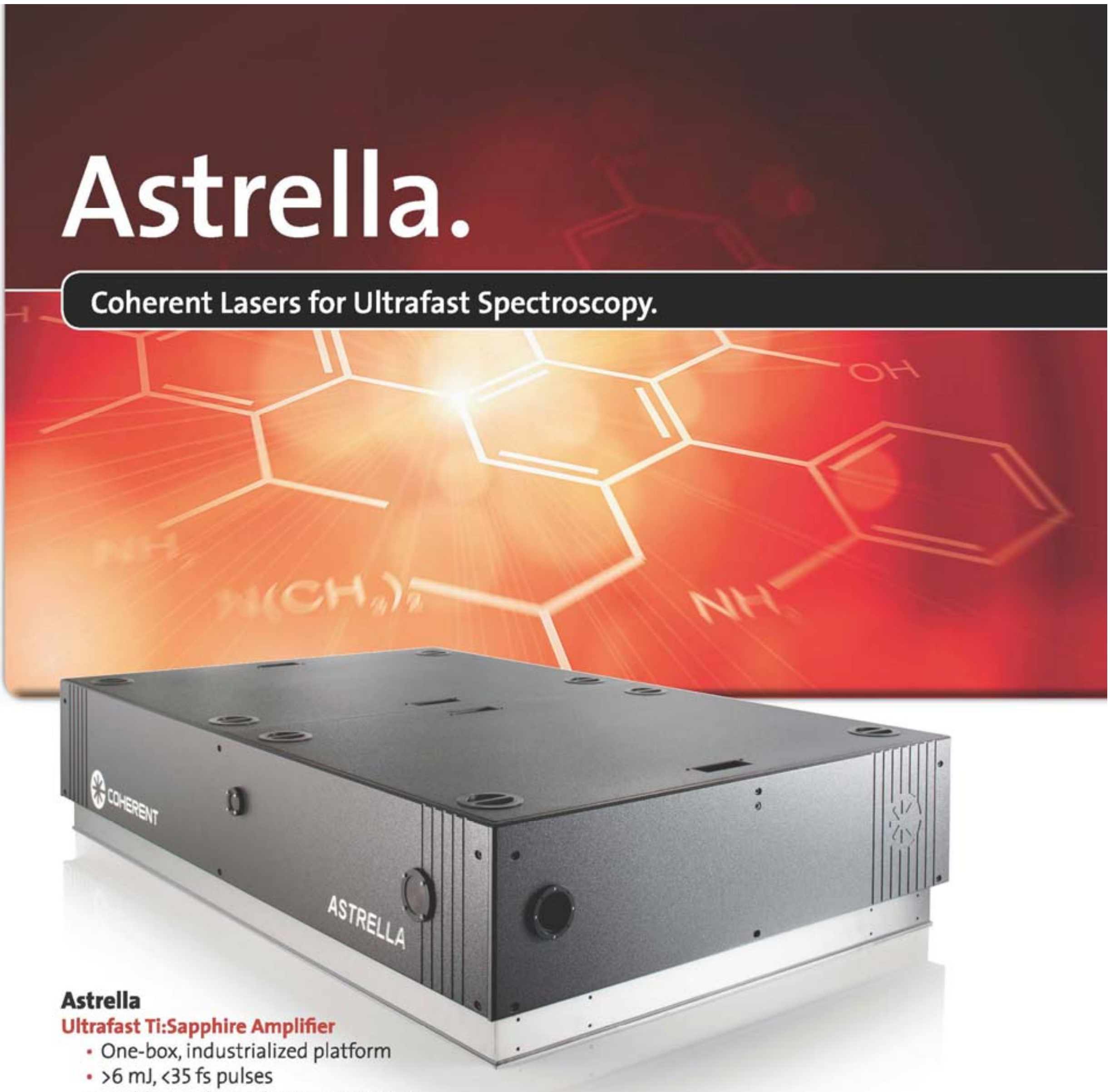
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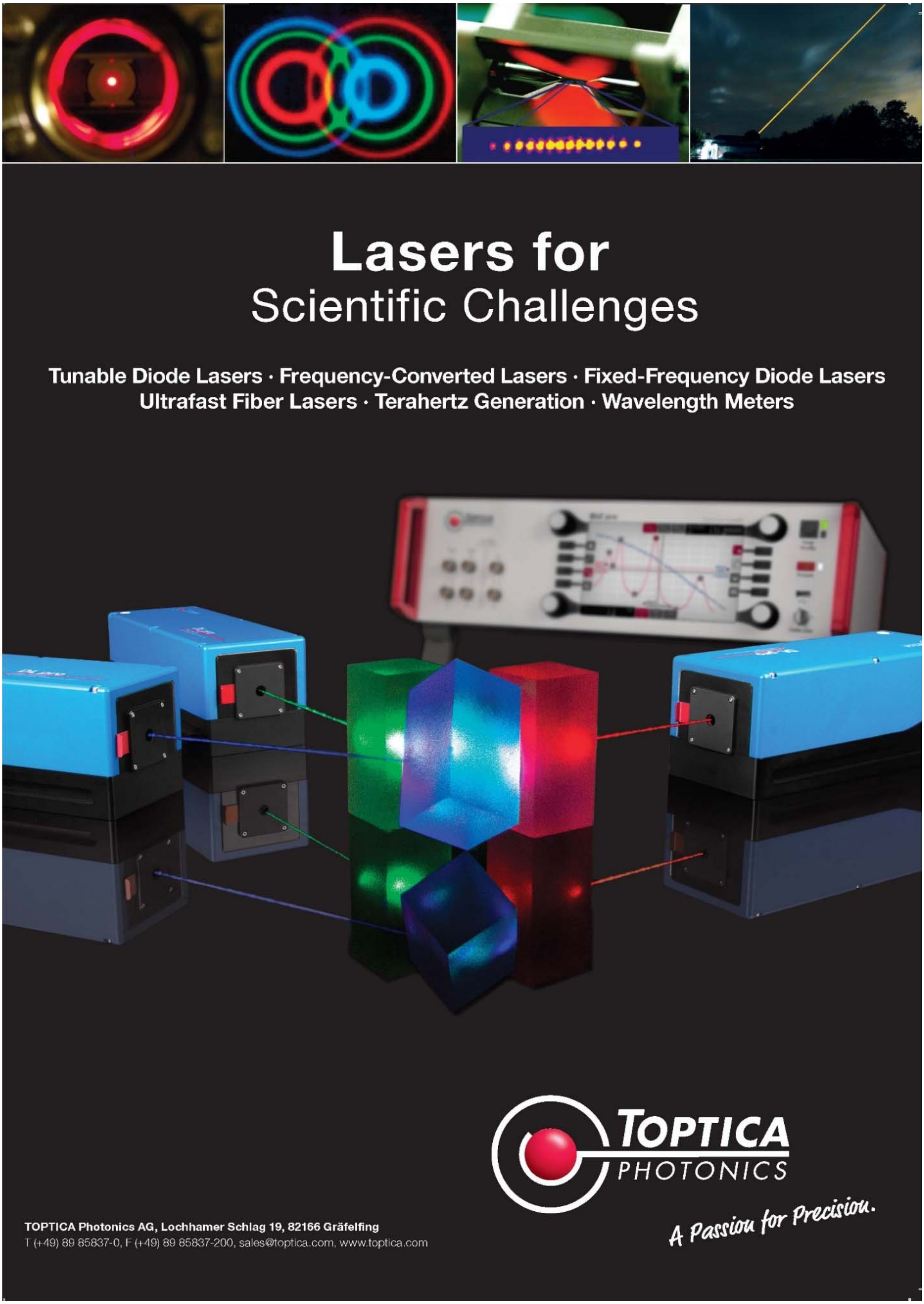

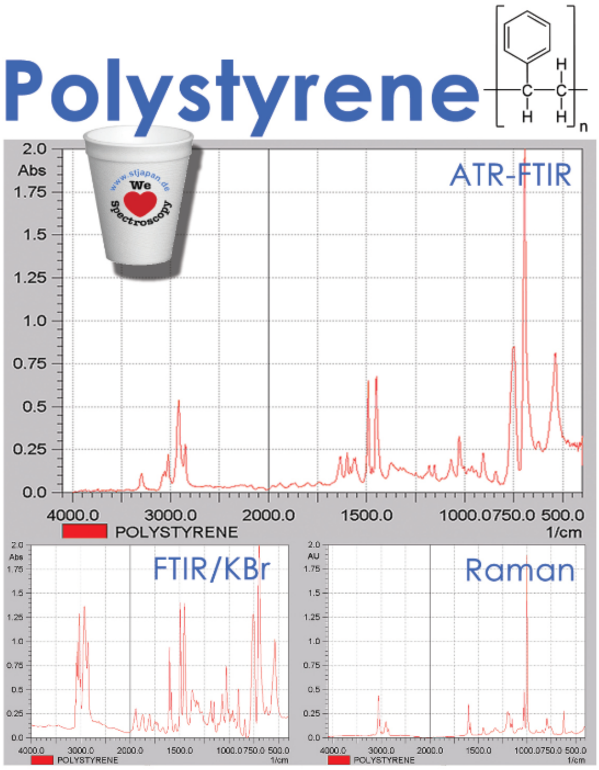
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Preface

We welcome you to the 32nd European Congress on Molecular Spectroscopy 2014, taking place at the Heinrich-Heine-University in Düsseldorf for the first time. The conference series goes back to the year 1951 and was initiated by Sir Harold Thompson (London), Jean Lecomte (Paris) and Reinhard Mecke (Freiburg). Ernst Miescher (Basel) organized the first meeting on neutral Swiss ground after the Second World War.[1] Its initial intention was an integration and reconciliation of European scientists after WW2, an intention that was taken over in the period of the cold war, in order to facilitate and strenghten the connections and the mutual understanding between eastern and western European researchers.

The Heinrich-Heine-University in Düsseldorf is a relatively young university located in the capital of Northrhine-Westfalia and emerged from a medical academy in 1965. It was named in 1988 after the famous Düsseldorf born poet, journalist, and essayist, Heinrich Heine, whom we owe, apart from his example in courage against unlawful authorities the statement, that “Money is round and rolls away – formation stays”. Furthermore Heine declared that

The German Censors —— —— —— —— ——⍰—— —— —— —— —— —— ——
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Needless to say, that Heine terminated his last years in exile in Paris, where he had to flee from the Prussian reaction.

In times of reduced public funding for pure research, world wide international colaborations, using in an intelligent way already existing equipment and machinery, might turn this drawback even into an advantage. Since its foundation EUCMOS covers exactly the aspects of stimulating and inspiring cooperations and should be used not only for scientific exchange, but also initiating new international cooperations to overcome the obvious lack of public funding in this area.

We wish you a pleasant stay in Düsseldorf, and a fruitful and inspiring meeting. Carry the spirit of this congress into your working groups and enjoy the talks, poster sessions and discussions throughout the week.

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[1] Most of the information about the early times of EUCMOS comes from personal communication of Henry H. Mantsch and from his article “The road to medical vibrational spectroscopy – a history” in *Analyst*, 2013, **138**, 3863.

Sponsors

We thank all sponsors, who made this conference possible with their generous contributions. We acknowledge especially the contribution of our principal sponsor Shimadzu. All contributing companies and organizations are listed below. Our deepest gratitude to all of our supporters.

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Andrea Lotzwick – conference secretary
Brigitte Müller
Dieter Marx
Klaus Kelbert
Michaela Braun
Daniela Langer

Overview

Sunday 24. August	Monday 25. August		Tuesday 26. August		Wednesday 27. August		Thursday 28. August		Friday 29. August	
	Chair: Michael Schmitt		**Chair:** Sylvia Turrell		**Chair:** Peter Gilch		**Chair:** Henry Mantsch		**Chair:** Austin Barnes	
	9:00 - 9:45	Official Opening Austin Barnes (Chair of EUCMOS) Christel Marian (Dean of the Faculty) Lutz Schmitt (Prorector)	9:00 - 9:45	Plenary talk Anouk Rijs The use of intense FIR radiation for molecular structure and dynamics experiments	9:00 - 9:45	Plenary talk Michael Ashfolc Molecular photofragmentation dynamics in the gas and condensed phase: similarities and differences	9:00 - 9:45	Plenary talk Hugh Burrows Transient absorption spectra and theoretical studies of excited and charged states of organic materials for optoelectronics	9:00 - 9:45	Plenary talk Siva Umapathy Time resolved stimulated Raman spectroscopy
	9:45 - 10:30	Plenary talk Eberhard Riedle Understanding complex reactive molecular proceses: from kinetics to comprehensive transient spectroscopy on all relevant time scale	9:45 - 10:30	Plenary talk Sonia Melandri Conformations and Dynamics of flexible molecules, biomolecules and molecular complexes by rotational spectroscopy	9:45 - 10:30	Plenary talk Andrzej Sobolewski Juggling with protons: molecules and light in action	9:45 - 10:30	Plenary talk Pavel Hobza Noncovalent interactions: theory and applications	9:45 - 10:15	Invited talk Ozan Ünsalan Applications of Vibrational Spectroscopy in Cultural Heritage, a case study: Valence Aqueduct (İstanbul)
									10:15-10:30	István Pálinkó Introduction to XXXIII. EUCMOS 2016
	10:30 - 11:00	Coffee break	10:30 - 11:00	Coffee break	10:30 - 11:00	Coffee break	10:30 - 11:00	Coffee break	10:30 - 11:00	Coffee break
	Chair: Rainer Weinkauf		**Chair:** Michael Ashfold						**Chair:** Austin Barnes	
	11:00 - 11:30	Invited talk Leo Meerts Novel strategies for solving highly complex NMR spectra of solutes in liquid crystals	11:00 - 11:30	Invited talk Harold Linnartz Molecular astro-spectroscopy; bridging gas phase and solid state processes in space	11:00 - 13:00	Oral presentations Room 3A **Session 12** Hydrogen Bonding Room 3B **Session 13** Methods I Room 3C **Session14** Spectroscopy for Cultural Heritage	11:00 - 13:00	Oral presentations Room 3A **Session 15** Raman Spectroscopy Room 3B **Session 16** Spectroscopy of Polymers and Films Room 3C **Session 17** Methods II	11:00 - 11:30	Invited talk Hervé Vezin Ancient carboneous matter in the context of origin of life. Memory of the past. Perspectives to Mars Mission
	11:30 - 12:00	Invited talk Giorgos Voyiatzis Polarized raman spectra: opportunities & challenges - What about polarized SERS?	11:30 - 12:00	Invited talk Con Mallidis Medical applications of confocal raman microspectroscopy					11:30 - 12:00	Invited talk István Pálinkó Pristine and functionalised layered double hydroxides - syntheses, structural characterisation and catalytic applications
	12:00 - 12:30	Invited talk Maurizio Becucci Non bonding interactions in molecular clusters	12:00 - 12:30	Invited talk Matteo Tommasini Infrared spectroscopy of edges in molecular graphenes					12:00 - 13:00	Concluding remarks
	12:30 - 13:00	Invited talk Alexandre Dazzi Infrared Nanoscopy applied to microbiology	12:30 - 13:00	Invited talk Melanie Schnell Enantiomer identification of chiral molecules using broadband microwave spectroscopy						
	13:00 - 14:30	Lunch Meeting of the International Committee	13:00 - 14:30	Lunch Meeting of the editors of J. Mol. Spectrosc.	13:00 - 14:30	Lunch	13:00 - 14:30	Lunch	13:00 - 14:30	Lunch
15 - 19 Uhr Registration	14:50 - 16:30	Oral presentations Room 3A **Session 1** Spectroscopy of isolated molecules I Room 3B **Session 3** Environmental Applications in Spectroscopy Room 3C **Session 5** Medical Applications in Spectroscopy I Room 3D **Session 7** Theory I	14:50 - 16:30	Oral presentation Room 3A **Session 9** Spectroscopy of Isolated Molecules III Room 3B **Session 10** New Materials II Room 3C **Session 11** Dynamics and Time Resolved Spectroscopy I	15:00 - 21:30	Excursion	14:50 - 16:30	Oral presentations Room 3A **Session 18** Dynamics and Time Resolved Spectroscopy II Room 3B **Session 19** New Materials III		
	16:30-17:00	Coffee break	16:30-17:00				16:30 - 18:00	Postersession 2		
	17:00 - 19:00	Oral presentations Room 3A **Session 2** Spectroscopy of isolated molecules II Room 3B **Session 4** New Materials I Room 3C **Session 6** Medical Applications in Spectroscopy II Room 3D **Session 8** Theory II	17:00 - 20:00	Postersession 1						
19:00-21:00 Welcome Party Mensa							20:00 - 23:30	Conference Dinner		

Overview by Days

Monday 25. 8. 2014

9:00 – 9:45	Official Opening
9:45 – 10:30	**HS 3A** Plenary Talk P1: Eberhard Riedle *Understanding complex reactive molecular procceses: from kinetics to comprehensive transient spectroscopy on all relevant time scales.*
10:30 – 11:00	Coffee Break
11:00 – 11:30	**HS 3A** Invited Talk I1: W. Leo Meerts *Novel strategies for solving highly complex NMR spectra of solutes in liquid crystals*
11:30 – 12:00	**HS 3A** Invited Talk I2: Giorgos Voyiatzis *Polarized raman spectra: opportunities & challenges - What about polarized SERS?*
12:00 – 12:30	**HS 3A** Invited Talk I3: Maurizio Becucci *Non bonding interactions in molecular clusters*
12:30 – 13:00	**HS 3A** Invited Talk I4: Alexandre Dazzi *Infrared Nanoscopy Applied to Microbiology*
13:00 – 14:30	Lunch
14:50 – 16:30	***HS 3A Session 1 Spectroscopy of Isolated Molecules I***
14:50 – 15:10	S. Schiller *Precision Spectroscopy of the Simplest Molecules*
15:10 – 15:30	José Arturo Ruiz-Santoyo, Marcela Rodríguez-Matus, Leonardo Álvarez-Valtierra, José Luis Cabellos, Rafael Grande-Aztatzi, José Gabriel, Merino-Hernández, John T. Yi, and David W. Pratt *Rotationally Resolved Electronic Spectra of the Electronic Origin and Some Vibronic Bands of Guaiacol and Mequinol: Vibrational Assignment of Low-Frequency Bands*
15:30 - 15:50	J. Laane, E. J. Ocola, H. L. Sheu, H. J. Chun, P. Boopalachandran, and N. Meinander *Spectroscopic and Theoretical Investigations of Molecular Vibrations and Potential Energy Surfaces in Ground and Excited Electronic States*
15:50 – 16:10	P. Hemberger, A Trevitt, T. Gerber, E. Ross and G. da Silva *Isomer-Specific Product Detection of Xylyl Radical Rearrangement and Decomposition Using VUV Synchrotron Photoionization*
16:10 – 16:30	B. Stuhlmann, F. Gmerek and M. Schmitt *Determination of the Geometry Change of Benzimidazole upon Electronic Excitation*
14:50 – 16:30	***HS 3B Session 3 Environmental Applications in Spectroscopy***
14:50 – 15:10	Albert van Oyen, Jan Andries van Franeker, Uwe Oppermann, Marion Egelkraut-Holtus *Monitoring Plastic Waste Using FTIR Spectroscopy*
15:10 – 15:30	G. Renner, M. Egelkraut-Holtus, A. van Oyen and J. Schram *Characterization of Plastic Marine Litter Using FTIR Microscopy*

15:30 - 15:50	I. R. Ivascu, C. E. Matei, M. Patachia, A. M. Bratu and D. C. Dumitras *Trace Gases Photoacoustic Detection for Monitoring of Some Air Pollutants*
15:50 – 16:10	G. Zerbi, M. Tommasini *Vibrational Spectroscopy of Anthropogenic Carbonaceous Particles: A Difficult Problem*
16:10 – 16:30	A. Bagheri Garmarudi, M. Khanmohammadi, Z. Haji Seyed Razi *Crude Oil Geochemical Evaluation by Infrared Spectroscopy and Chemometrics*

14:50 – 16:30 HS 3C Session 5 Medical Applications in Spectroscopy I

14:50 – 15:10	S. Turrell, A. Uwimanimpaye, C. Kinowski, C. Masselot-Robbe, F. Cardon and O. Cristini *Sol-Gel Biocompatible Porous Materials for Local Controlled Drug Release in Treatment of Parkinsons's Disease*
15:10 – 15:30	Iryna Goncharova, Sergey Orlov, Pavlina Novotná, Marie Urbanová *Determination of the ligand-protein binding parameters by combination of circular dichroism and fluorescence spectroscopy*
15:30 - 15:50	S. Tamosaityte, M. Pucetaite, V. Hendrixson, Z. A. Kucinskiene and V. Sablinskas *FT-Raman Spectroscopy as a Non-Destructive Tool for Determination of Chemical Composition of Urinary Sediments*
15:50 – 16:10	C. Paluszkiewicz, P. Chaniecki, W. M. Kwiatek, J. Lekki, M. Rękas *Natural Lenses with Cataracts Studied by FTIR Spectroscopy*
16:10 – 16:30	Thorsten Vahlsing and H. Michael Heise *Spectral Bandwidth Limitations of Tuneable External-Cavity Based Quantum Cascade Lasers for Clinical Biofluid Analysis with Different Multivariate Calibration Strategies*

14:50 – 16:30 HS 3D Session 7 Theory I

14:50 – 15:10	Jörg Tatchen, Reuven Ianconescu, and Eli Polak *Semiclassical Computation of Vibronic and Vibrational Spectra Beyond the Harmonic Approximation*
15:10 – 15:30	Jan-M. Mewes , Vladimir Jovanović, Christel M. Marian and Andreas Dreuw *Electronic Structure and Molecular Mechanism of Non-Radiative Decay of Nitrobenzene*
15:30 – 15:50	Stavrov, Solomon *Relationship between Structure and Vibrational Spectra of* A_0*,* A_1*, and* A_3 *Conformational Substates of Carbonmonoxy Myoglobin*
15:50 – 16:10	Güneş Süheyla Kürkçüoğlu *Theoretical Studies on the Molecular Structure and Vibrational Spectra of 2-Pyridineethylamine*
16:10 – 16:30	Tony Ford *The Molecular Complexes of Boron Trifluoride with Nitrosyl Fluoride and Nitrosyl Chloride. Ion-Pair Formation*

16:30 – 17:00 Coffee Break

17:00 – 19:00 HS 3A *Session 2 Spectroscopy of Isolated Molecules*

17:00 – 17:20	James. R. Durig and Bhushan S. Deodhar *The Utilization of Rare Gas Solution for Making Vibrational Assignments and Conformation Stability Determinations of Three Membered Rings*
17:20 – 17:40	A. Stamm, M. Weiler, A. Brächer, K. Schwing, M. Gerhards *Excited state proton transfer reactions in isolated hydroxychromones investigated by different IR/UV techniques*
17:40 – 18:00	A. Bouchet, M. Schütz, B. Chiavarioni, M-E. Crestoni, S. Fornarini, O. Dopfer *Binding Motifs of a Microhydrated Neutrotransmitter: IR*

	Spectroscopy of Rare Gas-Tagged Protonated Phenylethylamine and its Water Clusters
18:00 – 18:20	A. N. Heays, J. M. Ajello, A. Aguilar B. R. Lewis and S. T. Gibson *Fluorescence of Electron-Excited* N_2
18:20 – 18:40	Martin Wilke, Josefin Wilke and Michael Schmitt *Manipulation of Electronically Excited States of Indole*

17:00 – 18:40 ***HS 3B Session 4 New Materials I***

17:00 – 17:20	Sloufova I., Prochazka M., Vlckova B. *Charge-Transfer Resonance Mechanism Contribution to SERS of 2,2′:6′,2′′-Terpyridine Chemisorbed on Ag Nanoparticles*
17:20 – 17:40	P. Smejkal, L. Hochmann, J. Pfleger, and I. Sloufova *SERS spectral probing of laser ablated nanoparticles prepared in alcohols*
17:40 - 18:00	Murat Taş, Mürsel Arıcı, Okan Zafer Yeşilel *Syntheses, Crystal Structures and Spectroscopic Properties of Cadmium(II) AND Manganese (II)-Azoxybenzenetetracarboxylate Complexes with 1,2-Bis(Imidazole-1Yl-Methyl)Benzene*
18:00 – 18.20	B. Kutus, A. Pallagi, G. Peintler, A. Bíró, I. Pálinkó and P. Sipos *Structure and Equilibria of Ca(II)–Gulonate Complexes Forming in Aqueous Solutions from Multinuclear NMR Spectroscopy, Potentiometry, Conductometry and Freezing Point Depression*
18:20 – 18:40	Maria Buchholz, Peter G. Weidler, Chengwu Yang, Hikmet Sezen, Fabian Bebensee, Stefan Heissler, Alexei Nefedov and Christof Wöll *Polarization- and azimuth-dependent Infrared Reflection absorption spectroscopy of metal oxide single crystals*

17:00 – 18:40 ***HS 3C Session 6 Medical Applications in Spectroscopy II***

17:00 – 17:20	E.Y.M. Bonnist, P.D.A. Pudney, P.J. Caspers, G.J. Puppels, C. Marriott, L.A. Weddell, F.L. Baines, S. Paterson, J.R. Matheson *Raman Spectroscopic Studies of the Scalp Skin, In Vivo*
17:20 – 17:40	Said Mohammed El Amin, Dahmane El Montausie, Naubron Jean-Valère, Vanloot Pierre, Bombarda Isabelle, Vanthuyne Nicolas, Dupuy Nathalie, Roussel Christian *Chiral Study of Artemisia Herba Alba by Vibrational Circular Dichroism*
17:40 – 18:00	Gjorgji Petruševski, Tomče Runčevski, Marina Čačorovska, Sonja Ugarkovic, Igor Micovski, Gordana Bogoeva-Gaceva, Gligor Jovanovski, Robert E. Dinnebier and Petre Makreski *Solvatomorphism and Crystal Structure of the Narcotic Analagesic Drug Codeine Phosphate Sesquihydrate*
18:00 – 18.20	M. Khanmohammadi, F. Mozaffari, A. Bagheri Garmarudi *Diagnosis of Cardiovascular Defect by Infrared Spectrometric Analysis of Blood Serum*
18:20 – 18:40	M.I. Oshtrakh, I.V. Alenkina, A.V. Vinogradov, T.S. Konstantinova and V.A. Semionkin *Mössbauer Spectroscopy of Liver and Spleen Tissues from Normal Human and Patients with Hematological Malignancies*
18:40 – 19:00	A.A. Kamnev, A.V. Tugarova, L.A. Kulikov, and Yu.D. Perfiliev *Emission Mössbauer Spectroscopy in Probing Cation-Binding Sites in Biocomplexes: from Small Biomolecules to Enzymes*

17:00 – 18:40	***HS 3D* Session 8 Theory *II***
17:00 – 17:20	A. El-Azhary, N. Al-Jallal *Conformational and Vibrational Analysis of Dibenzo-18-Crown-6*
17:20 – 17:40	Choi Jun-Ho[a] and Cho Minhaeng *Numerical Simulation of Vibrational Spectrum Under Aqueus Solution: Protein and Bulk Water System*
17:40 – 18:00	A. Wohlert, M. Schmitt *Franck-Condon Simulation of Hot Absorption Spectra at Arbitrary Temperatures*
18:00 – 18:20	C. G. T. Feugmo, V. Liégeois, Y. Caudano, F. Cecchet and B. Champagne *Toward modeling Infrared-Visible Sum-Frequency Generation (SFG) of organic monolayers on hydrogen-terminated Si(111)*
18:20 – 18:40	Valery Andrushchenko, Ladislav Benda and Petr Bouř *Improving the Precision of Ab Initio Spectra Modeling by Employing Molecular Dynamics Simulations*

Tuesday 26. 8. 2014

9:00 – 9:45	**HS 3A** Plenary Talk P2: Anouk Rijs *The use of intense FIR radiation for molecular structure and dynamics experiments*
9:45 – 10:30	**HS 3A** Plenary Talk P3: Sonia Melandri *Conformations and Dynamics of flexible molecules, biomolecules and molecular complexes by rotational spectroscopy*
10:30 – 11:00	Coffee Break
11:00 – 11:30	**HS 3A** Invited Talk I5: Harold Linnartz *Molecular astro-spectroscopy; bridging gas phase and solid state processes in space*
11:30 – 12:00	**HS 3A** Invited Talk I6: Con Mallidis *Raman Microspectroscopy in Medicine. Can it Solve the Sperm Condrum*
12:00 – 12:30	**HS 3A** Invited Talk I7: Matteo Tommasini *Digging Molecules out of Vibrational Spectra with DFT and Statistical Analysis*
12:30 – 13:00	**HS 3A** Invited Talk I8: Melanie Schnell *Enantiomer Identification of Chiral Molecules using Broadband Microwave Spectroscopy*
13:00 – 14:30	Lunch
14:50 – 16:30	***HS 3A Session 9 Spectroscopy of Isolated Molecules III***
14:50 – 15:10	J.-U. Grabow, Z. Glassman, R. J Mawhorter, A. Le, and T. C. Steimle *The microwave spectrum of the odd isotope of ytterbium fluoride,* ^{171}*YbF*
15:10 – 15:30	K. P. Rajappan Nair, Michaela K. Jahn, David Dewald, Alberto Lesarri, Vadim V. Ilyushin, Jens-Uwe Grabow *Internal Rotation in Molecules From Microwave Spectroscopy*
15:30 – 15:50	T. Betz, S. Zinn, M. Schnell *Ibuprofen: Conformers and Thermal Decomposition Products*
15:50 – 16:10	Josefin Wilke[a], Martin Wilke[a], Michael Schmitt[a] and Leo Meerts *Electronic Stark Measurements With Rotationally Resolved Laser Induced Fluorescence Spectroscopy*
16:10 – 16:30	Alcides Simão, Isabel Peña, Carlos Cabezas, and José Luis Alonso *L-Pipecolic Acid - the Conformational Behaviour of a Neuroactive Cyclic Aminoacid*
14:50 – 16:30	***HS 3B Session 10 New Materials II***
14:50 – 15:10	Éva G. Bajnóczi, Szabolcs Bálint, Ottó Berkesi, Tamás Körtvélyesi, György Dombi, Péter Forgó, Zoltán Kele, Ingmar Persson, Gábor Peintler, István Pálinkó, Pál Sipos *Comparison of the Structure of Sn(II) And Pb(II)-Hydroxido Complexes Forming in Hyperalkaline Aqueus Solutions*
15:10 – 15:30	M. Sipiczki, I. Hannus, Zs. Ferencz, O. Berkesi, P. Sipos, and I. Pálinkó *Structural Features of intercalated CaFe-layered double hydroxides Studies by X-Ray Diffractometry, Infrared Spectroscopy and Computations*

15:30 – 15:50	Sandra Dorotíková, Júlia Kožíšková, Peter Herich, Marek Fronc, Lukáš Bučinský, Dana Dvoranová *Copper(II) Complexes With Quinolone: Structure and Spectroscopic Characterization*
15:50 – 16:10	M. Sipiczki, T. Anitics, V. Bugris, E. Kuzmann, Z. Homonnay, P. Sipos and I. Pálinkó *Thermal Decompostion and Reconstruction of CaFe-Layered Double Hydroxide Studied by X-Ray Diffractometry and Mössbauer Spectroscopy*
16:10 – 16:30	H. Yurtseven[a], M. Kurt *Analysis of the Frequency and Bandwidth as a Function of Temperature for the Phase Transitions in* $LiKSO_4$
14:50 – 16:30	***HS 3C Session 11 Dynamics and Time Resolved Spectroscopy I***
14:50 – 15:10	B.M. Pilles, D.B. Bucher, Lizhe Liu, P. Clivio, W. Zinth, W.J. Schreier, P. Gilch *The Decay of Triplet Excitations in All-Thymine DNA Strands*
15:10 – 15:30	S. Fröbel, L. Buschhaus, T. Villnow, O. Weingart and P.Gilch *The Mechanism of Phthalide Formation: Femto- to Microsecond Kinetics of a Complex Photoreaction*
15:30 – 15:50	P. Praus, E. Kočišová, P. Mojzeš, J. Štěpánek, F. Sureau *Intracellular Monitoring of Uptaken Aptamer by Time-Resolved Microspectrofluorometry*
15:50 – 16:10	Jiří Pfleger, David Rais, Pavla Bláhová, Jiří Vohlídal, Jan Svoboda *Time-Resolved Transient Optical Absorption of Dynamers of Bis(tpy)Oligothiophenes with* Zn^{2+} *Ion-Couplers*
16:10 . 16:30	Lucille Mendonça, Andreas Steinbacher, Raphaël Bouganne, and François Hache *Comparative Study of the Folding/Unfolding Dynamics of Poly(Glutamic Acid) in Light and Heavy Water*
16:30 – 17:00	Coffee Break
17:00 – 20:00	Poster Session I

Wednesday 27. 8. 2014

9:00 – 9:45	**HS 3A** Plenary Talk P4: Michael Ashfold *Molecular photofragmentation dynamics in the gas and condensed phase: similarities and differences*
9:45 – 10:30	**HS 3A** Plenary Talk P5: Andrzej Sobolewski *Juggling with protons: molecules and light in action*
10:30 – 11:00	Coffee Break
11:00 – 13:00	***HS 3A Session 12 Hydrogen Bonding***
11:00 – 11:20	J. Saramak, M. Kozanecki *Water clusters in liquid alkaline chloride matrices - comparison of DFT calculations and experimental data*
11:20 – 11:40	A. Loewenschuss *More H-Bonded Complexes of Athmospheric Interest*
11:40 – 12:00	D. R. Galimberti, A. Milani, and C. Castiglioni *Charge Mobility and Hydrogen Bonding From IR Intensity Parameters*
12.00 – 12:20	B. P. Kar, W. Sander *Protic Ionic Liquid N-Propylammoniumformate: A Low Temperature IR Study*
12:20 – 12:40	Valentina Closca, Andreea Celia Benchea, Mugurel Closca, Cezarina Morosanu and Dana Ortansa Dorohoi *Statistical Model of Ternary Solutions Verfied by Spectral Means*
12:40 – 13:00	K. Csankó, K. I. Ruusuvuori, B. Tolnai, P. Sipos and I. Pálinkó *Structural features of pyridylcinnamic acids and their extended hydrogen-bonded aggregations*
11:00 – 13:00	***HS 3B Session 13 Methods I***
11:00 – 11:20	Itamar Malka, Salman Rosenwaks, and Ilana Bar *Photo-guided sampling for rapid detection and imaging of traces of explosives by a compact Raman spectrometer*
11:20 – 11:40	S. Rupp, T.M. James, H. Seitz-Moskaliuk, M. Schlösser, H.H. Telle and B. Bornschein *Capillary Raman Spectroscopy for High-Sensitivity Gas Analysis*
11.40 – 12:00	R. Mundt, T. Villnow , G. Ryseck and P. Gilch *Noise Reduction in Fluorescence Kerr Gating*
12:00 – 12:20	Hans Bettermann and Björn Fischer *The Development of an On-Line Raman Detector for Hyphenation With High Temperature-HPLC AND IRMS*
12:20 – 12:40	X. Stammer, S. Heißler and Ch. Wöll *FT-IR Spectroscopy in Ultrahigh Vacuum: Surface Science Approach for Understanding Reactions on Catalytic Oxide Powders*
12:40 – 13:00	Marcello Coreno *Photoionization of Atoms, Molecules and Cluster: From Energetics to Dynamics with Novel VUV Light Sources*
11:00 – 13:00	***HS 3C Session 14 Spectroscopy for Cultural Heritage***
11:00 – 11:20	Igor Lukačević, Ivona Ergotić , Marina Vinaj *Non-Destructive Analyses of 16^{TH} Century Printed Book "Osorio" with the Colorful Fore-Edge Miniatures*

13:00 – 14:30	Lunch
15:00 – 22:00	Excursion

Thursday 28. 8. 2014

9:00 – 9:45	**HS 3A** Plenary Talk P6: Hugh Burrows *Transient absorption spectra and theoretical studies of excited and charged states of organic materials for optoelectronics*
9:45 – 10:30	**HS 3A** Plenary Talk P7: Pavel Hobza *Noncovalent interactions: theory and applications*
10:30 – 11:00	Coffee Break
11:00 – 13:00	***HS 3A Session 15 Raman Spectroscopy***
11:00 – 11:20	M. Kozanecki, M.N. Olejniczak *Intermolecular Interactions in Hydrogel-NSAIDS Systems – Raman Spectroscopy Studies*
11:20 – 11:40	Dmytro Solonenko, Alexander Milekhin, Martin Panholzer, Kurt Hingerl, Ovidiu D. Gordan, Dietrich R.T. Zahn *Interference Enhanced Raman Scattering of F_{16}CuPc Films*
11:40 – 12:00	Paola Sassi, Silvia Corezzi, Stefania Perticaroli, Lucia Comez, Alessandra Giugliarelli, Marco Paolantoni, Daniele Fioretto and Assunta Morresi *Low Frequency Vibrations of Native ans Denaturated Lysozyme: A Raman Study*
12:00 – 12:20	P. Filipczak, M. Wadlewska, M. Kozanecki *Influence of Selected Inorganic Salts on Raman Resonance Phenomenon in Water*
12:20 – 12:40	E.A. Sagitova, P. Donfack, K.A. Prokhorov, G.Yu. Nikolaeva, P.P. Pashinin, N.D. Merekalova, V.A. Gerasin, and A. Materny *The Symmetric C-C Stretching Mode Splitting in Raman spectra of substances, containing alkylammonium ions*
12:40 – 13:00	K.A. Prokhorov, Yu.V. Zavgorodnev, G.Yu. Nikolaeva, E.A. Sagitova, T.V. Vlasova, P.P. Pashinin, T.M. Ushakova, L.A. Novokshonova, E.E. Starchak, P.M. Nedorezova, A.N. Klyamkina, P. Donfack, A. Materny *Raman Diagnostics of Copolymers and Polymer Blends*
11:00 – 13:00	***HS 3B Session 16 Spectroscopy of Polymers and Films***
11:00 – 11:20	Cosutchi Irina Andreea, Dimitriu Dan Gheorghe, Zelinschi Carmen Beatrice, Breaban Iuliana and Dorohoi Dana Ortansa *Optical Activity of Transparent Polymer Foils Characterized by Spectral Means*
11:20 – 11:40	Stefano Radice, Alberto Milani, Chiara *Castiglioni Tetrafluoroethylene Based Polymers; Spectroscopy Studies and Quantum Chemical Modeling*
11:40 – 12:00	Dr. Gernot Höhne, Dr. Mathias Boese, Eric Klein *Automated FTIR Microscopy in the Polymer Industry*
12:00 – 12:20	Mario Krieg and Hans Bettermann *Tracking of micellization by fluorescence spectroscopy*
11:00 – 13:00	***HS 3C Session 17 Methods II***
11:00 – 11:20	A. Kraus, R. Größle, S. Mirz *Precise and Accurate Transmission Spectra Computed by a Modified Data Analysis Procedure in FTIR Spectrometry*

11:20 – 11:40	R. Größle, A. Kraus and S. Mirz *Non Linear Effects in IR Absorption Spectroscopy of Liquid Hydrogen Isotopologues*
11:40 – 12:00	Martin Labus, Hans Bettermann *Online In-Situ Raman Studies of Processes in a High Temperature PEM Fuel Cell*
12:00 – 12:20	H. Yurtseven and H. Özdemir *Calculation of the Specific Heat Using the Raman Frequency Shifts for the Solid I-II Transition in Benzene*
12:20 – 12:40	S. Mirz, R. Größle, A. Kraus *Investigation of the Influence of ortho/para Cconversion on the Infrared Spectra of Liquid Hydrogen and Deuterium*
12:40 – 13:00	Sanjay Kumar *Comparative Study of Excited State Dipole Moment of Coumarin Laser Dyes: Solvent and Substituent Effect*
13:00 – 14:30	Lunch
14:50 – 16:30	***HS 3A Session 18 Dynamics and Time Resolved Spectroscopy II***
14:50 – 15:10	A. Mezzetti, E.Kish Perrin, R. Spezia, M. Mendes-Pinto, D. Bovi, L. Guidoni, M. Basire, R. Vuilleumier, B. Robert *Solute-Solvent and Pigment-Protein Interactions in Carotenoids. A Combined Resonance Raman, Time-Resolved FTIR and QM/MM Study of Peridinin*
15:10 – 15:30	T. Villnow, G. Ryseck , R. Mundt, S. Fröbel and P. Gilch *Thioxanthone – A Photophysical Chimera*
15:30 – 15:50	Glushkov Alexander, Kondratenko P.A., Svinarenko Andrey, and Sakun Tat'yana *Spectroscopy of Cooperative Laser Electron-γ-Nuclear Processes in Diatomics, Multiatomic Molecules and Clusters*
15:50 – 16:10	G. M. Greetham, I. P. Clark, D. Weidmann, M. N. R. Ashfold, A. J. Orr-Ewing and M. Towrie *Waveguide Enhanced 2D-IR Spectroscopy in the Gas-Phase*
16:10 – 16:30	Marek J. Wojcik *Dynamics of protons in hydrogen bonds studied by theoretical methods and vibrational spectroscopy*
14:50 – 16:30	***HS 3B Session 19 New Materials III***
14:50 – 15:10	M.N. Olejniczak, K. Piechocki, W. Kwiecinski, S. Kadlubowski and M. Kozanecki *Molecular Approach to a Role of NSAIDS in Changes of Volume Phase Transition Temperature in Thermo-Responsive Hydrogels*
15:10 – 15:30	A.A. Maksimova, M.I. Oshtrakh, E.V. Petrova, V.I. Grokhovsky and V.A. Semionkin *Comparative Study of Chelyabinsk LL5 Meteorite Fragments with Light and Mixed Light and Dark Lithology Using Mössbauer Spectroscopy*
15:30 – 15:50	P. Matějka and A. Pospíšil *Development of vibrational spectroscopic methods for analysis of cocrystals: What is the Information about Interactions of coformers with the active ingredient?*
15:50 – 16:10	N.D. Curmei, G.V. Klishevich, V.I. Melnik, A.G. Tereshchenko *Significance of symmetry in the formation of impurity centers in molecular crystals*
16:30 – 18:00	Poster Session II
20:00 – 23:00	Conference Dinner

Friday 29. 8. 2014

9:00 – 9:45	**HS 3A** Plenary Talk P8: Siva Umapathy *Time resolved stimulated Raman spectroscopy*
9:45 – 10:15	**HS 3A** Invited Talk I9: Ozan Ünsalan *Applications of Vibrational Spectroscopy in Cultural Heritage, a case study: Valence Aqueduct (İstanbul)*
10:15 – 10:30	**HS 3A** István Pálinkó *Introduction to XXXIII. EUCMOS 2016*
10:30 – 11:00	Coffee Break
11:00 – 11:30	**HS 3A** Invited Talk I10: Hervé Vezin *Ancient carboneous matter in the context of origin of life. Memory of the past. Perspectives to Mars Mission*
11:30 – 12:00	**HS 3A** Invited Talk I11: István Pálinkó *Pristine and functionalised layered double hydroxides - syntheses, structural characterisation and catalytic application*
12:00 – 13:00	Concluding remarks
13:00 – 14:30	Lunch

Plenary talks

P1: Understanding complex reactive molecular procceses: from kinetics to comprehensive transient spectroscopy on all relevant time scales

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Complex multi-stage relaxation and reaction pathways after optical excitation of molecules in solution make the disentanglement of the underlying mechanisms challenging. We present a state-of-the-art transient spectrometer with excitation fully tunable from the deep UV to the IR [1]. Probing from 225 to 1700 nm allows for an analysis with greatly reduced ambiguity [2]. The temporal resolution of about 50 fs allows to resolve practically all relevant processes. Sample molecules/reactions are used for demonstration of the capabilities that show a new twist in the sequence of relaxation steps results that had previously been overlooked. The examples range from seemingly simple photophysical processes, through electron and proton transfer, and from unimolecular bond cleavage via two competing channels [3] to real bimolecular reactions. For the latter cases the time range given by mechanical delay stages is not sufficient. We find that adding a precisely synchronizable ns-OPO allows us to scan the delay range out to hundreds of microseconds without any gap from the femtosecond setup. As detection light the same femtosecond continua are used. This renders an unprecedented matching and precision for the wavelength scale and the opportunity to observe spectral shifts as small 0.1 nm.

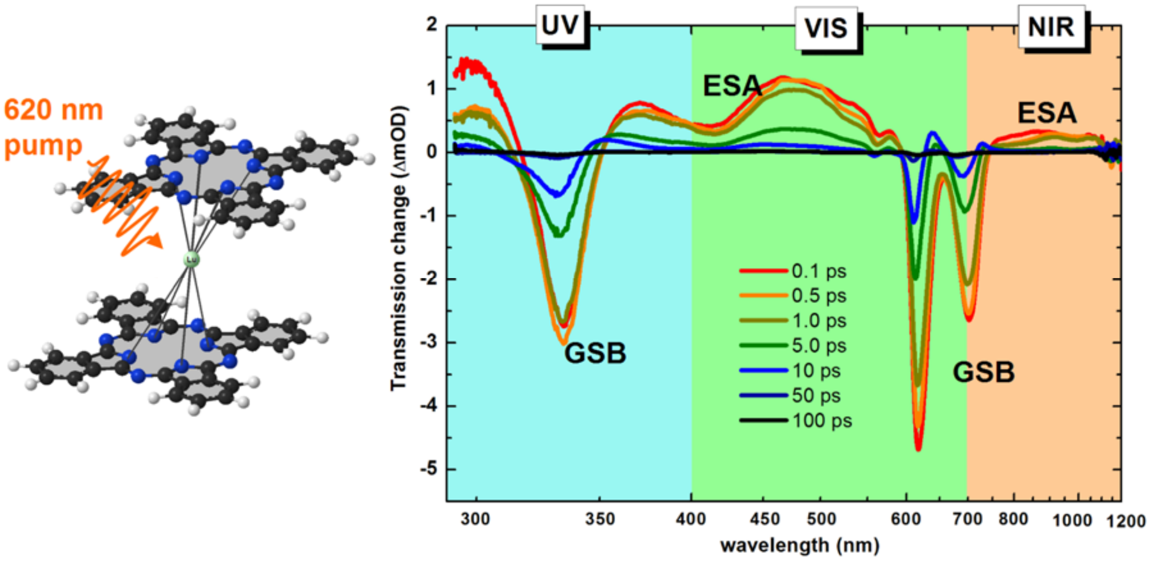

Fig 1 Transient spectroscopy of lutetium bisphthalocyanine anions after 620 nm excitation [4].

Keywords: time resolved optical spectroscopy; ultrafast chemical dynamics

References

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P2: Hard & Soft Matter Interactions in Peptides Probed by Far-IR Action Spectroscopy

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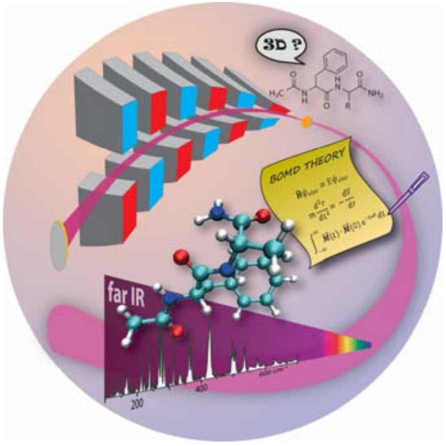
[b]*Universite d'Evry val d'Essonne, UMR 8587, Blvd F. Mitterrand, Bat Maupertuis, 91025 EVRY, France*

In nature, proteins combine soft and hard matter properties: function requires motion and a degree of floppiness, whereas stability requires stiffness. The step of forming a structural motif upon hydrogen bonding leads to a considerable stiffening of a peptide. The resulted secondary structures are expected to be directly visible in soft vibrational modes, which are typically delocalized over the entire peptide. A far-infrared spectrum, probing collective vibrations, is therefore expected to contain detailed information on the global conformational structure of peptides by combining IR action spectroscopy with quantum chemical calculations [1]. However, standard frequency calculations often perform poorly for these low-energy modes [2]. Here, we combine conformation-selective far-IR spectroscopic experiments with dynamical DFT simulations (Born-Oppenheimer Molecular Dynamics simulations (BOMD)) to provide an alternative approach to decipher this information.

We have applied this method to visualize the unique far-IR signatures of isolated gamma-turn peptides [3]. The combination of a high-resolution far-IR spectroscopy with BOMD have allowed us to document and assign low frequency vibrational motions, to reveal new details on the conformational structure, and distinguish between two almost identical secondary peptide structures. Recently, we have expanded our method to larger and more complex peptides in order to investigate the folding patterns of capped polyalanines. Where spectral congestion in the Amide I and II region prevents an unambiguous structural assignment, allow far-IR spectra us to picture structuration upon increasing intramolecular interactions via global backbone modes and hydrogen bond stretch vibrations!

The here presented combination of far-IR action spectroscopy and theory holds great promise for advanced structural analysis of peptides of increasing size and complexity and the understanding of functional vibrations. Additionally, the direct probing of intra- and intermolecular hydrogen bonds contributes to answering question concerning specificity and selectivity in molecular recognition.



***Keywords**:*
IR Action Spectroscopy; hydrogen bond interactions; peptide mimics, ATP, Structure elucidation; local and global motions

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P3: Conformation and Dynamics of flexible molecules, biomolecules and molecular complexes by rotational spectroscopy

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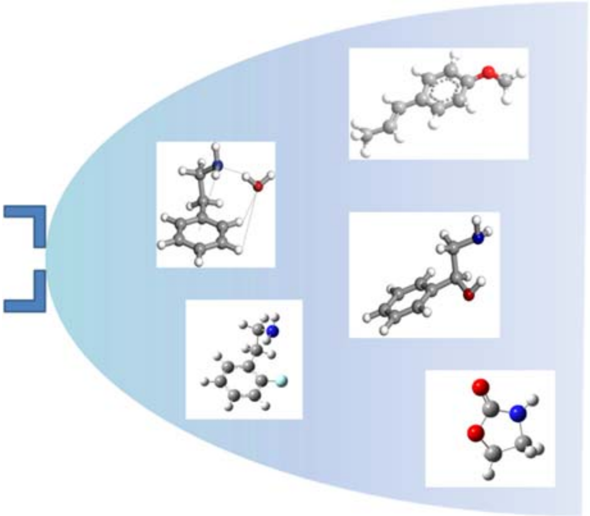
Some biomolecules are characterized by extreme conformational flexibility, originating from multiple torsional degrees of freedom, which makes folding and functionality possible.

While the topology of the molecules is determined by covalent forces, the conformational space of such systems is generally shaped by non bonding interactions occurring within the molecule or with the surroundings. The high number of low energy conformations and the presence of large amplitude motions taking place through shallow potential energy surfaces, are peculiar of these flexible molecules and their weakly bound molecular complexes and usually give rise to very complex rotational spectra, which represent a challenge for spectroscopic and computational methods.

Rotational spectroscopy of molecules of biological interest isolated in the gas phase in the conditions of a supersonic expansion gives very detailed structural and dynamical information on their intrinsic properties. These properties in turn can be directly compared to the outcome of high level ab initio calculations which are used to rationalize the results.



Chosen examples [1-4] and unpublished results will be given of rotational spectroscopy of flexible molecules, biomolecules and small molecular complexes studied in the isolated conditions of a free jet expansion. The examples include: adrenergic neurotransmitters, drugs, odorants and model systems. It will be shown how non-bonding interactions compete to shape the conformational space of the molecules and how these interactions can be drastically changed through substitution of even a single atom. Also, complexation with solvent molecules can influence the flexibility of molecules, locking some particular conformation, or changing the nature of the interactions, and thus the shape of the conformational surface.

Conformational surface, Non bonding interactions, Large amplitude motions, Rotational spectroscopy, ab initio calculations

References

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P4: Molecular photofragmentation dynamics in the gas and condensed phase: similarities and differences

Michael N.R. Ashfold

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Azoles and phenols are key components of the chromophores in nucleobases and aromatic amino-acids, which dominate the near-UV absorption spectra of many biological molecules. $\pi^*\leftarrow\pi$ transitions are responsible for these strong UV absorptions, but these molecules also possess excited states formed via $\sigma^*\leftarrow\pi$ electron promotions. These $\pi\sigma^*$ excitations have much smaller absorption cross-sections, but are attracting much detailed attention. Photofragment translational spectroscopy experiments and complementary *ab initio* theory have been applied to the study of H atom loss following UV photoexcitation of many such heteroaromatic molecules in the gas phase.[1] These studies show that X–H bond fission (X = heteroatom) following direct excitation to the $1^1\pi\sigma^*$ state (or, in phenols, by tunneling under the conical intersection between the $1^1\pi\pi^*$ and $1^1\pi\sigma^*$ potential energy surfaces) is often an important non-radiative decay channel, and that the resulting radical products are formed in a very limited sub-set of the possible vibrational states. Identifying these latter states can provide detailed insights into the non-adiabatic couplings that enable the evolution from photoexcited parent molecule to eventual fragments.

This presentation will (i) summarise the state of knowledge derived from such gas phase studies, (ii) highlight the extent to which such knowledge can inform our interpretation of ultrafast pump-probe studies of the UV photofragmentation of similar molecules ((thio)phenols, anisoles and ethers) in solution [2,3] and (iii) demonstrate how such solution phase studies offer a route to exploring photoinitiated ($\pi\sigma^*$ state mediated) ring opening of heterocyclic molecules like furans and thiophenes.

Keywords: Heteraromatic molecules, photofragment translational spectroscopy, ultrafast pump-probe spectroscopy.

References

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P5: Juggling with Protons: Molecules and Light in Action

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Proton is the lightest nuclei and its monatomic form (H_1) is the most abundant chemical substance in the Universe. The relative lightness and small size of this “quantum” particle explains the unusually high diffusion rate of the ‘excess’ proton through the hydrogen bond network of water molecules. We have shown recently that radiationless deactivation channel associated with conical intersection between the electronically excited state and the ground state for proton-transfer reaction along hydrogen bonds may provide a very effective mechanism for explanation of functionality of commercial organic photostabilizers, and the photostability of biological molecules such as DNA and proteins [1].

A question of control of proton motion with the aid of light fields is not only of fundamental interest, but may also results in some practical applications. Thus the mechanistic aspects of the excited-state intra-molecular proton-transfer (ESIPT) process may be utilized in construction of optically driven photostable molecular switches (a) [2], while the electron-driven proton-transfer (EDPT) phenomenon along the inter-molecular hydrogen bond(s) may provide a template for designing of macromolecular systems, which are able to oxidize water using solar radiation (b) [3].

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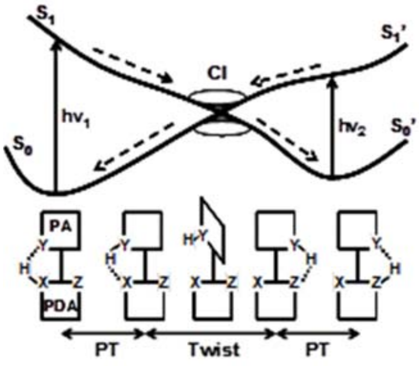
(a)



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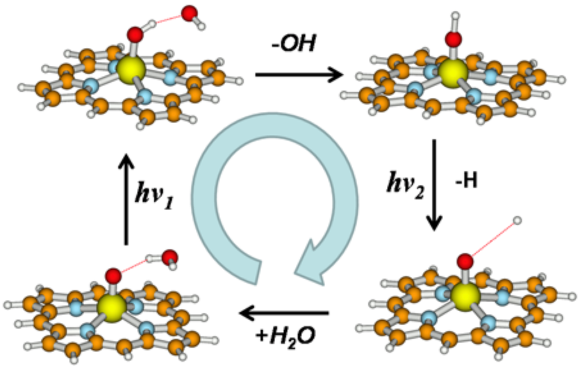

Keywords: proton transfer, molecular switch, water splitting

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P6: Transient Absorption Spectra and Theoretical Studies of Excited and Charged States of Organic Materials for Optoelectronics

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Organic semiconductors have emerged over the last three decades as commercially important materials for optoelectronic applications. They have the advantage over inorganic materials of possibilities of solution processing to produce cheap, large area devices, in addition, their properties can be readily tuned by appropriate chemical substitution. Typical applications range from various types of thin film transistors, through light emitting devices to flexible photovoltaic systems, chemical and biological sensors. Both polymeric and small molecule systems are used for these applications. Optimization of the properties requires a detailed understanding of the electronic spectral properties of both excited states and charged species.

Experimental results will be presented on the absorption spectra of excited singlet and triplet states of conjugated polymers, copolymers and oligomers with fluorene, thiophene and *p*-phenylene vinylene repeat units under conditions of isolated conjugated polymer chains. Results for fluorene based copolymers will be compared with DFT and TD-DFT calculations [1]. Conformational relaxation of the backbone is important deactivation pathway of excited singlet states of these systems [2]. Ultrafast time-resolved fluorescence studies on *p*-phenylene vinylene oligomers of different chain lengths will show how this can be separated from solvent reorientation effects [3].

Chemical, photochemical and radiation chemical routes have been used to prepare the one-electron oxidized and reduced species form these compounds, termed radical ions by chemists and polarons by semiconductor physicists. The advantages and limitations of each of these methods will be discussed. UV/vis/NIR spectra will be presented of charged states of a variety of polymeric and small molecule materials of relevance in optoelectronics. In keeping with the relatively localized excitation in these systems, negatively and positively charged species for each compound show very similar transient absorption spectra [4].

Acknowledgement: I am indebted to the work of many students, colleagues and collaborators, whose names are included in the references. I am grateful for funding from the FCT through the project Pest-OE/QUI/U10313/2014.

Keywords: Conjugated polymers and oligomers; Excited state absorption; Radical ion absorption

References

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P7: Noncovalent Interactions: Theory and Applications

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All life on our earth can be viewed as an application of supramolecular chemistry, with noncovalent interactions playing a central role. Noncovalent interactions are responsible not only for structure of molecular complexes but also of biomacromolecules and their complexes with ligands. To understand the function of biomacromolecules and their complexes one should first understand their structure.

Calculations of noncovalent interactions belong to the most difficult part of computational chemistry. Only the most advanced methods covering large portion of correlation energy provide reliable stabilization energies and geometries of various types of noncovalent complexes. Special position plays the coupled cluster CCSD(T) approach (covering single-, double- and triple excitations) which stands as the "gold standard" method of computational chemistry because of its outstanding accuracy for determination of various properties of noncovalent complexes. Accuracy of the method was tested by performing calculations of stabilization energy of various complexes at higher theoretical level, CCSDT, CCSDTQ, CCSDTQP and even full CI.

Highly accurate calculations going beyond the CCSD(T)/complete basis set (CBS) limit were used for determination of structure and binding energy (D_0) of HF dimer. The calculated D_0 agree excellently with the experimental value and the largest error originates in evaluation of ZPV energy. Harmonic approach (at the CCSD(T)/CBS level) provides substantial error and inclusion of anharmonicity is thus inevitable.

Databases based on CCSD(T) characteristics (e.g. S22, S66, X40 and A24 databases from our laboratory) are used for design, verification and parametrization of newly developed computational techniques allowing to treat extended complexes. Special position is played by semiempirical quantum mechanical methods since they can be applied to biomacromolecular complexes having more than 10 000 atoms. PM6-D3H4X method developed in our laboratory provides very good estimates of binding energies for protein - ligand complexes stabilized by different noncovalent motifs like hydrogen or halogen bonding. The method is the base of our scoring function used in *In silico* drug design and recent progress in this field will be summarized.

P8: Time Resolved Stimulated Raman Spectroscopy

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Understanding a chemical reaction requires detail knowledge of the molecular vibrational motions on a multidimensional potential energy surface. Typical time scale range for a molecular vibration is from 10 fs to 1 ps. In order to observe a chemical reaction in real time, high time (as fast as a vibration) and spectral resolution (vibrational line width) are a necessity. In addition, one needs to monitor the dynamics of many vibrational modes simultaneously to get a better understanding of the reaction mechanism. Ultrafast time resolved stimulated Raman spectroscopy has both time (~ 100 fs) and spectral resolution (~20 cm^{-1}) to observe dynamics of many vibrational modes in real time. This technique can also provide very useful information on the rate of energy flow which can be intra (IVR) and intermolecular (vibrational cooling) and details on the coupling of solute vibrations to the surrounding solvents. Based on this principle, femtosecond stimulated Raman spectroscopy (FSRS) technique has been applied to probe the dynamics of cis-trans isomerization, charge transfer dynamics, excited state proton transfer dynamics *etc*. [1], [2]. Ultrafast Raman loss spectroscopy (URLS) is a similar nonlinear Raman technique [3], [4]. A typical stimulated Raman experiment employs a narrowband Raman pump laser beam (pulse width of ~1 ps) and a broadband probe laser beam (pulse width ~ 100 fs), and a photo excitation pump beam (~ 100 fs). In such a case the temporal resolution is fully determined by the actinic pump-probe cross-correlation, while the spectral resolution is only set by the Raman pump pulse spectral width. In FSRS, the probe is a continuum Stokes field with respect to the narrowband Raman pump pulse, whereas in URLS the probe is chosen to cover the entire Stokes and anti-Stokes regions with respect to the Raman pump wavelength and the scattered light is only observed on the anti-Stokes side. We have studied the photo-isomerization of trans-Stilbene in different solvents after 280 nm (~ 100 fs) phot-excitaion (figure 1). The main marker band is C_{et}=C_{et} stretch (1560 cm^{-1}). Analysis of URLS spectra of this Franck-Condon active mode within 2 ps after photo-excitation shows oscillatory behavior (figure 1(b)). The origin of this oscillation is due to the coupling of Franck-Condon active mode with the low frequency modes.

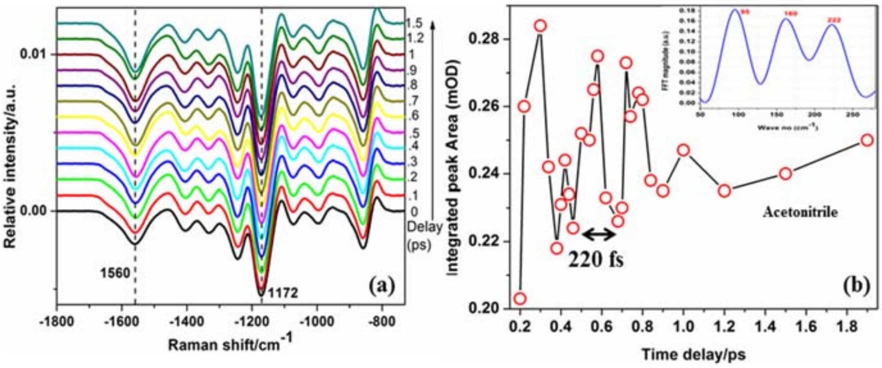

Fig. 1 Few URLS spectra of trans-Stilbene in the S_1 state are shown (a). Integrated intensity of 1560 is shown with respect to time delay. Inset is FFT of the observed oscillation. Main band observed in FFT plot are 90, 160, 222 cm^{-1} cm^{-1}

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Invited talks

I1: Novel strategies for solving highly complex NMR spectra of solutes in liquid crystals

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The NMR spectra of orientationally ordered molecules increases rapidly in complexity with the number of coupled nuclear spins. For example, the spectrum of n-pentane as solute in a nematic liquid-crystal solvent (12 coupled proton spins) consists of roughly 20,000 transitions, many of which overlap. As an example the NMR spectrum of n-butane is shown in Figure 1. The analysis of such complicated spectra by line-assignment techniques is fraught with difficulty.

However, application of the ideas of genetic evolution via evolutionary strategies makes possible the analysis of spectra [1], which are quite probably not solvable by ordinary methods. In particular, the covariance matrix adaptation evolution strategy (CMA-ES) [2] uses the idea of mutation and the results of previous trials to give solutions to quite complicated spectra [3]. The techniques described herein have already led to solution of NMR spectra that were not achieved with older techniques, and show promise for cracking even harder problems in the future.

An important aspect with NMR spectra of solutes in liquid-crystal solvents is the presence of a broad underlying baseline from the solvent protons. An automatic baseline removal method will be discussed [4].

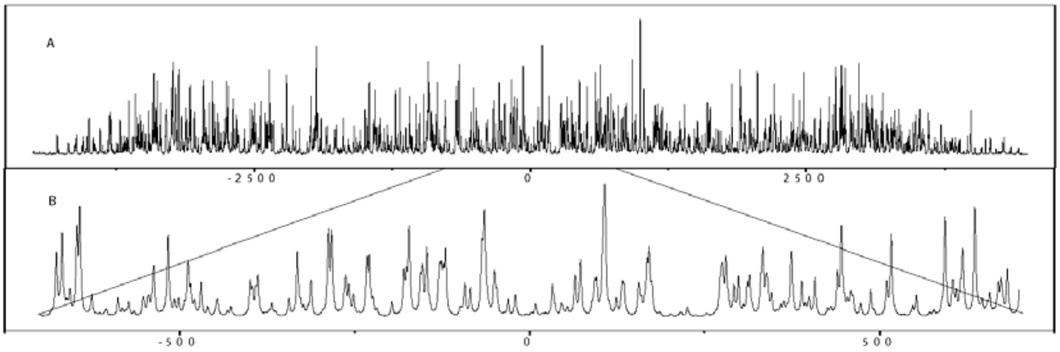

Figure 1. (A) NMR spectrum of n-butane in a 'magic mixture' liquid crystal at 298.5 K.. (B) An expanded region of the spectrum (B). The horizontal scale is in Hz.

Keywords: genetic algorithm, evolutionary strategy, evolutionary algorithm, NMR, spectral analysis, baseline removal, liquid crystal, ordered liquids, anisotropic

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I2: Polarized Raman spectra: opportunities & challenges – What about polarized SERS?

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The molecular orientation of uniaxially drawn active agent doped polymer films has been already suggested as a significant parameter for controlled release monitoring [1]. On the other hand, a novel surface enhanced Raman scattering excitation/collection configuration with a new oscillating cell combined with right angle scattering collection geometry has been also examined for quantitative Surface Enhanced Raman Scattering (SERS) measurements from nano-colloidal noble metal solutions [2]. Additionally, the SERS was recently introduced as a new method to monitor the level of drugs [3] as well as of multi-walled carbon nanotubes (MWCNTs) [4] at very low concentrations performing fast SERS measurements.

In this context, we try to correlate the molecular orientation, estimated by polarized Raman spectra and IR dichroic ratios, with the early/controlled release of non-steroidal anti-inflammatory drugs (NSAIDS) from biopolymer matrixes, like polypropylene (PP), see Fig. 1, and MAXON, probed by fast SERS measurements.

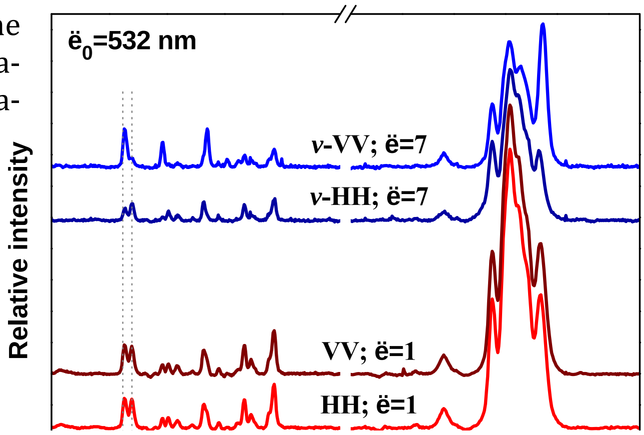

Fig.1 Polarized Raman spectra of an undrawn (λ=1) and a uniaxially drawn (λ=7) PP-2wt% Ibuprofen specimen

Furthermore, the Raman cross section was studied as a function of both nanoparticle aggregation (DLS & SEM) and polarization geometry (polarized SERS) in order to provide solid arguments for optimization of the detection limits of SERS.

Keywords: Release Monitoring; Drawn Samples; Quantitative Measurements; Nanoparticle Aggregation

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I3: Non Bonding Interactions in Molecular Clusters

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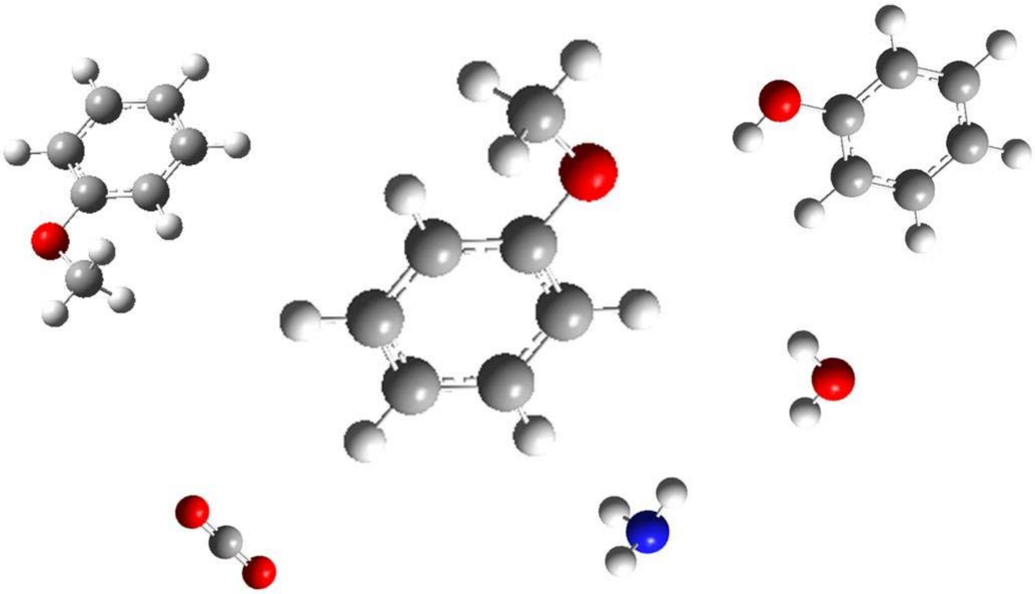
Structure and properties of molecular clusters are often regulated by a subtle balance of different interaction terms. Anisole (methoxybenzene) is a convenient reference chromophore for studies on clusters as it allows for dipolar and dispersion interactions while its capability to be involved in stronger interactions, such as hydrogen bonds, is limited to the role of proton acceptor.

Recent experimental results on different molecular clusters involving anisole obtained by REMPI-TOF spectrometry, high resolution LIF experiments and photoelectron spectroscopy will be discussed. These clusters are formed and studied in the gas phase by means of molecular beam techniques. Laser spectroscopy experiments provide many details on these systems both in the ground neutral and ionic states and in the first electronic singlet excited state.



Keywords: clusters;REMPI;LIF

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I4: Infrared Nanoscopy Applied to Microbiology

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We have developed an innovative infrared microspectroscopy technique, called AFM-IR, based on the coupling between a tunable infrared laser and an AFM (Atomic Force Microscope). This coupling allows us to perform ultra-local infrared spectroscopy and chemical mapping at the nanometer scale. The principle [1] is based on detecting the local thermal expansion of the sample, irradiated at the wavelength of its absorption bands. This expansion is detected by the AFM tip in contact mode like a damped oscillation. The technique can provide nanoscale IR absorption spectra and chemical maps by measuring the oscillation amplitude. We have validated this technique by comparing the infrared spectrum of a single *E.coli* bacterium and the corresponding FTIR spectrum, and showing the possibility to perform chemical mapping with sub-wavelength spatial resolution (50 nm) [2]. Later, better outcomes have been obtained in polymer science [3,4,5] with the nano-IR™ (AFMIR commercial version).

Our work is now mainly focused on microbiology [6,7] systems and cell imaging [8,9]. For example, we are now interested by the production optimization of bio-polymer (PolyHydroxyButyrate) done by a photosynthetic bacteria, *Rhodobacter sphaeroides.* The AFMIR technique allows us to easily detect the polymer (PHB) vesicles inside the bacterium due its specific absorption band (ester carbonyl at 1740 cm^{-1}) that is different from those of the bacterium. Similar studies are also provided on different bacteria like *Streptomyces* to optimize the production of bio-fuel precursor (triacylglycerols, ***Figure1***).

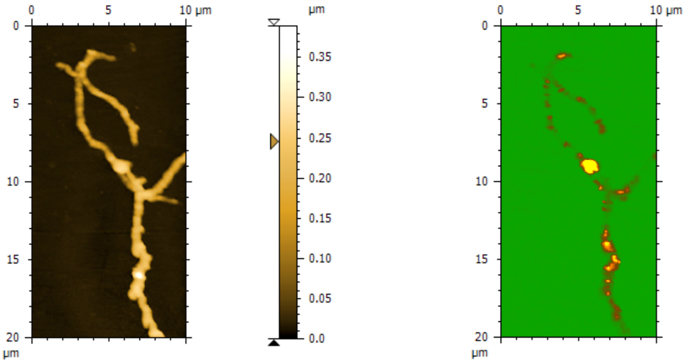

Figure1 : (Left), AFM topography of a *Streptomyces* bacterium filament. (Right) Corresponding AFMIR Chemical mapping at 1740 cm^{-1} revealing the lipids vesicles.

Keywords: Infrared spectroscopy, microbiology, atomic force microscopy

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I5: Molecular astro-spectroscopy; bridging gas phase and solid state processes in space

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Today, astrochemists explain the chemical complexity in space as the cumulative outcome of reactions in the gas phase, on the surfaces of interstellar grains, and in icy grain mantles. Gas phase models explain the observed abundances of molecules like the linear carbon chain radicals C_6H and $HC_{11}N$, but fail to explain the observed abundances of several stable species, e.g., water, methanol and acetonitrile - a closely related molecule for the simplest amino acid glycine - as well as larger compounds such as glycolaldehyde, dimethylether and ethyleneglycol. Evidence has been found that these and other complex, organic compounds form on icy dust grains that act as catalytic sites for molecule formation. External triggers are provided upon (non)energetic processing, such as irradiation by vacuum UV light, interaction with particles (atoms, electrons and cosmic rays), or heating.

This talk summarizes the outcome of recent spectroscopic work, focusing on both gas phase and solid state spectra of molecules of astronomical interests, and bridging the grain-gas-gap. New cavity based techniques are introduced as highly sensitive spectroscopic tools to study astrophysically relevant transients that are hard to generate in large abundances. It also shows how spectroscopy can be used to characterize *in situ* and in real time chemical processes in interstellar ice analogues, e.g. upon atom addition reactions and vacuum UV induced photoprocessing, and how this explains or guides astronomical surveys investigating the molecular inventory of the inter- and circumstellar medium.

Keywords:Laboratory Astrophysics;Interstellar chemistry;Plasma spectroscopy

I6: Raman Microspectroscopy in Medicine. Can it Solve the Sperm Condrum

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Relatively recently, Raman microspectroscopy has been introduced into the diagnosis, investigation and characterization of a myriad of medical conditions. A case in point is Reproductive Medicine, where despite technological and analytical advances, fertility clinics worldwide are confronted with the large disparity between high fertilization rates achievable by modern treatments yet concomitantly low pregnancy and/or “take home baby” rates. Modern analytical techniques have significantly increased the amount of information available, however the ability to non invasively and non destructively assess the integrity of sperm nuclear DNA (nDNA), then select a homogeneous sperm population, all of which are capable of successfully achieving a pregnancy and a healthy baby remains elusive. In fact, the sperm nDNA tests currently available are of limited clinical use as they destroy the sample.

For a number of years Raman microspectroscopy has successfully been used in the analysis and selection of living bacteria and stem cells without any apparent adverse reactions. We are an interdisciplinary collaboration of clinicians, researchers in male reproductive function, mathematicians and physicists who have undertaken a systematic appraisal of the method’s utility on sperm DNA assessment. In our initial studies we modified and optimized a confocal Raman microspectroscopic system and showed it was able to detect the presence, extent and location of oxidative, UV induced and naturally occurring nDNA damage as well as intact DNA in air dried sperm. In following up work, we found the assessments to be reproducible, accurate and similar to those of an independent spectroscopic method (FTIR) and the most validated sperm nDNA assay (Sperm Chromatin Structure Assay – SCSA).

Our aim is to develop an innovative automated system which can provide accurate information on a living sperm’s DNA status and thus provide a means of selecting and catering the treatment options to suit the individual patient/couple.

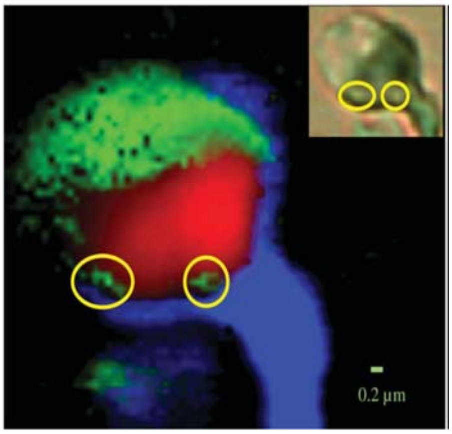

Figure 1: Hyperspectral Raman representation of a sperm

Keywords: Raman microspectroscopy;Medicine;Reproduction

I7: Digging Molecules out of Vibrational Spectra with DFT and Statistical Analysis

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Thanks to the exciting developments in computer hardware and computational quantum chemistry (notably Density Functional Theory methods) we are facing new scenarios in theoretical vibrational spectroscopy. On one side increasingly large molecular systems can be addressed by DFT so that the experimental vibrational spectra can be interpreted on the light of unprecedented theoretical data, enriching the existing empirical understanding of vibrational spectra of big molecules. On the other side, vast vibrational structure datasets can be computed in a relatively short time, thus opening new possibilities for approaching difficult conformational problems or the analysis of samples with a complex molecular structure. Statistical analysis tools prove to be extremely important for the efficient screening and rapid understanding of vibrational structure datasets composed by hundreds of entities, which would be otherwise very difficult to sort out by human inspection, on a one-by-one basis.

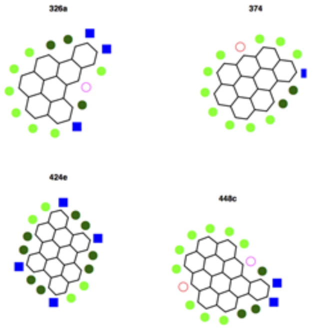

Fig.1 Structures of some of the PAHs considered, with different CH bonds.

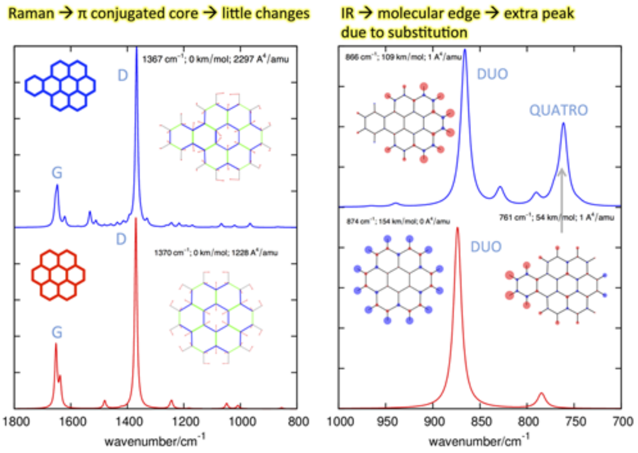

Fig.2 Slight PAH structure change mostly affects IR.

The vibrational structure of fifty-one Polycyclic Aromatic Hydrocarbons (Fig. 1) has been analyzed in order to find spectroscopic signatures useful for the molecular characterization of complex samples of combustion origin [1]. The outcome of this analysis, carried out with statistical tools, is the identification of spectroscopic markers in the IR (out-of-plane CH bending modes) that carry significant information about the topology of CH bonds at the molecular edge. These results show the usefulness of IR spectroscopy for the molecular characterization of several systems, ranging from combustion products, to π-conjugated polymers with aromatic moieties and molecular graphenes in materials science. For the latter systems Raman spectroscopy is the main vibrational spectroscopy technique usually considered, and it is an excellent tool for the characterization of graphene [2]. However, based on these findings, one can foresee that IR spectroscopy may add valuable information on the molecular structure of edges in condensed aromatic systems, to which Raman spectroscopy appears to be less sensitive (see Fig. 2).

Keywords: Density Functional Theory; molecular graphenes, Polycyclic Aromatic Hydrocarbons (PAH)

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I8: Enantiomer Identification of Chiral Molecules using Broadband Microwave Spectroscopy

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Chiral molecules have fascinated chemists for more than 150 years. The two enantiomers of a chiral molecule can have completely different (bio)chemical effects. For example, the active components of many drugs are of one specific handedness, such as in the case of ibuprofen. In nature as well as in pharmaceutical applications, chiral molecules often exist in mixtures with other chiral molecules. The analysis of these complex mixtures to identify the molecular components, to determine which enantiomers are present, and to measure the enantiomeric excesses (ee) still remains a challenging task for analytical chemistry, despite its importance for modern drug development.

We present here a new method of differentiating enantiomers of chiral molecules in the gas phase based on broadband rotational spectroscopy.[1,2] We exploit that the enantiomers of chiral molecules are mirror images of each other and so are their dipole moments. In our experiments, this mirror-image character of the dipole moments results in differences in the phases of the acquired signal by 180° for the two enantiomers. The phase also provides information on the absolute configuration of the particular enantiomer. Furthermore, the signal amplitude is proportional to the ee. A significant advantage of our technique is its inherent mixture compatibility due to the fingerprint-like character of rotational spectra. In this contribution, I will introduce the technique and present our latest results on chiral molecule spectroscopy and enantiomer differentiation.

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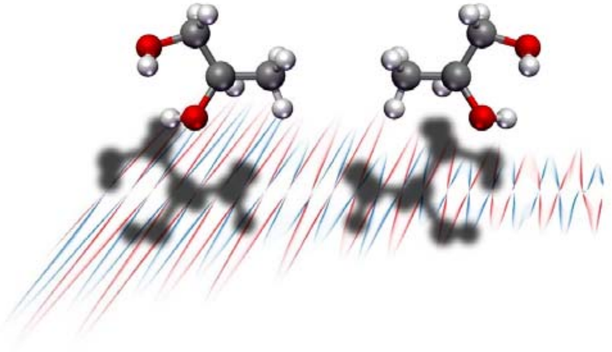

I9: Applications of Vibrational Spectroscopy in Cultural Heritage, a case study: Valence Aqueduct (İstanbul)

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This study involves Raman spectroscopic (250-1400 cm^{-1}), SEM-EDX and Geographical Information System studies of the pollutants on the walls of Valence Aqueduct (Bozdoğan Kemeri), Istanbul, Turkey. Raman spectroscopy is a useful analytical method in characterization of painting materials and corrosion products. Especially, when it is not possible to take the samples from the place they exist, handheld Raman spectrometers play an important role to identify the materials in these samples. Furthermore, more information could be gathered when it is combined with SEM-EDX studies. On the other hand, regarding the cultural heritage, it is crucial to determine precise coordinates of the historical peninsula and the samples which have been exposed to pollutants, by Geographical Information Systems in order to study them and take precautions for the future. Handheld Raman spectrometer (NanoRam by B&WTek) allows recording of acceptable and good quality spectra of a large majority of minerals outdoors. Raman spectra of minerals and pollutants in this study were obtained using 785 nm laser excitation source. Observed Raman bands are found at correct wavenumber positions within ±3 cm^{-1} compared to reference values in the literature. Taking into account the resolution of the spectrometer (10 cm^{-1}), the results are still reliable and applicable on such systems. Areas of potential applications of these instruments include all kind of common geoscience work outdoors.

Keywords: Valence Aqueduct, air pollution, Raman Spectroscopy, Information and documentation management, GIS (Geographical Information Systems)

I10: Ancient carboneous matter in the context of origin of life. Memory of the past. Perspectives to Mars Mission

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Carbonaceous material, whether land-based (coal, ancient cherts, etc ...) or extraterrestrial (carbonaceous meteorites) has paramagnetic defects which electron spins can be detected with high sensitivity by electron paramagnetic resonance (EPR) using microwave radiation.

In particular, we have recently shown that continuous wave EPR allows probing finely meteoritic and ancient cherts Insoluble Organic Matter (IOM). Pulsed EPR techniques but also EPR imaging techniques have allowed to demonstrate extreme deuterium enrichment of the radicals of the IOM for Orgueil meteorite. The very fine and nondestructive analysis of the carbonaceous material shows that it is a good marker of the memory of the past and can discriminate the terrestrial or extra-terrestrial nature of this matter. In the context of the origin of life in Mars, we will present the experimental challenge for detecting such carboneous matter in order to identify biosignatures.

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I11: Pristine and functionalised layered double hydroxides – syntheses, structural characterisation and catalytic applications

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Our recent activities in the synthesis and some applications of pristine as well as functionalised layered double hydroxides (LDHs) are overviewed.

Besides the usual synthetic methods (co-precipitation, dehydration-rehydration) a mechanochemical route for the synthesis of LDHs and their intercalated varieties, occasionally combined with ultrasound treatment, has been developed and applied. The strength of the method could be demonstrated *via* the straightforward synthesis of Ca(II)Sn(IV)-LDH, which was unsuccessful by the traditional wet chemical method. The mechanochemical methods worked well in the preparation of intercalated organic-inorganic host-guest complexes. It is to be noted, however, that the majority of the intercalated materials discussed here was made by the more commonly used dehydration-rehydration method.

During our work large variety of layered double hydroxides, both the hydrocalumite- and the hydrotalcite-types, were prepared. Some of the materials were used as-prepared, some were applied as host materials of various organic anions, others were used after heat treatment and, in some instances, the reconstruction behaviour of the heat-treated substances was also investigated. The obtained materials were thoroughly characterised by a range of state-of-the-art instrumental methods including scanning and transmission electron microscopies, energy-dispersive X-ray analysis, X-ray diffractometry, Fourier-transform infrared spectroscopy and dielectric relaxation spectroscopy. Molecular modelling was used to determine the orientation of the intercalated organic anions among the layer of LDH samples.

The detailed study on the rehydration of dehydrated CaFe-LDH (generally, this area of LDH research was largely neglected as the corresponding scientific literature attests) was performed with the combination of thermal methods, infrared and dielectric relaxation spectroscopies on partially rehydrated samples.

Catalytic studies using LDHs were conducted in two directions. One of them was the investigation of the applicability of the as-prepared LDH. The other one was the most common usage, *i.e.,* destroying the layered structure with heat treatment; then, partially crystalline mixed oxide is formed with many defects, and then, use this material as catalyst.

Pristine, uncalcined LDHs could serve as nanoreactors in photoinitiated [2+2] cyclisations of various cinnamate derivatives.

Exploiting the intercalation ability of the LDHs, various organic-inorganic nanohybrids were prepared, where the organic anions possessed secondary nitrogen. The presence of this moiety makes them potential organocatalysts, however, without the LDH they work in the same phase as the reactants and the products, and they are sacrificed during the reaction. Intercalation made these materials potential heterogeneous catalysts with the advantage of easy recycling.

Keywords: layered double hydroxides, detailed characterisation, various applications

Session 1: Spectroscopy of isolated molecules I

Session 1: Spectroscopy of isolated molecules I

SpIM 1.1 Precision Spectroscopy of the Simplest Molecules

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The molecular ions H_2^+, HD^+ and their relatives are fundamental quantum systems: three-body bound quantum systems that can be accurately calculated *ab initio* by Quantum Electrodynamics, using as input certain fundamental constants, in particular the Rydberg energy and the two mass ratios of the three constituent particles. A comparison between experimental transition frequencies and the ab initio results therefore provides a test of the validity of theoretical treatments, and/or a determination of these fundamental constants. At present, the experimental inaccuracies of the transition frequency measurements are still higher than the theoretical or fundamental constants inaccuracies, resulting in an on-going experimental challenge.

We perform high-resolution rotational and rovibrational spectroscopy as well as quantum state manipulation of HD^+, which allows one-photon electric dipole transitions. The molecular ions are trapped in an ion trap and sympathetically cooled by laser-cooled atomic ions (Be^+) to 10 mK in order to reduce line broadening. We developed a novel frequency-comb-based, continuous-wave 5 μm laser spectrometer [1] and performed spectroscopy at the Doppler limit [2]. To our knowledge, the achieved spectral resolution is the highest obtained so far in the optical domain on a molecular ion species. We were thus able to optically resolve the hyperfine structure.

Recently, the coefficients of the systematic shifts of the transition frequencies of H_2^+ and HD^+ due to external fields have been computed *ab initio* and it was estimated that under realistic experimental conditions experimental fractional inaccuracies of selected rovibrational transition frequencies could be at the 1×10^{-17} level [3,4,5]. This opens up the prospect of using these molecules to test whether the ratio of electron and proton masses is indeed a time-independent fundamental constant.

Keywords: *ion trap, rovibrational spectroscopy, laser cooling, precision measurements*

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SpIM 1.2 Rotationally Resolved Electronic Spectra of the Electronic Origin and Some Vibronic Bands of Guaiacol and Mequinol: Vibrational Assignment of Low-Frequency Bands

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The molecular structure of guaiacol (2-methoxyphenol) and mequinol (4-methoxyphenol) is studied via high resolution electronic spectroscopy in a supersonic jet and contrasted with theoretical ab initio calculations. Guaiacol was determined to be planar (C_s symmetry) in its ground electronic state with an inertial defect of -3.459 u*Å^2, and upon electronic excitation the molecule gets less planar (C_1 symmetry) with an inertial defect of -4.132 u*Å^2. Furthermore, we did examine two low frequency vibronic bands of guaiacol; which are assigned to an out-of-plane vibration and to a combination of low-frequency modes of the molecule, respectively; this provides an explanation for the two high resolution spectra exhibited by the molecule in the second vibronic band. Two bands of the mequinol molecule were also studied and assigned to the electronic origins of the two possible conformers of the molecule, trans- and cis-, respectively.

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Session 1: Spectroscopy of isolated molecules I

SpIM 1.3 Spectroscopic and Theoretical Investigations of Molecular Vibrations and Potential Energy Surfaces in Ground and Excited Electronic States

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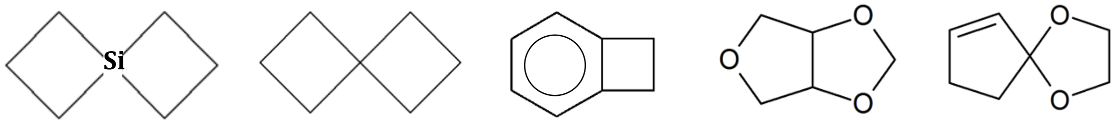
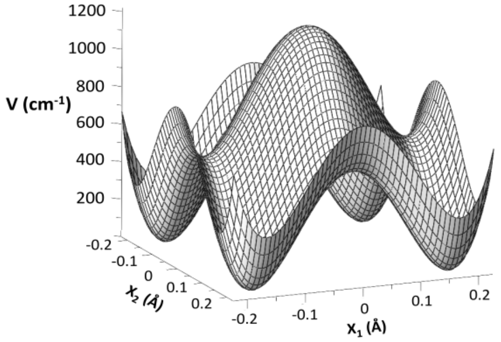
Vapor-phase infrared and Raman spectroscopy have been utilized to study molecular vibrations of selected molecules in their electronic ground states while laser induced fluorescence (LIF) and ultraviolet (UV) absorption spectra have been used to study the electronic excited states. *Ab initio* and DFT calculations were used to complement the experimental work. The two-dimensional ring-puckering potential energy surface (PES) of 4-silaspiro(3,3)heptane (**I** in Fig. 1) has been calculated. Fig. 2 shows the PES in terms of the two ring puckering coordinates. Both four-membered rings are puckered with dihedral angles of 34°, and the rings are tilted by 9° relative to each other. The quantum state energies and wavefunctions (Fig. 3) have been calculated for this surface. The vibrational spectra confirm the distorted symmetry of the molecule. Similar results were found for spiro(3,3)heptane (**II**). The infrared, Raman, LIF and UV studies of benzocyclobutane (**III**) have also been completed and the results for its ground and excited states have been compared to similar bicyclic molecules.



I **II** **III** **IV** **V**

Fig.1. Molecules of Interest

The infrared and Raman spectra of **IV** and **V** have also been investigated and theoretical calculations have been carried out to calculate the energy differences between the conformers. **IV** can exist as two different conformers while **V** has four conformations all at different potential energies. The two-dimensional PESs for both molecules have been calculated in terms of their out-of-plane vibrational coordinates. The corresponding energy levels and wavefunctions were also obtained. The UV spectra and theoretical calculations of pyridine and several fluoropyridines show that these molecules have barriers to planarity in their excited states. For pyridine it is only 3 cm^{-1}, but the fluoropyridines are much more puckered.



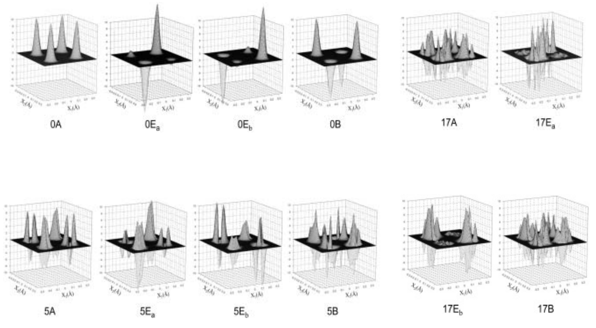


Fig. 2. PES for the ring-puckering motions of **I**

Fig. 3. Selected wavefunctions of **I**

Keywords: Potential energy surfaces; Infrared; Raman; Excited states; Theoretical calculations.

SpIM 1.4 Isomer-Specific Product Detection of Xylyl Radical Rearrangement and Decomposition Using VUV Synchrotron Photoionization

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Petrol additives such as xylenes (dimethyl benzenes), existing in three different isomers, are applied due to their high octane ratings and energy density. However their combustion properties differ strongly, although the first reaction step, the abstraction of an H atom and formation of the corresponding xylyl (methyl benzyl) radical, is shared. Shock tube experiments revealed that xylyl decomposition to xylylenes differs markedly depending on which isomer of the radical is present.[1] This motivated us to conduct this study.

Xylyl radicals were produced isomer-selectively from the corresponding methyl benzylbromides in a tubular pyrolysis reactor. At higher temperatures, the radicals can decompose by H atom loss. Vacuum ultraviolet (VUV) synchrotron radiation, as soft ionization method, coupled with mass-selected threshold photoelectron spectroscopy were used as an isomer-selective tool to study reactive intermediates and their decomposition products. Species were assigned according to their ionization potentials and vibrational structure by simulating these transitions in a Franck Condon approach.

o-Xylyl radicals show a very rich product variety. We identified four C_8H_8 species such as *o*-xylylene, benzocyclobutene, *p*-xylylene and styrene depending on the reactor temperature (Fig. 1). Furthermore, phenylacetylene and traces of benzocyclobutadiene, both C_8H_6 isomers, and smaller fragments like propargyl and acetylene are also present in the reaction mixture.

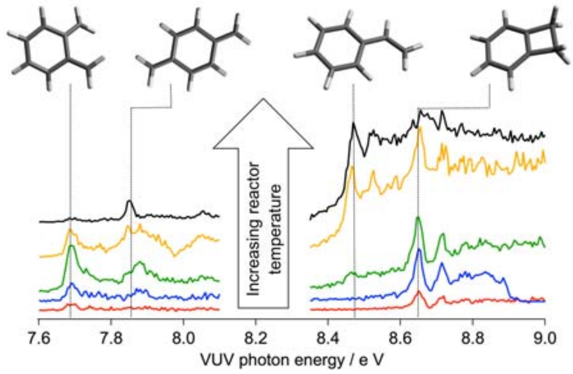

Fig.1 Temperature dependent mass selected threshold photoelectron spectra

Styrene is also formed in larger quantities upon oxidation of *o*-xylene compared to the *meta* and *para* isomers.[2] The key to understanding these differences lies within the decomposition and isomerization mechanism of the intermediate radical species. A comprehensive potential energy surface, showing the complex chemistry of *o*-xylyl radicals, complemented this experimental work.[3] This study can help to untangle the reaction channels appearing in the early stage (few hundred microseconds) of the radical decomposition in a combustion engine.

Keywords : Xylyl radicals; mass selected threshold photoelectron spectroscopy; decomposition dynamics

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SpIM 1.5 Determination of the Geometry Change of Benzimidazole upon Electronic Excitation

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Following the Franck-Condon principle, emission and absorption spectra of a molecule are directly linked to its structure. This is based on the approximation that the intensities of spectral bands are proportional to the Franck Condon factors, which are obtained from the overlap integrals of the wavefunctions in electronic ground and excited state.

Further information about geometry changes in molecules can be derived from the changes of rotational constants because they depend on the center of mass and the orientation of the inertial axes.

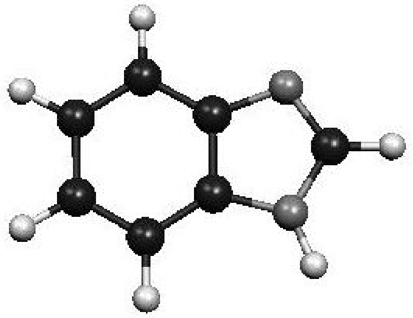

Fig. 1: Structure of Benzimidazole

Combining the information contained in Franck-Condon factors and rotational constants, the complete heavy atom geometry changes of benzimidazole upon electronic excitation have been determined[1].

The rotational constants used to fit this geometry changes have been measured for the electronic ground state and lowest electronically excited singlet state of four different isotopo-logues[2].

The Franck-Condon factors were obtained by single vibronic level fluorescence spectroscopy of the electronic origin and of seven vibronic bands between 0,0 and 0,0 + 1265 cm^{-1}. These measurements allowed to use the intensities of 182 vibronic emission bands and of 8 rotational constants for a combined Franck-Condon/rotational constants fit.

Furthermore, strong deviations from the Franck-Condon behavior in emission have been observed for vibronic bands about 1000 cm^{-1} above the electronic origin. Herzberg-Teller coupling contributes to this effect. 1300 cm^{-1} above the origin, the onset of intramolecular vibrational redistribution could be detected in the emission spectra.

Keywords: Franck-Condon analysis; Benzimidazole; Structure; Herzberg-Teller

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Session 2: Spectroscopy of isolated molecules II

SpIM 2.1 The Utilization of Rare Gas Solution for Making Vibrational Assignments and Conformation Stability Determinations of Three Membered Rings

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The use of rare gas solutions in the field of vibrational spectroscopy has been rather slow to develop for several reasons. Firstly, rare gases are liquids only at relatively low temperatures which requires infrared and Raman cells be maintained at relative low temperatures during the experiment. Therefore, the use of rare gas solutions to obtain spectroscopic data is not routine. Another disadvantage is the solubility in rare gas solutions is relatively low and rather poor for very polar molecules.

Nevertheless there are a number of advantages for many samples which makes rare gas solutions good. For example, there is very little interaction of the solvent with solute molecules so the frequencies observed for the bands in solution are hardly shifted from the values observed in the gas. Also the rare gases do not absorb infrared radiation so it is possible to use infrared liquid cells with path lengths of several centimeters such as 10 cm. Thus the solutions can be very dilute i.e. 10^{-4} molar, which drastically reduces the association of the solute molecules. Therefore variable temperature studies can be carried out on alcohols, amines, and acids where it is nearly impossible with conventional solvents. In fact it is nearly impossible to obtain enthalpy differences for these molecules with conventional solvents. Therefore some examples will be provided which will demonstrate the ability to determine conformational stabilities and vibrational assignments.

Keywords:Raman; Infrared;Conformational stability

Session 2: Spectroscopy of isolated molecules II

SpIM 2.2 Excited state proton transfer reactions in isolated hydroxychromones investigated by different IR/UV techniques

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Photochemical reactions as the excited state proton transfer are of great interest due to their importance in chemical and biological processes. Molecular beam investigations combined with double, triple and newly introduced quadruple resonance IR/IR/UV/UV and IR/UV/IR/UV spectroscopic techniques are very powerful tools to analyze these photochemically induced reactions. In comparison with (TD)-DFT calculations direct structural information on the electronic ground and electronically excited states of isolated molecules and clusters are obtained. Here we present studies on the photochemically reactive 3-hydroyxychromene and substituted systems (3-hydroxyflavone and 2-(2-naphthyl)-3-hydroxychromone) as well as their clusters with water. In order to analyze different isomers with overlapping UV transitions in different electronic states, the quadruple resonance methods yield unambiguous results. The investigated molecules and clusters show significant differences with respect to their structures, excited state life times and anharmonicities of OH stretching frequencies depending on the substitution of the hydroxychromones and the size of the investigated cluster.

Furthermore we had been able to observe a proton wire reaction in an isolated system, the 3-hydroxyflavone$(H_2O)_2$ cluster, by applying combined IR/UV spectroscopy in a molecular beam experiment. This was the first application of a structure sensitive IR method to a proton wire in the electronically excited state of an isolated cluster. The observation of the proton wire reaction depends on the excess energy within the electronically excited state and based on DFT calculations an assignment to the structure which undergoes a proton wire reaction could be given.

Keywords: molecular beam; Infrared; electronic spectroscopy

Session 2: Spectroscopy of isolated molecules II

SpIM 2.3 Binding Motifs of a Microhydrated Neutrotransmitter: IR Spectroscopy of Rare Gas-Tagged Protonated Phenylethylamine and its Water Clusters

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The characterization of the three-dimensional structure of biologically relevant molecules, the role played by inter- and intramolecular interactions, especially with water which is ubiquitous in physiological media, and their ability to form charged groups, are key issues to be addressed to deepen the understanding of recognition phenomena at the molecular level in biological environments. Biomolecules are generally not neutral in physiological media, but protonated or zwitterionic. The conformation of these charged molecules and their solvation shell is thereby modified compared to neutral species. Here, vibrational spectroscopy, associated with quantum chemical calculations, has been applied on a protonated neurotransmitter, phenylethylamine (PEA), and its water clusters isolated in the gas phase. The results obtained on the Ar-tagged PEA show that the protonation induces conformational locking of the monomer into a folded structure via a strong intramolecular NH···π interaction. Monohydrated protonated PEA reveals that a very stable inclusion structure is experimentally generated, in which the water molecule is inserted between the positively charged amino group and the phenyl moiety of PEA, acting both as an hydrogen bond acceptor (NH···O) and hydrogen bond donor (OH···π, see figure). A second isomer, for which the water is H-bonded to an external NH group is also found. The study of clusters formed by the addition of further water molecules allows for an accurate description of the first solvation shell of this protonated model neurotransmitter, mimicking its closest natural environment.

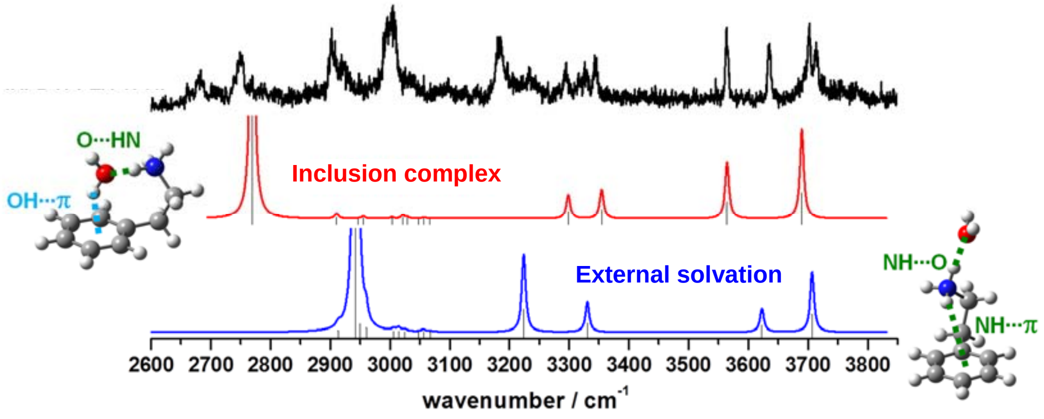

Figure: IR photodissociation spectrum of the Ar-tagged H^+PEA monohydrate (top) compared with the B3LYP-D3/aug-cc-pVTZ calculated frequencies of the two lowest-energy isomers of the hydrated cluster.

Keywords: Hydrogen bonds; Micro-hydration; Protonation; Neurotransmitters; Gas phase IR photodissociation spectroscopy; DFT calculations.

Session 2: Spectroscopy of isolated molecules II

SpIM 2.4 Fluorescence of Electron-Excited N_2

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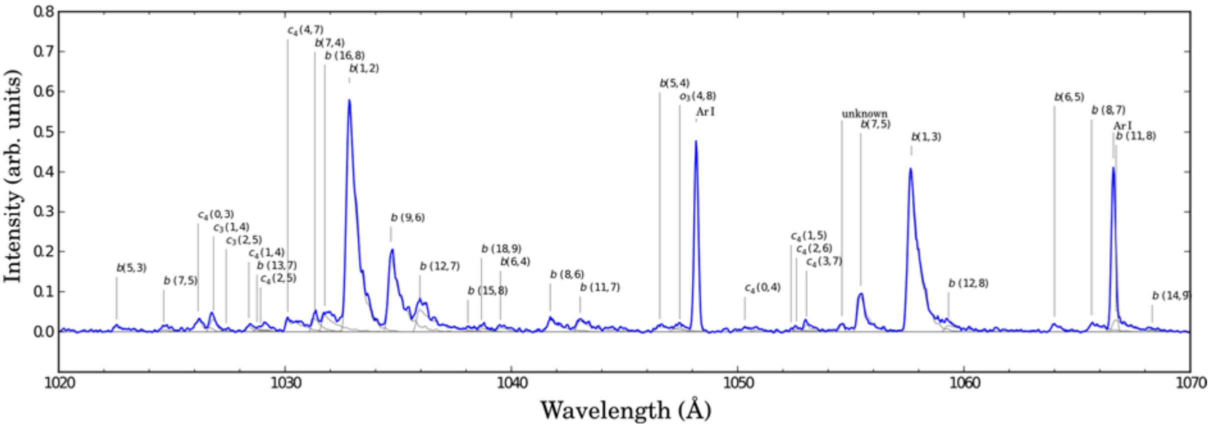
Vacuum ultraviolet (80 to 135nm) photoemission following the electron-excitation of N_2 was recorded at the Jet Propulsion Laboratory at high resolution (FWHM=0.02nm)[1]. The resultant spectrum of molecular bands is highly blended and overlapped even though the predissociative nature of N_2 excited states means many excited levels do not fluoresce.

By using an accurate coupled-channels model of N_2 states we simulated the rotational-profile of each emission band appearing in the experimental spectrum. The cross sections deduced for each emission progression were used to infer internuclear-distance-dependent electronic transition moments connecting the coupled excited states and ground state in our model. Using these transition moments, we are then able to reliably simulate emission from bands not observed in the laboratory and for other rotational temperatures.



Some of the bands appearing in the N_2 emission spectrum.

The excitation of molecular nitrogen by electrons and protons is an active process in solar atmospheres. The resultant molecular and N-atom emission recorded in the atmosphere of Titan by the Cassini spacecraft were compared with our laboratory and model emission spectra.

Nitrogen: Electron impact; Photoemission; Dissociation

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SpIM 2.5 Manipulation of Electronically Excited States of Indole

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In solution the position of the two lowest electronically excited singlet states of indole called L_a and L_b in the nomenclature of Platt [1] can be changed easily by varying the polarity of the solvent.

In a similar way we tried to affect the order of the excited states by adding different substituents at the indole chromophore in the gas phase. Therefore, several singly substituted indole derivatives were investigated using rotationally resolved electronic spectroscopy [2-6]. For the determination of the electronic nature of the electronically excited states the transition dipole moment orientation can be used. This was done experimentally and with high level *ab initio* calculations for 4-, 5-, and 6-substituted indoles. Depending on the character of the substituent and the effect exerting to the indole chromophor it could be shown at the biologically important position 5 that it is possible to manipulate the order of the electronically excited states.

The expansion of this study at other positions aims for a systematic manipulation of the electronically excited state and the possibility to create a library for increment rules to predict the shift of the excited state for every substituent at all of the positions at the benzene moiety.

Keywords: Indole; Rotationally Resolved Laser Induced Fluorescence Spectroscopy

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Session 3: Environmental Applications in Spectroscopy

EAS 3.1 Monitoring Plastic Waste Using FTIR Spectroscopy

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The production of plastic has reached an all-time high, for instance in 2012 there has been 288 million ton (MT) produced worldwide[1]. According to the United Nations Environment Program it is estimated that annually 6.4 Mt plastic ends in our seas and oceans worldwide. Estimates of the total volume in our oceans exceed more than 100 Mt [2] but more and more research assumes this is an underestimation.

In the environment degradation of plastic takes place. Under influence of UV-radiation and the ocean waves, big pieces of plastic are grinded into microplastics (< 5 mm). A large amount of these plastics will wash up the beaches where the sand is abrasive. The sand stores a lot of heat and exchanges this with the plastics, which accelerates the degradation.

An FTIR spectrum of a Polyethylene (PE) fragment in the environment differs strongly from the virgin state of PE as it was produced. The result of degradation are lot of new peaks. At this time, it's a well adopted opinion that degradation of PE mainly takes place on the surface. The plastic fragments on beaches getting sanded and small pieces released of the surface, are forming an invisible pollution. The plastic soup is becoming a plastic bouillon. Experimental work is in progress for analyzing the micro particles.

Marine biota mistakes plastic for food. Well known are the pictures of Chris Jordan [3] of albatross chicks which died of hunger but having a stomach full of plastics. Nowadays more and more researches are concentrating on the stomach content of fish and birds. About 95% of the North sea fulmars have plastic in their stomach. In the 1980s about half of these ingested plastic were industrial pellets, but nowadays 80% by mass is consumer waste, mostly PE.

For interpretation of FTIR spectra currently the majority of the polymer- or plastic libraries are using spectra of prime materials and are very useful for prime materials, polymer production waste, pre-consumer recyclates but insufficient for post consumers recyclates and plastic found in the environment.

Plastics are not inert but change over time as they are thermodynamically metastable. Plastics are losing their preferred and desired mechanical and thermal properties. Therefor the plastic recycle market is limited by the thermo dynamical state of the wasted plastics. The identification of plastic in our environment needs an updated determining method.

FTIR-ATR is a strong tool for identifying plastic over a long period of time, or even better over a degradation period. With the right library, FTIR-ATR is a helpful tool for polymer industry as well as for pre- and post- consumer plastic waste recycler, and for the researchers who are describing the plastic waste in our environment.

Keywords: FTIR-ATR Spectroscopy; Plastic; Environment, Wildlife

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EAS 3.2 Characterization of Plastic Marine Litter Using FTIR Microscopy

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Plastics and its residues are washed into sea with severe consequences for the marine environment [1],[2]. Due to the similar structure of some natural and synthesized polymer compounds (e.g. polyamides) it is difficult to estimate the dimensions of plastic marine litter [2]. However, the use of a reference spectra library does not succeed in combination with contaminated and degenerated samples. Furthermore, the samples could be too small for standard techniques like attenuated total reflection. A new high spatial resolution FTIR microscopy method, using spectroscopic data in second derivative to get specific characteristics for qualitative analysis, is introduced in the present study.

Several polymer types (LDPE, HDPE, PP, PET, PA, natural polymers) in different sizes (granulate, macroparticles, microparticles) and different qualities (new, pre- / post-consumer recycling, plastic marine litter) are measured in transmission and reflection with FTIR microscope (5-25 repeats, R=2 cm^{-1}). Due to conservation of chemical species information, no specific sample preparation is performed. The basis of characterization is the connection between physico-chemical properties, molecular structure and pattern of vibration bands [3]. To compare different chemical species, baseline correction is performed by derivative of the second order. A positive side effect is a significant increase of sensitivity for peak pattern, due to the enhancement effects for profile shape factors and inflection points as a result of this mathematical transformation. The single vibration bands are fitted with Voigt functions in second derivative and the pattern information can be described numerically by calculated peak areas. All calculated areas of one measurement are divided by each other for internal normalization. A high characteristic plot of all pattern ratios with wavenumbers as x- and y-axis and ratios as z-axis as a result of applying this method forms the basis for further evaluations (e.g. multivariate cluster analysis).

In application all measured samples can be classified by their similarities and differences. Even small effects like HD- and LD-PE or outer surface and inner core of LDPE are plotted correctly. The principal components of differentiating HD- and LD-PE include the ratio of the two rocking vibration bands at 730 and 720 cm^{-1}, which can be confirmed by reference literature [4]. The differentiating components of outer surface and inner core include frequency ranges of absorbed water. Differences of synthetic and natural polyamides consists of variations on polymer distribution resulting in specific vibration band pattern. This method recognizes these effects and classifies the broad distribution of natural and narrow distribution of synthetic polyamides correctly. Furthermore, contamination products (e.g. algae, sand) can be identified.

Keywords: FTIR; microscopy; plastics; chemometrics; polymers

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EAS 3.3 Trace Gases Photoacoustic Detection for Monitoring of Some Air Pollutants

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The new living standards imposed by the modern civilization consequently rises attention to the environmental preservation, especially to the environmental air quality, in order to prevent hazardous effects on health.

In this paper we present an analysis of pollutant trace gases based on laser photoacoustic spectroscopy detection with the final aim to perform accurate measurements of the environmental air quality from close space belonging to urban or rural sides. The photoacoustic spectroscopy offers valuable advantages including high selectivity, large dynamic range, locally sampling and multicomponent capability [1]. Based on the selective absorption of laser radiation by specific molecules, this technique became one of the most sensitive techniques in the world, being able to measure gas concentrations at sub-ppb levels (partial pressure of 10^{-10} atm) [2]. For this purpose a tunable CO_2 laser with a wavelength spectrum (9.2 ÷ 10.8 μm), covering the molecular absorption spectra of a multitude of air pollutants is employed as a source in the measurement chain. Our experiments start with monocomponent analysis of various pollutants existing in air, mainly represented by: ethylene, ethanol and methanol. The molecular absorption characteristics and the minimum detectable concentrations of the individual target compounds with respect to the 53 vibrational-rotational lines of CO_2 laser spectrum are investigated. The experiments are extended to multicomponent detection having as main goal the assessment of the absorption interference behavior in gas mixtures. A series of experiments on different mixtures of calibrated gases are carried out in order to prove the multicomponent ability of our detection scheme, the analysis being completed with theoretical considerations.

The obtained results are valuable for further measurements and validation of the theoretical analysis of more complex gas mixtures. These results could be applied to various domains: monitoring of air pollution in both urban (rush hours of underground Bucharest network) or rural (green houses) areas; controlling the indoor atmosphere of industrial spaces, where the presence for long term of such pollutants in the ambient air, even at low level of concentration (ppm range), could affect the people health.

Keywords: CO_2 laser, photoacoustic detection, air pollutants.

Acknowledgements: This work was supported by a grant of the Romanian Ministry of Education, CNCS – UEFISCDI, project number PN-II-RU-PD-2012-3 - 0207.

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EAS 3.4 Vibrational Spectroscopy of Anthropogenic Carbonaceous Particles: A Difficult Problem

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Particulate of anthropogenic origin is an ubiquitous material found in atmospheric dusts, smokes, car exhausts, deposited as powder or cohesive agglomerates on surfaces of any type, internalized in biological cells, *etc.* Within this context carbonaceous particles are matter of great anxiety when their threat is considered by environmental science, dealing with problems that span from human health to cultural heritage. Conversely, carbonaceous particles produced with specific properties are of great interest in the car industry (as rubber charge in tires or wear material in carbon fiber brakes) and the pharmaceutical industry (as filters or absorbers).

The atmospheric particulate can be described as a material consisting of microparticles (or nano particles) made up by an inorganic fraction, a poly-functional organic fraction soluble in organic solvents and by an insoluble fraction consisting of large Polycyclic Aromatic Hydrocarbons (PAH) forming aggregates. The chemical characterization of the insoluble fraction is a very difficult problem.

Based on our previous experience in the vibrational analysis (infrared and mostly Raman) of PAH, graphite and graphenes we tackled the problem of recording and interpreting the vibrational spectra of a large variety of carbonaceous particles collected from the environment, from the world of combustion and from the field of cultural heritage. These materials show the typical Raman spectrum of a graphitic sample, *i.e.* they show the G line near 1600 cm^{-1} and the D line near 1300 cm^{-1}. The frequency of the D line shows dispersion with the exciting wavelength and exhibits a multiplicity of broad lines, which can be associated to different "*ramanophores*" yet to be identified. The D line originates from the normal modes of the atoms at the edges of the graphitic domains. A systematic analysis of the spectra of about 50 different samples of various origin has been carried out using a statistical approach through multivariate analysis which provides a systematic procedure for detecting the spectroscopic similarities among the samples and group them based on the relative concentration of the *ramanophores*. The method of analysis, the problems and the results will be presented and discussed.

Session 3: Environmental Applications in Spectroscopy

EAS 3.5 Crude Oil Geochemical Evaluation by Infrared Spectroscopy and Chemometrics

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Crude oils are different in chemical composition, based on their origins, transformation, unexpected events like adulteration, etc. Difference in chemical composition affects their refining procedure, quality parameters and finally marketing. So, crude oil characterization and crude assay are important parts of petroleum industry. Petroleum industry demands robust powerful analytical approached which could support the quality inspection, structure investigation, forensic analysis and even economic evaluation [1,2]. Considering the useful capability of infrared (IR) spectroscopy as a rapid, economic and non-destructive method for identification of chemical samples, a practical approach was investigated for analysis of petroleum samples based on their informative spectral features in mid-IR region. In this work, totally 85 samples from 3 different sources: 2 petroleum reservoirs and one production for export were compared in binary models, by Fourier transform infrared (FTIR) spectroscopy and least square support vector machines (LS-SVM). Variable selection based on genetic algorithm (GA) was utilized as preprocessing method to improve the reliability of proposed method. Results of binary comparisons were obtained from conducted classifications. More test accuracy values steams from more differences and reversely less test accuracy values refers to more similarities between different fields. The accuracy values for binary classification were between 91.3-97.1 %

Keywords: Petroleum, ATR-FTIR, Geochemical, Diagnosis

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Session 4: New Materials I

Session 4: New materials I

NM4.1 Charge-Transfer Resonance Mechanism Contribution to SERS of 2,2':6',2''-Terpyridine Chemisorbed on Ag Nanoparticles

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The chemical mechanism of surface-enhanced Raman scattering (SERS), namely the charge transfer (CT) mechanism, complements the principal electromagnetic mechanism of SERS provided that the wavelength of the exciting radiation obeys simultaneously with the resonance condition of the localized surface plasmon excitation also the resonance condition of a metal to molecule or molecule to metal photoinduced CT excitation [1,2]. Consequently, the measurements and interpretation of the excitation wavelength dependence of SERS spectra of molecules chemisorbed on plasmonic, e.g. Ag nanoparticle (NP) surfaces is of principal importance for revealing the CT mechanism contribution to the overall SERS enhancement [2]. Additionally, factor analysis (FA) has been proved to be an invaluable tool for identification of different surface species formed by the same adsorbate [3].

In this study, SERS spectra, their excitation wavelength dependence in the 445-780 nm range and factor analysis (FA) were used for identification of two Ag-2,2':6',2''-terpyridine (tpy) surface species, Ag$^+$-tpy and Ag(0)-tpy, on Ag NPs in systems with unmodified and/or purposefully modified Ag NPs originating from hydroxylamine hydrochloride-reduced hydrosols. Ag$^+$-tpy is a spectral analogue of [Ag(tpy)]$^+$ complex cation, and its SERS shows virtually no excitation wavelength dependence. By contrast, SERS of Ag(0)-tpy generated upon chloride-induced compact aggregate formation and/or in strongly reducing ambient shows a pronounced excitation wavelength dependence attributed to a CT resonance (the chemical mechanism) contribution to the overall SERS enhancement. Both the resonance (λ_{exc}= 532 nm) and the off-resonance (λ_{exc}=780 nm) pure component spectra of Ag(0)-tpy obtained by FA are largely similar to the recently reported SERRS (λ_{exc}=532 nm in resonance with ^{1}MLCT transition) and SERS (λ_{exc}=780 nm) spectra of [Fe(tpy)$_2$]$^{2+}$ complex dication [4]. Consequently, the Ag(0)-tpy pure component spectral pattern at 532 nm is attributed to SERS with the CT resonance contribution stemming from a Ag(0) /Fermi level of Ag/$\rightarrow\pi^*$ (tpy) CT transition, i.e. to the concerted operation of the EM and chemical mechanisms of SERS, while the spectral pattern at 780 nm excitation is ascribed to SERS enhancement by entirely the electromagnetic mechanism. On the basis of these results, the analogies between the SERRS spectra of the synthetically prepared [Fe(tpy)$_2$]$^{2+}$ complex dication and the SERS spectra of Ag(0)-tpy surface complex involving the CT resonance contribution will be discussed in detail.

Financial support by the P208/10/0941 grant (Czech Science Foundation).

Keywords: SERS; charge-transfer resonance; Ag nanoparticles, surface complex, 2,2':6',2''-terpyridine (tpy), adsorption sites, factor analysis.

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NM4.2 SERS spectral probing of laser ablated nanoparticles prepared in alcohols

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Laser ablation in liquid media [1] is a perspective method of preparation of nanoparticles. The procedure is based on irradiation of a target from suitable material by high energy laser pulses (Fig. 1). The principal advantage of such a way of preparation (especially in water) is a relatively clean surface of prepared nanoparticles in comparison to those prepared by chemical ways [2]. The laser ablation process can be influenced by a variety of parameters, for example by laser fluence, pulse duration, frequency of laser pulses, the liquid ambient where the laser ablation is performed and other parameters.

In this contribution, we focused on characterization of surfaces of gold nanoparticles prepared by laser ablation in alcohols (butan-1-ol, propan-2-ol and ethanol) using surface-enhanced Raman scattering. The prepared gold nanoparticles were also characterized by TEM and surface plasmon extinction spectra measurements. While direct measurements of SERS spectra from nanoparticle sols in cuvettes were not possible due to the strong Raman peaks of the alcohols, measurements from sediments deposited on glass slides resulted in well-defined spectra of the selected adsorbates. The SERS activity of prepared colloids was evaluated by two different adsorbates, in particular 2,2'-bipyridine and cis-bis(isothiocyanato)bis(2,2'-bipyridine-4,4'-dicarboxylato)-ruthenium(II). The SERS spectral testing showed that surface of the prepared nanoparticles is occupied by Au$^+$ adsorption sites, similarly to the hydrosols prepared by laser ablation in water. The presence of alcoholate ions and/or alcohol molecules on the surface of nanoparticles was not observed. On the other hand, the stability of the colloids showed an efficient formation of the electric double layer around the nanoparticles. Nevertheless, SERS spectra have demonstrated that the stabilizing ions can be easily replaced by the testing adsorbates, so as they are relatively poorly adsorbed on the surface of Au nanoparticles.

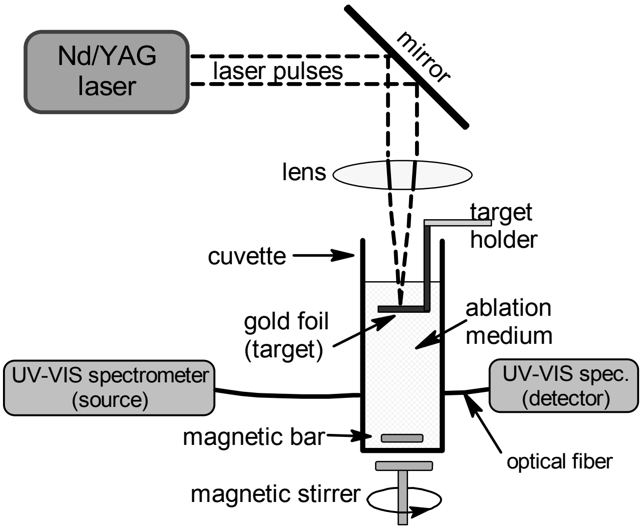

Fig. 1 Laser ablation set-up

Acknowledgement: Financial support by P208/10/0941 grant awarded by Czech Science Foundation is gratefully acknowledged.

Keywords: SERS; Surface-enhanced Raman Scattering; gold nanoparticles; nanoparticle surface probing; laser ablation

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NM4.3 Syntheses, Crystal Structures and Spectroscopic Properties of Cadmium(II) AND Manganese (II)-Azoxybenzenetetracarboxylate Complexes with 1,2-Bis(Imidazole-1Yl-Methyl)Benzene

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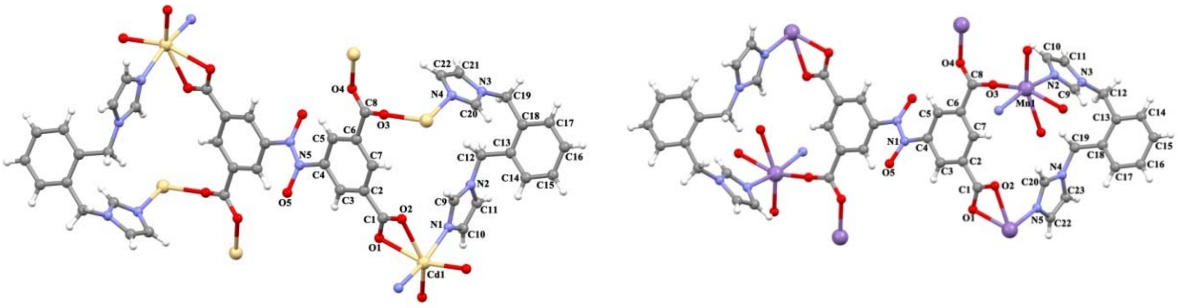
The design and synthesis of coordination polymers constructed with transition metals and organic linkers have received much attention due to their fascinating structures and potential applications [1]. The general strategy for designing of coordination polymers relies on the utilization of multidentate ligands which can act as bridging ligand. In this study, two new coordination polymers, namely, $[Cd_2(aobtc)(1,2\text{-}bix)_2]_n$ and $[Mn_2(aobtc)(1,2\text{-}bix)_2]_n$ (H_4aobtc=3,3´,5,5´-azoxybenzenetetracarboxylic acid, 1,2-bix= 1,2-bis(imidazole-1ylmethyl)benzene) were synthesized and characterized by single crystal X-ray diffraction, spectroscopic techniques (IR and photoluminescence), thermal analysis and elemental analysis.

Complexes **1** and **2** were synthesized by the reaction of $M(NO_3)_2{\cdot}4H_2O$ (M=Cd and Mn), H_4aobtc, 1,2-bix and HNO_3 at 100 °C in the mixture of $DMF{:}H_2O$ (10:1). The crystal structures of **1** and **2** with the atom labeling are shown in Fig. 1. Single crystal X-ray diffraction of analyses demonstrate that complexes crystallize in the triclinic system with the space group P-1. In complexes **1** and **2**, the aobtc ligand acts as a bridging ligand to form 2D layers. Topological analysis results showed that complex **1** and **2** had a two-dimensional (2D) 3,6-connected 2-nodal net with 3,6L19 topology. Complexes are stable up to about 350 °C. Moreover, photoluminescence property of complex **1** was investigated at solid state at room temperature.



(1) **(2)**

Fig. 1. The crystal structures of 1 and 2 with the atom labeling.

Keywords: Coordination polymers, azobenzenetetracarbozylate, Cd(II) and Mn(II)-complexes.

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Acknowledgements

This work has been supported by The Scientific and Technological Research Council of Turkey (Project No: 113Z313).

NM4.4 Structure and Equilibria of Ca(II)–Gulonate Complexes Forming in Aqueous Solutions from Multinuclear NMR Spectroscopy, Potentiometry, Conductometry and Freezing Point Depression

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It is well known, that Ca^{2+} ions form weak complexes with sugar derivatives in neutral solutions and high stability ones in (hyper)alkaline medium. The structure of these complexes in solution has only been studied sporadically. Recently, we have been involved in studying the structure and equilibria of Ca^{2+}–gluconate and Ca^{2+}-heptagluconate complexes in aqueous solutions, using a broad range of Ca^{2+} and sugar concentrations and ionic strengths [1-3] at room temperature. Structural information was derived from multinuclear NMR measurements and stability constants were quantitatively estimated with the help of the PSEQUAD program [4].

L-Gulonate (Gul^-) is a diastereomer of D-$Gluc^-$, with different configuration on C2 and C5. To reveal the structure and equilibria of complexes formed between Ca^{2+} and Gul^-, multinuclear NMR measurements were performed which were supplemented with potentiometric (Ca-ISE and H_2/Pt) and conductometric titrations as well as with freezing point depression measurements. Experiments were performed in neutral (or close to neutral) as well as in hyperalkaline aqueous solutions. ^{1}H NMR measurements revealed, that the binding sites on Gul^- are different from those identified on $Gluc^-$, which strongly indicates the important role of configuration in the complexation. Ca-ISE potentiometric titrations indicated that the formation constant of the $CaGul^+$ complex (which is the only complex that can be identified under these conditions) is very similar to that of $CaGluc^+$. In hyperalkaline media, formation of very stable complexes were observed, which clearly indicated the involvement of the deprotonated OH moieties in the metal binding. The observation, that the complexation in hyperalkaline medium is accompanied with hydroxide consumption, was confirmed with conductometric titrations. Freezing point depression measurements attested that complexes are formed in these solutions both in neutral and in alkaline conditions.

In summary, Ca^{2+} was found to interact with Gul^- in aqueous solutions in a way similar to that found for $Gluc^-$, except for the donor groups binding to the metal ion.

Acknowledgements: This research was financed by the OTKA NK106234 and the OTKA 83889 grants. The financial help is highly appreciated.

Keywords: Ca-gulonate complex; multinuclear NMR spectroscopy; freezing point depression, conductometry, solution structure

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NM4.5 Polarization- and azimuth-dependent Infrared Reflection absorption spectroscopy of metal oxide single crystals

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Infra-red Reflection Absorption Spectroscopy (IRRAS, RAIRS) studies of molecule adsorption on metal oxide single crystals are extremely scarce due to the fact that the reflectivity of such samples is two orders of magnitude lower than of metal single crystals. In contrast to metals, the classic surface selection rule for IRRAS does not apply on bulk oxide crystals and hence, vibrational bands can also be observed for s-polarized light. Since p-polarized light has a tangential and a normal component, because of the different reflectivity differences, positive and negative vibrational bands are visible in the spectra.

In this contribution we present the outcome of IRRAS studies carried out under UHV conditions on various metal oxide single crystals (ZnO, TiO_2, CeO_2). In consideration of reflectivity calculations the adsorption geometry of different small molecules (CO, CO_2, HCOOH…) can be determined by polarization- and azimuth-dependent IRRAS[1]. Here, we demonstrate the huge potential of IR-spectroscopy for investigations on oxide single crystal surfaces by considering all three components of the incident polarized light separately. A comparison to data reported previously for oxide nanoparticles provides important insight into the role of defects in the surface chemistry of powder particles.

Keywords: IRRAS; polarization; metal oxide single crystal

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Session 5: Medical Applications in Spectroscopy I

MAS5.1 Sol-Gel Biocompatible Porous Materials for Local Controlled Drug Release in Treatment of Parkinsons's Disease

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Parkinson's disease, an illness of the central nervous system, is characterized by a progressive degeneration of dopaminergic neurons in the brain. However, dopamine cannot be used as replacement therapy for this disease because it does not cross the blood-brain barrier. The precursor for dopamine, L-hydroxyphenylalanine (L-dopa), on the other hand, has good brain penetration and would be a most efficacious treatment except that during long-term use, patients develop motor response fluctuations which often lead to forced discontinuation [1],[2]. Though some tests show that slow release of L-dopa can reduce the side effects, the treatments now available can only offer symptomatic relief for Parkinson's disease patients.

Alternative approaches to treatment involve a development of controlled drug-release systems in order to reduce drug dosage and to make the drug available at the target sites [3]. Oxide nanomaterials, particularly silica-based materials, attract much attention because of their biocompatibility, controlled rate of bio-erosion and simple engineering. Sol-gel derived silica xerogels are hence excellent possibilities as hosts for controlled drug-release systems.

Previous reports using porous silica substrates have all been sol-doped systems. To minimize interaction between the host and the medicine, we propose an approach previously unreported, that of post-doping biocompatible silica gels with the adequate therapeutical agent. With this in mind, we have begun tests first to determine the capacity of the gels to absorb the molecular agents and then, in a second step, to test the ability of the gels to release their absorbed molecular agents to the environment. Tests involve the use of Raman and UV-visible absorption spectroscopies.

In the present work, attention has been focused on silica xerogels post-doped with aqueous and alcohol solutions of several drug molecules. The isotherm studies have shown that these biocompatible silica materials have high surface areas and pore-sizes which are sufficiently large to make them good matrices for post-doping. It is found that soaking the gels in drug solutions causes an increase of the total pore volume and of the specific surface area. Raman spectra show evolutions of the pore structures of the silica matrices and that after post-doping, the drug molecules are indeed entrapped within the matrix. While, in some cases there are indications of interactions between the matrix and the dopants, the released molecules are indeed in their active forms. Use of Beer-Lambert curves for the UV-visible spectra of drug solutions and of water used for soaking the doped samples has made it possible to quantify the amount of drug released from the loaded gels. The release profiles show two release steps, a first fast and sustained, and another very slow and fixed, with a release which continues up to 4 weeks. These results point to the possibility of developing these carrier substrates as slow-release drug-delivery materials.

Parkinson's disease; drug delivery; sol-gel derived carrier materials

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MAS5.2 Determination of the ligand-protein binding parameters by combination of circular dichroism and fluorescence spectroscopy

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The binding parameters - stoichiometry and binding constant - are very important for the understanding of the ligand-protein interaction. In some cases their determination is not plain. The efforts to simplify this determination can lead to incorrect results.

In our work we present the methodology for the estimation of the binding parameters by combination of different molecular spectroscopy techniques. The investigation provides the first complete characteristic of the linear tetrapyrroles binding on the serum albumin. The binding constants were calculated by circular dichroism spectroscopy and fluorescence enhancement and quenching methods. Förster's resonance energy transfer (FRET) was used to specify distances between Trp-214 and the bound pigments. We extended circular dichroism method to assign the relative affinities of the pigment binding sites. Their locations were estimated in displacement experiments using marker ligands. The measurements were interpreted on the basis of molecular docking performed to determine the topography of the binding sites. Provided data present new insight on mechanism of action and efficiency of the linear tetrapyrroles as antioxidant agents.

Keywords: binding constant, circular dichroism, fluorescence, bile pigments, serum albumin

MAS5.3 FT-Raman Spectroscopy as a Non-Destructive Tool for Determination of Chemical Composition of Urinary Sediments

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FT - Raman spectroscopy is chemically specific technique for investigation of molecular properties of the sample. In a combination with optical microscopy it holds the possibility to acquire chemical information of micro-scale samples which is especially beneficial in biomedical diagnostics [1]. Urinary deposits are usually in dimensions of several tens of micrometers. Their standard assessment in medical practice is currently based on visual inspection of morphology; however the risk of visual misinterpretation is high. We used Raman microscopy to determine the chemical composition of urinary sediments and kidney stones of 15 patients with urolithiasis and inspected whether correlation between the stones and the sediments exists.

The urine was filtered and the crystals or crystals clusters (of dimensions ranging 5 -100 μm) were investigated by means of FT – Raman spectroscopy. Samples were excited with a Nd:YAG laser of 1064 nm wavelength to produce Raman scattered radiation.

We were able to record Raman spectra and identify the chemical composition of urinary sediments no matter their morphological structure. The investigation of the Raman spectra confirmed the main kidney stone forming materials were present in urine of patients with kidney stone disease: (i) Calcium oxalate monohydrate $CaC_2O_4{\cdot}H_2O$ (5 samples) (ii) Urates - uric acid $C_5H_4N_4O_3$, uric acid dehydrate $C_5H_4N_4O_3{\cdot}2H_2O$, and ammonium acid urate $C_5H_7N_5O_3$ (4 samples); (iii) Brushite $CaHPO_4{\cdot}2H_2O$ (4 samples); (iv) Struvite $(NH_4)MgPO_4{\cdot}6H_2O$ (1 sample). Those were single-component sediments. One of the urinary deposits was composed of three different components: calcium oxalate monohydrate, hydroxyapate and calcite (Fig. 1). Correlation between kidney stones and urinary sediments occurred in 11 of 15 cases.

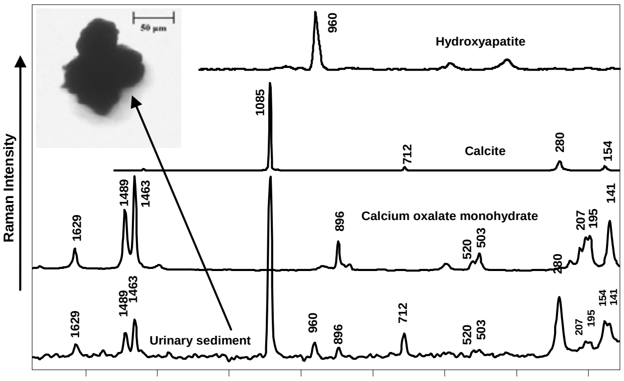

Fig. 1 Optical image of urinary deposit (top left corner), Raman spectra of the deposit (bottom), and reference chemical compounds. indicating calcium oxalate monohydrate, calcite and hydroxyapatite.

It was shown that FT - Raman spectroscopy is a reliable method for determination of the chemical composition of both single component and multi - component urinary deposits. Thus, FT-Raman spectroscopy can be considered a relevant technique to be brought to medical practice for the early identification of kidney stone formation.

Keywords: Raman microscopy, Urinary sediments, Kidney stones

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MAS5.4 Natural Lenses with Cataracts Studied by FTIR Spectroscopy

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One of the popular contemporary diseases is cataract. The number of patients with cataract is increasing exponentially. This illness manifested by a decrease in visual perception [1]. There are various number of cataract causes which differently affects the chemical structure and phase composition of the lens. Thus it requires surgical intervention for removing the cloudy lenses and eye lens polymer is placed instead.

In this work we will present analyses of degraded parts of human lens obtained from patients during routine surgical intervention.

The materials were analyzed by FTIR spectroscopy using Nicolet iS5 spectrometer equipped with DTGS detector, and ATR attachment with ZnSe crystal. The data were collected in transmission mode (KBr technique) and internal reflection mode from 600 cm^{-1} to 4000 cm^{-1}. The spectral resolution was set to 4 cm^{-1}. Spectra were normalized and converted into second derivatives in order to improve the quality of assignments and pull out the small subtleties. The fitting program was applied to locate the position of the overlapping components of the amid bands and to assign them to different secondary structures.

In our study we have paid the attention to investigate the relations between bands in the region from 1000 cm^{-1} to 1900 cm^{-1}[2,3]. Analysis in the scope of amide bands and the bands connected with methyl groups not only enables to indicate differences in the structure of the lenses, but it can also be an efficient tool to evaluate the reason for the appearance of cataract.

The results obtained will be correlated with the clinical patients parameters such as: visus, tonus, glucose level and LOCS.

Acknowledgements
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Keywords: Cataract; FTIR; Lens

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MAS5.5 Spectral Bandwidth Limitations of Tuneable External-Cavity Based Quantum Cascade Lasers for Clinical Biofluid Analysis with Different Multivariate Calibration Strategies

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In many publications, infrared spectroscopy has shown its excellent performance in quantitative multi-analyte analysis of biofluids. However, its applicability for point-of-care use or bed-side monitoring has been limited due to the still bulky size of conventional FTIR-spectrometers compared to single-analyte biosensors. With the recent development of room temperature operated quantum cascade lasers, utilising an external cavity for broad tuneability, infrared laser spectroscopy became feasible for quantitative biofluid analysis. For an optimized sample pathlength, the noise performance of EC-QCL based spectrometer systems has been shown to be at least equal to the state of the art of FTIR-instrumentation [1]. However, the nowadays available spectral bandwidth of about 200 cm^{-1} for a commercially available one-laser system is much smaller compared to the full mid-infrared range accessible with FTIR-devices. For this work, we applied a bandwidth constraint to previous FTIR-studies on spectroscopic assays of blood plasma [2], dialysates of biofluids [3] and aqueous solutions of common interfering drugs. An additional strategy was a spectral variable selection based on the extreme values of the PLS regression vectors. Quantitative results are given for various clinically relevant plasma and dialysate compounds. For the most important blood glucose with its substantial band structure in the fingerprint region, there was no impairment, provided that collinear spectral interferents such as hydroxyethyl starch used as plasma expander were absent. For other analytes of interest, such as lactate and urea, the required tuneability is about 400 cm^{-1} for optimum performance with a second laser needed for a simultaneous glucose assay.

Keywords: infrared spectroscopy, clinical chemistry, point-of-care diagnostics, quantum cascade lasers with external resonator, spectral bandwidth limitation, multi-analyte assay, blood glucose monitoring

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Session 6: Medical Applications in Spectroscopy II

Session 6: Medical Applications in Spectroscopy II

MAS6.1 Raman Spectroscopic Studies of the Scalp Skin, *In Vivo*

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Raman spectroscopy has long been suitable for *in vivo* skin research [1-3] in a clinical setting [4-5] because of the non-invasive nature of the technique. In the studies to date scalp skin is an under-explored area, perhaps because a dense covering of hair makes it difficult to access with conventional instrumentation. Nevertheless the scalp remains of great interest to the personal care industry. There is evidence to suggest that scalp skin differs from the skin at other body sites [6] and so a better understanding of the scalp skin would greatly facilitate the design of improved hair and scalp products.

We demonstrate successful measurement of the scalp skin *in vivo* using the recently developed Raman probe [7]. Our results show lower levels of Natural Moisturising Factor (NMF) in scalp stratum corneum (SC) compared with the volar forearm and axilla [6]. Also we observe that the surface sebum layer on the scalp, which is comprised of unsaturated and disordered lipid types, penetrates into the upper SC. We have also studied the skin of people suffering from dandruff [8]. Dandruff SC has NMF levels that are lower still, compared with non-dandruff scalp, and also has differences in the levels of lipid, urea, lactic acid and water. The amounts of these distinguishing components of dandruff normalise to those of the non-dandruff skin when the dandruff condition is treated with an anti-dandruff shampoo. This work shows the potential of Raman spectroscopy in assessing scalp health.

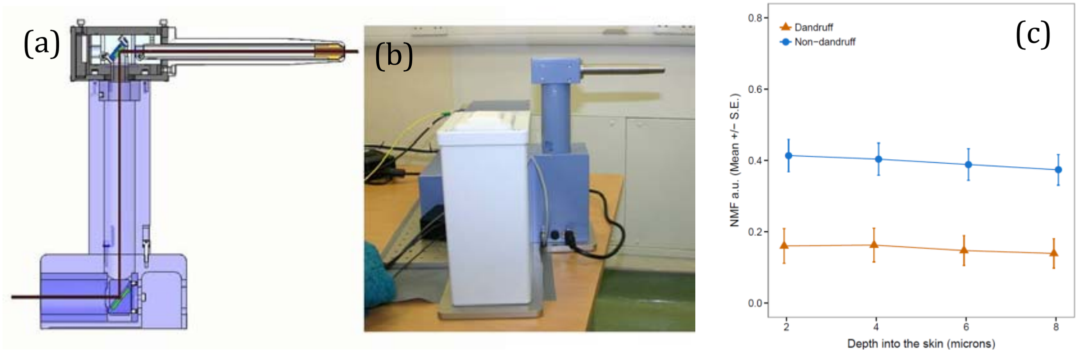

Figure 1. (a,b) the *in vivo* Raman probe (c) concentration profiles for Natural Moisturising Factor in dandruff and non-dandruff scalp skin

Keywords: Stratum Corneum; Scalp; Dandruff; Natural Moisturising Factor, Lipids

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MAS6.2 Chiral Study of *Artemisia Herba Alba* by Vibrational Circular Dichroism

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Artemisia herba alba (*AHA*) is a species belonging to the Asteraceae family. It is well represented in North Africa and in part of Asia. It grows in arid and semi-arid climates around Mediterranean Sea. It is typically found in the steppes and Middle East deserts (Egypt and Sinai desert), North Africa (Algeria, Tunisia and Morocco), Spain, extending into Northwestern Himalayas.[1] Essential oil (EO) obtained by steam distillation of the aerial parts of the plant are widely used in traditional medicine to treat diabetes, bronchitis and other diseases such as jaundice, and in pharmaceutical industries. [2],[3] The chemical composition of the essential oils (EOs) from three samples of *Artemisia herba alba*, grown in Algeria and Morocco, were determined by gas chromatography coupled to mass spectrometry (GC–MS) and chiral HPLC. The major chiral compounds identified in the oils were (–)-α-thujone, (+)-β-thujone and (-)-camphor.[4], these pure molecules and crude EOs were analyzed using vibrational circular dichroism (VCD) which provides their chiral signatures. Particularly, the VCD spectrum of EOs is a linear weighted combination of the individual spectra of chiral molecules that compose the sample. The objective in this work is to study the chiral signatures of *AHA* EOs, For this purpose, we developed a method based on the use of VCD spectra of the major compounds ((–)-α-thujone, (+)-β-thujone and (-)-camphor), VCD spectrum of the EOs and Multi Linear Regression (MLR) to model the VCD spectra of *AHA* EOs. Using this innovative method, the absolute configuration of the major chiral constituents of *AHA* EOs can be determined without using classic chiral chromatographic techniques.

Keywords: Artemisia herba alba, Essential oil, Vibrational Circular Dichroism, chirality.

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MAS6.3 Solvatomorphism and Crystal Structure of the Narcotic Analagesic Drug Codeine Phosphate Sesquihydrate

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Codeine phosphate is one of the most intensively used narcotic analgesic and antitusic active pharmaceutical ingredient (API) worldwide. Two commercial hydrate forms (hemihydrate and sesquihydrate) of this API are described by European Pharmacopoeia [1].

Detailed solvatomorphism study of codeine phosphate sesquihydrate is reported [2]. The crystallization from several medium to high polarity solvents clearly exhibited its low affinity towards building solvates. The materials obtained after crystallization were investigated by vibrational spectroscopy (infrared and Raman), thermoanalytical methods (DSC and TG/DTG) and X-ray powder diffraction (XRPD). It was observed that after absolute ethanol, ethyl acetate, acetone and acetonitrile crystallization, anhydrous codeine phosphate was obtained. When *N,N*–dimethylformamide was used as crystallization medium, transformation to the hemihydrate form was observed whereas in methanol solution the compound formed mixed hydrate-methanolate solvate. Tentative stoichiometry was established and the latter compound was identified as codeine phosphate sesquihydrate methanolate.

Due to the observed inability of codeine phosphate sesquihydrate to form single crystals, the crystal structure of this important API was solved by means of X-ray powder diffraction [3]. Dedicated study was conducted on the hydrogen bonding network, and the comparison with the corresponding feature within the crystal structure of the hemihydrate form was outlined. The influence of the hydrogen bonding properties on the internal crystal structure and how it reflects onto the external crystal shape is reported. It was observed that, at room temperature, the hemihydrate and the sesquihydrate are the only sufficiently stable codeine phosphate forms explaining their intense pharmaceutical application.

Keywords: codeine phosphate, solvatomorphism, crystal structure, hydrogen bonding

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MAS6.4 Diagnosis of Cardiovascular Defect by Infrared Spectrometric Analysis of Blood Serum

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Heart defect is main cause of death in Iran, according to the report of ministry of health. Early diagnosis of heart disease may help in prevention of heart attack and reduce the rate of death due to these types of health problems. Currently there are many methods for early diagnosis of heart disease while some of these methods are tedious, invasive and expensive and some would provide low accuracy [1]. However, novel comfortable and more accurate methods are required. In this work an infrared spectroscopic method has been proposed for diagnosis of heart disease by quantitative determination of choline as an important correlated biochemical in blood samples. Choline is a biomarker which can be determined and evaluated as indicator of normal biology, pathogenic process, or pharmacological response to therapeutic intervention [2]. ATR-FTIR spectrometry was used for determination of choline in 82 blood serum samples. Preprocessing methods such as standard normal variate (SNV), multiplicative scatter correction (MSC) and orthogonal signal correction (OSC) were performed and the calibration model was formed based on partial least squares. Effect of three processing methods on final quantitative evaluation of spectral data was compared. Root mean squared error of prediction (RMSEP) for the MSC-PLS model, SNV-PLS model and OSC-PLS model were 62.89%, 42.27% and 0.25% respectively. The most robust calibration model was obtained by OSC-PLS. Data classification was also conducted to diagnose the illness pattern. Partial least squares – discriminant analysis (PLS-DA) which has often been used for classification and discrimination problems was performed to the data set, Performing PLS-DA to the data set, the 1st PCs contain 99.58% and 13.44% of variance X-block and Y-block respectively. The pattern recognition results show reliable discrimination between healthy and patient samples. Obtained results demonstrate that ATR-FTIR spectrometry is feasible as a reliable tool for rapid and simple preliminary diagnosis of heart defects.

Keywords: ATR-FTIR, Cardiovascular, Serum, Diagnosis

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MAS6.5 Mössbauer Spectroscopy of Liver and Spleen Tissues from Normal Human and Patients with Hematological Malignancies

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Iron plays an important role in the living systems. Iron is accumulated in iron storage proteins ferritin and hemosiderin in the form of nanosized ferric hydrous oxide cores surrounded with protein shells. Liver and spleen tissues contain a large amount of iron storage proteins. However, the content of these proteins in liver and spleen as well as amount of iron in the core may vary in some diseases, for instant in case of the iron overload diseases. Moreover, the nanosized iron core structure in these proteins may also vary in case of some molecular diseases. The presence of iron in liver and spleen tissues permits to apply Mössbauer spectroscopy for studying any variations in the iron cores in iron storage proteins from normal and patients' tissues. Therefore, we used Mössbauer spectroscopy with a high velocity resolution [1] for comparative study of human liver and spleen tissues obtained from healthy persons and patients with some hematological malignancies.

Spleen tissues were obtained from healthy person and patients with from three patients with mantle cell lymphoma stage IVB, acute myeloid leukemia subtype M4 and primary myelofibrosis. Liver tissues were obtained from healthy person and from three patients with mantle cell lymphoma stage IVB and acute myeloid leukemia subtype M4. These samples were lyophilized and powdered. Mössbauer spectra of these samples were measured at room temperature using precision Mössbauer spectrometric system with a high velocity resolution. Mössbauer spectra were fitted using two approaches: i) with one quadrupole doublet within the homogeneous iron core model and ii) with several quadrupole doublets within the heterogeneous iron core model (see [2]). In both approached a comparison of Mössbauer parameters for normal and patients' tissues demonstrated variations in the iron content and possibly some differences in the iron core structure in iron storage proteins.

Keywords: Mössbauer spectroscopy; Liver and spleen tissues; Hematological malignancies

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MAS6.6 Emission Mössbauer Spectroscopy in Probing Cation-Binding Sites in Biocomplexes: from Small Biomolecules to Enzymes

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The sophisticated, extremely sensitive and informative emission variant of Mössbauer spectroscopy (**EMS**), with the most widely used ^{57}Co radionuclide, has been used largely in materials science and nuclear chemistry. Nevertheless, its sensitivity can also be helpful in revealing fine structural features of biological complexes, whenever the $^{57}Co^{2+}$ cation can be used as a substitute for native cobalt or other metal ions (for a recent review, see [1]).

Within the last decade, our studies have shown for the first time [2] that EMS can give unique structural information on the cation-binding sites in enzyme active centres [1–3]. Since biological applications of EMS have so far been quite rare [1], for a more reliable interpretation of emission Mössbauer spectra of sophisticated $^{57}Co^{2+}$-doped systems (such as enzyme active centres, or metabolically transformed $^{57}Co^{2+}$ species in live bacterial cells [4, 5]), a series of model studies would also be necessary involving small biomolecules (with different donor atoms or functional groups as ligands for the cation). This is also important, as the electron-accepting properties of the $^{57}Co^{2+}$ coordination microenvironment determine the so-called after-effects of the $^{57}Co \rightarrow ^{57}Fe$ nuclear transformation, which can complicate the resulting emission Mössbauer spectra with additional appearing lines (see, e.g. [1–5]). A series of $^{57}Co^{2+}$ complexes in aqueous solutions (rapidly frozen in liquid nitrogen) and in the dried state were studied involving different small biomolecules (some aromatic and non-aromatic amino acids, alkylresorcinol, α-amino-γ-butyrolactone). The Mössbauer parameters calculated from the spectra were assigned to various types of coordination. In some instances, similar Fe^{2+} complexes were comparatively studied by transmission Mössbauer spectroscopy. In many cases, tetrahedral coordination of high-spin cobalt(II) was implied, featured by lower isomer shift values. This was found also for $^{57}Co^{2+}$ cations bound in two different cation-binding sites within the active centres of bacterial glutamine synthetase (**GS**) [3] in a low adenylylation state, while its increase resulted in a more saturated $^{57}Co^{2+}$ coordination. This has implications for explaining GS activity regulation via adenylylation-deadenylylation [1].

This study was supported in part by The Russian Foundation for Basic Research (Grant # 13-04-01538-a), as well as under the Agreement on Scientific Cooperation between the Russian and Hungarian Academies of Sciences for 2011–2013 (Project # 28).

Keywords: Emission Mössbauer spectroscopy; Cobalt biocomplexes; Cation-binding sites

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Session 7: Theory I

Session 7: Theory I

Th7.1 Semiclassical Computation of Vibronic and Vibrational Spectra Beyond the Harmonic Approximation

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Modern ab initio and density functional theory (DFT) methods facilitate accurate calculations for complex systems in both the ground and the excited electronic state. Excited-state geometry optimizations can nowadays be performed routinely with highly efficient single-reference methods. Employing harmonic Franck-Condon-Herzberg-Teller theory, vibronic spectra are accessible and extensive comparison between theory and experiment becomes possible. Often, though, excited states exhibit multiple-well potential energy surfaces (PES) with shallow barriers; accordingly, the harmonic approximation is inapplicable for many important problems. Anharmonic treatments of vibrational and vibronic structure are up to now very expensive and are limited to very small molecules.

Semiclassical coherent state propagators [1] offer a promising way for calculating anharmonic spectra by means of a time-dependent, dynamic approach. They describe the time-dependent wave function solely on the basis of classical trajectories and monodromy matrices. In contrast to fully quantum dynamical methods, only local information about the PES is needed for integrating these quantities. In principle, the whole propagation can be performed on-the-fly via linking the dynamics to quantum-chemistry program packages. Applications are presented for the $S_0 \rightarrow S_1$ radiative transition and the $S_1 \rightarrow S_0$ internal conversion in formaldehyde H_2CO.[2,3] Here, time-dependent DFT is employed for the S_1 state PES.

In order to significantly reduce the number of single-point TDDFT calculations which are needed for the dynamics calculations we also explore a modified Shepard interpolation technique [4] (see Figure 1). Applications focus on infrared spectra. Finally, a renormalization procedure to improve the convergence properties of the semiclassical propagator is presented.[5]

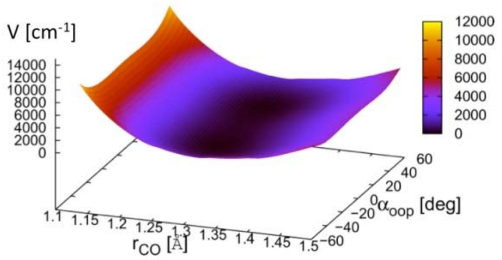

Fig.1: Plot of the Shepard-interpolated *S_1* state surface for formaldehyde. r_{CO} denotes the CO stretching internal coordinate, α_{oop} is the out-of-plane bending angle.

Keywords: Frozen Gaussians; vibronic and vibrational spectroscopy; quantum chemistry

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Th7.2 Electronic Structure and Molecular Mechanism of Non-Radiative Decay of Nitrobenzene

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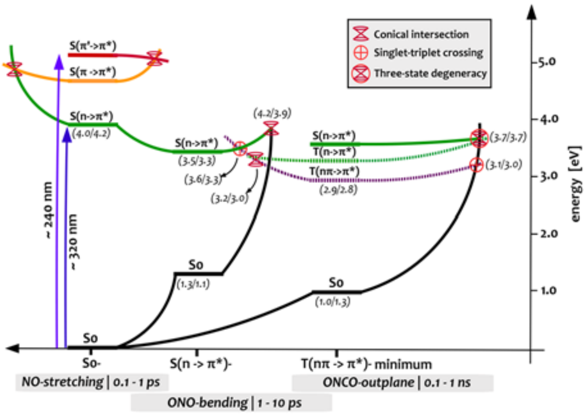
The electronic structure and non-radiative relaxation pathways of nitrobenzene have been investigated with a number of theoretical methods ranging from basic configuration-interaction singles to highest level third-order methods. Surprisingly, the high-level theory is necessary to obtain a reliable and sufficiently accurate theoretical description of this seemingly simple molecule. The reason for failure of first- and second-order methods is found in the complicated electronic structure of the low-lying states which are very important for the mechanism of non-radiative relaxation.[1]

Based on these high-level calculations we propose a mechanism for the non-radiative decay of nitrobenzene that conclusively explains the experimental findings.[2] This proposed mechanism involves internal conversion (IC) and inter system crossing (ISC) along three dominating internal coordinates of the nitro group. Of this, symmetric NO stretching and ONO bending modes have not been considered yet, but we found them to be most relevant for initial IC and ultrafast ISC into the triplet manifold. Moreover, we corroborate the suggestion of Takezaki *et al.*[3] that relaxation from the lowest triplet state *via* ISC occurs along the out-of-plane bending coordinate of the nitro group. The ultrafast ISC in nitrobenzene is possible because of a presence of singlet-triplet crossing in combination with significant spin-orbit coupling between the respective states.



Keywords: Nitrobenzene; Non-radiative decay; Internal conversion; Inter-system crossing; Electronic structure

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Th7.3 Relationship between Structure and Vibrational Spectra of A_0, A_1, and A_3 Conformational Substates of Carbonmonoxy Myoglobin

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It is known from the infrared absorption spectra of complex of myoglobin with carbon monoxide (MbCO) that MbCO has at least three conformational substates, characterized by different spectra of infrared absorption in the region of C-O absorption [1]. However, structures of these substates were unknown.

At the same time recent results of the high-resolution X-ray study of MbCO manifested presence of three different sub-structures of MbCO [2].

To check if these sub-structures correspond to the conformational substates observed in the vibrational spectra we performed DFT quantum chemical calculations [3] of the MbCO active center with its closest distal environment. The structure of the distal environment, which corresponds to each of the refined sub-structures, was taken from the X-ray study [2]. Frequencies of vibrations of the Fe-C-O unit were computed for each of the structures under consideration.

The calculations showed that, in general, the vibrational frequencies of the Fe-C-O unit are very sensitive to the distal environment, and, in particular, the observed different X-ray sub-structures correspond to the A_0, A_1, and A_3 substates.

It was also shown that electronic structure of different parts of the heme environment notably depends on the electrostatic interactions between them. This conclusion questions reliability of results of the standard molecular dynamics approach to determination of the structure and dynamics of the heme environment and explains the failure in the of MbCO [4]

Keywords: Heme proteins; resonance Raman spectroscopy; protein dynamics.

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Th7.4 Theoretical Studies on the Molecular Structure and Vibrational Spectra of 2-Pyridineethylamine

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In this study, the structural and spectroscopic investigations of 2-pyridineethylamine (abbreviated as aepy) have been experimentally and theoretically investigated. The optimized geometric parameters, conformational equilibria, normal mode frequencies and corresponding vibrational assignments of aepy are examined by means of B3LYP hybrid density functional theory (DFT) method together with 6-31G(d) basis set. Moreover, reliable vibrational assignments have been made on the basis of potential energy distribution (PED). Calculated wavenumbers and intensities are compared with FT-IR and Raman spectra of aepy in the range of 4000-250 cm^{-1}. Time depended density functional theory (TD-DFT) method using 6-31G(d) basis set is used to determine the minimum energy structure of aepy. Additionally, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of aepy are predicted with time depended density functional theory (TD-DFT) method using 6-31G(d) basis set. Calculations are carried out employed for different conformations of aepy in gas phase. According to the calculated results, the vibrational wavenumbers and excitation energies show an excellent agreement with the experimental data.

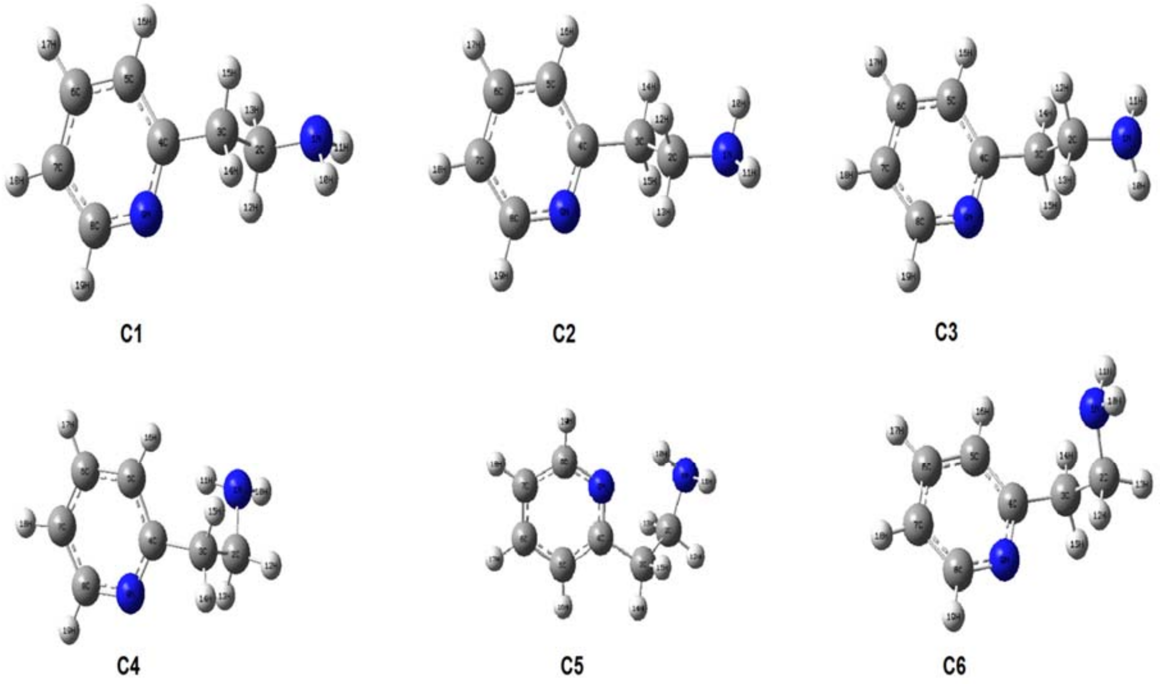

Fig. 1. Six different conformations and numbering of aepy

Keywords: 2-Pyridineethylamine; FT-IR spectra; Raman spectra; DFT; B3LYP; PED

Th7.5 The Molecular Complexes of Boron Trifluoride with Nitrosyl Fluoride and Nitrosyl Chloride. Ion-Pair Formation

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The electron donor-acceptor complexes formed between boron trifluoride and the nitrosyl halides ONF and ONCl have been studied by means of *ab initio* molecular orbital theory at the second order level of Møller-Plesset perturbation theory and with Dunning's augmented correlation-consistent polarized valence triple-zeta basis set. The focus of the calculations was on the structures, interaction energies and vibrational spectra of the complexes. A variety of trial structures were examined, with electron donation occurring from the oxygen, nitrogen and halogen atoms, in an attempt to establish the most favourable site for interaction. In addition, a number of rotational isomers for each adduct were investigated. It was found that, in both cases, the halogen atom was the preferred donor atom. Several of the optimized structures suggested that the formation of ion pairs would lead to stable complexes, and three separate ion pair structures were included among the possible associated species for each combination of interacting molecules. In those cases the computed spectra were more consistent with those of the NO^+ and BF_4^- or $BClF_3^-$ ions than of the corresponding neutral complexes. The relative stabilities of the two families of complexes have been rationalized and some differences between the properties of the ONF and ONCl adducts have been observed and explained.

Keywords: ab initio calculations; molecular complexes; boron trifluoride; nitrosyl halides.

Session 8: Theory II

Th8.1 Conformational and Vibrational Analysis of Dibenzo-18-Crown-6.[a]

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We performed conformational analysis of dibenzo-18-crown-6 (db18c6) using the CONFLEX conformational search method. Ab initio computations were performed for the predicted conformations in the gas phase and solution using the PCM model. The computations were performed at the B3LYP, PBE1PBE and MP2 levels and for some selected low energy conformations at the G3MP2 level. The DFT functionals were used with and without the dispersion correction DFT-D3 method. The vibrational, IR and Raman, spectra of db18c6 were measured. Comparison between the measured and calculated vibrational spectra using scaled-quantum-mechanical force field of some of the low energy conformations aided in the prediction in what conformation db18c6 exits. Use of the dispersion correction seemed to have almost no effect on the calculated vibrational spectra.

Keyword: dibenzo-18-crown-6; conformational analysis; vibrational analysis.

[a] Supported by NPST program by King Saud University, Project Number: 12-ENV2680-02.

Session 8: Theory II

Th8.2 Numerical Simulation of Vibrational Spectrum Under Aqueus Solution: Protein and Bulk Water System

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Considering solvent effects is crucial in numerical simulation of vibrational spectrum for a given IR probe such as amide I mode in peptide and OH stretch mode in water. The frequency of vibrational mode is shifted due to hydrogen bonding interaction with water molecules and the motional narrowing is made in its vibrational spectrum. Molecular dynamics (MD) simulation provides microscopic information on varying configuration of solute-solvent system in time. Quantum mechanical (QM) calculation is needed to obtain vibrational properties of frequency and vibrational transition dipole moment for a given vibrational mode. But it is not practical to perform QM calculation considering explicitly solvents effects for solute-solvent system which requests long computational time due to numerous configurations to be treated with.

Recently, we developed a systematic way to numerically simulate vibrational spectrum for IR and VCD dealing considering explicitly solvent effects.[1] QM calculation was performed with respect to a series of clusters containing IR probe molecule and surrounding water molecules and some parameters associated with solvatochromic frequency shift were determined with a proper fitting procedure.[1] The fluctuating IR probe frequency in liquid water was calculated against all the configurations within MD trajectory without any additional QM calculation. (see Figure 1)

This combined method was suucessfully applied to determine varying frequency shift of amide I mode in protein [1] and CO stretch mode in Myoglobin [2] under solution, and OH mode [3] in liqid water. The vibratinal spectra for IR, VCD and 2D IR spectroscopy were numerically simulated and comparison with experimental results was made.

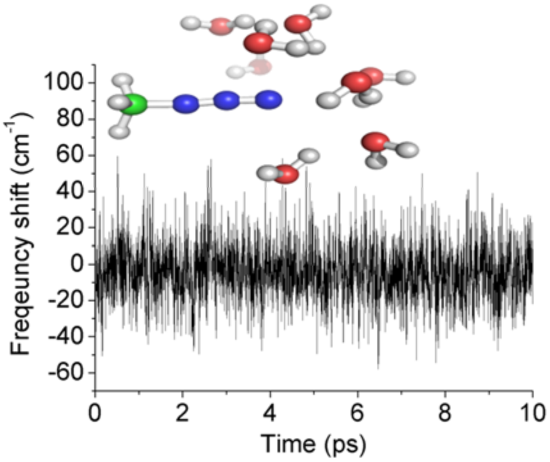

Fig. 1 Fluctuating frequency in liquid water

Keywords: IR; 2D IR; Protein; Water; MD simulation; QM calculation

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Th8.3 Franck-Condon Simulation of Hot Absorption Spectra at Arbitrary Temperatures

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To simulate an electronic absorption spectrum at an arbitrary temperature for an organic molecule, hot bands need to be considered. They allow for the identification of Franck-Condon forbidden transitions, and carry important information about how hot intermediates are formed during the measurement. Thermally excited states are well populated at room temperature and therefore influence the rate constants of all radiative and nonradiative deactivation processes [1]. Calculating spectra at arbitrary temperatures is therefore of great interest.

To calculate the intensities of vibronic transitions the calculation of the multidimensional vibrational wavefunctions (Franck-Condon integrals) is necessary. Our software performs the calculation of these Franck-Condon integrals via the recursion formulae of Doktorov et al. [2,3].

The capability to analyse the vibronic fine structure of electronic absorption spectra at different temperatures was integrated into our Franck-Condon analysis software [4], in accordance with an approach by Berger et al. [5]. To simulate an absorption spectrum at arbitrary temperatures, the population probability of the individual initial vibronic states is taken into account, and a Boltzmann distribution is assumed for the system. The relative Intensities calculated via Franck-Condon analysis are multiplied by the population probability and the Boltzmann factor to yield the spectrum at a given temperature. With the energetic thresholds provided by our software, i.e. the different approach to the generation of initial and final states for the Franck-Condon integrals, the computational effort compared to the approach of Berger et al. was reduced.

Using the procedure to simulate an absorption spectrum comparable to the experimental spectrum of benzimidazole, it was necessary to give different temperatures to the individual initial states of the spectrum to yield a simulation that would fit the experimental absorption spectrum. Since the laser-induced-fluorescence spectrum is measured in a molecular beam experiment, this is an indicator for the fact, that the temperature of the probe molecules within the beam is not distributed linearly.

Keywords:franck-condon simulation; hot bands; absorption spectra; benzimidazole

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Th8.4 Toward modeling Infrared-Visible Sum-Frequency Generation (SFG) of organic monolayers on hydrogen-terminated Si(111)

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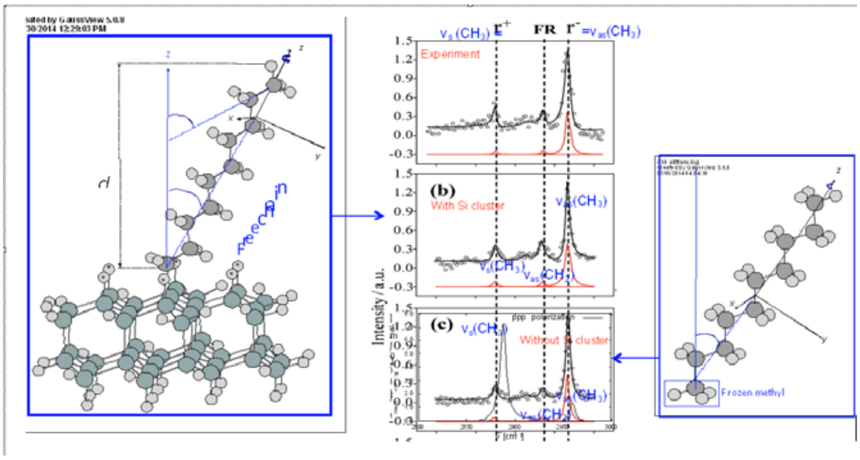
We present recent developments on the simulation of the sum frequency generation (SFG) spectra and its applications to study the structure and dynamics of organic layers at interfaces. Indeed, owing to its sensitivity to non-centrosymmetric organization at the interface, (vibrational) SFG spectroscopy is a powerful tool to probe the structure organization but the complexity of the spectra calls for the development of simulation and interpretation tools. A general method has been developed. It combines density functional theory calculations to evaluate the molecular properties with a three-layer approach to determine the macroscopic response of the organic monolayer. The later step, which accounts explicitly for the nature of the surface [1], has been implemented in a homemade code. In addition to its detailed presentation, the method is illustrated in the case of 1-dodecene covalently bonded to hydrogen-terminated Si(111) [2]. We demonstrate that the consideration of the nature of the surface greatly improves the agreement with experiment, which allows using the comparison between theory and experiment to unravel the monolayer structure. So, the tilt angles of the alkyl chain (θ) and of the terminal CH_3 (α) with respect to the surface normal (laboratory Z axis) are estimated to 28° and 67°, which is close to the 35° and 70° literature values [2], respectively. Moreover a monolayer thickness (*d*) of 10.7 Å has been calculated while the azimuthal angle (ξ) amounted to -104° for the alkyl chain.



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Th8.5 Improving the Precision of Ab Initio Spectra Modeling by Employing Molecular Dynamics Simulations

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Theoretical modeling of vibrational spectra of nucleic acids significantly enhances the amount of structural information obtained by spectroscopic methods [1]. Assignments of spectra becomes much more straightforward and allows to establish a dependable spectra-structure relationship. Additionally, computations provide an understanding of spectral features and theirs changes based on the first principles. However, despite a significant success in modeling of vibrational spectra in the nitrogen base region, dependable calculations of spectral response of polar groups, such as carbonyl and particularly sugar-phosphate backbone are extremely challenging [1]. The phosphate groups in nucleic acids are exposed to the solvent and ions and are more flexible than the bases, which largely diminishes the value of static simulations with continuum solvent models widely used to date. Both the solvent/ion effects and dynamics must be accounted for in accurate spectral calculations of the phosphate group.

Recently we have developed an advanced multiscale methodology, which allows to account for the effects of environmental factors and dynamics on the spectra of DNA oligonucleotides [2]. It is based on preliminary molecular dynamics (MD) simulations followed by precise calculations of vibrational spectra for a number of MD snapshots at the density functional theory (DFT) level (MD/DFT). In the present study we enhanced and fine-tined this approach and applied it to perform extensive spectra simulations of dimethylphosphate (DMP) as a model of nucleic acid phosphate group. We investigated the effect of MD forcefield, solvent, its dynamics, presence of cations, conformational flexibility of DMP and chemical substitution on its calculated spectral features. The developed protocol allows for an accurate modeling of vibrational spectra (IR and Raman) for such a challenging system as the phosphate group and can be extended to other molecules.

Keywords: Vibrational spectroscopy; Spectra modeling; Nucleic acids

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Acknowledgements

Support from the Czech Academy of Sciences (grant M200550902) and Grant Agency of the Czech Republic (grant 14-03564S) is gratefully acknowledged.

Session 9: Spectroscopy of Isolated Molecules III

SpIM9.1 The microwave spectrum of the odd isotope of ytterbium fluoride, ^{171}YbF

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Recent interest in the properties of ytterbium monofluoride, YbF, is primarily motivated by parity non-conservation (PNC) studies, and particularly the determination of electric dipole moment (e-EDM) of the electron, d_e [1]. The advantages of utilizing heavy metal containing polar molecules like YbF for PNC measurements were recognized approximately 40 years ago and primarily stem from the very large obtainable internal electric fields, E_{int}, and the closeness of levels with opposite parity. The latter implies that the molecule can be fully polarized under application of a modest external field and the internal field realized is near the E_{int} value.

The pure rotational spectrum of a minor isotopologue of ytterbium fluoride, ^{171}YbF, in the $X^2\Sigma^+$ (v=0) state, Fig.1, has been recorded using Fourier transform microwave (FT-MW) spectroscopy and pump/probe microwave optical double resonance (PPMODR) spectroscopy. The spectra were analyzed to produce an improved set of fine and hyperfine parameters for ^{171}YbF. Isotopic relationships and the determined ^{171}YbF parameters are used to predict the pure parameters and rotational transition frequency of ^{173}YbF.

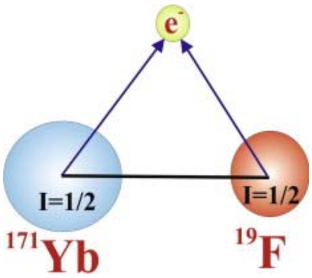

Fig.1 ^{171}YbF $X^2\Sigma^+$

Keywords: Ytterbium fluoride; odd isotope; Rotational spectrum

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SpIM9.2 Internal Rotation in Molecules From Microwave Spectroscopy

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Microwave spectroscopy plays a major role in elucidating accurate molecular structure and molecular interactions. Although best known for its ability to provide precise values of bond lengths and bond angles, microwave spectroscopy has also been one of the best means to obtain other molecular parameters such as dipole moments, nuclear quadrupole coupling constants, nuclear mass ratios, molecular magnetic moments, low lying vibrational states, barrier to internal rotation, conformation and energy difference in rotational isomers and has helped extensively in the identification of known and unknown molecules. We have recently studied the internal rotation in many substituted toluenes and in substituted phenols by Fourier Transform Microwave Spectrometer at Hannover. The results on the study of 2,6- and 3,5 difluorotoluenes, and inversion in 3,5 difluorophenol will be presented.

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Session 9: Spectroscopy of Isolated Molecules III

SpIM9.3 Ibuprofen: Conformers and Thermal Decomposition Products

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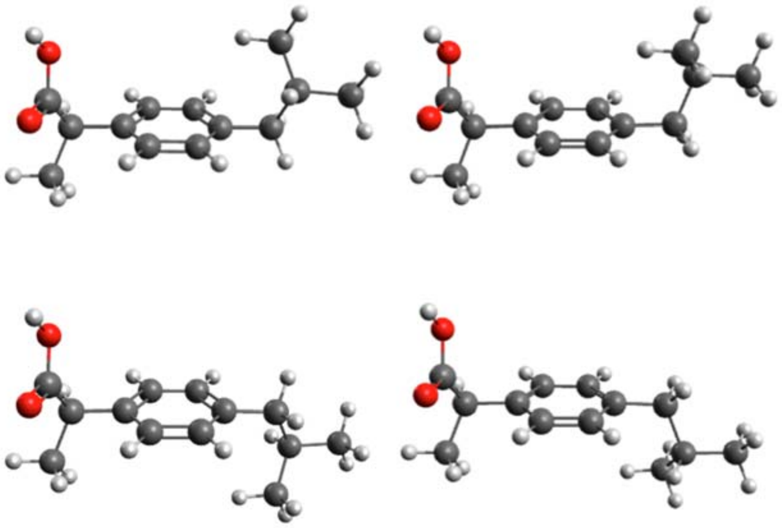
Ibuprofen acts in biological systems as an antiflammatory drug and is today one of the most important pain-relievers used in modern pharmacy. Interestingly, only one enantiomer of this molecule shows this medical effect and thus the function of this molecule is highly correlated to its structure.

In this contribution, the results of a broadband rotational spectroscopy study of ibuprofen in the range of 2 to 8 GHz under supersonically expanded conditions are presented. The four lowest energy gas-phase conformers of ibuprofen, differing in the orientation of the isopropyl group, were identified. Based on these results the conformational properties and the stabilizing, intra-molecular interactions of ibuprofen are clarified. In addition the rotational spectra of two thermal decomposition products of ibuprofen were observed. Their line splitting, probably due to internal rotation, and challenging identification are discussed as well.



SpIM9.4 Electronic Stark Measurements With Rotationally Resolved Laser Induced Fluorescence Spectroscopy

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In general, the photophysic in the low energy regime of indole is governed by two excited singlet states, called ^1L_a and ^1L_b in the nomenclature of Platt [1]. In the gas phase they may change their energetic order due to the influence of different substituents. High resolution laser induced fluorescence spectroscopy can be used to assign the electronic nature of the excited singlet states.

Therefore, several molecular parameters like the orientation of the transition dipole moment, the changes of the bond lengths or the frontier orbital contribution upon excitation gave the possibility to distinguish the electronic nature. Also, the excited states differ in their permanent electric dipole moment. To determine this we modified our existing experimental setup by inserting two Stark plates and a half wave plate. The Stark plates consist of a nickel wire grid which ensures a good transmission of 95 %. They are located in the region of the laser-molecular beam interaction, as it was done before by Korter et al. [2]. By moving the half wave plate into the laser beam its polarization can be rotated about 90° so that different selection rules can be applied.

The Stark spectra of several indole derivatives have been measured and analyzed using an evolutionary algorithm. Thereby the nature of the excited state can be discussed by means of its dipole moments.

Keywords: Electronic Stark Measurement; Indole; Rotationally Resolved Laser Induced Fluorescence Spectroscopy

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SpIM9.5 L-Pipecolic Acid - the Conformational Behaviour of a Neuroactive Cyclic Aminoacid

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L-Pipecolic acid (L-PIPA, Figure 1) is a non-proteinogenic, cyclic aminoacid, which can be synthetized via L-lysine[2] and is a homologue of proline.[3,4] It can be found in human physiological fluids, fungi and plants.[5,6,7] Although there is still a hot debate about its role in humans, evidence has pointed out that it has a functional role in the mammalian central nervous system, similar to that of GABA.[6,7] However, until now, a dedicated characterization from a physicochemical point of view has been lacking. The present work represents the first effort to characterize L-PIPA conformational behavior in gas phase, using broadband chirped pulse Fourier transform microwave spectroscopy (CP-FTMW), and to understand what factors contribute to their relative stability. So far, a total of seven conformers have been detected.

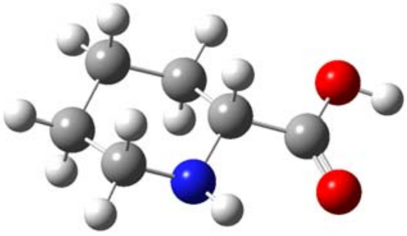

Fig.1 The most stable conformer of L-PIPA4

Keywords: Pipecolic Acid; Neurotransmission; Conformer; Microwave Spectroscopy

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Session 10: New Materials II

NM10.1 Comparison of the Structure of Sn(II) And Pb(II)-Hydroxido Complexes Forming in Hyperalkaline Aqueus Solutions

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Investigations of metal hydrolysis usually take place in the 2 < pH < 13 range (especially between 5 < pH < 8, because of the environmental aspects). Therefore the structure of hydroxo complexes formed in extremely alkaline (or hyperalkaline) solutions (pH > 13) are mostly unknown. The aim of this work was to extend the knowledge and understanding of aqueous chemistry of tin(II) and lead(II) in extremely high pH and to extract information from the experimental findings, which makes the comparison of the structure of the complexes formed possible.

The structure of tin(II)- and lead(II)-hydroxo complexes forming in alkaline (up to 8 M NaOH) aqueous solutions have been investigated by Raman spectroscopy, ^{117}Sn and ^{207}Pb NMR spectroscopy, XAFS and ESI-MS. Theoretical calculations were also carried out for the Raman and NMR spectrum.

The Raman spectra obtained for solutions with 1-8 M NaOH and 0.1-0.25 M metal-ion concentration attested that only one dominant species is present in these strongly alkaline solutions. The spectrum has the same features for both metal ions. According to the theoretical calculations the characteristic absorption bands are typical for a species with C_{3v} symmetry. The ^{117}Sn and ^{207}Pb NMR and the mass spectrometry measurements further confirmed these findings and XAFS measurements indicated, that in the complexes formed, unusually short M–O distances are present. These, together with the theoretical calculations suggest, that the predominant complex for both metal ions is an $[M(OH)_3]^-$ species with a piano-chair like structure.

Keywords: Tin(II), Lead(II), hyperalkaline, Raman spectroscopy, NMR, ESI-MS, XAFS

Acknowledgements: This research was financed by the OTKA NK106234 and the OTKA 83889 grants. The financial help is highly appreciated.

NM10.2 Structural Features of intercalated CaFe-layered double hydroxides Studies by X-Ray Diffractometry, Infrared Spectroscopy and Computations

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During the work leading to this contribution, our main interest was to gain insight in the mode of intercalation of various aromatic, partially or fully saturated N-contaning heterocyclic anions (indole-2-carboxylate, (*S*)-(-)-indoline-2-carboxylate, DL-2-piperidine-carboxylate and L-prolinate) in the interlayer space of layered double hydroxides (LDHs). The orientation of intercalated anions may be an important factor in the catalytic properties of these potential organocatalysts immobilised in the interlamellar space of LDHs[1].

The organic anion–LDH hybrids were synthesized by the dehydration-rehydration method, utilising the memory effect [2]. For the elucidation of the interlayer configuration of the anions X-ray diffractomery and infrared spectroscopy were applied. In addition, calculating the dimensions of the anions from quantum chemical models was of great help in envisaging the steric orientation of the anions in the interlayer space. Particular attention was paid to the influence of solvent mixture used during preparation; various solvent mixtures resulted in different interlayer distances and thus different arrangements of the anions between the layers.

After verifying that the organic anions were intercalated indeed, whichever solvent mixture was used, through the combination of the interlayer distance values and the dimension data of the organic anions a schematic representation of the possible arrangement of the anions between the layers are given. The infrared spectra of the various intercalated substances were used for verifying the successful formation of the host-guest complex, but on closer look, experimental evidence could be gained on the orientation of the anions between the layers.

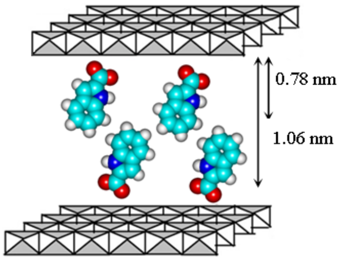

Fig.1 Schematic representation of a possible arrangement of indole-2-carboxylate in the inter-layer space of CaFe-LDH

Acknowledgements: This research was financed by the OTKA NK106234 and the OTKA 83889 grants. The financial help is highly appreciated.

Keywords: L(ayered)D(ouble)H(ydroxide), intercalation, steric arrangement, infrared spectroscopy

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NM10.3 Copper(II) Complexes With Quinolone: Structure and Spectroscopic Characterization

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Copper(II) complexes with the fluoroquinolone (FQ) and selenadiozoloquinolone (SeQ) in the presence of a nitrogen donor heterocyclic ligand 1,10-phenanthroline (phen) and/or 2,2-bipyridine (bipyr) have been prepared and characterized. It was found, that the combination of copper(II) with phen/bipyr increase the biological activity [1] of Cu(II) FQ/SeQ complexes. The crystal structures of copper(II) complexes have been determined with X-ray crystallography. According to the quantum chemical calculations and X-ray data, the copper atom is five-coordinated with the slightly distorted square pyramid which is built of a bidentate coordination of FQ/SeQ and phen/bipyr and a monodentate Cl^-/H_2O ligand.

The complexes have been studied with electron paramagnetic resonance spectroscopy (EPR) in solid state at room and low temperatures (110-280 K). The UV/vis spectra of the complexes have been recorded in aqueous and methanol solutions. The complexes exhibit in the visible region one asymmetric broad d–d transition band with maximum at approximately 645 nm.

The infrared spectra of synthesized complexes exhibited major changes compared to the free ligands. The strong band at ~1720 cm^{-1} in the spectra of FQs and SeQs was assigned to the C=O stretching vibration of carboxyl group. After complex formation with Cu(II) ions, this vibration has been replaced with two very strong characteristic bands in the range of 1587–1602 cm^{-1} and 1364–1387 cm^{-1} attributed to asymmetric and symmetric (O–C–O) stretching vibrations. The separation between these vibrations further confirmed the coordination to the Cu(II) ion via pyridone (O1) and carboxylate oxygen (O2) atoms (see Fig. 1) [2].

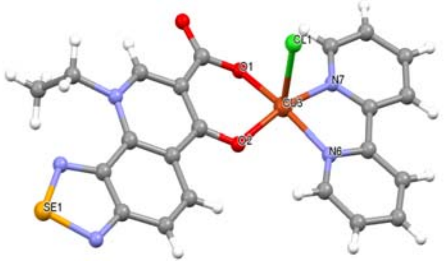

Fig. 1 Structure of [Cu(SeQ)(bipyr)Cl] SeQ=9-ethyl-6-oxo-6,9-dihydro[1,2,5] selenadiazolo[3,4-*h*]quinoline

Keywords: copper(II); quinolone; EPR; UV-VIS; IR spectroscopy; quantum chemical calculations

Acknowledgement
This work was financially supported by the Research and Development Agency of the Slovak Republic under the contracts No. APVV-0202-10 and APVV-0339-10 and the Scientific Grant Agency (VEGA Project 1/0289/12 and 1/0679/11). The calculations were performed at HPC center, SUT Bratislava (SIVVP project, ITMS code 26230120002, funded by the European region development funds) and Computing Centre SAS, code 26210120002 (Slovak infrastructure for high-performance computing) supported by the Research & Development Operational Programme funded by the ERDF. Kristína Plevová, Maroš Bella and Viktor Milata are gratefully acknowledged for synthesis of investigated derivatives.

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NM10.4 Thermal Decompostion and Reconstruction of CaFe-Layered Double Hydroxide Studied by X-Ray Diffractometry and Mössbauer Spectroscopy

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In this contribution results concerning the dehydration-rehydration process of CaFe-layered double hydroxide (CaFe-LDH) is described using X-ray diffractometry and ^{57}Fe Mössbauer spectroscopy. A peculiar property of LDHs is the so-called memory effect [1]. It is known that LDHs lose their layered structure on heat treatment. The procedure may be monitored by thermogravimetry and the dehydrated structure is often found to be only partially crystalline. It is also known that in an environment saturated with water vapour, if the temperature of heat treatment was not too high (generally lower than ~873 K, but the accurate value depends on the particular LDH), rehydration occurs and the layered structure is more or less regained as verified by, *e.g.,* X-ray diffractometry [2,3]. This phenomenon has been observed for various LDHs [4], and it is particularly characteristic to MgAl-LDHs [5].

^{57}Fe Mössbauer spectroscopy is very-well suited to follow the dehydration-rehydration process for CaFe-LDH, since it is sensitive to the chemical environment of iron, which obviously changes during these processes.

During our experimental work, the samples were annealed at various temperatures in the 373–973 K range and the X-ray diffractograms as well as the ^{57}Fe Mössbauer spectra were recorded. Rehydration experiments were performed in environments with preset and controlled humidity values and again the diffractograms and the Mössbauer spectra were taken. When thermal treatment was performed at temperatures 773 K, very stable $M(II)M(III)_2O_4$ spinel and M(II)O phases were formed and the LDH structure could not be reconstructed. Even though heat treatment at 500 C^o in inert atmosphere afforded spinel-like structure, it still could be rehydrated and complete structural reconstruction took place as the X-ray diffractogram and the ^{57}Fe Mössbauer spectrum attested.

Acknowledgements: This research was financed by the OTKA NK106234 and the OTKA 83889 grants. The financial help is highly appreciated.

Keywords: layered double hydroxide, rehydration procedure, Mössbauer spectroscopy

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NM10.5 Analysis of the Frequency and Bandwidth as a Function of Temperature for the Phase Transitions in $LiKSO_4$

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Analysis of the infrared frequencies and the linewidths of various modes is performed at high (300-850 K) and low (1.5-300 K) temperatures using the experimental data from the literature for $LiKSO_4$ which exhibits the sequence of phase transitions. The temperature dependences of the frequency and the bandwidth which are derived from the anharmonic self energy, are fitted to the observed peak positions and the linewidths of the S-O stretching modes (internal ν_3 modes at 1135 cm^{-1} and at 1180 cm^{-1}), peak position of the S-O bending ν_4 (internal) modes, the peak position and the linewidth of the Li mode at 429 cm^{-1} (external mode) and of the infrared band at 363 cm^{-1} for $LiKSO_4$.

Our calculated frequencies (peak position) and the bandwidths, which are in good agreement with the observed data show that the anharmonic self energy model describes adequately the observed behaviour of the successive phase transitions in $LiKSO_4$.

Keywords: Infrared frequency; Bandwidth; LiKSO4

Session 11: Dynamics and Time Resolved Spectroscopy I

Dyn11.1 The Decay of Triplet Excitations in All-Thymine DNA Strands

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Triplet excitations and their relation with photo-lesions have been a topic of DNA photobiology for decades [1]. For the most abundant UV lesion the cyclobutane pyrimidine dimer (CPD) formed by thymine bases adjacent on the DNA strand both singlet and triplet excitations were considered as precursors. Femtosecond UV pump / IR probe spectroscopy performed by the present authors gave conclusive evidence that the primary singlet excitation holds responsible for (most of) the CPD lesions formed in all-thymine DNA single strands [2]. Experiments with triplet sensitizers indicate that to some extent triplet excitations also contribute to the CPD formation [3]. In this contribution (see also ref. [4]) experiments on the fate of triplet excitations in an all-thymine single strand ((dT)$_{18}$) will be described. They show that the contribution of triplet states to the CPD formation is small.

(dT)$_{18}$ dissolved in buffered D$_2$O was subject to nanosecond UV (250 nm) pump / IR probe spectroscopy. The instrument featured a time resolution of ~ 1 ns thereby accessing a time range often neither open for femtosecond (< ~3 ns) nor nanosecond (> ~100 ns) spectroscopy. The transient IR spectra feature a band at 1596 cm^{-1} characteristic for the local triplet state of thymine. The band decays with a time constant of 12 ns. This decay feeds a species with a resonance (among others) at 1624 cm^{-1}. It prevails for 59 ns. Comparison of its IR spectrum with a computed one (DFT) suggests that the species is a triplet bi-radical (see Fig. 1). In this bi-radical thymine bases are linked by a single bond between the two C6 atoms. During the decay of the bi-radical no rise of the marker bands characteristic for the CPD [2] is observed. Taking the noise level of the experiment and the triplet yield into account this implies that at most 0.15 of the triplet excitations may result in CPD formation – most of the triplet states decay non-reactively.

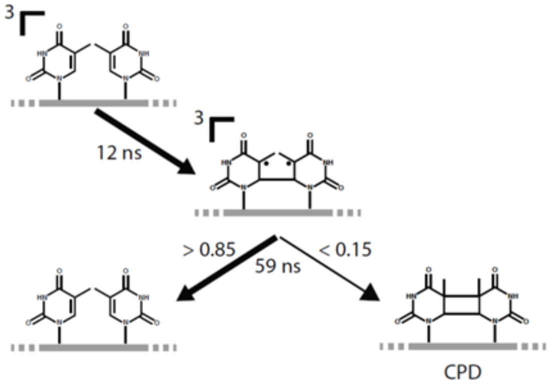

Fig.1 Kinetic scheme of the triplet decay in (dT)$_{18}$.

Keywords: DNA photo lesions; triplet states; time resolved IR spectroscopy

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Dyn11.2 The Mechanism of Phthalide Formation: Femto- to Microsecond Kinetics of a Complex Photoreaction

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The photoreaction of *o*-acylbenzaldehydes to phthalides has been under investigation for decades [1-3]. Nevertheless, the course of the reaction is not yet well understood. This can mostly be attributed to the fact that it contains multiple ultrafast processes, which could not be resolved in preceding work on this formal ring-closure reaction.

To obtain a complete picture of such a reaction, the photoconversion of *o*-acetylbenzaldehyde (oABA) to 3-methylphthalide (3MP) in acetonitrile is studied by means of femto- and nanosecond spectroscopy. Femtosecond UV/Vis spectroscopy reveals that at least five processes occur within a few nanoseconds after excitation. Femtosecond stimulated Raman spectroscopy, quantum chemical computations and experiments on the non-reactive *meta*- and *para*-derivatives are employed to unravel the nature of these processes. A ketene-enol species, which is formed *via* excited state hydrogen transfer, is identified by its ~ 400 nm absorption and unambiguous Raman bands. It is populated on two time scales, by a singlet and a triplet channel. The kinetics to this point surprisingly closely resembles the one previously observed for a nitrobenzene protecting group [4].

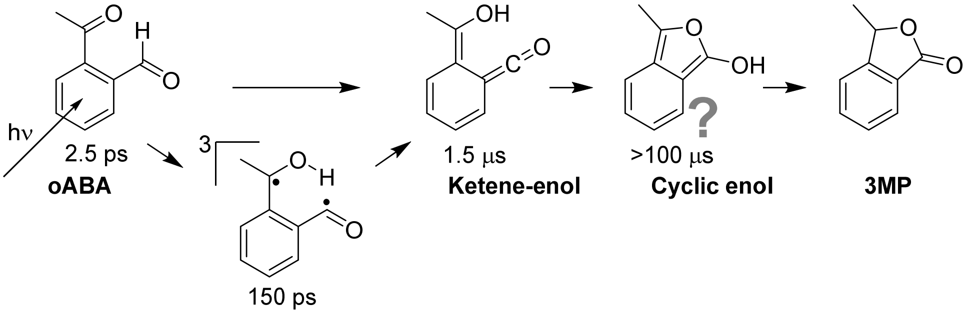

Fig.1 Suggested scheme for the photoreaction of oABA to 3MP in acetonitrile. The time constant for the decay of each species is indicated.

Since this ketene persists throughout our time window of ~ 3 ns, laser flash photolysis is employed to monitor its decay. In agreement with literature on similar compounds, we observe that within about 1.5 μs it transforms into another species absorbing around 370 nm [2,5]. Previously, this conversion was explained by *Z* to *E* isomerization of the ketene. We bring up arguments against this explanation and suggest that a different intermediate, a cyclic enol [1], is observed here (see Fig. 1).

Keywords: Femtosecond Spectroscopy; Organic Photoreactions; Laser Flash Photolysis; Ketene Intermediate

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Dyn11.3 Intracellular Monitoring of Uptaken Aptamer by Time-Resolved Microspectrofluorometry

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Different oligonucleotide strategies (e.g. antisense strategy, aptamer strategy) using the sequences of synthesized deoxyribo- or ribonucleotides to regulate gene expression reveal considerable therapeutic promise. Aptamers (from the latin word *"aptus"* meaning to fit) form at appropriate conditions a specific three-dimensional structure and after binding to their key targeted protein (often with a high affinity) elicit demanded biological response [1].

AS1411 is an advanced aptamer with therapeutic potential in the anticancer healing. It is a guanine-rich 26-mer sequence (5'-GGTGGTGGTGGTTGTGGTGGTGGTGG) with a natural (phosphodiester) backbone that in the presence of K^+ adopts a quadruplex structure. This aptamer molecule has been previously found to inhibit proliferation and induce cell death in many types of cancer cells with a little effect on normal cells [2].

In this work, time-resolved microspectrofluorometry was employed to investigate AS1411 labeled by ATTO-425 in human brain tumor U-87 cells. Confocal microspectrofluorometer adapted for time-resolved intracellular fluorescence measurements by using a phase-modulation principle with homodyne data acquisition was employed to acquire intracellular emission spectra. Experimental setup is suitably arranged for lifetime determination from selected sites inside the cell [3]. Acquired time-resolved fluorescence data from both the solution and the intracellular space (Figure 1) demonstrate the possibility in monitoring the aptamer localization and its interactions with biological structures inside the cell.

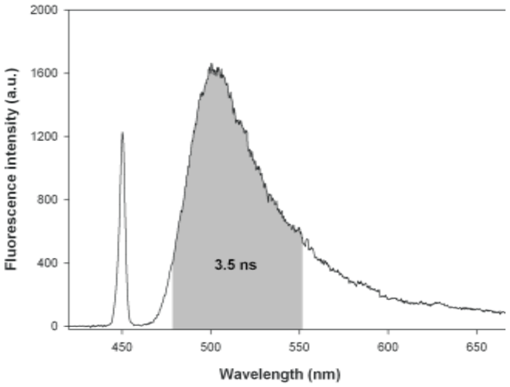

Fig.1: Emission spectrum of ATTO-425 labeled aptamer obtained from U87 cell nucleus. Elastic light scattering (band at 445 nm) is used as a zero lifetime reference. Shaded area of the broad emission band corresponds to 3.5 ns lifetime.

Keywords: time-resolved fluorescence; aptamer; fluorescence imaging

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Dyn11.4 Time-Resolved Transient Optical Absorption of Dynamers of Bis(*tpy*)Oligothiophenes with Zn^{2+} Ion-Couplers

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Constitutional-dynamic polymers, referred to as dynamers [1] are composed of well-defined oligomer molecules with specific end groups linked reversibly into chains by non-covalent interactions or appropriately labile coordination or covalent bonds. An ideal dynamer should exhibit a high thermodynamic stability in the solid state but it should be kinetic labile in a certain solution (at ambient or increased temperature). The dynamers constituted of oligomer molecules reversibly linked into chains via coordination of their end-groups to metal ions (through "ion couplers") are usually referred to as metallo-supramolecular polymers [2].

In the presented study a femtosecond time resolved transient optical absorption spectroscopy was performed on a series of α,ω–terpyridyl oligo[thiophene]s with the central block constituted of oligothiophene dimers and trimers, which were substituted with hexyl groups at various positions, and on their complexes with Zn^{2+}, forming thus the corresponding dynamers. In order to gain understanding of the fundamental processes on a molecular level the measurements were first done on the isolated constituent units (oligomers) in solutions and, then, we measured the kinetics of the excited states in solid state and analysed the exciton annihilation. Transient spectra of all these compounds showed common features: negative band assigned to the ground state bleaching, stimulated emission from the S1 state (SE), instant S1 – S2 excited state absorption (ESA) and a delayed absorption assigned to the T1-T2 electronic transitions of long living triplet states (TTA), respectively. Hexyl substituents shifted the SE towards longer wavelength within the time domain 1-100 ps, probably due to the planarization of the molecule upon excitation, and the ESA showed vibronic structure, which relaxed in the time domain 1-100 ps, shifting the maximum towards shorter wavelengths. Formation of complexes of the ligands with Zn^{2+} ions in solution resulted in a strong increase in observed intersystem crossing rate, decreasing the fluorescence lifetime to about 6 ps in case of hexyl substituted bis-terpyridine(terthiophene). The lifetime of triplet states was also decreased by metal complex formation and the risetime of the TTA was found to be sensitive to the presence of the hexyl substituents. As opposed to the DMSO solutions, in thin films of zinc complexes we observed a sign of mutual annihilation of excitons. This suggests that in DMSO solutions the formation of long self-assembled metallo-supramolecular polymer is not probable. In the case of zinc-complexed oligomers with longer π-conjugated bridge consisting of three thiophene heterocycles the ISC rate is faster in thin films than in the DMSO solutions. The relation of the kinetics to the molecular dynamics of the system will be discussed.

Financial support of the Czech Science Foundation (P108/12/1143) is gratefully acknowledged.

Keywords: Constitutional-dynamic conjugated polymers; transient optical absorption spectroscopy

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Dyn11.5 Comparative Study of the Folding/Unfolding Dynamics of Poly(Glutamic Acid) in Light and Heavy Water

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Secondary structure formation dynamics remains an important issue with respect to the much broader protein folding understanding. Indeed, experimental as well as computational evidences reveal that complex protein folding often starts with the formation of secondary structures which then arrange to shape the tertiary structure of the protein. Especially α-helices are very common in proteins and they are known to be the most-rapidly forming secondary structures. Poly(glutamic acid) (PGA) in heavy water has been thoroughly studied as an archetype of helical polypeptide [1],[2]. In this paper, we investigate the folding/unfolding equilibrium in PGA by two complementary sets of experiments: temperature-dependent steady-state circular dichroism spectra one the one hand and time-resolved circular dichroism measurements coupled with a T-jump experiment on the other hand [3]. Circular dichroism spectroscopy has two assets : it yields quantitative information on the helical fraction in the peptides and it can be used in *light* and *heavy* water as well. The experiments were performed for PGA dissolved in water for various pH values as well as in heavy water, allowing a fine comparison of the two solvents. The kinetic and thermodynamic parameters extracted from these measurements are shown to be markedly different between light and heavy water, which is assigned to the difference in hydrogen bonds energies in both solvents.

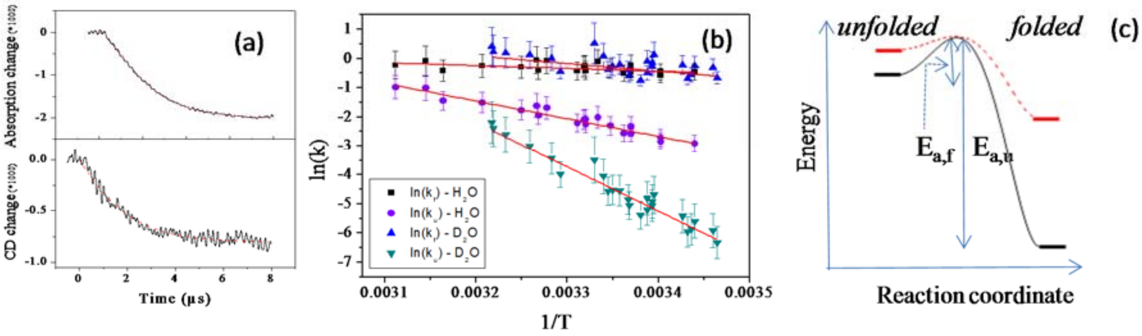

Fig. 1: (a) Transient absorption and circular dichroism at 220 nm after a 5° T-jump;
(b) Arrhenius plots for the folding and unfolding processes in light and heavy water;
(c) Schematic of the energy profile of the *unfolding* ⇔ *folding* reaction in light and heavy water.

Keywords: protein folding; circular dichroism; T-jump

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Session 12 : Hydrogen Bonding

HB12.1 Water clusters in liquid alkaline chloride matrices - comparison of DFT calculations and experimental data

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Theory of water clusters has been still extensively developed [1-4]. Most of quantum-mechanics (Q-M) studies considered clusters containing no more than twenty water molecules in vacuum or in continuum with constant dielectric permitivity using the integral equation formalism model (IEFPCM) [5]. The biggest chalange is to compare the stucture optimised with usage of Q-M methods with experimental data.

This work is devoted to water molecules in a serie of alkaline chlorides differ on dipole moment: CH_2Cl_2, $CHCl_3$, CCl_4. Various water clusters containing 2-6 water molecules are considered. Two calculation procedures were used to simulate an organic enviroment (i) molecules of alkaline chlorides were introduced to the system explicitly, (ii) and they were modeled by usage of IEFPCM. In the case of first way, an effect of the first and second solvatation spheres on water vibration will be discussed.

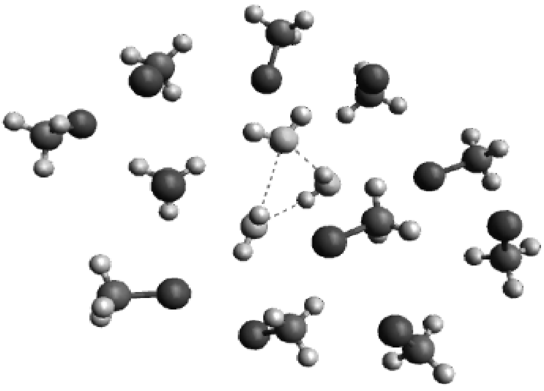

Fig. 1. Clustering of water molecules in chloromethane-water system.

Optimisation of geometry as well as the calculation of vibration modes are done at the DFT/B3LYP level of theory expressed in the 6-31G(d) basic set as implemented in Gaussian 09 package. Peak positions determined by Q-M calcuations are compared to the experimental ones found by vibrational spectroscopy for water dispersed in mentioned above alkaline chlorides.

Acknowledgments
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Keywords: quantum mechanics calculations, intermolecular interactions, vibrational spectroscopy, water clusters

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HB12.2 More H-Bonded Complexes of Athmospheric Interest

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We recently studied H-bonded complexes of atmospheric relevance. Here we report the infrared spectra of the matrix isolated complexes formed between In continuation of our studies of sulfuric acid H-bonded with trimethyl and of sulfuric acid with methanol. However, the study of this system is complicated by the inevitable presence water in the vapor and in the matrix, resulting matrix layers containing three species capable of forming H-bonded complexes.

The complex formed between trimethyl amine and sulfuric acid is of ionic character due to proton transfer of the H^+ proton from sulfuric acid to $(CH_3)_3N$ to form a new N-H bond and the replacement of the intramolecular O-H bond in H_2SO_4 by a strong intermolecular NH···O hydrogen bond. The complex is further stabilized by hydration. The skeletal modes show clear bisulfate related bands, only slightly affected by hydration. The ν(OH) region shows a rich band scheme, explained by a structure involving (at least) three H_2O molecules. A broad spectral feature spanning the 1700cm^{-1} - 500 cm^{-1} is assigned to a double-well potential quasi-symmetric, "Zundel-like", ionic species containing a $(CH_3)_3\text{-N}\cdots H^+\cdots \text{N-}(CH_3)_3$ configuration.

The matrix isolated sulfuric acid/methanol/water clusters show bands in the *ν*(OH) region compatible with a closed ring structure of the dominating complex, with methanol simultaneously playing the role of proton donor (to water) and donor acceptor (from sulfuric acid). The skeletal mode region shows evidence of bisulfate formation.

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HB12.3 Charge Mobility and Hydrogen Bonding From IR Intensity Parameters

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The description of the molecular charge distribution is fundamental in chemical physics, materials science, and molecular biology, since it has direct effects on the intra and inter-molecular interactions which determine the properties of the molecule and its arrangement at the nanoscale. Phenomena such as polarization of the electronic cloud, charge transfer between chemical groups, localization of electronic charge on specific molecular sites are indeed crucial in molecular interactions. To this aim, many methods have been proposed to describe the molecular charge distribution [1,2]. The Equilibrium Charges Charge Fluxes (ECCF) model proved to be particularly effective in the interpretation of both intra and inter-molecular effects (e.g., inductive effects, charge backdonation, hyperconjugation, formation of hydrogen bonds, or strong electrostatic interactions) [1]. While many studies focused mainly on the analysis of equilibrium charges [2], in this contribution we present a method for the derivation of the whole set of vibrational charge fluxes in planar molecules, calculated as numerical second derivatives of the molecular dipole moment [3]. This model is consistent with the partitioning of the atomic polar tensors into atomic charges and charge fluxes and it is directly related to experimentally measurable quantities such as IR intensities. We tested our model for several small benchmark molecules: high accuracy current state-of-the-art *ab initio*/Density Functional Theory (DFT) calculations were carried out and the complete set of charge fluxes were calculated for each molecule. The values thus obtained have been analyzed, shedding light on some peculiar molecular properties. We also applied the model to study intermolecular H-bond. We demonstrated that the computed atomic charges and charge fluxes provide a rationalization of hydrogen bonding effects in terms of molecular charge distribution and its mobility. Furthermore, a detailed interpretation of the enhancement of the X–H stretching band observed upon aggregation behavior can be obtained. Our results show that both principal and non-principal charge fluxes have an important role for the rationalization of the spectral behavior; in particular the occurrence of a dynamical charge transfer between the two molecules is predicted and quantitatively determined. Moreover, we demonstrated that the modulation of the charge distribution during vibrational motions of the –XH· · ·Y– fragment is not localized exclusively on the atoms directly involved in hydrogen bonding. In these grounds, we established some correlations between IR intensities, interaction energies and charge fluxes.

Keywords: Hydrogen-bond, Normal modes, charge transfer

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HB12.4 Protic Ionic Liquid N-Propylammoniumformate: A Low Temperature IR Study

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Emerging researches on ionic liquids (ILs) have discovered these as alternate green mediums for many applications. Protic Ionic liquids (PILs), a class of ILs, which form due to the proton transfer reaction between Brønsted acids and Brønsted bases, have also been studied for their applications on proton conducting membranes for fuel cell, nonaqueous electrolytes, amphiphile self-assembly media, in organic synthesis as a solvent and catalyst, chromatography and as solvent in study of biological phenomena like protein renaturation.

In other hand, structural behavior, ionicity and proton transfer in PILs are also in discussions among scientific communities. The extent of proton transfer from acid to base provides the ionicity in PILs and also its structure. It has been observed that for a primary amine, $\Delta pK_a^{aq} > 2$ is required to have 90 % proton transfer, whereas, for a tertiary amine, to have a strong proton transfer, the value of ΔpK_a^{aq} should be 6 or more [1]. The fact has been explained as, in case of primary amines the cation has three H-bond donor sites which interact with anion through H-bonding and solvate it, whereas in case of tertiary amine, the similar solvation is missing due to presence of only one proton donor site in cation.

In order to better understand the H-bonding and proton transfer in case of primary amines, the PIL n-propylammoniumformate (PAF) has been studied here experimentally using low temperature IR with and without matrix isolation and computationally. Matrix isolation studies on PAF have shown that the vapor phase of the PIL contains the neutral molecular species, formic acid (FA) and propylamine (PA). These have also provided the evidence that no proton transfer takes place between FA and PA with one molecule each, rather they form a H-bonding complex with a H-bond between the acidic H-atom of FA and N-atom of PA. Low temperature experiments without any matrix have revealed that the proton transfer reaction occurs due to the solvation of rightly oriented acid and base molecules to provide a three-dimensional H-bonding network. The collective phenomena of a large number of H-bonds are the cause of complete proton transfer and the ionic behavior in the condensed phase of primary amine based ionic liquids. DFT computations have been carried out to corroborate the experimental results. Computations have also shown that each ion is stabilized when it is H-bonded with three counter ions and vice versa.

Keywords: Proton transfer; ionic liquid; propylammoniumformate; low temperature; matrix isolation; IR.

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HB12.5 Statistical Model of Ternary Solutions Verfied by Spectral Means

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In ternary solutions achieved by two transparent solvents and a spectrally active substance as solute, a competition of the solvent molecules takes place in order to minimize the potential energy [1],[2]. The first solvation shell of the spectrally active molecules must be characterized by the minimum of the potential energy in the stabilized solution. But, the energy of the intermolecular interactions in liquid phase is of the same order of magnitude with thermal energy at room temperature. For these reasons, the ternary solutions are treated by statistical methods.

The solvent average statistic weights in the first solvation shell usually differ from the molar concentration in the entire solution, demonstrating the ternary solution non-homogeneity [3],[4]. Some dipolar molecules of cycloimmonium ylids were solved in a mixture of two different solvents in order to verify the statistical model of the ternary solutions.

The non-homogeneity of the ternary solutions has been emphasized.

The difference between the potential energy in pairs of molecules has been estimated on the basis of statistical model of ternary solutions [5],[6].

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Keywords: ternary solution, electronic absorption spectra, statistic model of ternary solutions, cycloimmonium ylids.

HB12.6 Structural features of pyridylcinnamic acids and their extended hydrogen-bonded aggregations

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For some time, the family of cinnamic acid and its heteroatom-containing derivatives has been in the focus of our interest due to their structural features allowing short- as well as long-range ordering both in the liquid and in the solid state, respectively [1–5]. They are significant molecules of pharmacology [6,7], and important intermediates in the chemical synthesis of pharmacologically active compounds as well [8].

In most of our previous studies, the combination of spectroscopic methods and molecular modelling was applied for the characterisation of the structure-forming interactions taking place in solution as well as the solid state. It was shown that the fundamental unit of the acids was the dimer kept together by the strong OH...O hydrogen bonds, while the aggregation of the dimers occurred *via* the weaker CH…X (X: O or S) interactions [1,4,5].

For the N-containing derivatives, only calculations were performed (assuming again that the dimer was the fundamental unit) [2,3], since the syntheses of the molecules were not successful. Since then, we have found ways for the preparation of some of the pyridyl-containing derivatives and now, the combined experimental and computational approach became feasible. Results of this work are communicated in the followings.

The conformational as well as the structure-forming properties of *E*-3-(*x*-pyridyl)propenoic acids (x = 2, 3 or 4) have been studied by the combination of computational and spectroscopic methods. IR spectroscopy revealed that in the solid state the zwitterionic species predominated, while by NMR measurements it was found that dimers, kept together by strong OH…O hydrogen bonds, were formed in a dipolar aprotic solvent (DMSO). In concentrated solution, extended aggregation occurred through the cooperative effect of (aromatic)C–H…N weak hydrogen bonds. Conformational search and geometry optimisation of the zwitterionic forms and the acid dimers were performed at the level of HF/6-31G**. The intermolecular forces between the dimers could also be modelled properly at the HF/6-31G** level. Molecular modelling provided reasonable geometric arrangements as well as energy data for the dimers of the dimers.

Keywords: pyridylpropenoic acids, spectroscopic methods, conformational search, intermolecular hydrogen bonds

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Session 13: Methods I

M13.1 Photo-guided sampling for rapid detection and imaging of traces of explosives by a compact Raman spectrometer

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Motivated by the obvious need to unravel traces of hazardous materials in real-time, a modular, compact Raman spectrometer, based on a green laser pointer, an air cooled intensified charged coupled device and a *x,y* motorized translation stage was developed. Its performance was tested for point and proximal detection and for rapid acquisition of Raman spectra and Raman spectral maps. This system was found to be highly sensitive and by using photo-guided sampling it allowed Raman mapping of samples in reduced time compared to raster scanning. The point and real-time detection capabilities of the spectrometer, together with the portability that it offers, make it a potential candidate for replacing existing Raman microscopes and for field applications.

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M13.2 Capillary Raman Spectroscopy for High-Sensitivity Gas Analysis

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Raman spectroscopy is an inline, non-contact and non-destructive compositional gas analysis tool that allows one to precisely detect multiple species simultaneously, without the need for multiple-wavelength laser sources. Raman systems, based on a conventional 90°-collection configuration, have been set up by our group over the past years and were successfully developed towards high measurement precision and sensitivity [1]. The sensitivity reported therein is believed to be close to the ultimate reachable limit for that configuration. In order to enable real-time applications, e.g. in process control, or the detection of trace amounts of gases even at low total pressures (in the mbar/sub-mbar range), it is necessary to further increase the sensitivity beyond that of the conventional technique. Consequently, alterations to the current 90°-implementation are required.

One promising approach to enhance the sensitivity of Raman systems is the use of a hollow glass capillary, with a highly-reflective inner coating, acting as the gas cell [2]. Laser radiation coupled into the capillary is reflected along its entire length, so that the whole capillary acts as the Raman interaction region. Likewise, the Raman radiation is reflected and collected over the full length. Thus, this elongated scattering volume vastly enhances the Raman signal compared to conventional setups.

Direct comparison measurements of our group yielded a signal enhancement of two orders of magnitude. Using a capillary Raman prototype for the compositional analysis of gas mixtures, it was possible to detect hydrogen isotopologues with partial pressures of < 0.5 mbar within 5 s overall acquisition time, for a laser power of 1.75 W (532 nm cw laser). These results compare favorably with those of other groups, who have been using various non-capillary Raman systems for measurements of gaseous hydrogen and report throughout inferior detection limits, although they sample for longer acquisition times (see e.g. [3,4]).

The caveat is that the sensitivity of capillary Raman systems is usually limited by non-negligible fluorescence background, which leads to a considerably increased shot-noise compared to the 90°-configuration. Said fluorescence is generated both in the optical components in the laser beam path and in the glass capillary itself. Therefore, we have investigated methods to minimize the fluorescence background in the setup whilst maximizing the collected Raman signal. These methods included successful fluorescence suppression measures such as the optimization of the number and thickness of optical components in the laser beam path, as well as the investigation of alternative capillary-like gas cells made of metal. The latter do not reach the same signal intensities as glass capillaries, probably due to a lower surface smoothness and thus lower reflectivity, but they exhibit a much lower background. As a result, sensitivities seem to be comparable to those reached with glass capillaries; in addition, one is able to use higher laser powers. Some preliminary results will be shown.

Keywords: Raman spectroscopy, gas analysis, sensitivity enhancement

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M13.3 Noise Reduction in Fluorescence Kerr Gating

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In order to observe ultrafast photochemical and –physical processes, one needs methods of measurement which supply a suitable time resolution down to several femtoseconds (fs). One method for this purpose is fs-fluorescence spectroscopy based on optical gating. The optical Kerr gate is one realization of this concept. It essentially consists of a pair of crossed polarizers (P, A) with a Kerr medium (K) in between (Fig. 1).

The presented set-up relies on the one described by Schmidt et al. [1]. Due to the predominantly reflective optics (Fig. 1, C = cassegrainian objective), the passage through material is reduced to a minimum (2 mm). The result is a nearly dispersion-free measurement with a time resolution of ~150 fs. But the used optics lead to problems for long-lived fluorophores: Due to geometrical and physical effects [2,3] there is light leaking through the closed gate. This results in a decreased signal-to-noise ratio in time resolved measurements, especially for late delay times. The disturbing effects will be discussed and a solution presented.

A second challenge in measuring long-lived fluorophores is the duration of the measurement period. Laser fluctuations on short as well as long time scales raise the magnitude of noise. In particular, the variations on longer time scales impair the quality of the decay traces (Fig. 2). Use of reference diodes helps to correct the measurements for fluctuations of pump and gate pulse and thereby reduce the noise.

Measurements on thioxanthone (TX) in selected solvents will illustrate the performance of the set-up. In accordance with transient absorption experiments the fluorescence proves to be very solvent sensitive.

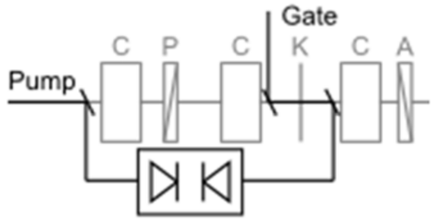

Fig.1: Application of reference diodes in optical Kerr gating (schematic).

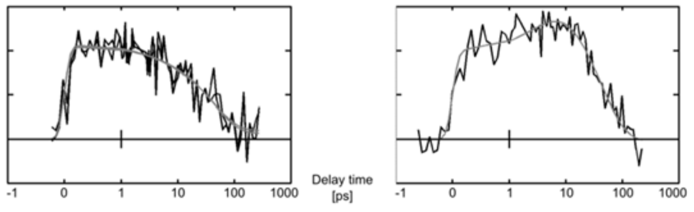

Fig.2: Illustration of laser fluctuation problem: Fluorescence decay of TX in acetonitrile at different days of measurement. Time trace for 440 nm.

Keywords: fs-Spectroscopy, Fluorescence, Kerr gate, Thioxanthone

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M13.4 The Development of an On-Line Raman Detector for Hyphenation With High Temperature-HPLC AND IRMS

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Criminal statistics of product and trademark piracy have increased dramatically in recent years. Beside the substantial economic damage, fake articles in foodstuffs, pharmacy and cosmetics exhibit potential risks for health.

Considering this background an analytical method was developed to collect information about origin and authenticity of chemical compounds. The technique proposed in this contribution links high-temperature high performance liquid chromatography (HT-HPLC) with isotope ratio mass spectrometry (IRMS). The compounds are first separated by HPLC and then analyzed by IRMS to receive their $^{13}C/^{12}C$ isotope ratios. Isotope ratios of compounds enable to identify their origin and authenticity. Since commercially available HPLC devices are usually equipped with detectors based on UV-VIS absorption spectroscopy, a direct coupling of HPLC and IRMS does not provide any structural information about the separated compounds. To circumvent this lack, a Raman cell was set between HT-HPLC and IRMS to provide an online identification of compounds.

To establish on-line Raman detection a specific sample cell was developed. The centerpiece of the detector was a liquid core waveguide which was equipped with T-pieces at both ends. The T-pieces first enabled that the mobile phase of the HT-HPLC as light guiding medium passed through the waveguide and in addition they served for the insertion of laser light into the waveguide at one end and enabled to take out the Raman scattering at the other end. For this, the laser light was directed to the waveguide by a microscope objective and Raman scattering was routed to the monochromator/camera unit via a fiber.

Due to the flow of analyst through the liquid core waveguide, detection times of Raman signals were about 10 s. For this detection time interval the detection limit was in the range of 1-4 mg L^{-1} (< 10^{-5} M). According to this high capacity of the liquid core waveguide to collect Raman photons, this device is about 100x to 1000x more sensitive than usual Raman spectrometer. The method was for instance applied to distinguish among dietary supplements.

The development of the Raman device was part of a close and fruitful cooperation in which the HT-HPLC was optimized by the Institute of Energy and Environmental Technology (IUTA, Duisburg, Germany) and the IRMS was adapted by the Institute of Analytical Chemistry (University Duisburg–Essen, Germany).

Keywords: Raman spectroscopy, hyphenation, product piracy

M13.5 FT-IR Spectroscopy in Ultrahigh Vacuum: Surface Science Approach for Understanding Reactions on Catalytic Oxide Powders

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FTIR spectroscopy has been frequently used to characterize catalytic oxide surfaces, since it can be well combined to the density functional theory (DFT) calculations and has scarcely the limitations marking the other investigation methods used till now. To achieve the highest sensitivity of spectroscopy and to fulfill the standard handling conditions for single crystalline oxides FTIR spectrometer can be adapted to a UHV equipment.

The fundamental advantage of using FT-IR spectroscopy in vacuum is to avoid the absorption of atmospheric moisture and other gas species. Furthermore, the UHV-FTIR adaption enables the closely combination of FT-IR technique with other UHV experimental methods, such as scanning tunneling microscopy, electron energy loss spectroscopy, thermal desorption spectroscopy, low energy electron diffraction and X-ray photoelectron spectroscopy.

An UHV-FTIRS apparatus dedicated to the spectroscopic characterization of oxides, single crystal as well as powders was developed [1]. It combines a Bruker VERTEX 80v vacuum FTIR spectrometer with a PREVAC UHV system.

Using this established equipment the amount of defects on rutile surface has been determined with the help of DFT calculations and the accordant catalytic activity of the oxide surface was deduced. For the first time IR data achieved for powder particles can be compared with single crystal reference system [2].

Keywords: FT-IR spectroscopy; catalysis; oxide; IRRAS;

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M13.6 Photoionization of Atoms, Molecules and Cluster: From Energetics to Dynamics with Novel VUV Light Sources

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For more than fifteen years the Gas Phase beamline of the Elettra synchrotron radiation laboratory (Trieste, I) [1] has enabled thorough photoionization studies of isolated systems, even with low density targets such as vapours of biomolecules [2] and clusters [3]. More recently the interest of the Elettra physical chemistry-chemical physics community has been attracted by the opportunity of exploring the temporal dynamics of isolated systems by means of novel state-of-the-art light sources. For this purpose two new beamlines capable of delivering ultrafast VUV photon pulses are currently under commissioning in the framework of the FERMI@Elettra Free Electron Laser (FEL) project: the Low Density Matter beamline at FERMI [4] and CITIUS [5], a state-of-the-art fs-VUV source, based on laser High Harmonic Generation on rare gases.

Recent experiments on photoionization spectroscopy of gas phase molecular targets of increasing complexity will be presented, as well as research opportunities opened in the field of atomic, molecular and cluster physics by these novel ultrafast light sources.

Keywords: Photoionization Spectroscopy; Photoelectron Spectroscopy; Synchrotron Radiation

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Session 14: Spectroscopy for Cutural Heritage

SfCH14.1 Non-Destructive Analyses of 16TH Century Printed Book "Osorio" with the Colorful Fore-Edge Miniatures

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In our study we are trying to illuminate the palette used by the artist who decorated the fore-edge of the Middle Age printed book description of the military campaign of the Spanish king Emanuel Hieronymus Osorio and try to give a temporal boundary on the moment of their creation. Our experiments show that a pigment palette is a common one for the period between 16th and 19th century. Several pigments were identified, like vermilion and minium, white lead and massicot. Further, we identified the ink used for the book cover inscriptions. Three complementary, non-invasive spectroscopic techniques were used: micro-Raman spectroscopy, PIXE spectroscopy and UV-VIS FORS spectroscopy. The challenges which occurred during the study are presented, such as the positioning of the book underneath the microscope or even the fiber optic probe holder, the roughness of the fore-edge surface and the thinness of the color layers.

Keywords: medieval pigments; non-destructive analyses; Raman spectroscopy; PIXE spectroscopy; UV-VIS FORS spectroscopy

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Session 15: Raman Spectroscopy

RS15.1 Intermolecular Interactions in Hydrogel-NSAIDS Systems – Raman Spectroscopy Studies

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Fast development of polymer stimuli responsive systems is mainly stimulated by increasing needs in the fields of biomaterials, Micro Electro-Mechanical Systems (MEMS) and carriers for controlled drug release [1,2]. Currently a great attention is focused on the thermo-responsive, bio-inert hydrogels exhibiting volume phase transition (VPT). Resulting from metastable balance between hydrophobic and hydrophilic interactions VPT leads to abrupt pull of water outside a collapsing polymer network. The temperature of VPT (T_{VPT}) depends mainly on chemical structure of polymer but also on a presence of ionic additives [3]. The last one is the most important for drug delivery systems, as a bioactive substances are commonly used in salt form.

In this work we present the results of Raman spectroscopy studies of intermolecular interactions in two thermo-sensitive hydrogels based on poly[2-(2-methoxyethoxy)ethyl methacrylate] and poly(vinyl methyl ether). The role of water – polymer and water – drug interactions are especially interesting, taking into account strong impact of used drugs on T_{VPT} and weak attraction between a drug and a polymer network (as it will be shown). An influence of selected non-steroidal anti-inflammatory drugs (NSAIDS) on redistribution of intermolecular interactions and water structure in mentioned systems will be discussed.

Acknowledges
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Keywords: thermo-responsive hydrogels; water structure; hydrogen bonds

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RS15.2 Interference Enhanced Raman Scattering of $F_{16}CuPc$ Films

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The effect of interference enhanced Raman scattering (IERS) first described by Nemanich *et al.* [1] became a powerful characterization tool for inorganic [2] and organic [3] thin films and helped to overcome the low Raman scattering response from ultra-thin films due to the small probed volume. It is especially useful for *in situ* Raman measurements of organic semiconductor thin films deposited by organic molecular beam deposition (OMBD) under ultra-high vacuum conditions. In order to conduct a systematic study of the IERS effect as a function of the SiO_2 oxide layer thickness a thin film (7±2 nm) of $F_{16}CuPc$ molecules was deposited on top of the SiO_2 layer using OMBD. Spectroscopic ellipsometry was used to determine the oxide and the organic film thicknesses. We performed the experiment in backscattering geometry using a piezoelectric stage for precise movement along the wedge-shaped sample in the direction of increasing SiO_2 thickness. Periodic enhancement of the $F_{16}CuPc$ Raman mode intensities with increasing SiO_2 thickness was observed with the maxima related to oxide thickness values corresponding to multiples of 1/4 of the excitation wavelengths [1] used, namely 325 nm of a He-Cd laser, 514.7 nm of a DPSS Cobalt® laser, and 632.8 nm of a He-Ne laser. We observed that the enhancement factors (EF) for $F_{16}CuPc$ Raman mode intensities in the spectra are independent of the $F_{16}CuPc$ optical constants, which contradicts the theoretical predictions [1,2,4]. The differences in the EF values for different Raman modes might be due to the different Raman selection rules. The model used for simulating the IERS effect was thus supplemented by taking into account all parameters (the numerical aperture of the objective and the s- and p- polarizations, respectively) of the system under study providing an improved description of the IERS effect and its application to ultra-thin organic films.

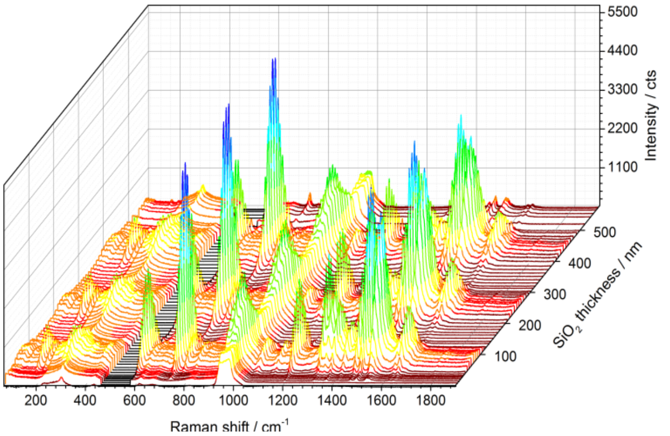

Figure 1. Series of Raman spectra of a 7 nm thick $F_{16}CuPc$ film, measured along the substrate with gradually varying SiO_2 layer thickness using 514.7 nm excitation wavelength (the strong contribution from Si peak at 521 cm^{-1} was cut out).

Keywords: interference enhanced Raman scattering, phthalocyanine, ultra-thin film

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RS15.3 Low Frequency Vibrations of Native ans Denaturated Lysozyme: A Raman Studay

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The low frequency Raman spectra of lysozyme aqueous solutions have been collected in HV geometry in the 25-85°C range [1]. Short and long exposures to high temperatures have been used to modulate the competition between thermally induced reversible and irreversible denaturation processes. A peculiar temperature evolution of spectra has been observed at temperatures higher than 65°C thus allowing distinguishing between effects caused by unfolding and aggregation on the collective vibrations of the globular protein.

Solvent free (SF) spectra have been obtained after subtraction of elastic and solvent components, and assigned to a genuine vibrational contribution of hydrated lysozyme. A straight similarity is observed between SF THz Raman feature and the vibrational density of states as obtained by molecular dynamics simulations [2]. In accordance with the model proposed for interpreting the low-lying vibrational modes of the native BSA [3], we suggest to consider the lysozyme molecule as a three dimensional, elastic nanoparticle with aperiodic charge distribution, and describe the SF profiles as a distribution of phonon-like vibrations.We relate the temperature evolution of this feature with the expansivity of lysozyme molecular volume and compare the results of this spectroscopic analysis with densitometric data. From this comparison an important description emerges of the role of the hydration shell respect to the effective protein volume in the pre-melting region.

Keywords: THz Raman; lysozyme; unfolding, protein aggregation

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RS15.4 Influence of Selected Inorganic Salts on Raman Resonance Phenomenon in Water

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Resonance effect is a phenomenon that strongly enhance Raman signal from the sample and strictly depends on excitation wavelength. It occurs when energy of an incident electromagnetic wave is close to an energy difference between stationary states.

First demonstration of Raman resonance effect in liquid water was presented by Pastorczak *et al.* [1]. Intensity ratio of two main components of OH stretching modes with maxima around 3200 and 3400 cm^{-1} (assigned to strongly and loosely hydrogen-bonded water molecules respectively) is assumed to be characteristic of water microstructure. This ratio depends on the excitation wavelength in the visible range. It results in the assumption that the Raman resonance effect in water directly corresponds to the supramolecular structure of liquid water.

Factors like high temperature, pH, ions etc. lead to reorganisation of local water structure. In Raman spectra, it effects in change of intensity ratio of 3400 and 3200 cm^{-1}. Terpstra *et al.* studied influence of ions size and concentration on the dynamical properties of water [2]. Their work shown that the biggest changes in OH stretching modes region in series of aqueous salts solutions: KCl, NaCl and LiCl follow the increasing order of cation size: $Li^+ < Na^+ < K^+$.

In this work we studied the impact of selected inorganic salts (alkali chlorides) on Raman resonance in liquid water. The effect of the cation size will be discussed.

Acknowledgments
This work was financially supported from grant no. 2013/09/B/ST4/03010.

Keywords: Raman resonance effect; water structure; inorganic salts

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RS15.5 The Symmetric C-C Stretching Mode Splitting in Raman spectra of substances, containing alkylammonium ions

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Raman spectroscopy is a powerful tool for the detection of substances containing CH_2 chains. Raman spectra of CH_2-chain molecules (n-alkane, polyethylene, alkylammonium surfactants *etc.*) have actually been studied in detail. Nevertheless, we recently observed a new effect in the Raman spectra of alkylammonium surfactants and their organo-clay hybrids, which are used as fillers for polymer/clay nanocomposites.

In our contribution, we present a rather interesting and unexpected behavior of the symmetric C-C stretching vibrational band in Raman spectra of substances containing alkylammoniun ions. This band splits into two modes when two types of *trans* CH_2 segments coexist in the alkylammoniun ions. These two types of *trans* segments differ in their chemical composition. Especially, the *trans* segment of the first type consists of a sequence of CH_2 groups with a terminal $(CH_3)_k$-N-unit. The *trans* segment of the second type contains only CH_2-groups (without a terminal $(CH_3)_k$-N- unit) and appears as a result of a bend of the CH_2 chains in the alkylammonium molecule.

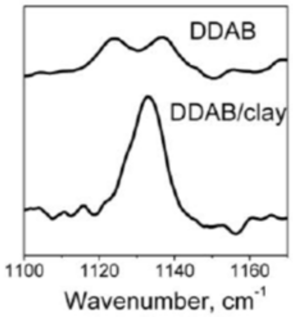

Fig.1 The C-C mode splitting

The illustration in Fig. 1 shows Raman spectra of polycrystalline DDAB $[(CH_3(CH_2)_{13})_2\ N^+(CH_3)_2Br^-]$ (the upper spectrum) and montmorillonite clay modified by DDAB (the lower spectrum). The Raman spectrum of polycrystalline DDAB reveals the symmetric C-C stretching mode splitting. Also, we have observed the splitting of this band in other substances, including montmorillonite clays modified by CTAB $[CH_3(CH_2)_{15}N^+(CH_3)_3Br^-]$ or DODAB $[(CH_3(CH_2)_{18})_2\ N^+(CH_3)_2Br^-]$, polycrystalline DODAB, and liquid di-n-octylamine hydrochloride $[(CH_3(CH_2)_6CH_2)_2\ N^+H_2Cl^-]$.

Here, we discuss the relationship between the extent of the observed band splitting and the respective lengths of *trans*-segments, which cause the splitting. In addition, we demonstrate that the splitting can be used as a versatile hint in order to validate computer-simulated conformational states of alkylammonium ions intercalated into confined space.

This work is supported by the Russian Foundation for Basic Research (project codes 12-02-00238-a).

Keywords: Raman spectroscopy; C-C stretching mode splitting; alkylammonium ions; clay

RS15.6 Raman Diagnostics of Copolymers and Polymer Blends

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Raman spectroscopy is a convenient and highly informative technique for the structural analysis of polymers, because it provides the ability to characterize various phase, configurational and conformational states of molecules.

Polyethylene (PE), isotactic polypropylene (PP), and polyvinylchloride (PVC) are the most important industrial polymers. Nowadays, the development of PE-, PP-, and PVC-based materials, including copolymers, blends, and nanocomposites, is a fast growing and promising field. The structure and, consequently, key properties of these new materials can be purposefully tuned in a wide range by altering the synthesis conditions. In addition to their high practical importance, these materials are of significant interest for fundamental research, since they demonstrate new interesting features in their molecular and supramolecular structure, their physical and chemical properties, and in their vibrational spectra.

Long time ago, Raman spectroscopic methods were already introduced for the evaluation of the phase composition, conformational order and macromolecular orientation for neat PE, isotactic PP, and PVC. However, realistic Raman structural diagnostics of their modern modifications (copolymers, blends, and nanocomposites) requires not only the elaboration of already existing approaches for the neat polymers, but more importantly also the consideration of the mutual influence of both the basic polymer (or matrix) and the incorporated substance (comonomer, filler, second polymer) on the vibrational fingerprints.

In this report we present the development of Raman methods aimed at the study of a wide range of PE-, PP-, and PVC-based materials, such as copolymers and polymer blends. The relationships between the synthesis and processing conditions, the structure and properties of these materials have been established. In our studies we have observed that the phase and conformational composition and the orientational order of macromolecules strongly depend on the content and nature of the imbedded substances, the synthesis conditions, in particular, on the type of catalyst.

We have found that the degree of crystallinity calculated from the Raman spectra of the materials is in a good agreement with the data of differential scanning calorimetry (DSC) and X-ray diffraction analysis. The alterations observed in the temperature-dependent Raman spectra of the materials under study and the comparison with the Raman spectra of low-molecular-weight compounds also support the applicability of our approach.

This work is supported by the Russian Foundation for Basic Research (14-02-00832-a, 12-02-00238-a) and the Grant of the President of the Russian Federation for the Support of Leading Scientific Schools (451.2014.2).

Keywords: Raman spectroscopy, polyethylene, polypropylene, polyvinylchloride, copolymer, polymer blend

Session 16: Spectroscopy of Polymers

SpP16.1 Optical Activity of Transparent Polymer Foils Characterized by Spectral Means

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The channeled spectrum method, validated for inorganic optical active layers [1]-[4], is used now to determine the optical activity of some transparent optical active polymer solutions in different solvents. By using the measurements of wavenumbers in the channeled spectra of hydroxyl propyl cellulose in water methanol and acetic acid, the circular birefringence, the dispersion parameter and the specific rotation were estimated in the visible range.

The experiments showed the dependence of specific rotation on the polymer concentration in solution and also on the solvent nature.

The decrease of the specific rotation with the increase of the wavelength in the visible range was evidenced [3].

The method has the advances as the rapidity of the experiments and the large spectral range in which it can be applied. One disadvantage is the fact that the channeled spectrum does not allow the rotation sense of the electric field intensity.

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Keywords: optical activity, specific rotation, optical rotatory dispersion, polymer solutions.

Session 16: Spectroscopy of Polymers

SpP16.2 Tetrafluoroethylene Based Polymers; Spectroscopy Studies and Quantum Chemical Modeling

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The research for innovative materials in high tech demanding applications located in the Fluorinated Polymers family different possible answers and solutions. Fluorinated polymers constitute a wide class of materials showing several outstanding performances; among them, the Tetrafluoroethylene (TFE: CF_2CF_2) based copolymers may be the best choice when final applications are very demanding in terms of aggressive chemical environment or high temperature of use. With the insertion of suitable co-monomers in the polymer chain backbone it is possible to get a fine tuning of physical-chemical properties (for example melting temperature, crystallinity). Vibrational Spectroscopy (including far/mid/near infrared and Raman) proved to be a valuable tool to investigate the effects of the presence of co-monomers in the TFE based polymers (fig.1), and its combination with Quantum Chemical (QC) modeling allows to give unambiguous interpretation of the recorded spectra and new insight into the physical-chemical properties of the materials. Here we show some results dealing with the conformational features and the determination of order/disorder content obtained both experimentally and from theoretical conformational analysis of different models miming the 15/7 perturbed helix chain backbone [1].
Moreover, an important aspect from the analytical point of view is the possibility to identify and quantify the polar end groups, for example those containing carbonyl moieties. The kind and the abundance of end groups may be an important feature which affects the overall performances of such materials in the final applications. In particular, the copolymer of TFE and 2,2,4 Trifluoro, 5 trifluoromethoxy 1,3 dioxole (TTD) (known commercially as Hyflon® AD copolymer) has been considered. IR spectra clearly evidenced the presence of carbonyl groups belonging to a variety of chemical groups, generated in the copolymer as a results of different chemical processes. With the support of QC modeling a wide set of functional groups have been considered and explored. The approach allowed us to propose some new bands assignments, useful both for analytical application and for the interpretation of the behavior of this class of polymers while undergoing severe working conditions and treatments.

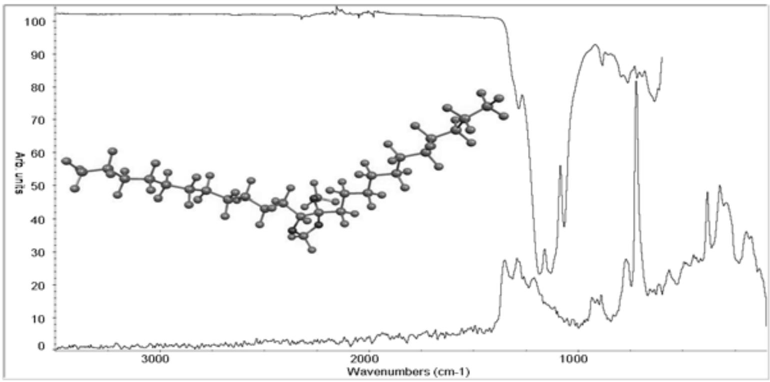

Fig. IR and Raman spectra of a TFRE/TFD copolymer(Hyflon ® AD copolymer)

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Session 16: Spectroscopy of Polymers

SpP16.3 Automated FTIR Microscopy in the Polymer Industry

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FTIR microscopy is a very established analytical method for investigating polymers and many different types of substrates with polymer coatings.

In recent years the size of analytical tasks even in industrial applications has decreased from "visible to the eye" (>100 µm) to the µm range which requires the use of an IR microscope. Typical applications are the determination of the chemical composition in laminates, the investigation of the homogeneity in polymer coatings, and the analysis of failures in polymeric structures. To study polymeric samples by FTIR in transmission thin (5-15 µm) sections have to be prepared by a microtome. In contrast, ATR-FTIR microscopy allows the analysis of bulk polymer samples and polymer coatings mostly without sample preparation. Conventional FTIR microscopes could be optionally equipped with ATR crystals which had to be placed and removed manually to change between IR and VIS mode.

Bruker has now launched the first fully automated FTIR microscope.

In this new system all movable components are motorized and electronically coded, ensuring highest user comfort and ease of operation. A major innovation is the motorization of the ATR crystal in the objective. Due to this feature, the system switches from transmission or reflection into the ATR mode without interaction of the operator, and is capable of measuring fully automated sample and background spectra, even in ATR mode.

A further enhancement is the complete integration of hard- and software components into a guided "wizard"-type functionality. This decreases the amount of time till the operator can run the system autonomously and leaves almost no room for measurement procedure uncertainties.

In this contribution, the automated mapping and imaging analysis of polymer laminates is shown. Dark samples were analyzed by Germanium-ATR microscopy. The laterally resolved information of IR images was evaluated by univariate and multivariate data reduction (e.g. PCA, 3D cluster analysis, RGB-WTA). The system was further applied for analysing the homogeneity of thin polymeric coatings as well as for determining small inclusions in polymers.

Keywords: FTIR, microscopy, xy-resolved chemical imaging

SpP16.4 Tracking of micellization by fluorescence spectroscopy

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Surface coverages generated by surfactants can be both characterized and modified by surface pressure–surface area isotherms. These are generated by measuring the surface pressure (difference between surface tension of water and of a solution) when the surface area is continuously reduced. Keeping the concentration of surfactant solution constant, the first derivative of these isotherms with respect to the area expresses the compressibility of the surface layer and shows two minima. Minima of compressibility indicate an upcoming reorganization of molecules within the layer if compression is continued. The first minimum at low concentrations enables the determination of the effective area which single molecules take up in the monomolecular layer with minor interference with adjacent molecules. The second minimum at higher concentrations but far below the cmc marks a conversion of the monomolecular layer to a multi-layered covering or to a detachment of molecular aggregates or micelles. To establish the latter path, the water insoluble tetraphenylporphyrin (H2TPP), which can be recorded by its fluorescence, was added to the surface layer. If the area is then decreased and the second minimum of compressibility is passed, a certain amount of H2TPP could be recorded on the backside of the barrier that reduced the size of surface. This demonstrates that TPP molecules are attached by surfactants and transferred via the bulk phase to the backside.

The transport of H2TPP molecules via micellization depends on the composition of the surfactants. Micelles built up by molecules with long hydrophobic chains (e.g., E6C16) can affiliate H2TPP molecules while aggregates made from molecules with shorter hydrophobic chains (e.g., E10C12) detached from the layer without carrying H2TPP molecules.

Concluding these experiments may give a certain insight in the aggregation behavior of surfactants.

Keywords: fluorescence microscopy; micellization; transport phenomena

Session 17: Methods II

Session 17: Methods II

M17.1 Precise and Accurate Transmission Spectra Computed by a Modified Data Analysis Procedure in FTIR Spectrometry

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Nuclear fusion reactors like the international thermonuclear experimental reactor (ITER) and demonstration power plant (DEMO) require a fuel cycle with infrastructure for gas recycling. Part of this infrastructure is a facility that separates the six hydrogen isotopologues H_2, HD, D_2, DT, T_2 (Q_2) by cryogenic distillation. For this system, an inline, non-invasive method for real-time monitoring of the Q_2 concentrations is needed. The tritium absorption infrared (TApIR) experiment [1] was developed and set up at the TLK in order to test the suitability of IR absorption spectrometry for this purpose.

The method of measurement in the TApIR experiment is Fourier transform infrared (FTIR) spectrometry; intensity spectra are computed from measured interferograms by a software that applies a discrete Fourier transform (DFT).

The conventional data analysis procedure in FTIR spectrometry (division of sample by reference spectra) yields wrong results when applied to the TApIR data, due to different refraction effects at the sample windows with filled and empty cell. This can be avoided by modifying the data analysis procedure with an additional filter that removes these effects.

A rolling circle filter (RCF) [2] is a suitable algorithm for this task. RCFs depend on two filter parameters, radius and ellipticity, which we optimized to obtain filtered spectra with high trueness. However, RCFs significantly change the statistical and systematic errors of the final spectra, which have to be determined to obtain results with high trueness.

From the sample transmission functions resulting from this modified analysis procedure, calibration quantities, like integrated absorbances, can be computed. These can be used for a calibration with Q_2 concentrations, which are measured externally by an independent Raman system [3]. If a calibration exists, Q_2 concentrations in unknown sample mixtures can be determined. The trueness of these concentration values improves with knowledge of the statistical error in the sample transmission functions above, while the correction of the systematic uncertainties is necessary when the resulting spectra are used for investigations of the underlying physics.

In this talk, the current data analysis procedure will be presented, the optimizations will be described and results for sample transmission functions with systematic error corrections will be shown.

Keywords: Fourier transform infrared spectrometry; liquid hydrogen isotopologues; signal decomposition

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Session 17: Methods II

M17.2 Non Linear Effects in IR Absorption Spectroscopy of Liquid Hydrogen Isotopologues

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For future fusion facilities like ITER and DEMO, which will consume up to several 100 g of tritium per day [1], an IR absorption system for tritium measurement and accountancy is being developed at Tritium Laboratory Karlsruhe (TLK) [2]. Due to a burn-up fraction below 3%, the estimated throughput of tritium in fusion fuel cycles will be in the range of some kg per hour. One important aspect of these tritium fuel cycles is to reprocess unburned fuel and to purify tritium and deuterium. For processing of hydrogen isotopologue ({H_2, D_2, T_2, HD, HT and DT} = Q_2) mixtures the Isotope Separation System (ISS) as part of the TRitium Enrichment Test Assembly (TRENTA) is under development at TLK [3]. The ISS is using cryogenic distillation columns, which are operated at 20 to 25 K. Therefore, a reliable method for the precise and accurate compositional analysis of the liquefied hydrogen isotopologues needs to be identified and tested.

A promising method is infrared absorption spectroscopy which is being developed and tested at the TRENTA facility. The actual R&D work is focusing on the questions how such an inline system can be calibrated. For this purpose a cryogenic sample cell has been developed (Fig.1) and measurements with the system have started. Two major issues for understanding the spectra are the identification of appropriate absorption lines and the dependence of the absorption spectra on the isotopologic composition. A laser Raman system, that is measuring in gaseous phase at around 300 K, is available for cross calibration[4]. This Raman setup is an ideal instrument for cross calibration measurements due to the fact, that it is sensitive to the same parameters like the IR spectroscopy in liquid phase. One major difference between the two methods is, that Raman spectroscopy in gaseous phase is linear, while IR in liquid phase is nonlinear. This nonlinearity has a major impact to the overall composition of IR absorption spectra. One very obvious effect is the appearance of fully new lines in mixtures of deuterium and hydrogen where no lines are visible in pure samples (fig. 2). This contribution will show first results and impacts from the nonlinear effects on the calibration of the TApIR experiment (Tritium AbsorPtion Infrared Spectroscopy). *Keywords: IR spectroscopy; liquid hydrogen; nonlinear effects*

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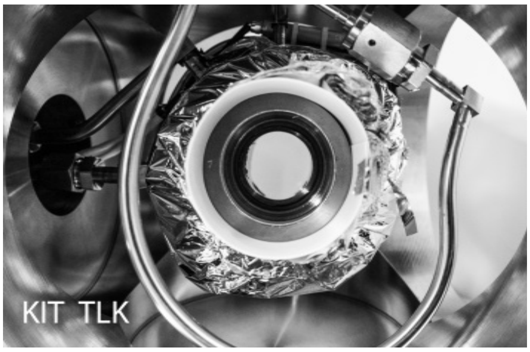

Fig.1 Cryogenic sample cell of the TApIR experiment.

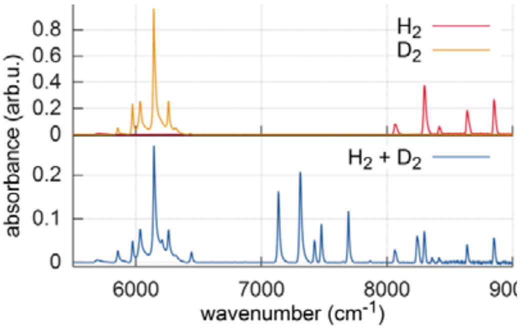

Fig.2 Comparison of absorption spectra from pure H2 and D2 samples with a mixture of the two isotopologues.

M17.3 Online In-Situ Raman Studies of Processes in a High Temperature PEM Fuel Cell

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In recent years various physico-chemical methods have been considered to study HT-PEFCs in operation. These methods dominantly record global electric parameters. This contribution intends to show that chemical processes can be locally resolved by applying in-situ Raman spectroscopy.

An optical port was generated by drilling a hole into the ligament between parallel flow field canals on the cathode side. A quartz rod (diameter: 730 µm) was inserted into the hole and was fed in contact with the poly-(2,5-benzimidazole) membrane doped with phosphoric acid. A beam of a He-Ne laser was focused into the rod by a microscope objective to locate the beam waist within the membrane. The Raman signals passing the rod were directed to the detection unit consisting of a spectrograph of high luminosity and a Peltier-cooled CCD-camera.

The spectra were recorded under OCV (open circuit voltage) condition and different current densities. Although excited by red laser light, the membrane did fluoresce strongly. Despite this drawback, the Raman bands could be extracted from the fluorescence emission. Against expectations, the measurements reveal that only small amounts of orthophosphoric acid were present. The main contribution originated from pyrophosphoric acid [1]. This acid is generated at higher temperatures by condensing two phosphoric acid molecules under elimination of one water molecule. To a small amount polyphosphoric acid could also be identified. In addition $H_4PO_4^+$ cations were discovered. Due of its large Raman signals it is thought that charge transfer is carried out by $H_4PO_4^+$ cations to a large extent. Changes of current consumption directly induced significant changes in the concentration of pyrophosphoric acid and $H_4PO_4^+$. The aforementioned fluorescence of the membrane material was analyzed with respect to changes of temperature, tensile stress and dopant concentration.

Keywords: Raman microscopy; Fuel cells; Proton exchange membranes

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M17.4 Calculation of the Specific Heat Using the Raman Frequency Shifts for the Solid I-II Transition in Benzene

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The specific heat C_P is calculated as a function of temperature using the observed Raman frequency shifts of the six lattice modes at constant pressures of 0 and 0.1 GPa for the solid I-II transition in benzene. This calculation is performed using the volume data through the mode Grüneisen parameter of each lattice mode which we determined as functions of temperature and pressure.

The specific heat C_P due to the contributions of the six lattice modes, increases with the increasing temperature, as expected at constant pressures (P=0 and 0.1 GPa), which can be compared with the experimental measurements for the solid I-II transition in benzene.

Keywords: Specific heat; Raman frequency shifts; Benzene

M17.5 Investigation of the Influence of ortho/para Cconversion on the Infrared Spectra of Liquid Hydrogen and Deuterium

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One important part of the fusion fuel cycle of facilities like ITER (International Thermonuclear Experimental Reactor) and DEMO (DEMOnstration Power Plant) is the isotope separation system (ISS). The purpose of the ISS is to separate mixtures of all six hydrogen isotopologues Q_2 (H_2, HD, D_2, HT, DT and T_2) with a throughput of several kg per day [1]. The technical implementation of this separation using cryogenic distillation at temperatures around 20 K, is under development at the Tritium Laboratory Karlsruhe as part of the TRitium Enrichment Test Assembly (TRENTA) [2].

For the monitoring of the amount of accumulated tritium in the bottom of the distillation column an inline and real time analysis method able to measure the isotopologic concentration is needed. As a test experiment for this analysis method the Tritium Absorption Infrared experiment (TApIR) has been set up to simulate the conditions of the cryogenic distillation column inside a cryogenic sample cell [3]. The TApIR experiment is able to liquefy hydrogen and to analyse them using infrared (IR) absorption spectroscopy. To deduce the gas composition from the recorded IR spectra a calibration with known mixtures is required. The calibration and analysis procedure has been proven in a first calibration measurement with equilibrated H_2-HD-D_2 mixtures [4]. A major systematic uncertainty on the calibration of the TApIR experiment is caused by metastable populations of the energy states of the investigated Q_2, due to the ortho/para modifications of H_2, D_2 and T_2. A change in the odd J fraction caused by ortho/para conversion has a direct influence on both line strength and line position of the infrared absorbance spectrum, as shown in fig. 1.

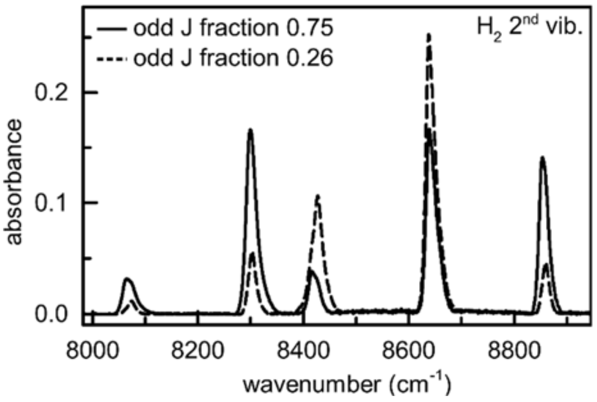

Fig.1 Influence of the ortho/para conversion on the line strength and line position of the 2nd vibrational branch of H_2.

This contribution will give an overview over the first Raman [5] and FTIR spectroscopic measurements to qualify the influence of ortho/para conversion on the calibration of the TApIR experiment.

Keywords: infrared spectroscopy; ortho/para conversion; liquid hydrogen

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M17.6 Comparative Study of Excited State Dipole Moment of Coumarin Laser Dyes: Solvent and Substituent Effect

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In the present work an array of novel substituted 2H-chromen-2-one (coumarin derivatives abbreviated as C-337, C-480, C-540A) has been subjected to photophysical analysis. Although the influence of the electron donating groups such as amino, substituted amino, hydroxyl, alkoxy groups etc. at position 7 of the coumarin ring system has been extensively studied, However coumarin moieties with substituent at position 3 have not been explored much. Attempt is made to explain the effect of electron donating and electron accepting substituent on excited state and ground state dipole moment. The ground state (μ) and excited state (μ^*) dipole moment of C-337, C-480, C-540A coumarin are estimated from solvatochromic shift of absorption and fluorescence spectra as a function of the dielectric constant and refractive index using Bakhshiev and Kwaski-Chamma Viallet equ. μ^* and μ for all the reported coumarin are also calculated using Reichardt correlation method. The small angle is also reported between the ground and excited state dipole moment suggesting they are almost parallel to each other. Excited state dipole moment is observed larger than ground state dipole moment for all the coumarin studied indicating substantial π- electron density redistribution.

Keywords: Coumarin Laser Dyes, absorption and fluorescence spectroscopy, organic solvents, excited state, ground state, dipole moment

Session 18: Dynamics and Time Resolved Spectroscopy II

Dyn18.1 Solute-Solvent and Pigment-Protein Interactions in Carotenoids. A Combined Resonance Raman, Time-Resolved FTIR and QM/MM Study of Peridinin

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Peridinin is the main light-harvesting carotenoid found in dinoflagellates, and show peculiar photophysical properties, which are strongly dependent on the protein microenvironment. We used Resonance Raman spectroscopy and time-resolved step-scan FT-IR spectroscopy (two techniques that can give precise information on pigment-protein and solute-solvent interactions, and on the mechanism of photochemical reactions at an atomic scale [1,2]), coupled to QM/MM and DFT calculations, to investigate how Peridinin interacts with its surrounding microenvironment in Peridinin-Chlorophyll-a-Proteins (PCPs) and in several organic solvents with different physicochemical parameters (which were used as prototypical environments) [3, 4].

In particular, experiments in organic solvents showed that the stretching frequency of the lactonic C=O moiety of Per is extremely sensitive to the polarity of its surrounding environment due to three key factors: I) H-bonding dynamics between hydrogen-bond donor solvents and the lactonic C=O moiety [3];II) the effect of the dielectric constant of the solvent [3]; III) a Fermi resonance effect between the C=O and a C-H wagging mode [4]. The lactonic C=O becomes therefore a tool to distinguish among different Peridinins in PCPs (where several Peridinins are simoultaneously present). This made it possible to follow more deeply PCP photophysics, in particular the process of triplet formation. We found evidence that at low temperature the triplet is localized on Per 612 and/or Per 622 (whose C=O group is in a polar but aprotic environment [3, 5]). The results will be discussed in the framework of the study of light-harvesting and photoprotective mechanism in photosynthesis, as well as in the framework of the technological applications of Peridinin and PCPs.

Keywords: Peridinin; QM/MM; Resoance Raman; step-scan FTIR

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Dyn18.2 Thioxanthone – A Photophysical Chimera

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Experiments employing thioxanthone as a sensitizer for photolabile protecting groups revealed a chimeric behavior: Photo-excited thioxanthone (dissolved in methanol) can simultaneously emit fluorescence and act as a triplet energy donor[1]. The behavior was attributed to a rapidly established equilibrium between the bright $^1\pi\pi^*$ and the dark $^3n\pi^*$ state (see Fig. 1). This requires the two states to be isoenergetic within k_BT. High level quantum chemical computations[2] on thioxanthone in methanol show that the adiabatic energies of these two states are indeed equal within the computational error.

The fluorescence lifetime is known to be on the nanosecond time scale. For this to be feasible –considering the established equilibrium– the $^3n\pi^*$ state has to be depopulated on this time scale. Therefore, either the internal conversion (IC) rate between the upper ($^3n\pi^*$) and lower ($^3\pi\pi^*$) triplet or the equilibrium constant $K = \frac{[^3n\pi^*]}{[^1\pi\pi^*]}$ might be responsible for this surprisingly slow decay.

Seeking further insight into this unusual behavior we presently conduct extensive femtosecond absorption and fluorescence experiments. Measurements in different solvents reveal a strong influence of their polarity and proticity on the decay times. This is in line with quantum chemical computations[2], which predict a strong impact of these properties on the energetic positions. Temperature dependencies show that at least the internal conversion process is activated. The fluorescence quantum yield decreases and the $^3\pi\pi^*$ yield increases with rising temperature (see Fig. 2).

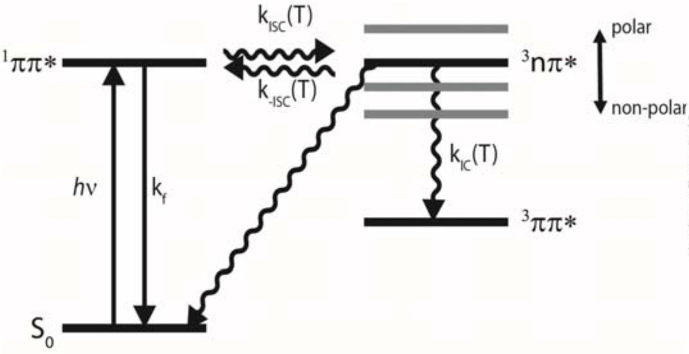

Fig. 1: Kinetic Scheme: After excitation a fast equilibrium between the $^1\pi\pi^*$ and $^3n\pi^*$ is established. Thioxanthone will radiate until the $^3n\pi^*$ is depleted.

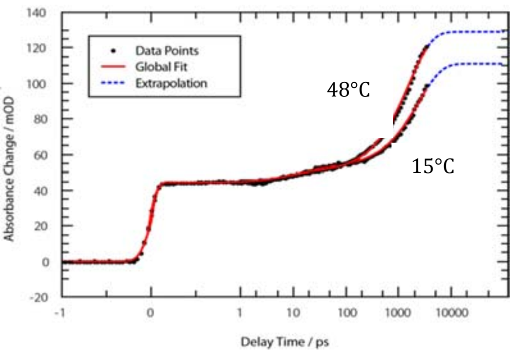

Fig. 2: Time trace at 600 nm (center of the $^3\pi\pi^*$ absorption band) for thioxanthone in methanol reveals the temperature dependency of the internal conversion and the triplet quantum

Keywords: Thioxanthone; Femtosecond; Transient Absorption; Delayed Fluorescence; ISC

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Dyn18.3 Spectroscopy of Cooperative Laser Electron-γ-Nuclear Processes in Diatomics, Multiatomic Molecules and Clusters

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In the modern molecular spectroscopy it is intensively studied a new class of problems, connected with discovery and modelling the cooperative laser-electron-γ-nuclear processes. It includes a calculation of the probabilities and energies of the mixed γ-optical transitions in molecules, intensities of the complicated γ-transitions due to the changing of the molecular excited state population due to the laser field effect. The first qualitative estimates of the cooperative effects parameters were earlier presented (see [1-3] and refs. therein). We develop an advanced quantum approach to calculation of laser-electron-γ-transition spectra (e-vibration satellites) of nucleus in diatomic and multiatomic molecules, based on density functional (DF; one version) and model potemtial (second version) methods and energy approach [3]. Decay and excitation probability are linked with imaginary part of the molecule - field system.

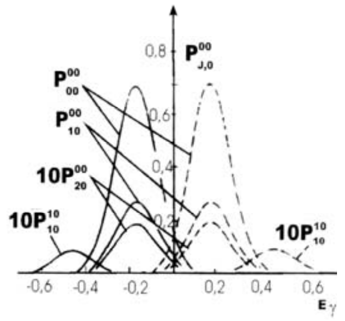

Fig.1 Emission &absorption spectrum of ^{127}I in H^{127}I (mol. init. state: ν_a=0, J_a=0)

New data on the electron-nuclear γ-transition spectra of the nucleus in some multiatomics are presented for a number of molecules: 3-atomic XY_2 ($D_{\infty h}$), 4-atomic XY_3(D_{3h}), 5-atomic XY_4(T_d), 7-atomic XY_6(O_h) ones.

As example, in fig.1 the theoretical emission (solid curve) and absorption spectrum of nucleus ^{127}I in H^{127}I is presented. In table 1 our data on probabilities of the first several vibrational-nuclear transitions in a case of the emission and absorption spectrum of ^{188}Os ($E^{(0)}_\gamma$= 155 keV) linked with molecule *OsO_4* are listed.

Table 1 . Probabilities of vibration-nuclear transitions for molecule *OsO_4* (see text)

Vibration transition	Probability
$v_3^a ,v_4^a – v_3^b, v_4^b$	$\overline{P}$ ($v_3^a ,v_4^a – v_3^b, v_4^b$)
0,0 – 0,0	0.795
1,0 – 0,0	0.018
0,1 – 0,0	0.074
1,0 – 1,0	0.750
0,1 – 0,1	0.673

Keywords: Cooperative molecular spectroscopy; Laser-electron-gamma-nuclear effects; Chemical bond effect

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Dyn18.4 Waveguide Enhanced 2D-IR Spectroscopy in the Gas-Phase

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2D-IR spectroscopy [1] follows changes in structure and/or vibrational energy transfer by monitoring ways in which the vibrational spectrum of a sample varies with time and/or pump wavelength. Time-resolved 2D-IR spectroscopy measurements on gas-phase samples were made in a square hollow IR waveguide (fig. 1A) [2] to overcome difficulties of low concentration of a gas sample (relative to more commonly studied condensed-phase samples) [3].

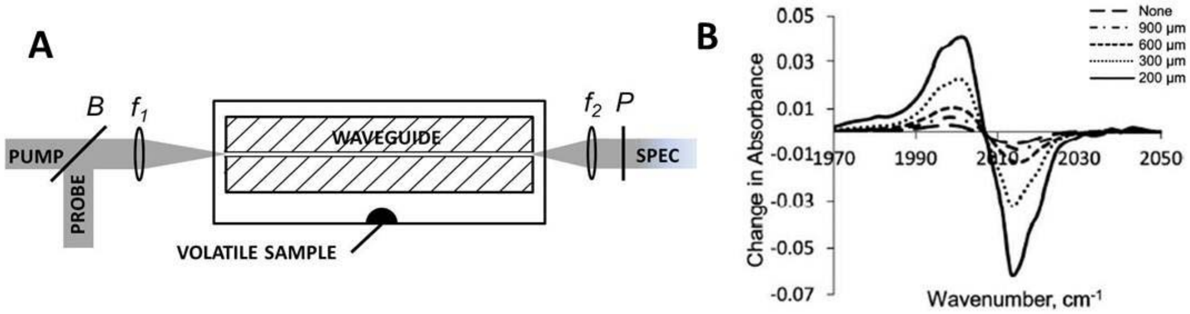

Fig.1 **A**. Experimental setup for waveguide-enhanced 2D-IR of gas-phase samples. **B**. 2D-IR signal waveguide-enhancement

Transient pump – probe spectroscopy techniques, such as 2D-IR, require focusing of the beams onto the sample to generate significant population of excited state species to probe. This requirement to use focused beams (typically 100 µm diameter) normally limits the path length of a measurement to a few millimetres in the IR. By waveguiding the beams, this path length was extended to several centimetres, enhancing signal intensity by more than an order of magnitude (fig. 1B).

This technique provides opportunities to study molecular dynamics in the gas-phase. We performed time-resolved 2D-IR measurements on the fluxional motion of iron (0) pentacarbonyl ($Fe(CO)_5$). 2D-IR spectra were taken of $Fe(CO)_5$ vapor in free space and in a range of waveguide widths, showing increasing signal intensity with decreasing waveguide width. The 2D-IR spectra of this and other metal carbonyl samples have been well studied in solution phase for comparison [4]. However, the present measurements reveal new insights into the dynamics of $Fe(CO)_5$ fluxional motion

Keywords: time-resolved infrared spectroscopy; 2D-IR; gas-phase spectroscopy; waveguide

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Dyn18.5 Dynamics of protons in hydrogen bonds studied by theoretical methods and vibrational spectroscopy

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Theoretical model is presented for the X-H(D) stretching vibrations in hydrogen-bonded systems. The model takes into account an adiabatic coupling between the high-frequency X-H(D) stretching and the low-frequency intermolecular X...Y stretching modes, linear and quadratic distortions of the potential energy for the low-frequency vibrations in the excited state of the X-H(D) stretching vibration, resonance interactions between hydrogen bonds, and Fermi resonance between the X-H(D) stretching and the overtone of the X-H(D) bending vibrations. The effects of deuteration and temperature on spectra are successfully reproduced by the model. Comparison between experimental and theoretical spectra is presented for hydrogen- bonded crystals, liquids, gaseous complexes, as well as for ices and aqueous ionic solutions.

Multidimensional proton tunneling in symmetric hydrogen-bonded systems is described by two-dimensional model potentials. The potentials have been fitted to quantum-mechanically calculated two-dimensional grid of energies, and used to analyze proton dynamics in tropolone. The model PES quantitatively reproduce experimentally observed promotion of the tunneling by the excitation of the planar modes and suppression by the excitation of the out-of-plane modes.

Session 19: New Materials III

NM19.1 Molecular Approach to a Role of NSAIDS in Changes of Volume Phase Transition Temperature in Thermo-Responsive Hydrogels

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Polymer stimuli responsive hydrogels - a new class of functional materials - react of even small modification in environmental conditions such as temperature, pH, electric or magnetic fields [1]. In a case of thermo-responsive hydrogels reversible volume phase transition (VPT) above specific temperature called lower critical solution temperature (LCST)may be observed. A temperature raising above LCST results in an imbalance between hydrophobic and hydrophilic interactions in gel consisting of amphiphilic polymer. Therefore phase separation occurs and water is pushed out. The VPT temperature (T_{VPT}) depends on many factors like presence of additional substances [2].

The main area of presented research includes investigations of an influence of sodium salts of selected non-steroidal anti-inflammatory drugs (NSAIDs) on T_{VPT} of poly(2-(2-methoxyethoxy)ethyl methacrylate) ($PMEO_2MA$) hydrogels. This polymer is commonly regarded as a good candidate for biomedical applications because of its biocompability and non-toxicity [3]. Exemplary results for ibuprofen sodium salt are presented in Figure 1. The reasons of this unique behavior will be discussed in the light of spectroscopic results. Raman spectroscopy was used to characterize the specific intermolecular interaction between water-polymer networks and selected NSAIDs.

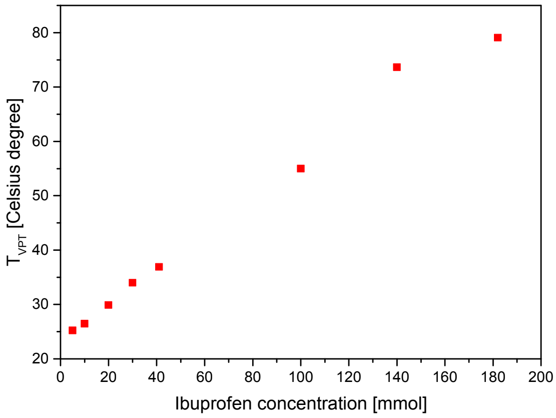

Fig. 1 The relationship between the T_{VPT} of $PMEO_2MA$ hydrogels and drug concentration.

Acknowledges
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Keywords: poly(oligo-(ethylene glycol) methacrylate); thermo-responsive hydrogels; water-polymer interactions; hydrogen bonds

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NM19.2 Comparative Study of Chelyabinsk LL5 Meteorite Fragments with Light and Mixed Light and Dark Lithology Using Mössbauer Spectroscopy

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It was a meteorite rain in Chelyabinsk region of Russian Federation on February 15, 2013. The Meteoritical expedition of the Ural Federal University immediately started the search of meteorite fragments and collected a lot of meteorite pieces. This meteorite was named Chelyabinsk and classified as ordinary chondrite LL5 group. It was observed that various meteorite fragments have different lithology. Therefore, two fragments of Chelyabinsk LL5 with light and probably mixed light and dark lithology were chosen for comparative study using Mössbauer spectroscopy with a high velocity resolution. This technique demonstrated higher precision of Mössbauer spectra measurement with at least 8 times smaller instrumental (systematic) errors for hyperfine parameters and more reliable fit of complicated spectra than those obtained using conventional spectrometers [1].

Two fragments of Chelyabinsk LL5 ordinary chondrite with light and mixed light and dark lithology were used for slices preparation for analysis by metallography and scanning electron microscopy. The powdered samples of both fragments were studied using X-ray diffraction and Mössbauer spectroscopy with a high velocity resolution at room temperature. The main iron-bearing phases identified in both fragments were olivine $(Fe, Mg)_2SiO_4$, pyroxene $(Fe, Mg, Ca)SiO_3$, troilite FeS and metal (Fe–Ni–Co alloy). Metal grains contain α-Fe(Ni, Co) and γ-Fe(Ni, Co) phases with various Ni and Co concentrations. The minor iron-bearing phase was related to chromite $FeCr_2O_4$. The Mössbauer spectra of Chelyabinsk LL5 fragments with light and mixed light and dark lithology were better fitted using different number of spectral components. These components were related to the iron-bearing phases. A comparison of these results demonstrated different relative amount of corresponding iron-bearing phases in both fragments as well as different composition of the metal grains with various relative content of α-Fe(Ni, Co) and γ-Fe(Ni, Co) phases and variations in Ni concentration. The results obtained indicated that Chelyabinsk LL5 ordinary chondrite has a breccia structure formed in the space after a number of impacts between/with asteroids resulted in formation of a composition of pieces of matter from different parent bodies.

Keywords: Mössbauer spectroscopy; Chelyabinsk LL5 ordinary chondrite; Light and mixed light and dark lithology

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NM19.3 Development of vibrational spectroscopic methods for analysis of cocrystals: What is the Information about Interactions of coformers with the active ingredient?

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Pharmaceutical cocrystals were defined as structurally homogeneous crystalline materials that are constructed from at least two neutral molecules containing an active pharmaceutical ingredient (API) and other solid components (coformers) with a well-defined stoichiometry, in which APIs and coformers are not sustained by the covalent forces but by hydrogen-bond, halogen-bond, π-π stacking, and other non-covalent interactions. Like other solid forms, cocrystals possess intellectual property issues and can be protected by legal issues that confer cocrystals with unique commercial advantages and wide development space [1]. The bioavailability and stability of the API can be improved by tuning its solubility and the melting point through the appropriate cocrystallization. Cocrystal characterization is an important constituent part within cocrystal research. The basic physicochemical properties of cocrystal can be characterized by powder X-ray diffraction (PXRD), single crystal X-ray diffraction (SXRD), infrared spectroscopy (IR), Raman spectroscopy, differential scanning calorimetry (DSC), solid state nuclear magnetic resonance spectroscopy (SSNMR), scanning electron microscopy (SEM), and terahertz spectroscopy [2].

The goal of this study is a comprehensive vibrational spectroscopic approach based on combination of Raman, mid-infrared (MIR) and in this field rarely used near-infrared (NIR) spectroscopy. Agomelatine (Fig. 1), a drug for treatment of severe depression, was selected as a model API to study its interactions with several known or potential coformers of different chemical nature, e.g. acetic acid, glycolic acid, ethylene glycol, methyl-4-hydroxybenzoate, i-sonicotinamide and urea. The band shifts, changes of band intensities and band widths were analyzed in details to distinguish between common trends and coformer-specific effects. Both the API and coformer spectral features are affected by mutual interactions. Though the interpretation of NIR spectra is more complex than in the case of MIR and Raman spectra, the NIR spectra exhibit for several cocrystals (e.g. with methyl-4-hydroxybenzoate) very narrow features which can be assigned straightforwardly to specific overtones or combination bands.

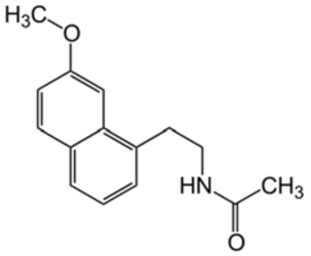

Fig.1 Structure of Agomelatine

We can conclude that not only MIR and Raman spectroscopy are powerful tools for characterization of cocrystals and description of interaction between API and coformer, but the NIR spectroscopy represents a quite fast and reliable tool for identification of cocrystals. We propose, NIR spectroscopy can be used for quality control of cocrystals production.

Keywords: Cocrystal; Raman Spectroscopy; Near-Infrared; Mid-Infrared

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NM19.4 Significance of symmetry in the formation of impurity centers in molecular crystals

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Molecular crystals are characterized by high values of the molecule packing factor. Hence, it is possible that solid solutions according to the type of substitution will be formed when two organic substances are mixed. In [1] it is demonstrated that some monosubstituted derivatives of naphthalene (alpha naphthalene fluoride and beta naphthalene fluoride) generate the impurity centers of two types when such derivatives are inserted into a naphthalene crystal. Each of the impurity centers is represented by the corresponding series of spectral bands in the crystal absorption and fluorescence spectra. It is demonstrated that the method for determining the number of impurity centers of different types, proposed in [1], can be used in the case of semisubstituted naphthalene derivatives in naphthalene, specifically in the case of a 1,5 naphthalene dichloride molecule. This molecule is formed as a result of the substitution of two hydrogen atoms at positions 1 and 5 of a naphthalene molecule by chlorine atoms. Due to the symmetry of atom groups in a free molecule (D_{2n}) and a crystal (C^5_{2h}), the hydrogen atoms at positions 1 and 5 are not affected or are transferred to other equivalent positions.

In a case of a free molecule:

$$\left.\begin{array}{l} E(H_1H_5),\ i(H_1H_5),\ C^7_2(H_1H_5)\ \text{и}\ \sigma_{xy}(H_1H_5) \longrightarrow H_1H_5,\ \mathbf{k} = 4 \\ \\ C^x_2(H_1H_5),\ C^y_2(H_1H_5),\ \sigma_{xz}(H_1H_5)\ \text{и}\ \sigma_{yz}(H_1H_5) \longrightarrow H_1H_5,\ \mathbf{k} = 4 \end{array}\right\} \quad \mathbf{n} = 2,\ \mathbf{N} = \mathbf{k} \cdot \mathbf{n}$$

For molecules in the crystal:

$$E(H_1H_5),\ i(H_1H_5),\ C^7_2(H_1H_5)\ \text{и}\ \sigma_{xy}(H_1H_5) \longrightarrow H_1H_5,\ \mathbf{k} = 4,\ \mathbf{n} = 1,\ \mathbf{N}' = \mathbf{k}' \cdot \mathbf{n}'$$

where **n** is the number of the equivalent positions of a hydrogen atom in a naphthalene molecule, **k** is the repetition factor for each position, and **N** is the order of symmetry.

As is evident, the substitutions of the hydrogen atoms at positions 1, 5 and 4, 8 by chlorine atoms are equivalent in a free molecule and nonequivalent in a crystal. In this case, the number (m) of impurity centers of different types is determined as follows:

$$m = \frac{n}{n'} = \frac{N}{N'} \cdot \frac{k'}{k}$$

The results obtained are in agreement with the experimental data.

Additionally, the analysis was performed for determining the intensity of fluorescence and phosphorescence for the previously detected impurity centers of fluoroderivatives in crystalline naphthalene [1]. It is determined that the drastic decrease of intensity of radiation, determined for two impurity centers, begins at temperatures of 25 K and 50 K, correspondingly, in the case of singlet exiton radiation and at temperatures 5 K and 7 K, correspondingly, in the case of triplet exiton radiation.

The results obtained are discussed with consideration for transfer of excitation centers to the impurity centers and for the thermoactivation processes providing transfer of excitation centers to the zone of singlet and triplet exitons.

Keywords: impurity centres; molecular crystals; 1,5 naphthalene dichloride

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Postersession I

Po1.1 RAMAN AND INFRARED SPECTROSCOPIC STUDY OF CARBONATE MINERALS FROM DJEBEL KELLAL, CONSTANTINE, NORTH-EAST OF ALGERIA

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Orientale Algeria, particularly Djebel Kellal in Constantine region; is characterized by a superposition of several thrust sheets, we can observe the development of several caves and a variety of sedimentary rocks such as limestone and others...

Limestone, the principal raw material for cement manufacture forms one of the most important mineral deposits of Algeria and provides a solid base for the industrial prosperity of the country.

Calcite is the most abundant form and widely distributed in the Earth's crust followed by calcite and dolomite with some impurities. The aim of this paper is to characterize limestone rocks by Raman and FTIR spectroscopy techniques, and compare the results obtained by the two techniques.

The X-ray diffraction (XRD), Optical Microscopy, Environmental Scanning Electron Optical and electron microscopy (MEB, EDS) is required for morphological characterization of the existing phases. These techniques provide one of the most useful methods in the characterization of materials that are used in construction's field [1].

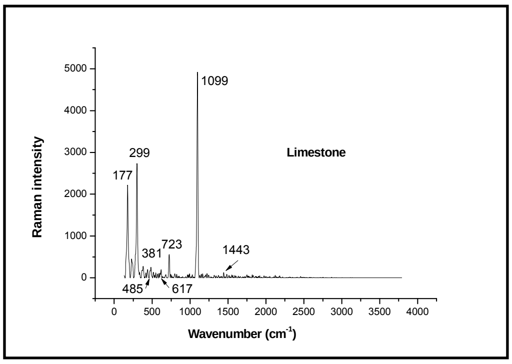

Fig.1 Raman spectra of limestone samples

The FTIR, spectral data of limestone samples have been compared, they shows that calcium carbonate in limestone, principally in the form of calcite, as identified by its main absorption bands [2], [3]. Raman spectroscopy, like FTIR spectroscopy, can be used for the identification of constituent materials of limestone as far as they provide information about characteristic vibrational levels. Multiple bands are observed for the antisymmetric stretching and bending region for these minerals.

Nevertheless, not all transitions between vibrational molecular levels are allowed. Some transitions can appear only in the infrared spectrum, some only in the Raman one and some in both of them at coincidental frequencies (1099/1098 cm^{-1}) [4], [5].

The results of this study, obtained by various analytical techniques give good informations on the existing phases. This work is a part of systematic studies of vibrational spectra of limestone in particular and carbonates in general and their synthetic analogs.

Keywords: Infrared; Raman spectroscopy, Limestone

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Po1.2 INFRARED AND RAMAN SPECTROSCOPY IN EXAMINATION OF SPRAY PAINTS ON PLASTER

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Mural painting is a well-known type of art. Graffiti or other daubs made by the use of spray paints destroy elevation of many buildings and are often a subject of forensic examination [1,2]. The layer of paint, which creates an inscription, smudge or a drawing, is thin and difficult to be separated from the base. Model examinations have been carried out aiming at the evaluation of the usefulness of spectroscopic methods (FTIR, Raman) in the identification of spray paints. It was checked if the different types of base influenced the spectrum of paint and also if there were differences between spectra of the applied paint from shaken and not shaken sprays.

Seven red spray paints, available on the Polish market were placed on the surface of glass plate and on a mineral plaster. Two groups of samples were prepared. In the first one the paint was applied from well shaken and in the second one from not shaken cans.

The infrared spectra were recorded using Digilab FTS 40Pro spectrometer combined with UMA 500 microscope in transmission mode. On the basis of the obtained IR spectra it was possible to identify the main polymers and fillers of paint samples. Raman spectra were measured by the use of an InVia Raman Microscope (Renishaw, UK) using three excitation lasers: 514, 633 and 785 nm. Spectra were recorded in the 200-2000 cm^{-1} region with an acquisition time of 10 s and 3 accumulations. Each paint sample was measured three times. Identification of pigments was based on the peaks wavelengths using a spectral reference database.

It was observed that within each group, IR spectra of the same paint placed on glass and plaster substrate showed no differences. However, significant changes were observed between IR spectra of shaken and not shaken sprays. The presence of additional peaks and differences in the intensity of bands indicated changes in chemical composition of samples. In addition, spectra of paint from not shaken sprays showed inhomogenity in concentration of pigments and other inorganic additives. The influence of the used substrates was observed for several samples in Raman technique. Additional, intensive broad band was present in spectra of paints applied on glass and a few additional peaks in spectra of paints applied on plaster. Worth mentioning is fact that there were no meaningful differences between Raman spectra of the same paint acquired for sprays from the first and the second group.

It was found that spray paints collected both from the glass plates and the plasters can be effectively differentiated in most cases by means IR and Raman spectroscopy based on the presence of specific minor and major compounds.

Keywords: FTIR microspectrometry, Raman microspectrometry, paint, forensic analysis

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Po1.3 SPECTROMETRIC ANALYSIS OF COLOUR TONERS

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Comparison of colour and establishing of chemical composition are the main problems in analysis of the forensic traces. One of the examined traces are printing materials on questioned documents. Nowadays the powder toners are very often used for printing. So, it is essential to find out methods, which provide useful information about the analyzed objects. To differentiate among colour toners (magenta, yellow, cyan and black) originated from different devices spectroscopic methods are applied. IR spectrometry allows to identify polymer binder, while Raman spectroscopy is useful in pigments or dyes identification. Spectroscopy in the visible range (MSP-Vis) enables colour parameter calculation and colour comparison [1, 2].

Four types of colour toners originated from colour printings (Ryc. 1) of 10 devices (HP 1025, 1312, 276, Konica Minolta 350,353, 650, Ricoh 105, 245 Oki C831, Olivetti d-Color MF920) were analysed using three micro spectrometric methods i.e. Raman, FTIR and MSP-Vis. The transmittance IR spectra were obtained using FTS 40Pro (Digilab, USA) coupled with a UMA 500 microscope (Digilab, USA). Toners particles were picked up from paper by a scalpel and deposited on KBr window. The reflectance Raman spectra were obtained using Renishaw inVia spectrometer (GB) equipped with a confocal Leica (Germany) microscope and three types of excitation source: Ar ion (514.5 nm), He-Ne (628.5 nm) and a near infrared (785 nm) semiconductor lasers. The reflectance spectra in the visible region (MSP-Vis) were recorded using J&M TIDAS spectrometer (Germany) combined with a C. Zeiss Axioplan 2 (Germany) microscope. For Raman and MSP measurements fragments of printed paper were put directly on the microscope stage.

Two types of binder were present in the set of the analysed samples, i.e. styrene-acrylate or polyester - bisphenol A copolymers. In each group IR spectra of different colour toners were similar but not identical. Pigment identification only on the basis of IR spectra was not possible. Looking at peaks position it was possible to divide MSP spectra of magenta toners into two groups and yellow toners into three groups. Spectra of cyan toners belonged to one group. MSP spectra of black toners were deprived of bands. The most information about pigments was obtained from Raman spectra measured at 785 nm excitation line. All samples of cyan toners contained the same type of blue pigment and these samples could not have been differentiated neither by Raman, nor by MSP. Nearly all samples of black toners contained only carbon black pigment and also could not have been differentiated. In cyan toners phtalocyanine blue pigment was identified. In identification of magenta and yellow pigments standards or spectra library was needed.

It was found that in toners examination of different devices the useful information was obtained, while examining magenta and yellow toners. The best results in comparison and differentiation were obtained applying all three of the discussed methods.

Keywords: toner, FTIR microspectrometry, Raman microspectrometry, MSP-Vis

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Po1.4 COMPREHENSIVE COMPARATIVE STUDY OF HEAVY METAL, TRACE AND MACRO ELEMENT LEVELS IN SKIN AND MUSCLE OF TWO COMMERCIAL SPECIES OF FISH HARVESTED OFF OF THE PERSIAN GULF USING ICP-OES TECHNIQUE

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This study was performed to determine the differences between two commercial species of fish harvested off the Bushehr shores of the Persian Gulf in terms of toxic metals, nutrients and trace elements. Samples were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES). The results showed that Ca, Li, Mg, P, Se, Sn, Sr and Zn concentrations were significantly different between the skin and muscle tissues of Indo-Pacific king mackerel but with the exception of P, there was no significant difference between element levels in the skin and muscle tissues of tiger tooth croaker. The Indo-Pacific king mackerel contained significantly higher levels of As, Sn, Se and P in the muscle tissue and Zn in the skin tissue compared to the muscle and skin tissues of tiger tooth croaker. The estimated daily intake of the toxic elements including As, Cd, Sb, Pb and Sn via consumption of these fish were below the established guidelines.

Keywords: Indo-Pacific king mackerel; Tiger tooth croaker; Heavy metals; Trace elements; Persian Gulf.

Po1.5 CORRELATION OF DUAL FLUORESCENCE PARAMETERS WITH REVERSIBILITY OF ESIPT REACTION

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At present, fluorescent probes based on molecules with dual fluorescence have been widely used [1,2]. A valuable property of that systems is the mutual change of the intensity of fluorescence bands depending on intermolecular interactions; the selfcalibration procedure of the response reaction to the properties of the environment is based on this property, which is widely used, e.g., in studies of various physicochemical objects with molecular probes that utilize the proton internal transfer reaction in the excited state (ESIPT). ESIPT reactions in organic fluorophores are among the fastest basic reactions known so far and their rates can be observed even on femtosecond time scale. Understanding of such reaction mechanism is crucial for correct description fluorescence response while probing different samples. Meantime in condensed media the intermolecular interactions and their dynamics result in frequently observed two separate bands in the steady-state emission spectra. There are two possibilities for their simultaneous observation: when the ESIPT reaction is slow on the time scale of emission or when the reverse reaction repopulating the reactant state is fast and leads to the excited-state equilibrium.

ESIPT reaction may occur in agreement with two mechanisms classified as kinetic or thermodynamic [3]. Kinetic type or slow irreversible reaction is the case when forward ESIPT is essentially faster in comparison with backward reaction. Due to the appreciable barrier the reaction occurs on a similar time scale of emission, so that the emission from initially excited state N* can be observed. In the case of fast reversible or thermodynamic reaction the origin of observation of emission from N* state is the fast rates of both forward and reverse reactions so that the distribution of intensity between two bands corresponds to the distribution of excited-state species at equilibrium. Discrimination of two abovementioned types of reactions is usually carried out on the basis of time resolved studies of fluorescence kinetics of the both bands of emission. We have derived here the analytical expression for dependence of the ratio of both bands intensities on the energy gap between excited singlet states of the normal and tautomer forms for ESIPT probe in the case of thermodynamic reaction. The expression obtained enables to discriminate type of reaction using simple spectroscopic measurements and reversibility of ESIPT can be identified in this case. Experimental data obtained for some derivatives of 3-hydroxyflavones and some other families appearing in thermodynamic ESIPT reaction were verified and very good correlations between reversibility of these reactions and the environment-dependent effects observed in fluorescence spectra have been observed.

Keywords: du lfluorescence; ESIPT; reversibility

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Po1.6 RAMAN FREQUENCY SHIFTS CALCULATED FROM THE VOLUME DATA IN NAPHTHALENE

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The Raman frequencies for modes of symmetry Ag and Bg are calculated as functions of temperatures (at atmospheric pressure) and pressure (at room temperature) using the observed volume data from the literature through the mode Grüneisen parameters in naphthalene. By determining the temperature and pressure dependence of the isobaric (γ_P) and isothermal (γ_T) mode Grüneisen parameters, respectively, the Raman frequencies of the modes which were calculated, are in good agreement with the observed frequencies considered in naphthalene. Our results show that the Raman frequencies for the modes studied, can be predicted from the volume data by means of the mode Grüneisen parameters. This also leads to predicting the temperature dependence of the thermal expansion (α_P) and the pressure dependence of the isothermal compressibility (κ_T) from the frequency shifts, , and , respectively, which can be measured accurately in naphthalene.

Keywords: Raman frequencies; Volume; Mode Grüneisen parameter; Naphthalene

Po1.7 SINGLE MOLECULE FLUORESCENCE STUDY OF THE CONFORMATIONAL STRUCTURE OF HIV RNA

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HIV-1 genomic RNA has a non-coding 5' region containing sequential conserved structural motifs that controls many parts of the lifecycle. Very limited data exist on their 3-dimensional conformation and then how they work structurally. Recently the novel 3-D structural information of this most highly conserved region of the virus was reported on a promising therapeutic target [1]. In order to learn more on the structure of this RNA, we use single molecule fluorescence, anisotropy imaging microscopy and RNAstructure modelling [2,3] together to monitor its conformational dynamics in physiological condition. We aim to understand with implications for RNA dimerization and protein binding during regulatory steps.

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Po1.8 RAMAN STUDY OF THE NECK REGION IN UNIAXIALLY DRAWN SINGLE-CRYSTAL MATS OF ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE

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Polyethylene (PE) is one of the most important industrial polymers due to its excellent characteristics and reasonable cost. With regard to the strength, the chemical, temperature and wear resistance, the friction coefficient and physiological inertness, ultrahigh molecular weight PE (UHMW PE) possesses even better properties as compared to ordinary PE grades. As a matter of fact, UHMW PE has been successfully applied in the production of prostheses, light-weight and high-strength fibers and some other products. However, UHMW PE application is limited by its low processability, which is due to the high viscosity of UHMW PE melt. Detailed investigations of UHMW PE deformation mechanism could be very useful for overcoming this limitation and expanding the field of application of UHMW PE.

Raman spectroscopy is one of the most suitable methods to study structural changes, which occur in polymers during deformation. This technique is non-destructive and highly informative about both the crystalline and amorphous states of molecules. Raman investigations do not require any sample preparation, which could affect the sample structure, and a spatial resolution of a few microns can be achieved on solid samples.

Uniaxial deformation of PE leads to the reorganization of its complex multi-level and multiphase structure, with the most significant alterations taking place in the so-called neck region. A number of investigations of PE neck region have been reported. However, there are practically no related Raman spectroscopic studies.

In this work, we present a Raman spectroscopic study of the deformation process of solution-crystallized single-crystal mats of UHMW PE. We study the neck regions of the films, drawn till the formation of the neck, on the one hand, and the films deformed to higher draw ratios till rupture, on the other hand. For the sake of comparison, we have also carried out Raman investigations of UHMW PE films produced by pressing of the industrial powder.

We have found that the uniaxial molecular orientation in the neck region of the single-crystal mat films develops slowly as compared to the films, prepared by pressing of the industrial powder. This finding could be explained by different structures of the amorphous phases in the samples: in the films, produced by pressing of the industrial powder, a large number of chain entanglements prevent the unfolding of chains during the uniaxial drawing and restrict the draw ratio. On the contrary, the amount of chain entanglements in single-crystal mats is relatively small, and hence the unfolding of chains of lamellar crystallites can easy occur during uniaxial deformation. The chain unfolding process presumably dominates over the process of improving the uniaxial orientation of macromolecules, which occurs in both crystalline and amorphous phases with participation of the tie molecules.

This work is supported by the RFBR (14-02-00832-a) and the Grant of the President of the Russian Federation for the Support of Leading Scientific Schools (451.2014.2).

Keywords: Raman spectroscopy, ultrahigh molecular weight linear polyethylene, single-crystal mats

Po1.9 CONFORMATIONAL AND SPECTROSCOPIC IDENTIFICATION OF 3-AMINOPHENYLBORONIC ACID MONOHYDRATE BY EXPERIMENTAL TECHNIQUES AND DENSITY FUNCTIONAL APPLICATIONS

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Boronic acids are known to bind diols through reversible boronate esters formation [1]. The 3-aminophenylboronic acid (APBA) is capable of reversibly binding with 1,2- or 1,3-diols; thus, boronic acid-functionalized nanoparticles may give access to valuable nanosupports for the optical detection, the transport or the separation of carbohydrates [2]. Moreover, it is as a receptor in favor for sugar recognition, and also can be employed for cell capture. However, literature survey shows that the complete structural and spectroscopic features of APBA have not been defined yet. In this study, the characterization of 3-aminophenylboronic acid monohydrate was evaluated using experimental techniques and density functional applications. The ground state conformation was optimized and compared with available recorded data. The vibrational and electronic transitions were determined by FT-IR, FT-Raman and UV spectroscopy and DFT or TD-DFT quantum chemical methods. The proton and carbon NMR spectra were measured in DMSO$_{\text{-d6}}$ solution in addition with the DEPT 135 NMR spectrum to determine the hydrogen bonded and non-bonded carbon atoms. All calculations were done for monomeric and dimeric forms and compared with the computed results.

Keywords: 3-aminophenylboronic acid monohydrate, DFT, Molecular spectroscopy

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Po1.10 Mn-AMINO ACID–CaAl-LDH NANOCOMPOSITES – SYNTHESES, STRUCTURAL CHARACTERISATION BY XRD, SCANNING ELECTRON MICROSCOPY, IR AND X-RAY ABSORPTION SPECTROSCOPIES

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Mn(II)-histidine, cysteine or cystine complexes were constructed in the interlayer space of CaAl-layered double hydroxide (LDH) with the final aim of building enzyme-mimicking complexes immobilised *via* intercalating in the LDH by ion exchange or on the outer surface of the delaminated LDH by adsorption. The composite materials may be efficient catalysts in redox reactions, and the constrained environment of the intercalated complex may also be beneficial in terms of increasing selectivity.

During the preparation of the composites, the amino acids, in anionic forms were introduced among the layers by ion exchange first; then, the composite was soaked in various solvents (aqueous isopropanol,acetone or DMF). In some experiments the layers were delaminated and the complex was allowed to interact with the separated layers. Then, restacking was attempted, thus forming a hierarchiral interlayer composite.

The synthesised substances were studied by mid and far IR spectroscopy, scanning electron microscopy and energy-dispersive X-ray analysis, X-ray diffractometry in order to gain as much structural information as it is possible.

It has been found that the composites, the delaminated-restacked materials as well, were of layered structure, and the complexes situated mostly among the layers.

Even though the above-listed methods are all valuable as far as structural characterisation is concerned, further structural information, regarding the quality of coordinating atoms, coordination numbers, and bond length values are only hoped from XANES/EXAFS measurements. They were performed in Max-Lab at beamline I811 at the Mn edge.

Together with measurements by the complementing methods, detailed information was obtained about the intercalation either with the ion-exchange or the delaminating-restacking method. The coordination environment of the central ion was determined as concerns both the quality of the coordinating atoms, the coordination numbers as well as bond distances.

Acknowledgements: This research was financed by the OTKA NK106234 and the OTKA 83889 grants. M.S. thanks for the support by the TÁMOP 4.2.4. A/2-11-1-2012-0001 'National Excellence Program'. All these financial supports are highly appreciated.

Keywords: CaAl-layered double hydroxides, characterisation by XRD, IR, SEM-EDX; characterisation by XANES/EDAX

Po1.11 ULTRASOUND-ASSISTED ADSORPTION/INTERCALATION OF PHENOL/PHENOLATE ON/IN CAFE-LAYERED DOUBLE HYDROXIDE

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Even though numerous wet chemical methods can be identified in the literature for the preparation of layered double hydroxides (LDHs), ultrasonically-assisted ones are rare [1, 2]. Working in the area of the synthesis and modification of these materials, especially in constructing hierarchically structured substances, it is our aim to expand the already available toolkit with the use of the cavitation phenomenon (ultrasonic waves), in order to increase the rate and efficiency of synthesis of Ca(II)Fe(III)-LDH and the intercalation of phenolate ions among its layers.

The pristine and the intercalated LDHs were prepared *via* combining ball milling and sonication. First, the starting materials were homogenised and mechanically activated in the mill; then, the sample was immersed into an ultrasonic bath, and sonication was carried out at 60 °C. Optimum parameters of the treatments were identified. Both the pristine and the modified LDHs were characterised by X-ray diffractometry (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), energy dispersive X-ray fluorescence (EDX) and infrared (IR) spectroscopies. The adsorbed and intercalated phenolate ions were quantified by UV-spectrophotometry.

The major characterisation method was XRD allowing the rapid checking of the results of varying the parameters in the sonochemical synthesis. It was found that the layered structure was formed indeed, even if the parameters were altered in a wide range. Thermogravimetric and infrared measurements also verified the formation of the LDH structure just like SEM–EDX measurements. In SEM images, the laminated and hexagonal crystal forms of the LDHs were clearly observable, even for phenolate ion intercalated samples. UV-spectroscopy measurements allowed the quantitative estimate of adsorbed and/or intercalated phenolate ions.

In conclusion, a novel method, the combination of ball milling and ultrasonic treatment, was developed for the fast synthesis of Ca(II)Fe(III)-LDHs, providing an efficient and comfortable tool for preparation of hierarchically-ordered nanostructures. Furthermore, sonochemically-assisted adsorption and intercalation in LDH proved to be a simple method to remove phenol in form of phenolate from drinking water.

Acknowledgements: This research was financed by the OTKA NK106234 and the OTKA 83889 grants. The financial help is highly appreciated.

Keywords: CaFe-layered double hydroxides, mechanochemistry, sonochemistry, characterisation, phenol/phenolate adsorption/intercalation

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Po1.12 DEPOSITED, LIQUID OVERLAYED Ag NANOPARTICLE AGGREGATES AS SUBSTRATES FOR SERS, SERRS AND SURFACE-ENHANCED LUMINESCENCE

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Localization of molecules into hot spots in the course of SERS and/or SERRS spectral measurements leads to large enhancements of Raman scattering by the electromagnetic mechanism, however, in some cases, e.g. [1], it also causes the adsorbed molecule decomposition. In this contribution, we demonstrate one of the possibilities how to overcome this drawback by preparation and spectral testing of deposited, adsorbate containing compact aggregates of chloride-modified Ag nanoparticles (NPs) overlayed by a thin layer of aqueous phase. The parent Ag NPs (of ~30 nm average size) hydrosols were prepared by reduction of $AgNO_3$ by $NH_2OH{\cdot}HCl$ [2]. For SERS, SERRS as well as for combined time-dependent SERRS/surface-enhanced fluorescence (SEF) measurements, the NPs in hydrosol were modified by addition of chlorides and the testing adsorbate. Resulting compact aggregates were transfered onto a glass slide with ca 10 μL of the residual liquid, immobilized by gravitational sedimentation, and their spectral measurements were performed by micro-Raman setup. SERS and SERRS spectral limits of detection at λ_{exc} = 532 nm of 2,2´-bipyridine (bpy) and free base 5,10,15,20-tetrakis(1-methyl-4-pyridyl)porphine (H_2TMPyP) testing adsorbates from a single deposited, liquid overlayed aggregate were found to be by one order of magnitude lower than those obtained from the corresponding hydrosol systems. Furthermore, fluorophores mutually differing by their fluorescence quantum yields (namely ZnTMPyP and CuTMPyP) were incorporated into the aggregates, and the time-evolution of their SERRS and SEF signals was followed in 1s interval and mutually correlated. Finally, deposited aggregates of chloride-modified Ag NPs overlayed by a thin layer of a luminophore, namely $[Ru(bpy)_3]Cl_2$, aqueous solution were found to be suitable substrates for luminescence lifetime imaging studies.

Keywords: bpy;H_2TMPyP; CuTMPyP; ZnTMPyP; $[Ru(bpy)_3]Cl_2$; SERS; SERRS; SEF; aggregate; Ag NPs;

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Po1.13 THE STUDY OF NAPHTHOQUINONES AND ITS COMPLEXES WITH DNA BY RAMAN SPECTROSCOPY AND SERS.

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Naphthoquinones represent the group of plant secondary metabolites with cytotoxic properties based on their ability to generate reactive oxygen species and interfere with the processes of cell respiration. There are many targets of cytotoxic action on the cellular level; however, DNA is a critical target of many cytotoxic compounds, such as medicinally used antineoplatics. . In our work, the Raman spectroscopy was used to determine the possible binding sites of the naphthoquinones on the DNA and to characterize the bond of naphthoquinone to DNA. Experimental data reveals the relationships between the perturbations of structure-sensitive Raman bands and the types of the naphthoquinones invole78dved. DNA interactions with some substances were studied and the results of our work were compared with the published data, e.g. [1-2]

All the studied DNA modifications by the selected naphthoquinones induced changes in the spectral part corresponding to the vibration of the sugar-phosphate backbone, in the areas of vibration of the bases, and also in the areas of vibration of each naphthoquinone. The modification of DNA by the studied naphthoquinones leads to the non-specific interaction, which causes the distortion of DNA from B-conformation of DNA to A-conformation except of plumbagin. It is also evident from the SERS spectra that the interaction between DNA and complexes takes places at the bases and not at the sugar-phosphate backbone. In the case of modification of the bases, the adenine and thymine was modified in all DNA changed by naphthoquinones. For each DNA modified by all studied complexes the intensity of the band near 1277 cm^{-1} increased, which is affected by the vibration of adenine and guanine. It is obvious from these results that all naphthoquinones are bound to DNA except of plumbagin. In the case of plumbagin, there were only some denaturation effects after the modification of DNA due to the methyl group in the naphthalene skeleton. The analysis of the difference spectra leads to the clear conclusions that bases have been modified, and these changes have pre-denaturation and denaturation character.

Keywords: naphthoquinones, cytotoxicity, DNA, DNA interactions, Raman spectroscopy

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Po1.14 TOWARDS A ROTATION-VIBRATION LINE LIST FOR METHYL CHLORIDE

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Accurate *ab initio* electronic structure calculations teamed with variational nuclear motion computations are playing an increasingly important role in high-resolution rotation-vibration spectroscopy. The process of generating comprehensive line lists detailing millions of transitions for small polyatomic molecules is nowadays fairly straightforward, and it can greatly assist spectral analysis in both terrestrial and astrophysical applications.

Here we present work on the calculation of a rotation-vibration line list for methyl chloride. A new nine-dimensional potential energy surface and dipole moment surface have been generated using the highest level of modern *ab initio* theory. The potential energy surface incorporates a range of higher-level additive energy corrections to account for scalar relativistic effects, core-valence electron correlation, higher-order coupled cluster methods, and the Born-Oppenheimer approximation.

Variational calculations of the rotation-vibration energy levels and corresponding transition intensities of CH_3Cl have utilized the computer program TROVE [1], whose functionality has been extended to handle molecules of the form XY_3Z. To approach experimental accuracy in ro-vibrational calculations, the potential energy surface must be empirically refined to existing experimental spectroscopic data. This combination of first principles quantum mechanical methods and empirical tuning can produce highly accurate and extensive line lists applicable for elevated temperatures.

Methyl chloride is the main source of natural chlorine in the Earth's atmosphere and plays a significant role in ozone depletion. It is a candidate biosignature in the search for life outside our solar system. A detailed rotation-vibration line list would no doubt assist the interpretation of high-resolution spectra of future terrestrial and astronomical studies.

This work is part of the ExoMol project [2], which is actively providing key spectroscopic data on all molecular transitions necessary for the study and modeling of exoplanet atmospheres.

Keywords: Rotation-vibration spectroscopy; Ab initio methods; Atmospheres

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Po1.15 HYDROTHERMAL SYNTHESES, CRYSTAL STRUCTURE AND SPECTRAL STUDIES OF $[Cd(\mu–pydc)(\mu–dpetan)0.5(H_2O)_2]_n$

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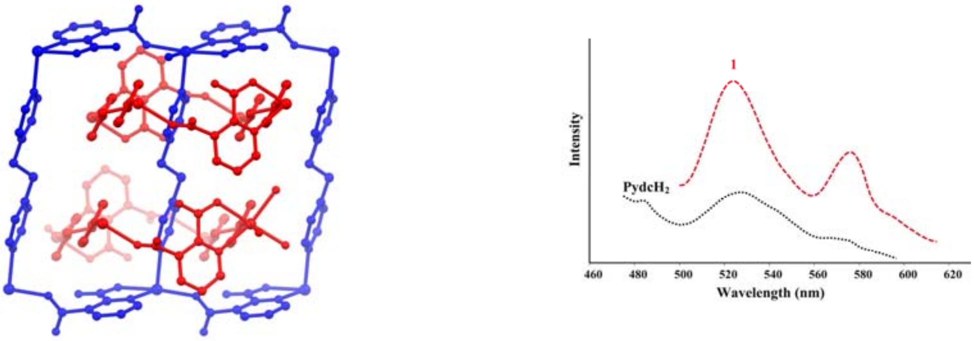
The synthesis and characterization of coordination polymers with various intriguing topologies have been of great current research interest, not only because of their intriguing variety of architectures but also because of their potential applications [1]. A novel coordination polymer, $[Cd(\mu–pydc)(\mu–dpetan)_{0.5}(H_2O)_2]_n$ (**1**) (pydc = Pyridine-2,3-dicarboxylate, dpetan = 1,2-bis(pyridyl)ethane) has been synthesized and characterized by elemental analysis, IR photoluminescence spectroscopy and thermal analysis.

Compound **1** was synthesized under mild hydrothermal conditions (130 °C and 72 hours). The IR spectrum of complexes show characteristic bands for antisymmetric-symmetric stretching of the dicarboxylate groups range of 1664, 1564 cm^{-1} and 1384 cm^{-1} respectively. The Cd(II) ions are μ-bridged by pydc ligands to generate 1D $[Cd(\mu\text{-}pydc)]_n$ coordination polymer. At the same time, the Cd(II) ions are connected by dpetan ligands, which bridge two 1D $[Cd(\mu\text{-}pydc)]_n$ chains generating 1-D ladder structure with rectangular, cavities dimensions of 8.213 x 14.042 Å (defined by Cd···Cd distances). Each square of the ladder interlocks neighbor square of the ladder to form 1D→2D inclined interpenetration of **1** (Fig 1(a))**.** The 1D ladder structures in **1** are connected each other by O-H···O hydrogen bonds between aqua ligands and carboxylate oxygen atoms to forming 2D hydrogen bonded (3,4)-connected supramolecular network 3,4L83 topology with the point symbol of $\{4^2{\cdot}6^3.8\}\{4^2.6\}$. The TG/DTA curves of complexes show that the dehydrated complex is stable up to 367 °C. Complexes **1** exhibits blue fluorescent emission bands at 402 nm and a shoulder at 487 nm upon excitation at ca. 350 nm (Fig 1(b)).



(a) (b)

Fig. 1. 1D→2D inclined interpenetrated structure of (a) 1 and (b) Emission spectra of pydc (blue), 3 (red) in recorded in the solid-state at room temperature

Keywords: Coordination polymers, Interpenetration, Pyridine-2,3-dicarboxylate.

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Po1.16 LOW pH INDUCED LacDNA STRUCTURAL CHANGES AS PROBED WITH UV RESONANCE RAMAN SPECTROSCOPY

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In this work we report an UV resonance Raman spectroscopic study on double-stranded and single-stranded DNA oligomers. Investigation of structural changes induced in a natural DNA recognition site, in the presence and absence of divalent metal ions (Mn^{2+}, Ca^{2+}) at two pH values (6.4 and 3.45), respectively, providing data about changes in the protonation state of AT and GC base pairs, are of interest [1]. The targeted DNA is a non-palindromic 22-mer duplex representing the primary cyclic AMP receptor protein (CRP) binding site of the *E. coli lac* promoter, d(TAATGTGAGTTAGCTCACTCAT)· d(ATGAGTGAGCTAACTCACATTA) (LacDNA) ([2] and references therein). Also, its corresponding single-stranded oligonucleotides, d(TAATGTGAGTTAGCTCACTCAT) and d(ATGAGTGAGCTAACTCACATTA) were investigated.

Large changes in the UV (275 nm) resonance Raman spectrum of LacDNA duplex were observed at pH 3.45, in the absence of divalent metal ions, as compared with the corresponding spectrum at pH 6.4. *Main changes are: adenine protonation, GC base pair protonation, DNA bases unstacking and changes in the hydrogen bonding strength between the strands of LacDNA complexes, respectively.* Divalent metal ions (Mn^{2+} and Ca^{2+}) were found to inhibit LacDNA protonation even at low concentrations. Manganese(II) ions are much more effective in this regard, as compared with calcium(II) ions. In this last case, only a small influence of the divalent metal ions on binding of proton to LacDNA has been found. Binding of Mn^{2+} ions to N7 of guanine and, possibly, in a lesser extent to adenine was observed as judging from the difference Raman bands at 1315, 1354 and 1493 cm^{-1}. Low affinity of calcium(II) ions for binding to LacDNA molecules, at a reduced pH value, has been found by us.

Further studies on DNA model systems with modified counterion distributions would provide information for a better understanding of the equilibria between protonated and non-protonated DNA base pairs. The possible significance of base pair protonation in cellular processes, will be clarified by such studies ([3] and references therein).

Keywords: LacDNA structure; LacDNA protonation; divalent metal ions; UV resonance Raman spectroscopy

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Po1.17 SPECTROSCOPIC, STRUCTURAL AND NONLINEAR OPTICAL INVESTIGATIONS ON 1-[(E)-{[4-(MORPHOLIN-4-YL)PHENYL]IMINO} METHYL]NAPHTHALEN-2-OL: A THEORETICAL STUDY

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Morpholine is an important heterocyclic compound that has a wide range of industrial applications such as rubber additives, corrosion inhibitors, solvents, optical brighteners, antioxidants and also in the manufacture of a number of drugs and herbicides. This heterocyclic compound exhibits diverse pharmacological and physiological activities such as antidiabetic, antiemetic, platelet aggregation inhibitors, antihyperlipoproteinemics, bronchodilators, growth stimulants and antidepressants. Due to these diverse applications, a number of papers have devoted morpholine derivates. Recently, Ranjith et al. have reported the crystal structure, FT-IR, UV-vis and FT-NMR spectra for 1-[(E)-{[4-(morpholin-4-yl)phenyl]imino} methyl]naphthalen-2-ol molecule. However, to the best of our knowledge, there is no theoretical study devoted to the title molecule. So as to eliminate this deficiency, theoretical geometry optimization and investigations of structural, spectroscopic, electric and electronic properties of MPIMN were performed by using Density Functional Theory calculations. All calculations were performed by Gaussian 09 package program. DFT calculations show that MPIMN exhibits significant nonlinear optical properties. Theoretical vibrational spectra were simulated, and obtained vibration modes were assigned by the application of potential energy distribution (PED) analysis. Intramolecular hyperconjugative interaction energies for MPIMN are evidence of the intramolecular charge transfer causing stabilization of MPIMN. Additionally, there is a good agreement between the theoretical and experimental results.

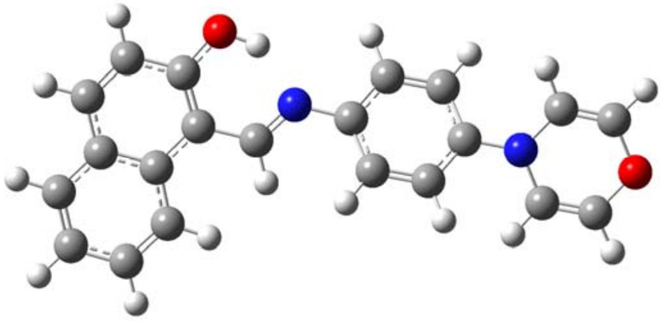

Fig. 1. Optimized structure of MPIMN obtained at B3LYP level

Keywords: 1-[(E)-{[4-(morpholin-4-yl)phenyl]imino} methyl]naphthalen-2-ol, IR, NMR, UV-vis, NLO

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Po1.18 THEORETICAL INVESTIGATIONS ON SPECTROSCOPIC AND ELECTRIC PROPERTIES OF 1-(2′-THIOPHEN)-3-(2,3,5-TRICHLOROPHENYL)-2-PROPEN-1-ONE (TTNP)

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Thiophene is a class of chemically stable compounds, and thiophene-based compounds have gathered great importance due to the potential applications in modern drug design, biodiagnostics, electronic and optoelectronic devices, and conductive and electroluminescent polymer. Recently, 1-(2′-thiophen)-3-(2,3,5-trichlorophenyl)-2-propen-1-one compound was synthesized by Manjunath et al., and its structure was investigated by FT-IR, FT-NMR and UV-vis spectroscopies [1]. However, to the best of our knowledge, there is no theoretical study concerning the structural, spectroscopic and nonlinear optical properties of TTNP. So, density functional theory calculations were performed to investigate optimized geometry, IR, NMR and UV-vis spectra, NLO properties and HOMO-LUMO energies TTNP. All calculations were performed by Gaussian 09 package program. Detailed assignments of vibrational modes were made by the application of potential energy distribution (PED) analysis. Obtained structural parameters show that DFT results can replace experimental ones. Small HOMO-LUMO energy gap implies that charge transfer occurs in title compound. It is well known that molecular charge transfer increases polarizability and hyperpolarizability properties [2,3]. So, TTNP display significant NLO properties.

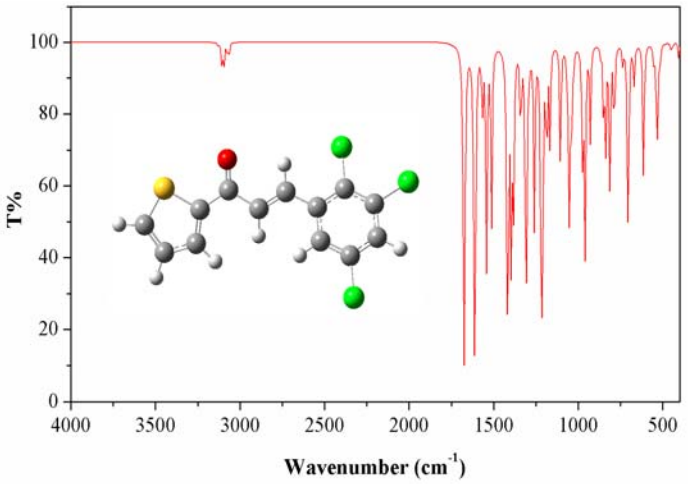

Fig.1. Optimized geometry and theoretical IR spectrum of TTNP

Keywords: 1-(2′-thiophen)-3-(2,3,5-trichlorophenyl)-2-propen-1-one, IR, NMR, UV-vis, NLO

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PO1.19 QUANTITATIVE STRUCTURAL CHARACTERIZATION OF POLYETHYLENE MATERIALS BY RAMAN SPECTRA IN THE REGION 2700-3200 CM^{-1}

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Polyethylene (PE) is the most widely used polymer among plastics. A great amount of new PE-based materials, including nanocomposites, copolymers, and blends, are increasingly being developed. To produce polymer material with pre-specified functional performance, the knowledge about many structural characteristics is needed. In particular, the mechanical properties of any polymer depend strongly on its molecular weight, the proportion of amorphous and crystalline phases, the amount of *trans*-conformers, *etc.*

Raman spectra in the region 1000-1600 cm^{-1} can allow a quantitative characterization of PE structure in terms of the phase composition and the amount of *trans*-conformers. Yet, the main limitation to PE and PE-based material diagnostics is the rather low intensity of Raman bands in the region 1000-1600 cm^{-1}. This can hinder the study of samples containing fluorescent impurities (filler or dye molecules). The highest intensity of Raman-active PE bands belongs to the spectral region 2700-3200 cm^{-1}. However, this region was previously not explored for quantitative characterization of the polymer structure.

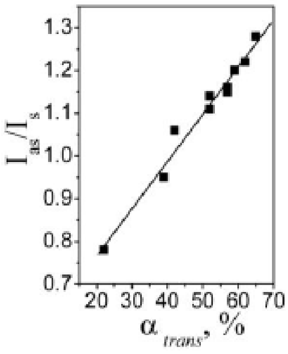

Fig.1 I_{as}/I_s *vs.* α_{trans}

In our contribution, we present the temperature-dependent Raman study of PE grades with various densities and PE/clay nanocomposites produced from these PE grades. We discuss the relationship between structural changes in PEs and PE/clay nanocomposites upon heating. To this end, we follow the evolution of the Raman spectra in the region 1000 – 3200 cm^{-1}. We have found that the intensity ratio (I_{as}/I_S) of the bands assigned to the asymmetric (at approx. 2883 cm^{-1}) and the symmetric (at approx. 2850 cm^{-1}) stretching vibrations of CH_2 groups depends on PE density and the amount of *trans*-conformers. If the content of *trans*-conformers exceeds 20%, the ratio I_{as}/I_s is proportional to the amount of *trans*-conformers. As an example, Fig. 1 shows the ratio I_{as}/I_s *versus* the content of *trans*-conformers (α_{trans}) for PE with a density of 0.935 g/cm^3 (squares symbols are experimental data for the ratio I_{as}/I_s and the straight line is the linear fit). Therefore, the ratio I_{as}/I_s can be used for the quantitative determination of the *trans*-conformer content above 20 % in PE and PE/clay composites.

This work is supported by the Russian Foundation for Basic Research (project codes 12-02-00238-a) and the Grant of the President of the Russian Federation for the Support of Leading Scientific Schools (project code 451.2014.2).

Keywords: Raman spectroscopy; temperature-dependent spectra; polyethylene; polyethylene-clay nanocomposites

Po1.20 FACILE SPECTROPHOTOMETRIC DETERMINATION OF SUNSET YELLOW DYE BY COMPLEXATION WITH COPPER (II) IONS IN COMMERCIAL FOOD PRODUCTS

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A facile, highly sensitive and selective spectrophotometric method has been developed for the determination of Sunset Yellow (SY) as a food colorant dye.

The method is based on the formation of binary complex of copper (II) ions with Sunset Yellow (SY). The results indicated formation of 1:1 metal dye species at pH = 9.5 exhibiting maximum absorbance at 350 nm with molar absorptivity 0.6×10^4 l mol^{-1} cm^{-1}. Under optimized experimental conditions, Beer's law is obeyed in the concentration range 9.047 – 99.52 μg/ml. The limits of detection (LOD) and the limits of quantification (LOQ) were found to be 4×10^{-4} and 0.01221 μg/ml; respectively. The proposed method was successfully applied for the determination of Sunset Yellow (SY) dye in commercial food products with some advantages: it reduce the number of analysis steps, it is a green method with less chemical waste. The concentration levels of dye in commercial samples were within the safe recommended limits[1,2].

Keywords: Food Colorant Dye; Sunset Yellow; Copper (II) Ions; Complexation; Spectrophotometric Analysis.

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Po1.21 VIBRATIONAL SPECTROSCOPIC INVESTIGATION OF SPINEL CHROMITES

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Transition metal oxides with spinel structure belong to the intensively studied compounds in solid-state sciences due to interesting physical and chemical properties, which make them attractive in many technological applications such as magneto-electric materials [1], super hard materials [2], high-temperature ceramics [3]. catalytic materials [4],humidity sensors [5] etc..

In general, the ACr_2O_4 phases crystallize in the normal spinel structure with the cubic $Fd\bar{3}m$ space group and the atoms of ACr_2O_4 occupy 8a (tetrahedral), 16d (octahedral) and 32e (oxygen) Wyckoff sites, respectively. These sites contribute to $F_{2g} + F_{1u}$, $A_{2u} + E_u + F_{2u} + 2F_{1u}$ and $A_{1g} + E_g + 2F_{2g} + F_{1g} + A_{2u} + E_u + F_{2u} + 2F_{1u}$ modes of the theoretical vibrational representation. From these modes, the A_{1g}, F_{2g} (triply degenerate) and E_g (doubly degenerate) are active in Raman spectra while the four F_{1u} (triply degenerate) are IR active and one remaining F_{1u} (acoustic mode) can not be observed in infrared spectra. The rest of modes are Raman inactive (F_{1g}) and infrared inactive ($2A_{2u}$, $2E_u$, and $2F_{2u}$). In our work, we focused on detailed study of nanocrystalline transition metal chromites by vibrational spectroscopies. The samples of ACr_2O_4 (A = Zn, Cu, Cd, Co, Mn and Fe) were obtained either as bare nanoparticles or nanocomposites constituted of nanoparticles embedded in amorphous silica matrix ACr_2O_4/SiO_2.

The lowering of the cubic O_h symmetry to the tetragonal D_{4h} symmetry ($I4_1/amd$ space group), which occurs due to Jahn-Teller effect below room temperature, is connected with splitting of the triply degenerate modes F_{1u} (to A_{2u} and E_u) and F_{2g} (to B_{2g} and E_g), and of doubly degenerate mode E_g (to A_{1g} and B_{1g}). However, the both symmetries were observed for nanocrystalline $NiCr_2O_4$ depending on the preparation method [6].

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Keywords: Metal chromites; vibrational spectroscopy; powder X-ray diffraction

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Po1.22 EFFECT OF THE POTENTIAL ELECTRODE ON SURFACE-ENHANCED RAMAN INTENSITIES OF 2-METHYLPYRAZINE

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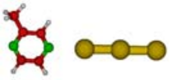
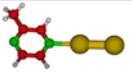
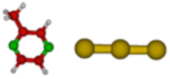
The effect of the electrode potential on Surface Enhanced Raman Scattering (SERS) intensities of 2-methylpyrazine (2MP) recorded under resonant charge transfer (CT) conditions is analyzed by using a simple theoretical model [1] in which the macroscopic surface charge in the metal is modeled by several metallic clusters with different number of silver atoms (n) and charges (q), $[Ag_n]^q$. Two and three linear silver atoms with zero and positive and negative charges, respectively, bounded to the 2MP through the nitrogen atom, have been taking into account.

In this way, a new microscopic parameter called the effective atomic surface charge (q_{eff}) is introduced being defined as the ratio between the charge and the number of silver atoms ($q_{eff}=q/n$). This parameter is directly related to the macroscopic charge excess in the electrochemical experiences. The selected charge excess range (q_{eff} = ±0.33) covers the usual experimental potential electrode range of 0-1.5 V [2]. Due to the non equivalent aromatic nitrogen atoms in 2MP, two different complexes have been considered, $[Ag_n\text{-}N1]^q$ and $[Ag_n\text{-}N4]^q$. Time-dependent density functional theory (TDDFT) with the M06HF/LanL2DZ level of calculation has been used in order to identify the CT states of the $[Ag_n\text{-}2MP]^q$ systems. After that, the SERS-CT spectra of these superficial complexes have been calculated by the independent mode displaced harmonic oscillator (IMDHO) method.

Table 1: Theoretical results for the $[Ag_n\text{-}N4]^q$ complex

	Model	**DFT Calculations (M06HF/LanL2DZ)**				**Experimental**		
q_{eff}	**$[Ag_n\text{-}N4]^q$**	**CT_0 /eV Energy**	**Δq**	**Intensity**		**Potential Electrode**	**Intensity**	
				8a	**8b**		**8a**	**8b**
-0.33		1.142	0.84	100	26	**-0.75V**	100	31
0.00		2.933	0.69	100	49	**-0.50V**	100	51
+0.33		5.324	0.51	100	12	**-0.25V**	100	20

The theoretical results (Table 1) reproduce satisfactorily the main experimental behavior, that is, the strong enhancement of the totally symmetric 8a ring-stretching mode, being the most enhanced band at any electrode potential. On the contrary, the weaker band corresponding to the other ring-stretching 8b mode reaches the maximum intensity at -0.50V and decreases at more negative or positive potentials.

Keywords: SERS spectroscopy; 2-Methylpyrazine; Charge transfer mechanism.

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Po1.23 A CRITICAL STUDY OF SPECTROPHOTOMETRIC METHODS FOR CHARACTERISATION OF POLYPHENOLIC COMPOUNDS

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Phenolic compounds are very big group of substances that have a biological effect on the humans´ health and they are irreplaceable in the modern medicine. They are important in prevention and in the treatment of civilization diseases. All these aspects have increased interest in the pharmaceutical research on the isolation, identification and determination.

Valuable information about the content of polyphenols in plant extract can be obtained by using the spectrophotometric methods. It is due to its simplicity, sensitivity and efficiency in time and economic aspects. The aim of our study was to provide a comparison of two selected spectral methods and to determine the reactivity of selected interfering substances, together with the interpretation of their influence. The most important criteria for selecting a Folin-Ciocalteu and Price-Butler methods for comparative analysis was their low interference with other compounds, possibility of a routine analysis of a large number of samples, the accuracy and sensitivity.

For both spectrophotometric assays was determinate the calibration curve of gallic acid, which is commonly used as the standard method by Folin-Ciocalteu and Price-Butler. Then measurements were performed at the same set of control samples with the addition of each individual interferents (Al^{3+}, Fe^{3+}, Fe^{2+}, cysteine, glucose). Selected spectrophotometric methods were applied for determination of total polyphenols in plant extract of oak bark. Results were analyzed by using the statistical methods.

PBM is not a sufficiently sensitive colorimetric assay for the higher concentration of phenolic compounds, especially for the problematic formation of precipitates, and the instability of a colored complex. Folin- Ciocalteau method is a good indicator of the content of polyphenols in the context of lower concentrations, and the effect of interfering substances in relation to the values of absorbance is insignificant.

The result of this study is to determine that the studied methods are not in practice sufficiently sensitive ind icator procedures without respecting the precise extraction techniques and measurement conditions. Their possible potential benefit is in the case of semiquantitative characterization of the sample in parallel using multiple techniques.

Keywords: spectrophotometric methods; polyphenols; Folin- Ciocalteau method, Price-Butler method

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PO1.24 MATHEMATICAL ANALYSIS OF ASYMMETRICAL SPECTRAL LINES

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The form of spectral lines and such line parameters as position of the maximum, intensity, width, and statistical moments, constitute a major body of data on physicochemical properties of substances under study. Since the effect of line asymmetry often impedes spectrum interpretation, various theoretical and empirical expressions of asymmetrical profiles have been suggested to overcome the difficulties. Each expression is usually appropriate for a particular class of spectra, while a general approach to the mathematical analysis of asymmetrical line profiles is lacking until now. Such approach allows establishing the main patterns of physicochemical processes by searching common properties of the models used to describe the spectral lines.

This study reports mathematical analysis of non-integral theoretical and phenomenological asymmetrical lines [1-6] performed by decomposing them into a product of their symmetrical and asymmetrical parts. To compare the spectral profiles under the same conditions, their x-coordinates were put on a normalized dimensionless scale. The decomposition errors were found to be negligible in the case of small asymmetry coefficients. The new concept of the integral angular function (IAF) of the asymmetrical part was introduced [7]. The dependences of the maximum peak positions and intensities, widths and truncated moments of the lines, and their symmetrical parts on the asymmetry parameter were obtained. The following new measures of asymmetry were proposed and studied: the ratio of the absolute values of the minimum and maximum amplitude of the first-order derivative of the line profile and the ratio of the satellite amplitudes of the second-order derivative of the line profile. A procedure of scaling to unique asymmetry was developed for comparing asymmetrical model lines. The scaled difference between the components of the IAFs to the left and to the right from the peak maximum was shown to be the most sensitive indicator of line asymmetry. The advantages and drawbacks of the proposed asymmetry measures are discussed.

Theoretical relationships between the line parameters and the asymmetry of the line wings [8] were considered in the framework of the approach to mathematical analysis of asymmetry lines proposed in the work.

A practical numerical method of decomposing asymmetrical lines into a product of their symmetrical and asymmetrical parts was developed. The results obtained may also be employed in asymmetrical line modeling performed for decomposing complex spectral profiles into elementary components.

Keywords: spectroscopy; asymmetrical lines; line profile parameters; normalization; approximation

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Po1.25 VIBRATIONAL STUDY OF THE INTERACTION OF 2,4 DICHLOROPHENOXY ACETIC ACID IN ACETONE SOLUTION

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We have studied from theoretical and experimental points of view the interaction of a powerful environmental herbicide agent [1], the 2,4 dichlorophenoxy acetic acid (2,4-D) compound in gas phase [2] and acetone solution. The characterization of the compound in acetone solution was carrying out by means of infrared and Raman spectroscopies. The structural and vibrational properties of the three conformers more stable of 2,4-D were predicted in both media by using the density functional theory (DFT) together with the 6-31G* and 6-311++G** basis sets while the solvent effect were studied at the same levels of theory by using the self consistent reaction field (SCRF) method with the polarized continuum model (PCM). The calculated geometrical parameters [3], the atomic charges, bond orders, main delocalization energies, the molecular electrostatic potentials, molar volume, solvation energies and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gaps for all the forms of 2,4-D were compared and analyzed among them. The results show that the C2 conformer is the most stable structure in acetone solution with a higher dipole moment value while in this medium the C3 conformer present the higher solvation energy value, as expected due to their higher volume variation. For C2 and C3, the HOMO-LUMO values by using both basis sets predicted a lower reactivity in acetone solution than in gas phase.

The harmonic vibrational wavenumbers for the more stable structures in acetone were calculated at the same theory levels and, then, the complete assignments of all the observed bands in the vibrational spectra were performed combining the DFT calculations with the Pulay´s scaled quantum mechanical force field (SQMFF) methodology in order to fit the theoretical wavenumber values to the experimental ones.

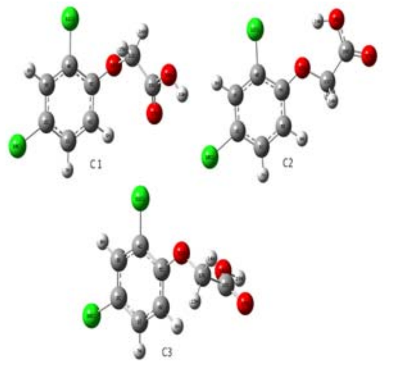

Fig.1 Theoretical structures of 2,4-D

Keywords: vibrational spectra, molecular structure, force field

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Po1.26 FERROUS ORBITAL T_{2g} SPLITTING DETERMINATION IN ILMENITE BY MÖSSBAUER SPECTROSCOPY

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Ilmenite is the naturally occurring form and the most stable polymorph of $FeTiO_3$ at ambient temperatures and pressures. The ilmenite structure is based on a hexagonal close packed oxygen lattice with metal atoms occupying two thirds of the available octahedral sites to form honeycomb-like layers of edge shared oxygen octahedra. The Fe and Ti ions form alternating bilayers perpendicular to the **c** axis, with –Fe–Ti–□–Ti–Fe– ordering (□: vacancy) along the threefold axes, reducing the symmetry to R3 [1].

Mössbauer spectra (MS) of an ilmenite were collected by the authors at temperatures between 4.2 K and 900 K. Below the magnetic ordering temperature of about 57 K [1], the MS were numerically analysed by a model-independent hyperfine field distributed component (B_{hf}) [2] of which the subcomponents were calculated from the diagonalization of the full nuclear interaction Hamiltonian [3]. The paramagnetic MS were numerically analysed by a model-independent quadrupole splitting distributed component (ΔE_Q). The adjusted parameter values (with highest probability in the distributions) are indicated in Table 1.

Accounting for the trigonally elongated Fe-site in ilmenite and the high-spin state of the Fe^{2+}, the lower T_{2g} level of the ferrous ^5D orbital level scheme is splitted in a higher singlet and a lower doublet. The latter is confirmed by the positive sign of the principal component of the electric field gradient (V_{zz}). However, the experimental value of the asymmetry parameter (η) does not match the assumption of trigonal symmetry, in which case η is indeed expected to be zero. V_{zz}, η and the Boltzmann occupation of the ^5D orbital levels determine the value of ΔE_Q. Therefore and taking the symmetry of the Fe-site into account, the splitting of the T_{2g} levels could be determined from the temperature (T) variation of ΔE_Q. The best description of the experimental $\Delta E_Q(T)$ curve was obtained in the assumption of a small rhombic distortion of the local trigonal symmetry [4] causing a small splitting of the lower lying doublet, yielding splittings for the T_{2g} triplet of (80±10) cm^{-1} and (500±50) cm^{-1} with respect to the lowest orbital level. This rhombic distortion also explains the value of η as derived from the 4.2 K MS, at least qualitatively.

Table 1: Relevant Mössbauer parameters with highest probability in the B_{hf}- and ΔE_Q-distributions at selected temperatures for ilmenite (δ: center shift; Γ: full width at half maximum; other symbols: see text)

T (K)	δ (mm/s)	ΔE_Q (mm/s)	V_{zz}	η	B_{hf} (T)	Γ (mm/s)
4.2	1.22	1.44	>0	0.37	45.6	0.31
80	1.19	1.00				0.26
295	1.07	0.65				0.26
900	0.62	0.24				0.26

Keywords: ilmenite, Mössbauer, magnetic splitting, quadrupole splitting, crystal field

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P01.27 THE INFLUENCE OF THE LONG-RANGE ORDER ON THE VIBRATIONAL SPECTRA OF ZEOLITES BASED ON SODALITE CAGE

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Zeolites are a group of tecto-aluminosilicates with numerous practical applications, e.g. gas separators, molecular sieves, sorbents. The unique properties result from nano-porous structure of chambers and channels which are built from smaller units - the so-called *Secondary Building Units (SBU)*, and sometimes even larger groups [1],[2],[3]. Among other, frameworks of naturally occurring sodalite and synthetic zeolite Y (FAU) and zeolite A (LTA) are built from sodalite cage (*β cage*). The last two, are characterized by one of the best sorption properties [4].

The aim of this study was the examination of the influence of long-range structure order on vibrational spectra of sodalite cage model units and comparison of the obtained results with the experimental spectra of chosen zeolites based on sodalite cage.

An *ab initio* calculations (geometry optimizations and vibrational spectra calculations) of sodalite cage were carried out by means of *Gaussian09* [5] (in the case of isolated molecules, *i.e.* hydrogen terminated sodalite cage), *Castep* [6] and *Crystal09* [7],[8] (for periodic structure) programs. The obtained results were compared with the experimental spectra of sodalite, zeolite Y and zeolite A crystal structures, synthesized under hydrothermal conditions with phase compositions confirmed by X-ray diffraction study. These results allowed analyzing of the long-range ordering influence on the vibrational spectra, as well as the identification of the characteristic vibrations in *β cage* based zeolites framework.

Keywords: zeolite; β cage; ab initio calculation, vibrational spectra

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Po1.28 EXPERIMENTAL AND THEOREITACL STUDIES OF CHOSEN S AND D BLOCK CATIONS INFLUENCE ON VIBRATIONAL SPECTRA OF ZEOLITE A

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Synthetic zeolite A (LTA) is one of the best sorbents and ion-exchange material used, among other, for the heavy metal immobilization. Accessible area per unit volume of this zeolite is about 1700 m^2cm^{-3}, maximum sorption capacity is 5.48 $meqg^{-1}$ and maximum diameter of a sphere that can be included is about 11 Å [1],[2]. As all zeolites, LTA is built from smaller units – the so-called *Secondary Building Units (SBU)*, and sometimes even larger groups, in that case: single eight ring (S8R), single six ring (S6R), double four ring (D4R), *α cage*, and the exchangeable cations may occupy various locations [1],[3],[4],[5].

The aim of this study was to investigate the influence of selected *s* and *d* block cations on the vibrational spectra of chosen *SBU* units, α cage and comparison of the obtained results with experimental spectra of different cationic form of zeolite A.

Zeolite A was synthesized in accordance with the procedure laid down in [6] with phase compositions confirmed by X-ray diffraction study. Sorption was carried out on sodium form of LTA using aqua solutions of selected nitrates. Experimental vibrational spectra of resulting samples were compared with calculated ones. *Ab initio* calculations (geometry optimizations and vibrational spectra calculations) of chosen *SBU* units with selected cations and *α cage,* were carried out by means of *Gausssian09* [7] (in the case of isolated molecules), *Castep* [8] and *Crystal09* [9],[10] (for periodic structure) programs and the changes of vibrational spectra of the zeolite A due to the sorption of particular cations were analyzed in detail.

Keywords: zeolite A; sorption; ab initio calculations, vibrational spectra

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Po1.29 THE USE OF SEMIEMPIRICAL CALCULATIONS FOR INTERPRETATION OF THE COMPLEX UV/VIS SPECTRA OF PROTONATED IMATINIB

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Imatinib (*N*-(4-methyl-3-{[4-(pyridin-3-yl)pyrimidin-2-yl]amino}phenyl)-4-[(4-methylpiperazin-1-yl)methyl]benzamide) (brand name Gleevec®) is a tyrosine kinase inhibitor used for treating chronic myelogenous leukemia (CML) and gastrointestinal stromal tumors (GISTs) [1]. Several nitrogen atoms in imatinib can undergo protonation as a function of pH and the main protonation route has been reported previously [2].

In the present study [3] we observed that the UV/Vis absorption spectra of imatinib exhibited different pattern depending on the pH of the solution. The absorption relationship between first two absorption maxima changed systematically and the growth of new absorption band occurred in the longer wavelength region with the decrease of solution pH.

These changes in the UV/Vis absorption spectra were interpreted using quantum chemical calculations. The geometries of various imatinib cations in the gas phase and in ethanol solution were optimized with the DFT/B3LYP method on the basis of experimentally determined crystal structure of imatinib (Fig. 1) and treated with the semi-empirical ZINDO/S-CI method to calculate the absorption lines and electronic transitions.

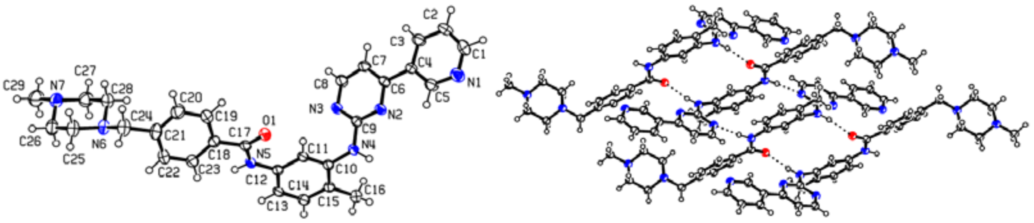

Fig. 1 The molecular and crystal structure of imatinib free base

Calculations suggested that the formation of the extra near-UV absorption band resulted from an increase of imatinib trication concentration in the solution, while the increase of the first absorption maximum at pH values below 2 could be attributed to both the tricationic and tetracationic forms of imatinib. The nonlinear change of the main absorption maximum relationship indicated an undistinguishable contribution from the various protonated states. This was confirmed by theoretical calculations that showed electronic transitions in the particular wavelength region for all the studied species.

Thus the present study demonstrates the theoretical calculations as an indispensable tool for the interpretation of the complex electronic spectra of multicationic API.

Keywords: Imatinib; UV/Vis spectrocsopy; ZINDO/S

Acknowledgments

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Po1.30 LOW TEMPERATURE PHASE TRANSITION IN $[Ca(H_2O)_4]Cl_2$ STUDIED BY INFRARED AND RAMAN SPECTROSCOPY AND NEUTRON SCATTERING

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Hexaaquacalcium chloride $[Ca(H_2O)_6]Cl_2$ is an interesting material at least from two points of view. Firstly, it is interesting because of the occurrence of different reorientational motions of the complex cations and H_2O ligands. Secondly, such compounds are extensively investigated because of its potential application as a Phase Changing Materials (PCM) [1,2]. The polymorphism of the mentioned above compound was investigated by us by means of differential scanning calorimetry (DSC). One phase transition at: T_c^h = 218 K (onset on heating) and T_c^c = 208 K (onset on cooling) was determined for $[Ca(H_2O)_6]Cl_2$ in the temperature range of 90–300 K. The thermal hysteresis of the phase transition temperature T_c equal to ca. 10 K and the heat flow anomaly sharpness suggest that the detected phase transition is a first-order one. The relatively high entropy change ($\Delta S \approx 8.5$ J·mol^{-1}·K^{-1}) connected with observed phase transition indicates high degree of dynamical disorder. At room temperature $[Ca(H_2O)_6]Cl_2$ has a hexagonal structure (space group No. 150, P321) with one molecule in the unit cell. The lattice constants are as following: $a = b = 7.8759$ Å, $c = 3.9545$ Å [3].

We have performed infrared (FT-MIR and FT-FIR), Raman (RS) and neutron scattering (IINS/QENS) measurements in order to establish relationship between the observed phase transition and reorientational motions of the H_2O ligands. Fourier transform middle and far infrared spectra were measured in the temperature range of 8–295 K. FT-MIR, FT-FIR and FT-RS measurements showed that bands associated with H_2O vibrations modes narrow continuously with temperature decreasing. This suggests that the observed phase transition (PT) is connected with a change in the speed of the H_2O reorientational motions. Moreover, apart from of the narrowing, the splitting of some bands can be seen below the phase transition. This suggests that during the phase transition crystal structure change take place. The neutron scattering (IINS, QENS) studies performed with NERA time of flight spectrometer (Dubna in Russia) in the temperature range of 10–295 K did not give the evidence of fast (correlation time $\tau < 10^{-11}$ s) stochastic reorientational motions of H_2O (180° flips) ligands in high and low temperature phases. The QENS peaks, registered at 250 and 200 K, does not show any broadening. The proton-weighted phonon density functions G(ν) obtained at temperatures 10, 200, 250 K show some separate peaks characteristic for ordered phase. We performed quantum chemical calculations of normal modes using periodic boundary conditions (CASTEP code [4]). We have obtained good agreement between calculated and experimental data (IR, RS and IINS spectra).

Keywords: Molecular reorientations; Raman scattering (RS); Fourier transform middle and far infrared spectroscopy (FT-MIR and FT-FIR); Inelastic and quasielastic incoherent neutron scattering (IINS and QENS)

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Po1.31 CORRECTION OF FREQUENCY SCALE OF RAMAN SPECTRA USING ABSOLUTE FREQUENCY STANDARDS

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Correct interpretation of Raman spectra requires elimination of spectral artifacts, e.g. removal of non-Raman background, subtraction of solvent contribution and optionally intensity normalization [1]. Before any such data pre-treatment, a proper frequency calibration of Raman spectra is necessary [2], especially if multivariate statistical methods are used for spectral analysis [1]. Time drifts of wavenumber scale may be responsible for dominant variability within a set of Raman spectra making thus their statistical treatment impossible or unreliable. The instability of Raman wavenumber scale becomes an increasing concern particularly for the repeated experiments conducted over a long period of time (days to weeks) or long-lasting Raman imaging experiments. Rather than trying to assure the highest possible absolute frequency accuracy (typically no better than 1-2 cm^{-1} [2], depending on the experimental design of a Raman spectrometer and the procedure for the frequency calibration), it is more desirable to ensure exact match (i.e. reproducibility) of Raman frequency scales between consecutive measurements.

Here we present practical procedure of the frequency scale correction that is fully automatic and requires only specification of a reference spectrum containing the same set of reference bands or lines as the spectra from dataset, relative to which the frequency scales of individual spectra from dataset will be adjusted. Explicitly, the optimal wavenumber shift between a given Raman spectrum and the reference spectrum is found using an iterative algorithm that is looking for the exact match in the positions of one or more selected spectral lines common for the reference spectrum and the spectra in dataset. As reference lines can serve Raman bands of internal frequency standards or emission lines of appropriate external standards, e.g. calibration lamps. Usability of the method will be demonstrated on the extensive Raman datasets acquired simultaneously with the spectrum of a neon glow lamp. Except for a few neon lines falling into the carefully selected spectral regions, neon emission was efficiently suppressed by a combination of short-pass, long-pass or band-pass filters assuring that the lines of calibration spectrum absolutely do not interfere with Raman bands in the regions of highest interest, typically parts of fingerprint or hydrogen-stretching regions. Excellent reliability of the correction method and improvement of the multivariate analysis results will be demonstrated on several examples including some model systems and datasets originating from Raman imaging of biological samples.

Keywords: Raman spectroscopy; Frequency scale calibration; Neon glow lamp; External standard

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This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (projects CZ.1.05/2.1.00/01.0030 and CZ.1.07/2.3.00/30.0041) and the Czech Science Foundation (P208/10/0941).

Po1.32 SOLVENT EFFECT ON THE ABSORPTION, ECD AND MCD SPECTRA OF THE AMINO ACIDS

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Electronic transitions in the ultraviolet and visible spectral region reveal precious information about molecular geometry and interactions. However, the modeling providing the necessary link between spectral shapes and the structure is often difficult.

To understand how conformational equilibria and solute-solvent interaction influence spectra, we collected absorption (UV-vis), electronic circular dichroism (ECD), and magnetic circular dichroism (MCD) spectra of phenylalanine, tyrosine and tryptophan in aqueous solutions. Energies and intensities of spectral bands were modeled by the time-dependent density functional theory (TD-DFT). The solvent was approximated by a continuum as well as clusters with explicit solvent molecules obtained from molecular dynamics.

The ECD signal was found to depend on molecular conformation the most, whereas UV-vis and MCD spectra were dependent less. All spectral intensities, however, were significantly influenced by the solvent approximation; for ECD and MCD the usual polarizable continuum solvent model did not provide satisfactory spectral shapes. On the other hand, averaging of the clusters obtained from molecular dynamics provided an unprecedented agreement with experiment.

Thus, it has been shown that interactions with explicit water molecules are necessary for proper modeling of the electronic spectra.

Keywords: DFT calculations, MCD, ECD, amino acids, solvent effect

Po1.33 VIBRATIONAL CIRCULAR DICHROISM OF CARBOXYL SIDE CHAINS IN POLY-L-GLUTAMIC FIBRILS

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Amyloid fibrils and similar protein aggregates are intensively studied because of their role in neurodegenerative diseases (Alzheimer, Parkinson, etc.),[1] and the general need to understand peptide folding and molecular interactions.[2]

Vibrational spectroscopy provides useful information about the structure of these systems. The theoretical calculations can be conveniently used to interpret IR or VCD spectra and to provide a link between geometry and spectral properties.[3,4]

In this work we concentrate on fibrils consisting of poly-L-glutamic acid (PLGA) strands and the carboxyl residues which provide unusually high VCD signal. We show that how reflects partial ordering of side chains in the fibrils using the means of molecular dynamic combined with quantum chemical calculations.

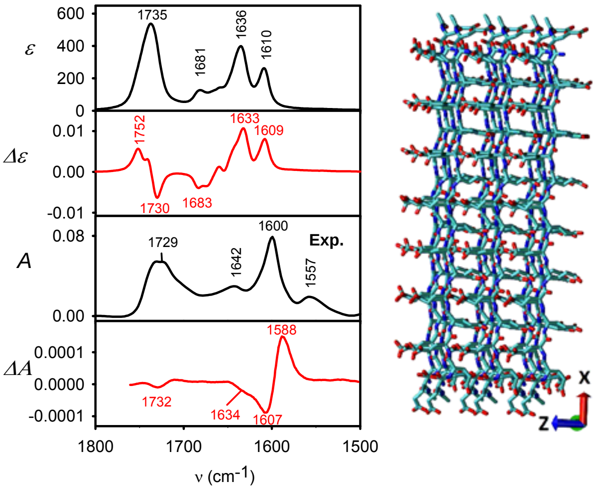

Fig.1: Theoretical model and its calculated (top) and experimental (bottom) IR and VCD spectra

Keywords: Vibrational Optical Activity; Fibrils; Molecular Dynamic

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Po1.34 TWO-DIMENSIONAL ZINC (II)-AZOXYBENZENETETRACARBOXYLATE COMPLEXES with 1,2-BIS(IMIDAZOLE-1YL-METHYL)BENZENE

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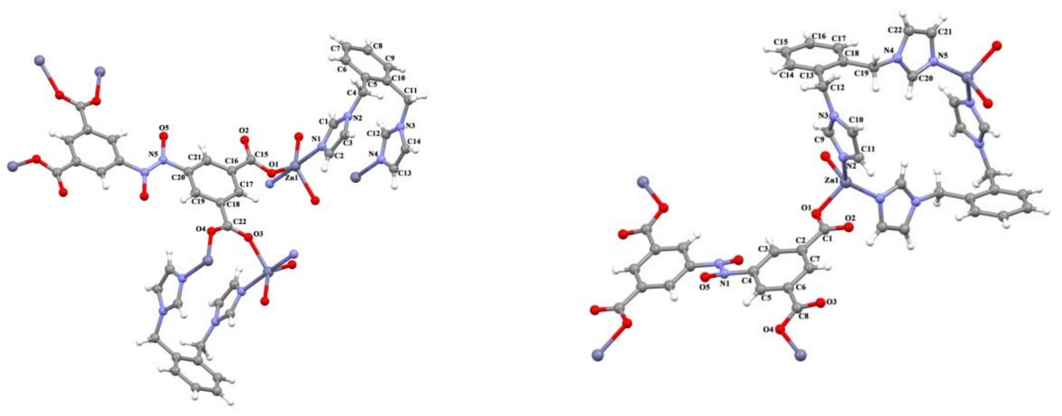
Synthesis and characterization of coordination polymers have attracted interest because of their tunable structure and potential applications in the fields such as gas adsorption/separation, catalysis, conductivity, magnetism and nonlinear optic [1]. The structure of coordination polymer changes depending on organic ligands, metal ions and supramolecular interactions between organic ligands or metal and organic ligands. In this study, two novel coordination polymers with the same close formula, namely, $[Zn_2(aobtc)(qauche\text{-}1,2\text{-}bix)_2]_n$ and $[Zn_2(aobtc)(anti\text{-}1,2\text{-}bix)_2]_n$ (H_4aobtc=3,3´,5,5´-azoxybenzenetetracarboxylic acid, 1,2-bix= 1,2-bis(imidazole-1ylmethyl)benzene) were synthesized and structurally characterized by single crystal X-ray diffraction, spectroscopic techniques (IR and photoluminescence), thermal analysis as well as elemental analysis. Moreover, topological studies were performed.

Complexes **1** and **2** were prepared by hydrothermal reaction of $Zn(NO_3)_2{\cdot}6H_2O$, H_4aobtc, 1,2-bix and HNO_3 at 100 °C. Single crystal X-ray diffraction of analyses reveal that **1** and **2** crystallize in the monoclinic and triclinic systems with the space groups P21/c, P-1, respectively. The crystal structures of **1** and **2** with the atom labeling are shown in Fig. 1. In complexes **1** and **2**, the aobtc ligand acts as a bridging ligand to form 2D layer. The aobtc ligand shows different coordination modes in **1** and **2**. 1,2-bix ligand adopt gauche and anti-conformation in complexes **1** and **2**, respectively. Topological analyses revealed that complex **1** and **2** had a two-dimensional (2D) 3,4-connected 2-nodal net with the point symbol of $\{4.6^2\}_2\{4^2.6^2.8^2\}$. Thermal and photoluminescence properties of the complexes were investigated in detail.



(1)

(2)

Fig. 1. The crystal structures of 1 and 2 with the atom labeling

Keywords: Coordination polymers, azobenzenetetracarbozylate, Zn(II)-complexes.

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Po1.35 CONSTRUCTION OF 2D NETWORK and 3D+3D INTERPENETRATED METAL ORGANIC FRAMEWORK of ZINC(II)-5-NITROISOPHTHALATE with 1,2-BIS(IMIDAZOLE-1YLMETHYL)BENZENE

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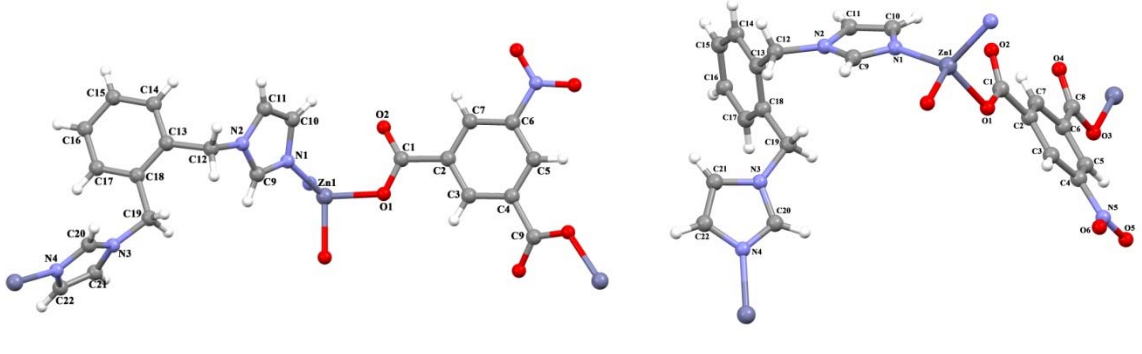
The rational design and construction of porous coordination polymers (PCPs) have attracted interest due to their fascinating structural topologies and potential applications in diverse fields such as gas adsorption/separation, molecular magnetism, catalysis, luminescence and nonlinear optic materials [1]. The challenge of designing porous coordination polymer is the formation of interpenetration leading to small pores or no pores, but they cannot prevent the possibility of open porous materials. In the design and synthesis of PCPs, the selections of metal ions, organic linkers and reaction conditions are the key factors. Aromatic dicarboxylates are widely utilized for synthesis of PCPs because of their diverse coordination mode and high structural stability. 5-nitroisophthalate which is a versatile aromatic dicarboxylate ligand can coordinate to metal ions in diverse coordination modes with two carboxylate groups with the bending angle of 120º. In this study, two novel coordination polymers with the same close formula, namely, $[\mathrm{Zn}(\mu\text{-5-nip})(\mu\text{-1,2-bix})]_n$ (5-H_2nip=5-nitroisophthalic acid, 1,2-bix= 1,2-bis(imidazole-1ylmethyl)benzene) were synthesized and structurally characterized by single crystal X-ray diffraction, spectroscopic techniques (IR and photoluminescence), thermal analysis as well as elemental analysis.

Complexes **1-2** were prepared by hydrothermal reaction of $Zn(NO_3)_2{\cdot}6H_2O$, 5-H_2nip, 1,2-bix at 170 ^{o}C. Complexes crystallized in the same beaker. The crystal structure of **1** and **2** with the atom labeling is shown in Fig. 1. The asymmetric units of **1** and **2** consist of a Zn(II) ion, one 5-nip ligand and one 1,2-bix ligand. **1** and **2** crystallize in the tetragonal and monoclinic systems, respectively. The coordination geometries around the Zn(II) ion can be described as a tetrahedral geometry. 1,2-bix ligand adopt conformation isomer in complexes **1** and **2**. Complex **1** exhibits a 2-fold interpenetrating 3D framework with 6^6-dia topology. Complex **2** displays 4-connected sql topology with the point symbol $4^4.6^2$. Thermal and photoluminescence properties of the complexes were investigated in detail.



(1) **(2)**

Fig. 1. The crystal structures of 1 and 2 with the atom labeling

Keywords: Coordination polymers, 5-nitroisophthalate, Zn(II)-complexes.

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Po1.36 NMR INVESTIGATIONS ON THE STRUCTURE OF COMPLEXES THAT FORM IN HYPERALKALINE SOLUTIONS OF CA^{2+} AND SMALL M_W HYDROXY CARBOXYLATES

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Polyhydroxy carboxylates (or sugar carboxylates) are known to form solution complexes with alkaline earth metal ions, like Ca(II) and Mg(II) [1]. These complexes are of small stability in neutral or close to neutral solutions. However, under hyperalkaline conditions, complexes with surprisingly high stability may be formed, where the metal ion is claimed to be bound *via* the carboxylate and alcoholate group(s) of the ligand [2,3]. At intermediate pH, proton loss from the OH group does not take place and the contribution of the alcoholic OH to the coordination (if any) is expected to be relatively small.

Recently, we have been involved in a comprehensive study concerning the solution structure and equilibria of Ca^{2+}-sugar type (D-gluconate, D-glucose and D-sorbitol) complexes in aqueous solutions, using a broad range of Ca^{2+} and ligand concentrations and ionic strengths at room temperature [4,5]. During these studies, structural information was derived from multinuclear (^{1}H, ^{13}C and ^{43}Ca) NMR measurements and from these spectra, stability constants were quantitatively determined as well. The measurements were supplemented with potentiometric, conductometric and polarimetric observations. The structure and composition of the complexes formed was derived from XAFS, ESI-MS measurements and *ab initio* quantum mechanical calculations.

To identify the structural unit, which is responsible for the strong metal ion binding in hyperalkaline medium, we embarked on systematic studies of Ca^{2+} complexation with small molecular weight ligands, such as D-tartrate, citrate and DL-malate. ^{1}H and ^{13}C NMR spectroscopies were the major experimental tools to find the complexation sites on the ligand and to elucidate the structure and also to characterise the equilibria of the complexes formed.

Acknowledgements: This research was financed by the OTKA NK106234 and the OTKA 83889 grants. The financial help is highly appreciated.

Keywords: Hydroxy carboxylates; Ca^{2+} complexes; ^{1}H, ^{13}C NMR

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Po1.37 THE COMPARATIVE VIBRATIONAL SPECTROSCOPIC STUDY OF CYPROHEPTADINE HCL AND MIANSERIN HCL

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Cyproheptadine hydrochloride, {4-(5H-dibenzo [a,d]-cyclohepten-5-ylidene)-1-methylpiperidine hydrochloride}, is an antihistaminic, antiserotonergic agent, known to have inhibitory activities for L-type calcium channels [1]. CYP HCl (Fig. 1a) contains a tricyclic nucleus with a 1-methyl-4-piperidylene ring attached to the central heptatriene ring. Its shape is similar to that of mianserin, with which it shares several common pharmacological properties, such as binding to central-nervous-system (CNS) 5HT-2 receptors [2]. Mianserin hydrochloride,{(±)-2-methyl-1,2,3,4,10, 14b-hexahydrodibenzo [c,f]pyrazino[1,2-a] azepine}, is a non-selective tetracyclic antidepressant with a prominent serotonergic profile and with moderate histamiergic side effects [3]

In this study, the FT-IR and FT-Raman spectra of cyproheptadine HCl and mianserin HCl have been recorded in 4000-400 cm^{-1} and 3500 cm^{-1}, respectively. The optimized geometry, energies, nonlinear optical properties and vibrational frequencies of these compounds have been determined using the density functional theory (DFT/B3LYP) method with 6-311G(d,p) basis set.

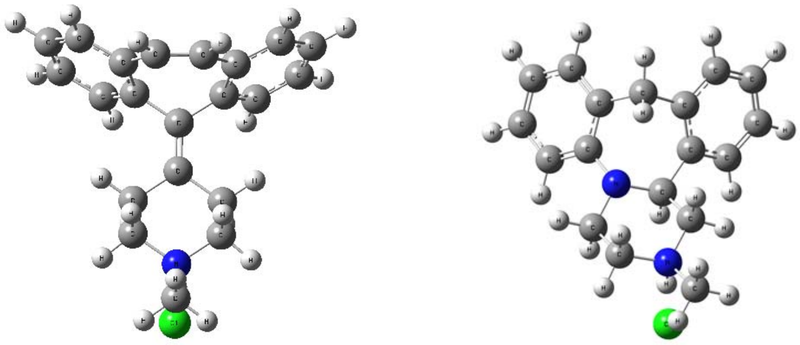

Fig 1. Optimized molecular structures of a) cyproheptadine HCl b) mianserin HCl calculated at the B3LYP/6-311G(d,p).

The comparisons of the experimental and theoretical results of cyproheptadine HCl and mianserin HCl indicate that the density-functional B3LYP method is able to provide satisfactory results for predicting vibrational properties. The experimental and calculated results for cyproheptadine HCl have also been compared with mianserin HCl.

Keywords: Cyproheptadine HCl ; Mianserin HCl ; Vibrational spectra

Acknowledgments

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Po1.38 $E \rightarrow Z$ PHOTOCONVERSION OF CROTONIC ACID IN SOLID XENON

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It has been shown that matrix-isolated acrylic acid ($H_2C=CCOOH$) undergoes conformational isomerization about the C_α–C bond when irradiated with UV light ($\lambda \sim 248$ nm), leading to a photostationary state where the population of the two experimentally observable conformers (*cc* and *ct*) are nearly equal [1]. Later, high-level correlated multiconfigurational *ab initio* and TD-DFT calculations allowed identification of the underlying mechanism for this photoprocess [2] and show that in the participating excited states the C_α–C_β bond has essentially a single bond character. Hence, besides the observed conformational isomerization, permutation of the two terminal hydrogen atoms can also be postulated to take place in acrylic acid upon UV excitation of the molecule. However, in acrylic acid the structure resulting from this process is indiscernible from the reactant species, precluding investigation of this transformation.

On the other hand, the $E \leftrightarrow Z$ isomerization in crotonic acids (*E*- and *Z*-$CH_3CH=CCOOH$) can be expected to be easily detectable spectroscopically [3], since the reactant and final product are, in this case, different species. Hence, in the present study, we have investigated the UV-induced isomerization processes undergone by *E*-crotonic acid isolated in inert cryogenic matrices.

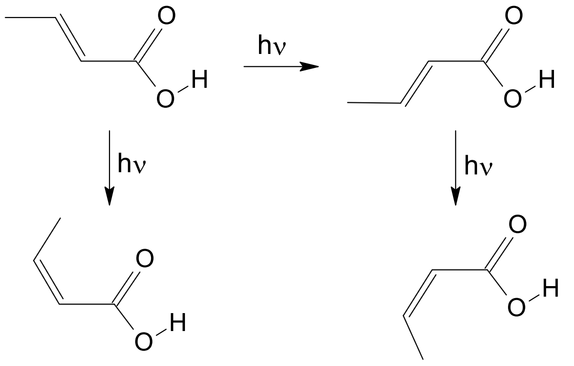

Fig. 1 Observed phototransformations of *E*-

The experimental results confirm that in gas phase *E*-crotonic acid exists in two low energy conformers, E_{cc} and E_{ct} (*top*, Figure 1) and that, upon *in situ* UV irradiation ($\lambda > 230$ nm) of the compound isolated in solid xenon, E_{cc} converts into E_{ct}. In addition, it could also be concluded that, concomitantly with the $E_{cc} \rightarrow E_{ct}$ conforma-tional isomerization, both *E*-crotonic acid conformers are also converted into their *Z*-analogue forms (Z_{cc} and Z_{ct}; *bottom*, Figure 1).

Acknowledgements: This work was supported by the Portuguese "Fundação para a Ciência e Tecnologia" (FCT; Research Projects PTDC/QUI-QUI/111879/2009 and PEst-OE/QUI/UI0313/2014, co-funded by QREN-COMPETE-UE. N. Kuş acknowledges FCT for the award of a post-doctoral Grant (SFRH/BPD/88372/2012).

Keywords: Crotonic acids;UV-induced isomerizations

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Po1.39 FT-IR AND DFT STUDY OF THE FREE AND SOLVATED 4-(IMIDAZOL-1-YL)PHENOL

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4-(imidazol-1-yl)phenol (4IP) is a non-linear molecule consists of 20 atoms which is used as a reactant in the synthesis of nitric oxides [1]. In this study, experimental FT-IR spectrum of 4-(imidazol-1-yl)phenol was recorded. Vibrational frequencies and modes of 4IP were determined. Vibrational assignments were proposed with the help of B3LYP/6-311++G(d,p) level of calculations. The solvent effects on the structure, vibrational frequencies, and atomic charges of the title ligand were studied theoretically. Water, dimethyl sulfoxide, and ethanol were the solvents considered. Experimental FT-IR spectrum in DMSO solution was recorded and compared with solid phase experimental data. DFT B3LYP combined with polarized continuum model (PCM) [2] was employed to characterize the solvent effects. PCM was used in both implicit and explicit consideration of solvent effects.

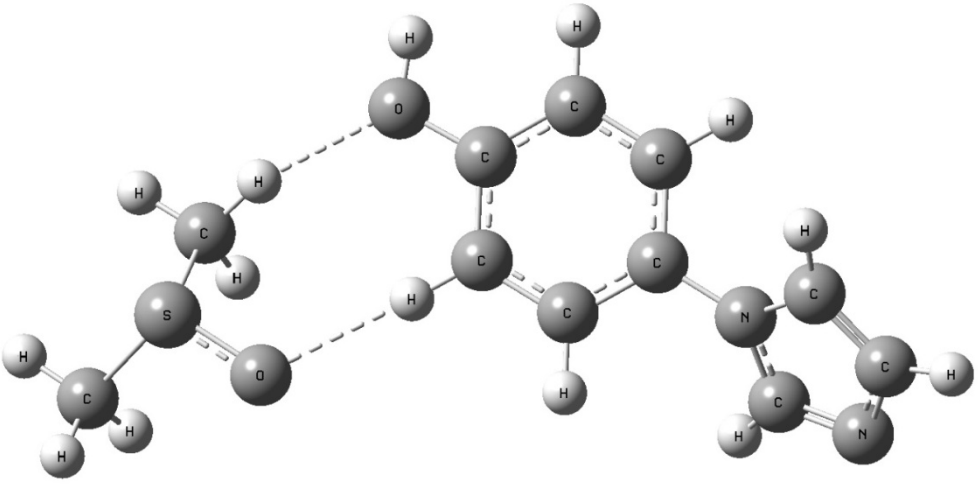

Fig.1 4IP:DMSO complex used in PCM calculations

Keywords: 4-(imidazole-1-yl)phenol; vibrational spectroscopy; DFT; solvent effects; PCM

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Po1.40 MIR-FIR SPECTROSCOPY IN ONE STEP – WIDE RANGE INFRARED TECHNOLOGY

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The extension of the mid IR towards the far IR spectral range below 400 cm^{-1} is of general interest for molecular vibrational analysis for inorganic and organometallic chemistry, for geological, pharmaceutical, and physical applications, polymorphs and crystallinity analysis as well as for matric isolation spectroscopy.

The achievable spectral range of an FTIR spectrometer is defined by the intersection of the efficiency ranges of the used source, beam splitter, and detector. The lower limit of the spectral range is very dependent upon the beam splitter, and is typically limited to 350 cm^{-1}. To extend the spectral range further into the far IR and THz spectral ranges one or more additional far IR beam splitters and detectors are required and because of this the user has to pause the measurement and as needed manually open the spectrometer optics bench.

Now available for the first time is the Bruker ***WRITE™*** (**W**ide **R**ange **I**nfrared **Te**chnology) option for VERTEX 70 FT-IR spectrometer which combines two Bruker innovative optic components the wide range MIR-FIR beam splitter [1] and the wide range DLaTGS detector. The ***WRITE™*** option enables in connection with the standard IR source the spectral range from 6000 cm^{-1} down to 30 cm^{-1} in one step for all types of transmittance, reflectance and ATR measurements. Utilizing the external water cooled mercury arc high power lamp the spectral range can be ultimately extended down to 10 cm^{-1}.

Keywords: IR spectroscopy; FIR; THz; wide range; FT-IR spectrometer

Reference

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Po1.41 SYNTHESIS, CONFORMATIONAL AND PHARMACOLOGICAL STUDY OF ESTERS DERIVED FROM 3-METHYL-3-AZABICYCLO[3.3.1]NONAN-9α(β)-OLS

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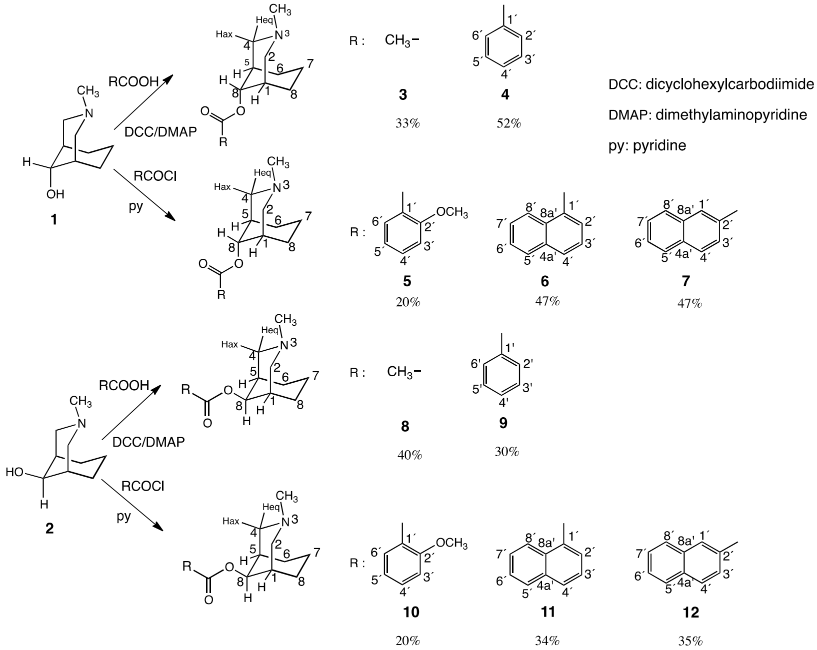
Following our research program related to the synthesis and structural study of potential pharmacologically interesting compounds we have synthesized some esters derived from 3-methyl-3-azabicyclo[3.3.1]nonan-9α(and β)-ols.



For compounds **3**, **4, 8** and **9** higher yields have been obtained starting from the alcohol and the corresponding acid, whereas the reaction between the alcohol and the acyl chloride is the best method to obtain the compounds **5-7** and **10-12**.

A study by ^{1}H and ^{13}C NMR has been done to determine the preferred conformations in solution. The assignments of proton and carbon resonances have been made on the basis of our data for related systems and double resonance experiments for compounds **4** and **9**.

Both α (**3-7**) and β esters (**8-12**) adopt in $CDCl_3$ solution a chair-chair conformation with the *N*-CH_3 group in equatorial position. ^3JH1(5)-H9(**8-12**) > ^3JH1(5)-H9(**3-7**); therefore, the piperidine ring adopts a flattened chair conformation in the case of the β-esters. The shape of the signals corresponding to the aromatic protons accounts for a free rotation of the aciloxy group around the C-O bond.

Finally, although compounds tested (**4**,**5**,**9** and **10)** showed analgesics properties they are much less active than the reference compound (morphine). Compound **9** showed the highest potency followed by compound **4**; therefore, the introduction of the *o*-OCH_3 substituent in the aromatic ring produces a decreasing of the analgesic activity.

Keywords: Bicyclic α- and β-esters; 3-Methyl-3-azabicyclo[3.2.3]nonan-8α(β)-ols ; Conformational Analysis

Po1.42 MATRIX ISOLATION INFRARED SPECTROSCOPIC, THERMODYNAMIC AND THEORETICAL STUDY OF 1-METHYLHYDANTOIN

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The structural, vibrational and photochemical study of 1-methylhydantoin (1-MH, $C_4H_6N_2O_2$; Fig.1) was undertaken by matrix isolation infrared spectroscopy (in argon matrix; 10 K), complemented by quantum chemical calculations performed at the DFT(B3LYP)/6-311++G(d,p) level of approximation. The theoretical calculations yielded the C_s symmetry structure, with planar heavy atom skeleton, as the minimum energy structure on the potential energy surface of the molecule. The electronic structure of this minimum energy structure of 1-MH was then studied in detail by means of the Natural Bond Orbital (NBO) and Atoms in Molecules (AIM) approaches, allowing for the elucidation of specific characteristics of the molecule's σ and π electronic systems. The infrared spectrum of the matrix-isolated 1-MH was fully assigned, also with the help of the theoretically predicted spectrum of the compound, and its UV-induced unimolecular photochemistry ($\lambda \geq 230$ nm) was investigated. The compound was found to fragment to CO, isocyanic acid, methylenimine and *N*-methyl-methylenimine. Finally, the thermal behavior of 1-MH, from 10 K till melting, was studied using infrared spectroscopy, differential scanning calorimetry and polarized light thermal microscopy. A new polymorph of 1-MH was identified.

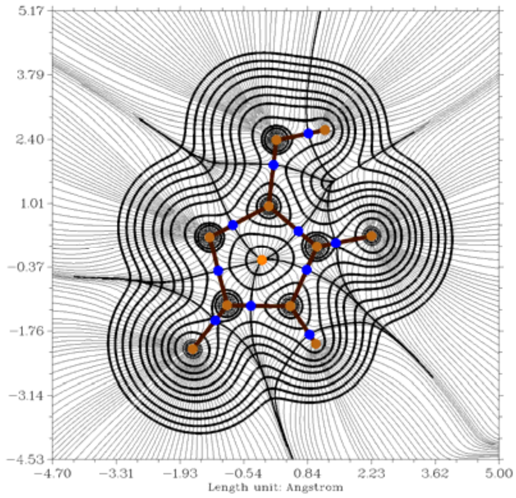

Fig. 1 - Contour map of the molecular charge density in the molecular plane of 1-MH, and the trajectories of the corresponding gradients. The figure shows also the location of the bond and ring critical points, and bond paths.

Acknowledgements: This work was supported by the Portuguese ''Fundação para a Ciência e Tecnologia'' (FCT) Research Project PTDC/QUI-QUI/111879/2009, and FCOMP-01-0124-FEDER-021082, co-funded by QREN-COMPETE-UE. The Coimbra Chemistry Centre (CQC) is supported by FCT through the project PEst-OE/QUI/UI0313/2014.

Po1.43 ORDER-DISORDER PHASE TRANSITION IN $[(CH_3)_2NH_2]Na_{0.5}Fe_{0.5}(HCOO)_3$ STUDIED BY IR AND RAMAN SPECTROSCOPY

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We report synthesis, structural and phonon properties of novel metal-organic framework (MOF) compound, $[(CH_3)_2NH_2]Na_{0.5}Fe_{0.5}(HCOO)_3$, which belongs to an interesting family of materials exhibiting unique properties due to order-disorder phase transition. Simple MOFs composed of one magnetic ion (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}) exhibit magnetic and ferroelectric order in the same phase [1,2]. Studied here compound was obtained by replacing of divalent metal ions by equimolar amount of Fe^{3+} and Na^{+} ions.

Single crystal diffraction pattern shows that presented material crystallizes at room temperature in *R3* trigonal space group in which $(CH_3)_2NH_2^+$ cations are dynamically disordered. Below $T_C \approx 166$ K the order-disorder phase transition takes place to lower symmetry phase.

Our temperature-dependent structural and phonon studies show weak anomalies in FWHM close to the phase transition temperature for the modes of metal formate framework. However, very pronounced changes in FWHM, intensity and shift with decreasing temperature are observed for the modes assigned to amino and methyl group vibrations. This behavior proves highly dynamic nature of $(CH_3)_2NH_2^+$ groups above T_C and increase of hydrogen bond strength below T_C.

Modes involving motions of metal formate framework show clear splitting into two or more components conforming that the phase transition is associated with a decrease of crystal symmetry. Our studies show that the ferroelectric phase transition is mainly driven by the ordering of $(CH_3)_2NH_2^+$ ions and coincident distortion of metal formate framework.

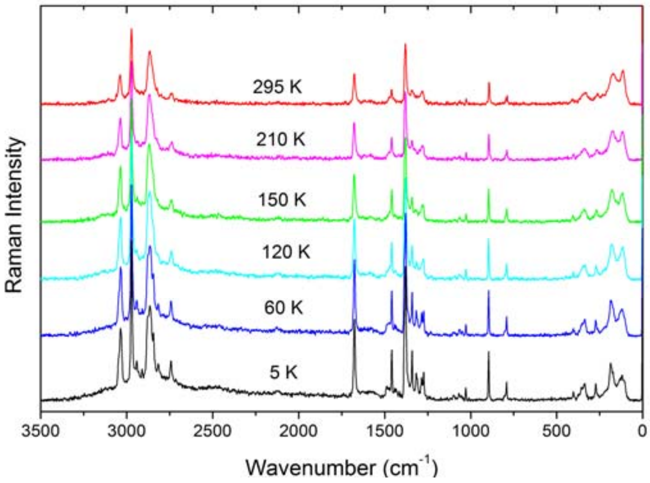

Fig.1 Raman spectra of $[(CH_3)_2NH_2]Na_{0.5}Fe_{0.5}(HCOO)_3$ recorded at various temperatures.

Keywords: MOF; Formate; Order-disorder; Phase transition

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Po1.44 SYNTHESIS, MAGNETIC AND VIBRATIONAL PROPERTIES OF $[NH_2\text{-}CH^+\text{-}NH_2][M(HCOO)_3]$ FORMATES (M=Co, Fe)

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In the present work we report synthesis of two novel Co and Fe formates, i. e., $[NH_2\text{-}CH^+\text{-}NH_2]Co(HCOO)_3]$ and $[NH_2\text{-}CH^+\text{-}NH_2]Fe(HCOO)_3]$. These compounds crystallize in the orthorhombic Pnna space group with formamidinium cations [FMD$^+$] located in the cavities of the metal formate framework and forming strong hydrogen bonds with the anionic framework. Divalent cobalt and iron ions have octahedral coordination, and are connected by formate ligands. Low-temperature magnetic studies have revealed that FMDCo and FMDFe compounds are weak ferromagnets with critical temperature of 13.0 K and 17.0 K, respectively.

We also report vibrational properties of FMDCo and FMDFe. Assigment of vibrational modes to the respective motions of atoms in the unit cell has been proposed through comparison with other known formates and DFT calculations performed for formamidine molecule and FMD$^+$ cation.

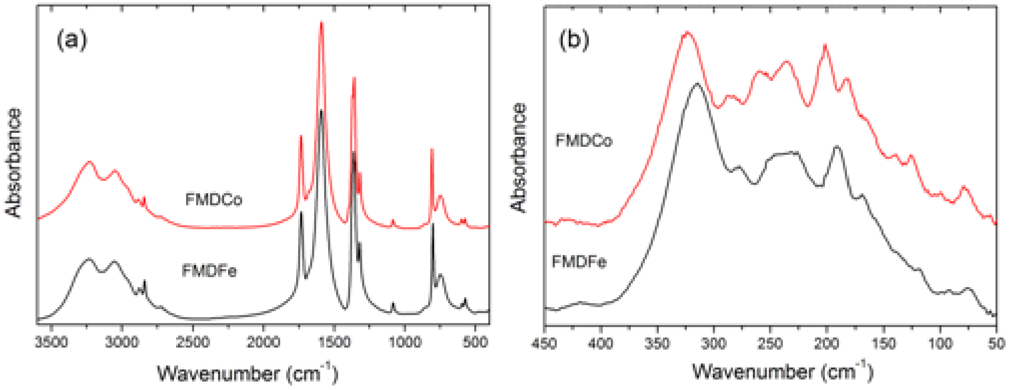

Fig.1 IR spectra results corresponding to the spectral ranges (a) 400-3600 and (b) 50-450 cm^{-1}

Our results show that FMDCo and FMDFe exhibit similar vibrational properties. However, the IR and Raman spectra show downshifts of some lattice modes when Co^{2+} is replaced by Fe^{2+} due to increasing size of the unit cell in the latter case.

In conclusion, we report the synthesis, structure, magnetic and vibrational properties of two novel formamidine - templated Co and Fe formates. These studies allowed us to better understand the relationship between size and type of divalent cation and structural as well as vibrational properties of metal-organic frameworks based on divalent cations linked by formate ligands and organic cations located in the cavities of the framework.

Keywords: MOF; Raman; IR; phase transition; multiferroic;

Po1.45 VIBRATIONAL SPECTROSCOPIC STUDIES ON 1-(P-TOLYLSULFONYL) PYRROLE

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Literature reveals that to the best of our knowledge DFT calculations and experimental studies on molecular structure and vibrational spectra of 1-(p-tolylsulfonyl)pyrrole (1PTSP) molecule have not been reported so far. Therefore, we have carried out detailed theoretical and experimental investigations on the molecular structure and vibrational spectra of 1PTSP molecule completely. We have utilized the B3LYP [1-3] with 6-311++G(d,p), cc-pVDZ and cc-pVTZ basis sets.

The FT-IR spectrum of 1PTSP molecule is recorded in the region 4000–400 cm^{-1} on Vertex 80 spectrophotometer. The FT-Raman spectrum of 1PTSP molecule has been recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 50-3500 cm^{-1} on the Thermo scientific DXR Raman Microscope. The ^{1}H and ^{13}C NMR spectra are taken in solutions and all signals are referenced to TMS on a **Bruker Ultrashield** FT-NMR Spectrometer. All NMR spectra are measured at room temperature.

The calculations were performed at DFT levels by using Gaussian 09 program package, invoking gradient geometry optimization [4-5]. In order to establish the stable possible conformations, the conformational space of 1PTSP molecule was scanned with theoretical methods. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. Then, vibrationally averaged nuclear positions of 1PTSP molecule were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies. In the present work, the vibrational modes were assigned on the basis of TED analysis for 6-311++G(d,p) basis set, using SQM program [6].

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Po1.46 PHYSICAL AND CHEMICAL CHARACTERIZATION OF POLY(MA-*ALT*-MVE)/ODA-MMT NANOHYBRID STRUCTURES

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Abstract- Novel bioengineering nanocomposites poly(maleic anhydride-*alt*-methyl vinyl ether)/octadecylamine-montmorillonite [poly(MA-alt-MVE)/ODA-MMT] were synthesized by exfoliation-absorption and graft polymerization of copolymer poly(maleic anhydride-*alt*-methyl vinyl ether) and organo clay octadecylamine-montmorillonite (ODA-MMT). Chemical and physical structures of synthesized nanohybrids were confirmed by FTIR, ^{1}H and ^{13}C NMR-Dept-135, MALDI-TOF-MS spectroscopy and XRD analyses. Surface or inner morphology of nanocomposites were studied by SEM and TEM analyses. Obtained results were shown that ODA-MMT clay take place dual functions as a nanofiller (layered silicate) and a catalyst component (or copolymer)/ODA-MMTcomplex.

Introduction-Nanocomposites are of great interest for many researchers due to their nontoxic, cell-compatible, biodegradable properties[1-3]. Poly(MA-*alt*-MVE) and some organic derivatives of MMT clay have been known to have bioengineering effects as well as a broad spectrum of antitumoral, antimicrobial, protein linkage activities[4]. In this study, to provide useful information for the biological function of copolymer / organoclay nanocomposite poly(MA-*alt*-MVE)/ODA-MMT [5, 6] .

Experimental-Poly (maleic anhydride-*alt*-methyl vinyl ether) / octadecylamine-montmorillonite [poly(MA-alt-MVE/ODA-MMT)] nanocomposites synthesized by exfoliation-absorption and graft polymerization methods. Chemical and physical structures of synthesized nanohybrids were confirmed by FTIR, ^{1}H and ^{13}C NMR-Dept-135, MALDI-TOF-MS spectroscopy and XRD analyses. Surface or inner morphology of nanocomposites were studied by SEM and TEM analyses.

Results and Discussion-Chemical structure of synthesized copolymers was studied by ^{1}H (^{13}C) NMR and FTIR spectroscopy **(Figure 1a-d)**. Surface or inner morphology of nanocomposites were studied by SEM and TEM analyses, respectively. These results indicate the formation of fine dispersed morphology in the nanosystem containing matrix copolymer with middle average-molecular weight. **(Figure 1 e-f).** Obtained results were shown that ODA-MMT clay take place dual functions as a nanofiller (layered silicate) and a catalyst component (or copolymer)/ODAMMTcomplex.

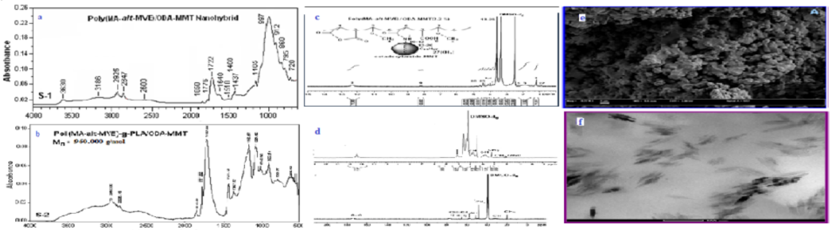

Figure 1: FTIR spectrum of Poly(MA-alt-MVE)/ODA-MMT nanohybrid structures, synthesized in dioxan (a) and in PLA (b) NMR (^{1}H) spectrum (c) in dioxan and (d) ^{1}H and ^{13}C-NMR spectrum (e) SEM and (f) TEM images of Poly(MA-*alt*-MVE)/ODA-MMT nanocomposite structures.

This work has attempted to develop novel bioengineering functional nanocomposites which contained free carboxylic and amine groups with an ability to conjugate with biomolecules, enzymes, proteins, are available to decolorization of reactive color substrates. These nanocomposites were synthesized by graft copolymerization and in situ exfoliation of graft copolymer chains between silicate galleries and formation of nanostructural hybrid systems.

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Po1.47 AB INITIO STUDY OF PROTON TRANSFER PATHWAY IN C—H···X HYDROGEN BONDS: STRUCTURE AND NMR PARAMETERS

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Hydrogen bonds such as C—H···X are very prevalent non-covalent interaction in organic chemistry (in particularly, in organic molecular crystals [1] or biological structures [2]). Formation of a hydrogen bond is considered as a first step in the process of proton transfer, one of the most ubiquitous reactions in nature, $\mathrm{CH + X \rightleftharpoons C\text{-}H\cdots X \rightleftharpoons C^{-}\cdots H\text{-}X^{+}}$.

Molecular and zwitterionic complexes in this reaction are often short lived transient species. As a result, the structure and spectroscopic parameters remain largely unknown. In this work we considered a couple of model complexes of strong CH proton donors with various bases (for example, a complex of 1,1-dinitroethane with pyridine, see f.e. [3]). A systematic *ab initio* study (B3LYP/6-311++G(d,p)) of proton transfer has been carried out. We have followed changes in carbon atom hybridization along the reaction pathway, as well as NMR spectroscopic parameters (isotropic chemical shifts and spin-spin coupling constants). We show that some NMR parameters can serve as sensitive indicators of complex's geometry. For example, for 1,1-dinitroethane and pyridine complex, geometry of hydrogen bridge can be described by spin-spin interactions between three atoms forming it [4], in this case $^{1}J_{CH}$, $^{1}J_{HX}$ and $^{2h}J_{CX}$. At the same time, hybridization state of acidic carbon (*sp*^{3} changes to *sp*^{2} with proton transfer, see fig. 1) is best reflected by changes of $^{1}J_{CC}$ coupling constant. Interestingly, after proton transfer in this complex the negative charge on carbanion is localized primarily on electronegative nitro groups, and hence proton accepting ability of carbon atom is strongly reduced. Those results is supported by preliminary NMR experiments.

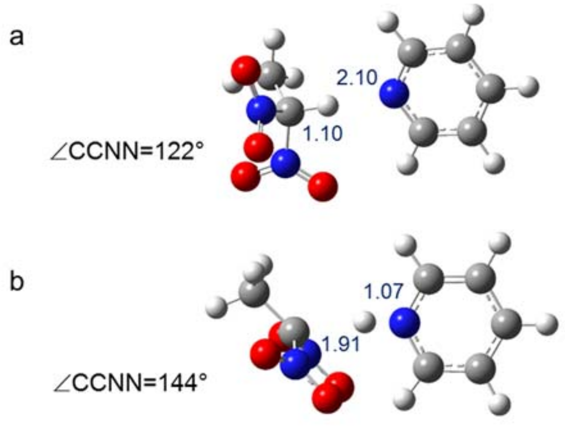

Fig. 1. Snapshots of 1,1-dinitroethane complex with pyridine: (a) equilibrium geometry, r_{CH} = 1.10 Å, (b) r_{CH} = 1.91 Å.

Keywords: ^{1}H, ^{13}C NMR; CH acid; hydrogen bond geometry; proton tautomerism; dinitroethane

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Po1.48 ROTAMERS OF 2,5-DIFLUOROPHENOL STUDIED BY RESONANT TWO-PHOTON IONIZATION AND MASS-ANALYZED THRESHOLD IONIZATION SPECTROSCOPY

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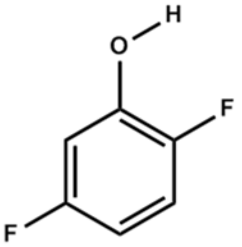
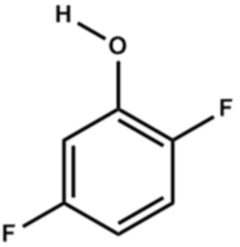
We applied the resonant two-photon ionization and mass-analyzed threshold ionization techniques to record the vibrational spectra of 2,5-difluorophenol in the first electronically excited S_1 and the cationic ground D_0 states. Due to the relative orientation of the hydroxyl with respect to the two fluorine substituents, 2,5-difluorophenol has two stable rotational isomers (rotamers).



cis-2,5-difluorophenol



trans-2,5-difluorophenol

The band origins of the $S_1 \leftarrow S_0$ electronic transition of the cis and trans rotamers are found to be 36 448 ± 2 and 36 743 ± 2 cm^{-1} and the adiabatic ionization energies are 71 164 ± 5 and 71 476 ± 5 cm^{-1}, respectively. The distinct spectral features mainly result from the in-plane ring deformation and substituent-sensitive bending vibrations. Spectral analysis suggests that the molecular geometry and vibrational coordinates of the cation in the D_0 state resemble those of the neutral species in the S_1 state for both cis and trans rotamers.

Keywords: Vibronic spectrum; Cation spectrum; Rotamer; Phenol derivatives

Po1.49 BILIRUBIN, MODEL MEMBRANES AND SERUM ALBUMIN INTERACTIONS: STUDY BY CHIROPTICAL METHODS

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Bilirubin (BR), the end product of the hem catabolism in the human body, is formed at a rate of about 300 mg per day and usually is effectively excreted from the body. Although, this pigment has been known for more than a century, its exact effects are still under debate. In the pathologic state, BR may accumulate and at higher concentrations its negative effects may turn up. One of the main negative effects of BR is its impact on nerve cell membranes which may result in cell apoptosis. These neurotoxic effects of BR are thought to be caused by its enantiodiscrimination on the membrane which results as a membrane damage.

BR belongs to the group of non-planar tetrapyrrolic pigments. Its rigid dipyrrole units form a helical structure, with either P- or M-sense of helicity. However, in homogenous solution BR exists as a racemate. As it is supposed that one of the forms interacts preferentially with the membranes, it is convenient to study these systems with methods enabling the observation of the enantiomeric excess.

Because of this, we employed chiroptical spectroscopic techniques, vibrational and electronic circular dichroism (VCD, ECD), for the studies of BR with model membranes. This combination of techniques enabled us to study the BR systems at different conditions: concentrations, pH, temperature, and also for different model membrane composition.

In some cases BR was found to penetrate inside the membrane. Our obtained results suggest that not only the structure of BR is influenced by the model membrane but that the effect is mutual and the membrane structure is also gravely modified. Besides of these results, the VCD spectroscopy, employed for the first time to study the interaction of BR with model membranes, provided information about functional groups that participated in the interaction.

However, in the human organism, BR is usually supposed not to be dangerous to health because its transport in the blood vessels is mainly ensured by the serum albumin transport protein to which BR has a very high binding constant ($K_A = 9.10^7$ l.mol^{-1}). Hence, we explored its influence on the BR-model membranes interaction. In addition, the effect of model membranes on the association of BR with albumin was quantified. The obtained results suggest that BR, which is bounded to the liposomes, is not released after the addition of albumin into the solution. This indicates that although the binding constant of BR to albumin is high, the elevated levels of BR in the human body may have effects where the interaction of BR with membrane may be involved.

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Keywords: Bilirubin; model membranes; circular dichroism

Po1.50 CONCENTRATION-DEPENDENT EFFECT OF DESMOSTEROL ON ZWITTERIONIC MODEL MEMBRANES: DIFFERENTIAL SCANNING CALORIMETRY AND FTIR SPECTROSCOPY STUDIES

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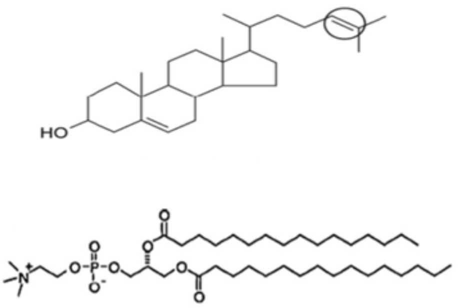

Fig.1 Chemical structures of desmosterol and DPPC

Desmosterol is a primary biosynthetic precursor of cholesterol in Bloch pathway of cholesterol biosynthesis and varies from cholesterol only in an additional double bond between carbons C-24 and C-25 of the flexible alkyl side chain [1,2]. Desmosterol consists of only trace quantities in most tissues, however it is an important component in spermatozoa, developing brain and accumulates during myotonia [3]. Dipalmitoyl phosphatidylcholine (DPPC) is the predominant phospholipid in natural lung surfactant and consists of two saturated 16-carbon fatty acid chains connected by a glycerol backbone with a zwitterionic headgroup [4,5]. The studies on the interaction of desmosterol with membranes at molecular level are very limited [1,6].

In the present study, concentration-dependent effect of desmosterol on zwitterionic dipalmitoyl phosphatidylcholine (DPPC) multilamellar vesicles (MLVs) was investigated for the first time by using differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. The result of DSC studies reveals that with the incorporation of increasing concentrations of desmosterol into pure DPPC MLVs, the pretransition and the main phase transition abolish. The result of FTIR studies shows that the addition of low desmosterol concentrations (1, 3 and 5 mol %) into pure DPPC MLVs increases the order slightly and decreases the dynamics in the gel phase, while high desmosterol concentrations (25, 30 and 40 mol %) decrease the order barely and increase the dynamics of DPPC membranes in the gel phase. In the liquid crystalline phase, low concentrations of desmosterol induce a reduction in the order and the dynamics of membranes, whereas high concentrations of desmosterol cause an enhancement in both of them. Desmosterol also induces a decrease in the wavenumber of the C=O stretching and PO_2^- antisymmetric double stretching bands of DPPC both in the gel and liquid crystalline phases, which points out hydrogen bonding in between the hydroxyl group of desmosterol and carbonyl group and head groups of DPPC membranes.

Keywords: Desmosterol; DPPC; DSC; FTIR

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Po1.51 MOLECULAR AND CRYSTAL STRUCTURE, VIBRATIONAL STUDIES AND CONFORMATION OF THE HYDRAZO BOND IN 3,3’,5,5’-TETRANITRO-2,2 HYDRAZOBIPYRIDINE

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The synthesis of 3,3’,5,5’-tetranitro-2,2-hydrazobipyridine (NHP) has been described. Its IR and Raman spectra have been measured and compared to those of similar compounds previously reported by us [1-4]. The 6-311G(2d,2p) basis set with the B3LYP functional has been used to discuss the optimized structure and vibrational dynamics of the studied compound. The vibrational characteristics of the hydrazo bond is reported with its relation to the conformation of the molecule.

The crystal and molecular structures of the studied compound have been determined by means of X-ray diffraction and quantum chemical DFT analysis. The crystallization of NHP from acetonitrile and also acetic acid solutions led to formation of two polymorphs, as a mixture of red blocks (majority) and orange plates (minority). The crystals of both forms belong to monoclinic space group *P*21/*c*, with one-half molecule in the asymmetric unit (Fig. 1). Crystal structure determined at 100 K reveals different structural hydrogen-bonded motifs that distinguish the polymorphs.

The IR and Raman wavenumbers have been calculated for the optimized geometry of possible structural models. Normal modes of hydrazo bond, nitro group and pyridine rings have been proposed together with the PED values. It was found that the characteristic vibrational bands observed in the range 3400-2900 cm^{-1} originate from the intramolecular N-H···O hydrogen bonds formed between the NH and NO_2 groups.

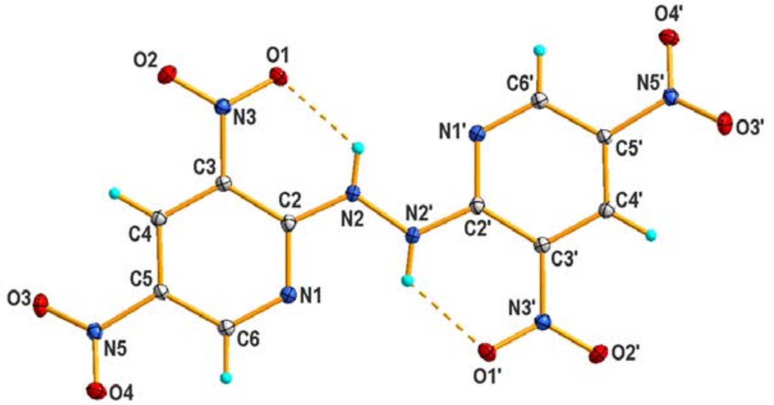

Fig. 1. The molecular structure of red polymorph, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry code: (') -x+1, -y+1, -z+1. Dashed lines indicate intramolecular N-H···O hydrogen bonds

Keywords: Hydrazobipyridine; Hydrazo bond; X-ray study; IR and Raman spectra

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Po1.52 THE CRYSTAL STRUCTURE AND HYDROGEN BONDS IN 1-N-PENTYL-HYDANTOIN STUDIED BY XRD, IR AND RAMAN METHODS AND CALCULATIONS

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The imidazolidine-2,4-diones, so called hydantoins, constitute an interesting family of compounds with bioactive properties. They found application as fungicides, herbicides as well as pharmaceutics: antitumor, anti-inflamatory, anti-HIV and anticonvulsant. Hydantoins are being examined as a potential treatment for prostate cancer.

The title compound, 1-N-pentylhydantoin (**5Hyd)** was synthesized by the chloroacethylurea reaction with pentylamine in n-propanol solution according to the procedure developed by Talik T. et al. [1] and characterised by means of FT-IR, FT-Raman and single crystal X-ray crystallography. In the crystal structure of **5Hyd** a pair of N-H···O hydrogen bonds, involving N3 atom as a donor and O1 atom (-*x*, -*y*, -*z*+1) as an acceptor, link two molecules into a dimer with the $R^2_2(8)$ ring motif (Fig. 1). The distances (N3···O1) and angles (N3-H3···O1) of the intermolecular hydrogen bonds are as follow: 2.781(5) Å, 177º which indicate that they are moderately strong. The structural changes due to complexation by H-bindings are observed in chemical calculations. A weakening of chemical bonds involved in formation of hydrogen bonds is observed by an increase in their distances. The C=O1 bond length, as a consequence of HB bonding, extends from 1.207 to 1.224 Å.

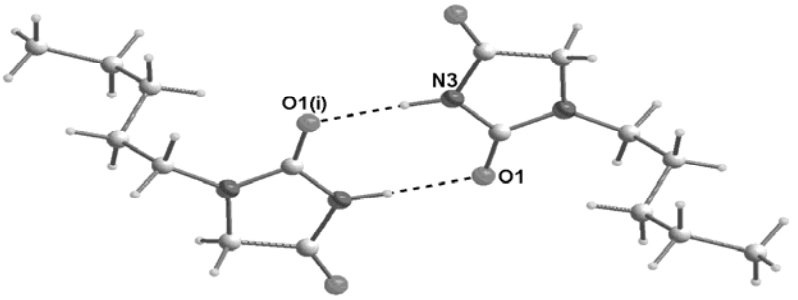

Fig. 1. The X-ray structure of 5Hyd dimer. Dashed lines indicates intermolecular hydrogen bonds.

FT-IR and FT-Raman spectra have been measured and discussed in terms of quantum chemical DFT calculations and literature data then related to the XRD data obtained for the **5Hyd** crystal. The vibrational characteristics of the N-H bond have been reported with their relation to the formed intermolecular hydrogen bonds. The wavenumbers of the characteristic bands of the HB in the studied compound were assigned at 3181-3138 cm^{-1} for N3-H3···O1, at 1775 cm^{-1} for C=O4 and at 1692 cm^{-1} for C=O1. These wavenumbers are close to the calculated vibration as well as to those described in the literature for hydantoin.

Keywords: Crystal structure of 1-N-pentylhydantoin; IR and Raman spectra; Hydrogen bond

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Po1.53 MOLECULAR STRUCTURE, VIBRATIONAL SPECTRAL INVESTIGATION AND THE CONFIRMATION ANALYSIS OF TRICHLOROISOCYANURIC ACID

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Trichloroisocyanuric acid is an organic compound with the formula ($C_3Cl_3N_3O_3$). It is used as an industrial disinfectant, bleaching agent and a reagent in organic synthesis [1, 2].This white crystalline powder, which has a strong "chlorine odour," is sometimes sold in tablet or granule form for domestic and industrial use. The compound is a disinfectant, algicide and bactericide mainly for swimming pools and dyestuffs, and is also used as a bleaching agent in the textile industries. It is widely used in civil sanitation, pools and spas, preventing and curing diseases in husbandry and fisheries, fruits and vegetables preservation, wastewater treatment, algicide for recycling water of industry and air conditioning, anti shrink treatment for woolen, treating seeds, bleaching fabrics, and organic synthesis.

Density functional method has been used to compute optimized geometry, vibrational wavenumbers of Trichloroisocyanuric acid (TCIC) and its tautomers [3-5] Three tautomers of TCIC were determined and optimized by Quantum Chemical Method. FT-IR and FT-Raman spectra of TCIC have been measured in the regions 4000-100 cm^{-1} and 3500-100 cm^{-1}, respectively. The vibrational modes were assigned on the basis of TED analysis for 6-311++G(d,p) basis set, using SQM program [5]. ^1H and ^{13}C NMR properties have been calculated for the most stable three tautomeric forms using the Gauge İndependent Atomic Orbital (GIAO) method.

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Po1.54 SURFACE-ENHANCED RAMAN SPECTROSCOPY OF THIOBENZOIC ACID ON METAL NANOPARTICLES

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Molecules adsorbed on some metal surfaces such as silver, copper and gold, can exhibit enormous *Surface-enhanced Raman Scattering* (SERS). The SERS effect has historically been associated with substrate roughness on two characteristic length scales [1,2]. Surface roughness on the 10 to 100 nm length scale supports the electromagnetic resonances which are the dominant mechanism of enhancement. A second mechanism often thought to require atomic scale roughness, is referred to as the chemical enhancement mechanism. This second mechanism involves the creation of new electronic excited states which result from adsorbate–substrate chemical interactions. These two mechanisms operate simultaneously making it difficult to isolate the role and magnitude of each one.

In this work the SERS spectra of thiobenzoic acid (TBA) adsorbed on several silver colloids are recorded by using different excitation wavelengths. Taking advantage of the fact that SERS spectroscopy is both, surface selective and highly sensitive, we have attempted to determine the molecular structure of the surface complex once TBA is adsorbed on the metal. The analysis of the vibrational wavenumbers of the Raman and SERS spectra suggests that this molecule shows unidentate coordination to the silver surface through the sulphur atom. In order to confirm this conclusion DFT calculations have been carried out for different TBA-silver complexes concluding that the unidentate coordination is the most likely interaction of TBA on the metal surface.

Wavelength-scanned SERS excitation spectroscopy involves the measurement of SERS signal by using several excitation wavelengths and it was recognized as a useful tool for checking the mechanisms responsible for the SERS enhancement [3]. We have studied the effect of the wavelength within the SERS spectra of TBA on silver colloid prepared by different methods and we have analyzed the intensity of the 8a vibrational mode of TBA recorded at about 1590 cm^{-1}. The intensity of this mode is noticeably higher in the spectrum recorded with the 514.5 nm line (Fig. 1). This result is attributed to the presence of a resonant Raman effect associated to a photoinduced charge-transfer process when using the most energetic excitation line.

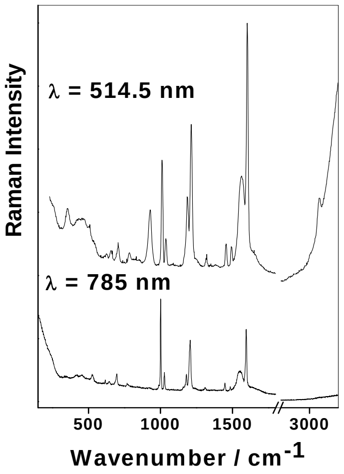

Fig.1. SERS spectra of TBA at different wavelengths.

Finally, it is important to mention the high affinity of TBA for the silver surfaces what allows for a detection limit estimated to be 0.01 μM.

Keywords: SERS, thiobenzoic acid, nanoparticles

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Po1.55 SPECTROSCOPIC STUDIES OF SILICATE LAYER DERIVED FROM DIFFERENT ORGANIC PRECURSORS

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The sol-gel method offers the possibility of obtaining silicate materials with different chemical compositions. When using $(SiOC_2H_5)_4$ or $C_7H_{19}O_3Si$ as organic precursor to silica capable of hydrolysis and poly-condensation, it is possible to use inorganic or organic precursors to produce other ingredients.

This work presents results of studying of silicate gels with the addition of calcium, in which the molar ratio of calcium to silicon was Ca/Si=x/(100-x), where x was, respectively: 0, 10, 20 and 40 (x=0 – control sample). The resulting gels were deposited on the metal substrate and (as well as the same gels) subjected to heat treatment, wherein the heating was carried out simultaneously in air or in argon. On the ground of infrared spectroscopy, X-ray (GID technique) and scanning electron microscopy (SEM) with X-ray microanalysis (EDS) measurements analysis the layers have been compared from the point of view of crystallinity and phase composition.

Due to the fine crystalline or amorphous nature of the resulting material, as confirmed in XRD - GID studies, the different bands on the IR spectra were characterized by large full width at half maximum. The analytic parameters of the resulting bands warranted the conclusion that there had been structural changes caused by the varying synthesis parameters. The resulting spectra were compared with spectra of crystalline pure phases for example: cristobalite, quartz, pseudowollastonite and tobermorite, which suggested the possibility of existence of rearranged areas [1].

All the layers were soaked in the simulated body fluid (SBF). The potential biological activity of the layers was estimated on the base of apatite growth possibility [2]. The presence of apatite on the layers surface was detected on the base of comparison of analogous spectra of the samples before and after SBF soaking. The detailed analysis of IR spectra confirmed the presence of bands characteristic of P-O bonds.

This work was funded under project no. 11.11.160.258 at the AGH University of Science and Technology in Krakow.

Keywords: sol-gel method, IR spectroscopy of calcium silicate gels, SBF soaking

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Po1.56 AN *AB INITIO* STUDY ON SPECTROSCOPY, STRUCTURE AND STABILITY OF 5-ATOMIC [C, C, H, N, S] ISOMERS

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Diverse small, highly unsaturated chemical compounds are commonly found in the interstellar medium. Molecules of the homologous series C_nS and $HC_{2n-1}N$ (*n=1,2,3,4…*) are relatively well known, in contrast to the HNC_nS species. HNCS is the simplest molecule of those latter; it has been both experimentally [1] and theoretically studied [2], and has also been detected in space [3, 4]. The interstellar synthesis proceeds through the cationic species $HNCSH^+$ and H_2NCS^+ [5, 6].

The titled 5-atomics include, among other possibilities, thioformyl cyanide HC(S)CN (hereafter: TFC) – a sulfur analogue of formyl cyanide HC(O)CN detected in the interstellar region Sgr B2 [7].

The systematic theoretical study described in this contribution was aimed at the molecules sharing the [C, C, H, N, S] stoichiometry. We present geometry, thermodynamic stability, and spectroscopic constants for a whole range of isomers, of both singlet and triplet multiplicity. The predictions on spectroscopy of the three most stable isomers include *i*) the energy and structures for the first singlet and triplet excited electronic states; *ii*) anharmonic vibrational frequencies and intensities for the fundamental, overtone and combination modes; *iii*) molecular parameters of direct interest to radio astronomers, i.e. rotational constants, equilibrium electric dipole moment values, quadrupole coupling constants etc. Abundances in typical cold, dense interstellar clouds have also been estimated, based on astrochemical kinetic models.

This study points to TFC as the lowest energy species among the three most stable compounds, within the discussed family of isomers. The other two are thioformyl isocyanide HC(S)NC and iminoethenethione HNCCS, less stable than TFC by, respectively, 80 and 140 kJ/mol. All three species are expected to have a reasonably high photochemical stability; their first few excited electronic states are bound. The ground state electric dipole moments are sufficiently high to expect radio astronomical detections.

Keywords: ab initio; astrochemistry; vibrational spectroscopy

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Po1.57 THE INFLUENCE OF SYNTHESIS PARAMETERS AND SIO_2 PRECURSOR TYPE ON STRUCTURE OF SILICA GELS AND THIN FILMS OBTAINED BY SOL-GEL METHOD

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Silica sols allows to synthesize coatings of different properties depending on the type of SiO_2 precursor. In this way antireflective coatings or thin films of high thermal resistance [1] and even hydrophobicity or high laser damage thresholds in case of methyl groups modifications [2] of sols can be obtained.

In this work, silica sols were prepared applying different synthesis parameters and different type SiO_2 precursors. The synthesis was performed as acid or basic catalyzed process, conducting in a way to achieve 5% weight of SiO_2 in the particulate sols. As SiO_2 precursors, the earlier mentioned tetraethylorthosilicate TEOS and also dimethyldietoxysilane DDS were used. DDS added into sols containing TEOS played the role of a pore dimensions modifier and enabled to posses a silica gel of the desired porosity.

Thin films were deposited by dip-coating technique on steel substrate and ceramized at 500°C in air. The gel samples were at first dried at ambient temperature and then annealed at 500°C and 1000°C in air.

FTIR spectroscopic structural studies were performed for synthesized thin films and gel samples. Additionally, XRD diffraction in a standard and in GID configuration was applied. The microstructure and the surface topography of thin films were analyzed by SEM and AFM microscopy.

In all FTIR spectra, in the range of 779–799 cm^{-1}, the bands ascribed to the symmetric stretching vibrations of Si-O-Si bond are observed, while bands in the range of 1027 – 1098 cm^{-1} are due to the asymmetric vibrations of Si-O(Si) connections. AFM images give the information of topography of samples surface in a nanoscale and allow to estimate the roughness and for particulate samples, the thickness of separate coatings deposited. The XRD measurements show the contribution of amorphous phase in samples and the tendency of their crystallization.

Acknowledgment

The financial support of AGH University of Science and Technology, grant no 11.11.160.258

Keywords: sol-gel method, silica coatings, TEOS, DDS, FTIR, SEM, AFM

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Po1.58 EFFECT OF Si AND Ca PRECURSORS ON THE PHASE COMPOSITION AND CRYSTALLINITY OF COATINGS ON METALLIC SUBSTRATE

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Coatings applied to the metallic surfaces of implants may advantageously modify their properties by improving biocompatibility and bioactivity of the material. The sol-gel method enables to obtain homogeneous sols with different chemical composition. Phase composition and crystallinity of coatings obtained on metallic substrates depends on several factors such as the type of substrate, sol composition, temperature and atmosphere of heat treatment.

This study concerns calcium silicate gels and coating obtained on stainless steel substrates or Ti6Al4V alloy in which the Ca/Si molar ratio was 1/3. Various organic silicon precursors and inorganic calcium precursors were used. The coatings were heat treated in air or argon atmosphere.

The resulting materials were examined with XRD PD to determine whether they are amorphous or crystalline; and in the case of crystalline materials, to determine their phase composition. Due to the fact that the samples obtained were very finely crystalline, unambiguous determination of phase composition was not possible. Infrared spectroscopy was used as the main examination method. Changes in the position, shape and width of the bands in IR spectra were analysed, depending on the method of heat treatment (temperature, time, and air or argon atmosphere) and the type of silicon and calcium precursor.

It was shown that silicate sols of the same predetermined target composition may form single- or multi-phase materials in which the predominant phase may be either calcium silicates (such as pseudowollastonite or tobermorite) as well as quartz or cristobalite. It was demonstrated that the structure and phase composition of gels and coatings depends mainly on the heat treatment atmosphere and the type of precursors used.

The study was financed under project No. 11.11.160.258 at the AGH University of Science and Technology in Krakow, Poland.

Keywords: calcium silicate gels; infrared spectroscopic studies of gels and coatings; phase composition of gels

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Po1.59 SPECTROSCOPIC AND STRUCTURAL PROPERTIES OF 2,2´-DIPYRIDYLAMINE, AND ITS PALLADIUM AND PLATINUM COMPLEXES

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The structural features such as geometric parameters, vibrational frequencies, intensities of the vibrational bands of 2,2´-Dipyridylamine (dpa), and its palladium (Pd(dpa)Cl_2) and platinum (Pt(dpa)Cl_2) complexes were studied by density functional theory (DFT). Theoretical calculations were carried out by using DFT / B3LYP method with 6-311++G(d,p) and LANL2DZ basis sets. All vibrational frequencies assigned in detail with the help of total energy distribution analysis (TED). Optimized bond lengths and bond angles were compared with the experimental X-ray data [1][2][3]. Using K_2PtCl_4 and Na_2PdCl_4, we have synthesized complexes of dpa. Then those complexes were characterized by elemental analysis, FT-IR (mid and far IR) and Raman spectroscopy.

Keywords: 2,2´-Dipyridylamine; platinum and palladium complexes; IR and Ra Spectra

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Po1.60 ORGANICALLY MODIFIED SILICATES DEPOSITED ON NATURAL POROUS SUBSTRATES - THE STRUCTURE AND MICROSTRUCTURE STUDIES

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Organically modified silicates deposited on porous substrate by an infiltration method caused the formation of a layer of good hydrophobic properties on the surface and through the upper part of porous samplel. Thus the ormosils find their applications as impregnants used for protection against the moisture in the preservation of historical monuments, in buildings and facilities. This hydrophobicity of organo-modified silica is connected with the presence of surface methyl groups in obtained coatings.

Four different suspensions were applied for the infiltration of porous mineral materials as limestone and common brick. Two of them: SILOXAN W290 and SARSIL®H-14/2 are commercially available while another two solutions were prepared with dimethyldiethoksysilane (DDS) and N-butanol with the modifying addition of an aluminium sec-butoxide. All samples were infiltrated under the same conditions and investigated by FTIR spectroscopy, XRD diffraction and SEM microscopy together with EDX analysis. The water contact angle was also measured as the parameter characterizing the hydrophobicity of speciments with coatings obtained after the infiltration. The speciments of limestone and brick without the infiltration process were also investigated as control samples.

The presence of methyl groups responsible for the hydrophobicity of samples is confirmed by IR spectra measured for the infiltrated samples and their comparison with the spectra obtained for non-infiltrated ones. SEM images show changes in morphology of samples after the infiltration while EDX microanalysis points out the local changes in a chemical composition of analyzed points. The values of water contact angle measured for the infiltrated samples are distinctly higher then those obtained for the control samples.

Acknowledgment
The financial support of AGH University of Science and Technology, grant no 11.11.160.258

Keywords: dimethyldiethoksysilane (DDS); coatings; hydrophobicity, limestone, brick

Po1.61 SELF-ASSOCIATION OF GUANOSINE-MONOPHOSPHATES A RAMAN STUDY

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Increasing recognition of biological [1] and nanotechnological [2] importance of guanine quadruplexes stimulated intensive research on their structural and conformational properties. In addition to structurally explicit methods providing ultimate structural information at atomic level, e.g. NMR spectroscopy and x-ray diffraction, a great part of our current knowledge comes from various methods of optical spectroscopy, particularly UV-vis absorption, chiroptical methods (CD and VCD) and fluorescence. Raman spectroscopy, a practical and well-established method for structural and conformational studies of nucleic acid in general [3], may contribute considerably to G-quadruplex field if exploited more frequently and systematically, and could be especially useful at least in the case of structures and processes where quadruplex concentration or physical state of the sample play a crucial role [4]. Raman spectroscopy can be applied throughout a wide range of DNA concentrations and various states (solutions, gels, crystals), therefore it can serve as a bridge between experimental methods restricted to low- and high-DNA concentrations, furthermore providing a benefit of more structurally rich information than other commonly used spectroscopic methods.

Since various guanosine-monophosphates (GMPs) at elevated concentrations can also form highly ordered supramolecular structures consisting of stacked guanine quartets [2], they are often employed as model systems for G-quadruplexes formed from oligonucleotides. Here, self-association of GMPs has been systematically studied by Raman spectroscopy to refine interpretational basis needed for Raman studies of more complex G-quadruplexes [3]. In order to critically review validity of quadruplex Raman markers indicative of hydrogen bonding within G-quartets, effect of ionic radius of a stabilizing cation and stacking interactions of G-quartets reported previously [3], Raman spectra of various GMPs in aqueous solutions throughout a wide range of GMPs concentrations as well as in solid states have been studied in the presence of Li^+, Na^+ and K^+ cations. A particular attention was paid to distinguish effects related to the formation of G-quartets and their self-associates from those connected with a formation of monomer self-associates. Results have been critically confronted with previous Raman [5] and NMR structural studies [6].

Keywords: G-quadruplex; G-quartet; Guanosine-monophosphates; Raman spectroscopy; Raman markers

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Po1.62 COMPARATIVE STUDY OF RAMAN ENHANCEMENT EFFECT FOR URIC ACID ON VARIOUS SERS SUBSTRATES

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Uric acid is an end product of purine metabolism. Its elevated or decreased concentration in various bodily fluids (blood, urine, tears) can suggest disorders such as gout, preeclamsia or cardiovascular disease [1]. Uric acid analysis in urine is performed in order to evaluate kidney function. Various methods have been used for the analysis: enzymatic method, spectrophotometry, liquid chromatography, etc. [1]. However, these methods are not sensitive enough when small concentrations of the sample molecules need to be detected.

Surface-enhanced Raman scattering (SERS) spectroscopy has been increasingly proposed as a method of choice for disease diagnosis and prevention [2]. Advantages of SERS over conventional Raman spectroscopy includes significantly increased signal which allows detection of trace amounts of substances in the sample and fluorescence quenching. On the other hand, if SERS spectroscopy is going to be used in routine analysis several problems, such as reproducibility of the enhancement factor, should be considered. In addition, suitable substrates should be selected according to the sample and available experimental conditions. The aim of this work is to test the suitability of various SERS substrates for uric acid analysis by means of Raman spectroscopy.

Several colloidal solutions of Ag spheres, Ag prisms, Au rods and Au branched nanoparticles of different sizes and concentrations were prepared. In order to form a substrate, a drop of the colloid was placed on a microscope glass slide covered with Al foil and dried. In addition, substrates of Au nanodendrites on graphite plates were produced. Finally, commercially available "Randa" Ag substrates (Integrated Optics) were used for the analysis. SERS spectra were recorded with FT-Raman spectrometer equipped with Nd:YAG excitation laser (1064 nm). SERS spectra presented in Fig.1 allows deducing that even low concentrations (10^{-5}-10^{-7} M) of uric acid can be detected on substrates produced from concentrated Ag prism colloid. Similar results were obtained with the commercial substrates. However, neither Au colloid nor Au nanodendrite substrates were SERS active. This could be due to adsorption properties of uric acid molecules; however, further analysis of this phenomenon is necessary.

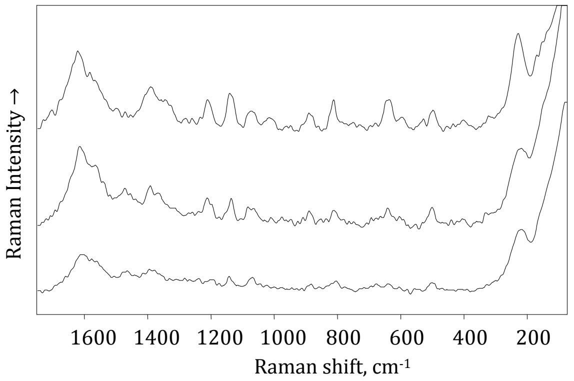

Fig.1 SERS spectra of uric acid obtained on substrates produced from concentrated Ag nanoprism colloid: top – 10^{-3} M, middle – 10^{-5} M, bottom – 10^{-7} M.

Keywords: SERS; uric acid; SERS substrate

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Po1.63 INFRARED SPECTROSCOPIC ANALYSIS OF URINARY SEDIMENTS: TRANSMISSION VS. ATR

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Urinary stone disease, or urolithiasis, is one of the most prevalent and, due to lack of effective individual-based preventive treatment, highly recurrent urinary tract disorder. Usually late discovery of the stones leads to painful symptoms, invasive and costly treatment which significantly affects quality of life [1]. In the oversaturated urine, the growth of urinary stones is initiated by nucleation and aggregation of crystals of different chemical compositions. Monitoring and chemical analysis of these crystals in the high risk patients would allow diagnosing urolithiasis in its early stages. Subsequently, preventive measures could be taken to inhibit further formation of the stone.

In our previous study we demonstrate that Fourier transform infrared microspectroscopy (μFT-IR) in transmission mode is a reliable method for chemical analysis of urinary sediments regardless of their state [2]. In addition, correlation between chemical composition of the sediments and urinary stone of the same patient has been confirmed. The disadvantage of the method is that the required thickness of the samples cannot be easily obtained and bands in the IR absorption spectra are saturated. Furthermore, future applications of μFT-IR in the routine analysis could be complicated as complex experimental equipments are required. The use of attenuated total reflection (ATR) method would allow overcoming both of the disadvantages; therefore, the aim of the study is to compare the results of these two techniques.

It can be seen in Fig.1a that IR absorption spectral bands of urinary struvite crystal are saturated and only few characteristic spectral bands can be distinguished. Meanwhile, spectral bands in the ATR spectrum of the same crystal (Fig.1b) could be successfully assigned to molecular vibrations of struvite. In the cases of thin sediment samples, the absorption spectra measured in transmition mode and the ATR spectra are comparable. Similar results were obtained for urinary sediments of various compositions. Taking into account simplicity and accessibility of the ATR technique it could be a method of choice for the chemical analysis of urinary sediments.

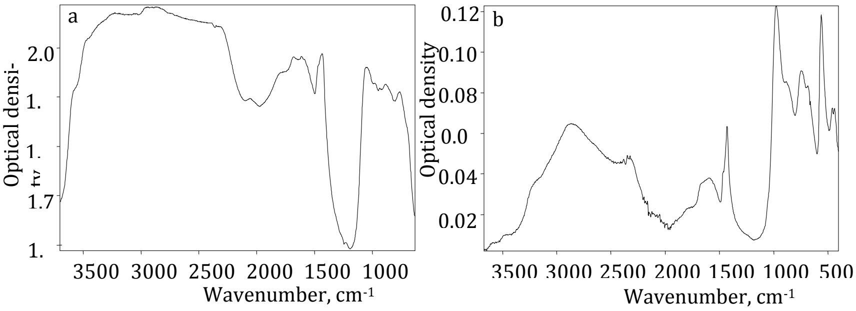

Fig.1 IR aborption (a) and ATR (b) spectra of urinary struvite crystal.

Keywords: μFT-IR; ATR; urinary sediments

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Po1.64 FREQUENCY COMB REFERENCED NARROW-LINEWIDTH MID-IR LASER SPECTROMETER FOR HIGH-RESOLUTION MOLECULAR SPECTROSCOPY

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We demonstrate a novel source for high-resolution molecular spectroscopy, a continuous-wave (cw) quantum cascade laser (QCL) stabilized to a ULE cavity and referenced to an optical frequency comb. The MIR laser wave (5.4 µm) is upconverted to 1.2 µm by sum-frequency generation in an orientation-patterned GaAs crystal [1] with the output of a standard high-power cw 1.5 µm fiber laser and subsequent amplification of the sum-frequency wave. The 1.5 µm laser is phase-locked to a standard Er:fiber frequency comb. The upconverted light at 1.2 µm is stabilized to a high-finesse ULE cavity by feed-back control of the QCL's frequency.

Both the 1.5 µm and the 1.2 µm frequencies are simultaneously measured, and thus the frequency of the QCL can be calculated. Its frequency can be tuned by frequency tuning of the 1.5 µm wave.

Stabilization of the QCL to the ULE cavity results in sub-kHz linewidth and frequency determination with sub-kHz inaccuracy relative to an atomic frequency reference, in this case a hydrogen maser long-term-stabilized via GPS

Keywords: QCL; Frequency comb; ULE; narrow-linewidth

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Po1.65 THE EFFECT OF FLUORINE SUBSTITUTION IN CHIRAL RECOGNITION: AN ***R2PI AND IR/R2PI*** SPECTROSCOPIC STUDY.

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Chirality is an essential element of life either at the molecular and at the supramolecular level. The transmission of chiral information, the recognition properties as well as the functionality of biomolecules rely substantially on non-covalent intra and intermolecular interactions and their study is of fundamental interest and deep impact in chemistry, biology, pharmacology, material science and even astrophysics. In combination with stronger non covalent interactions with high directionality, such as hydrogen bonding or metal coordination, *π*□*π* stacking forces and very weak XH□π (X = O, N and C) or CH□X interactions may also play an essential role in chiral discrimination processes.[1] Fluorine substitution[2] can endow novel interactions, such as CH□F or OH□F interactions, which still remain largely uncharacterized in molecular complexes. A large number of therapeutic and diagnostic agents contain strategically placed fluorine atoms which also allow simultaneous modulation of electronic and lipophilic parameters and affect binding affinity and relevant pharmacokinetic properties.

We report results of a comparative study in which we have investigated in detail the role of stereospecific interactions in the presence of fluorine atoms. Specifically, the molecular diastereomeric complexes between R-1-phenyl-1-ethanol and its fluorinated analogues with R and S-butan-2-ol, isolated in the gas phase under molecular beam conditions have been investigated by mass-selective resonant two-photon ionization (R2PI) and infrared depleted R2PI (IR-R2PI). The comparison of the systems allowed to highlight the significance of specific intermolecular interactions in the chiral discrimination process. The interpretation of the results is based on theoretical predictions mainly at the D-B3LYP/6-31++G** level of theory.

Our combined experimental/computational approach gives answers that help in understanding, at a molecular level, the influence of specific weak non covalent interactions in relation to the molecular and chiral recognition processes in these model systems.

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Po1.66 RAMAN SPECTROSCOPY AS A METHOD FOR THE DIFFERENTIATION OF INKJET INKS

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Raman spectroscopy was chosen as a method for the discrimination of inkjet inks in the field of forensic document examination as it is a non-destructive and rapid technique. It additionally has the advantage that pigmented inkjet inks, which nowadays are used by most printer manufacturers and which can not be analyzed by the established standard chromatographic methods, may be examined. The study involved the inspection of pure colored inks on different substrates as well as in form of color overlaying print-outs. Furthermore it was explored if the application of a gold colloid would yield a positive SERS effect. This poster will show the development of a customized method to be used as a basis for application in forensic examination of inkjet printed documents.

Keywords: Raman Spectroscopy; SERS; inkjet inks

Acknowledgements

The study was conducted at the Forensic Science Institute (Section Document Examination) of the State Criminal Investigation Office NRW (Landeskriminalamt Nordrhein-Westfalen).

Po1.67 NEW INSIGHTS INTO UV AND IR SPECTROSCOPY OF HNCS, CH_3NCS AND CH_3SCN – A JOINT CRYOGENIC, GAS PHASE AND COMPUTATIONAL STUDY

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We are interested in the spectroscopy, photochemistry, and astrochemistry of simple thiocyanates, R-NCS. HNCS [1] and HSCN [2] molecules have already been detected in the interstellar medium, along with the similar methylated thiocyanates: CH_3NC [3] and CH_3CN [4].

In this communication we report on the measured absolute IR and UV absorption intensities for HNCS, CH_3NCS, and CH_3SCN, together with the assignment of vibrational combination and overtone bands.

The cryogenic matrix isolation technique was used in the majority of presented experiments, as it offers a convenient environment for photochemical studies leading to unstable thiocyanate-related isomeric, radical or ionic species.

Keywords: UV and IR spectroscopy; thiocyanates; cryogenic matrix isolation

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Po1.68 THEORETICAL AND EXPERIMENTAL APPROACHES FOR IDENTIFICATION OF IMIDAZO[1,2-A]PYRIDINE-6-CARBOXALDEHYDE

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Molecular structures of imidazo[1,2-a]pyridine-6-carboxaldehyde (IM(1,2-a)P-6-C) and possible stable forms were studied theoretically, and experimentally using FT–IR. FT–IR spectra was recorded in the region of 4000–400cm^{-1}. The optimized geometric parameters, conformational analysis, normal mode frequencies and corresponding vibrational assignments of IM(1,2-a)P-6-C ($C_8H_6N_2O$) have been examined by means of B3LYP hybrid density functional theory (DFT) method together with 6–31++G(d,p) basis set. All vibrational frequencies were assigned in detail with the help of total energy distribution (TEDs). The experimental wavenumbers were compared with the scaled vibrational frequencies determined by DFT/B3LYP method. The results showed that the B3LYP/6–311++G(d,p) method predicts vibrational frequencies and the structural parameters effectively. The total electron density and molecular electrostatic potential surfaces of the molecule were constructed by using B3LYP/6–311++G(d,p) method to display electrostatic potential (electron + nuclei) distribution. The electronic properties HOMO and LUMO energies were measured. The lower energy band was assigned to the HOMO→LUMO transition. Natural bond orbital analysis of IM(1,2-a)P-6-C has been performed to indicate the presence of intramolecular charge transfer. Furthermore, solvent effects on IM(1,2-a)P-6-C molecule in different solvents were studied theoretically at the DFT/B3LYP level in combination with the conductor polarizable continuum model (CPCM) for the first time.

Keywords: Imidazo[1,2-a]pyridine-6-carboxaldehyde, Vibrational spectra, MESP, DFT, Solvent effect

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Po1.69 VIBRATIONAL SPECTRAL ANALYSIS AND THEORETICAL INVESTIGATION ON THE MOLECULAR STRUCTURE OF 1 – BROMO 2,4,6 – TRICYCLOHEXYL BENZENE

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The crystal structure of the title molecule was done by Joel T. Mague et. al. [1]. 1–bromo 2,4,6–tricyclohexyl benzene molecule , $C_{24}H_{35}Br$ (Figure 1), packs efficiently in the crystal structure with no solvent-accessible voids and several intermolecular H⋯H contacts approximating the sum of the van der Waals radii. The molecule is quite crowded. All cyclohexyl rings adopt chair conformations with the 'seat' of the chair inclined at approximately 57–81° to the mean plane of the benzene ring [1].

In this study, conformational search of the 1–bromo 2,4,6–tricyclohexyl benzene molecule has been performed. The FT – IR spectrum of this molecule was recorded in the region 4000–400 cm^{-1}. The FT- Raman spectrum was also recorded in the region 3500–50 cm^{-1}. The molecular geometry and vibrational frequencies of title molecule in the ground state have been calculated by using Density functional method (B3LYP) with LanL2MB, LanL2DZ and SDD basis sets. All calculations were performed by using Gaussian 09 and Spartan 12 program package, invoking gradient geometry optimization [2-4]. The total energy distributions TED among the symmetry coordinates of the normal modes have computed for the low energy structure of the molecule. The whole of vibrational assignments have provided on the basis of the calculated TED values.

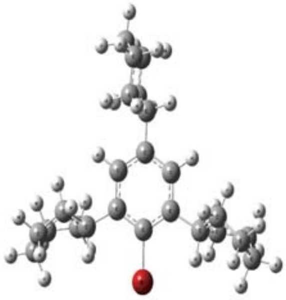

Fig.1 Structure of 1–bromo 2,4,6–tricyclohexyl benzene

Keywords: 1–bromo 2,4,6–tricyclohexyl benzene, Vibrational spectra, DFT, FT-IR, FT-Raman

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Po1.70 EXPERIMENTAL AND DFT METHODS FOR VIBRATIONAL SPECTROSCOPIC STUDIES ON 2-(5-PHENYL-2-OXAZOLYL) BENZOIC ACID

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Experimental and theoretical carried out vibrational spectra and electronic properties of 2-(5-phenyl-2-oxazolyl) benzoic acid. The FT-IR (4000–400 cm^{-1}), DXR Raman Microscope (3500–50 cm^{-1}) and FT-NMR spectra have been recorded and analyzed which measured at room temperature by using TMS on a **Bruker Ultrashield** FT-NMR Spectrometer. The molecular geometry, harmonic vibrational frequencies, chemical shifts, HOMO, LUMO energies and molecular electrostatic potential map of 2-(5-phenyl-2-oxazolyl)benzoic acid have been calculated by using DFT method we have carried out detailed theoretical and experimental investigations on the molecular structure and vibrational spectra of 2-(5-phenyl-2-oxazolyl)benzoic acid completely with 6-311++G(d,p), cc-pVDZ and cc-pVTZ basis sets. Total energy distributions of vibrational modes are calculated by using SQM method.

Keywords: 2-(5-phenyl-2-oxazolyl)benzoic acid, DFT, TED, SQM method, FT-IR, DXR Raman Microscope, and NMR spectra.

References

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Po1.71 APPLICATION OF IR AND RAMAN SPECTRA IN THE STUDIES OF ZEOLITES FROM 5-1 STRUCTURAL GROUP

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This work presents results of IR (MIR and FIR range) and Raman spectroscopic studies of zeolites belonging to 5-1 structural group after heavy metal cations (Ag^+, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} and Cr^{3+}) immobilization.

Changes in intensities and positions of the bands corresponding to the characteristic ring and Me-O vibrations have been observed. These rings occur in pseudomolecular complexes (built of [SiO_4] and [AlO_4] tetrahedra) which constitute the secondary building units (SBU) and form zeolite framework. Based on the results of DFT method calculations, normal vibrations of the 5-1 unit (Fig.1) terminated by different cations (Na^+, K^+) have been visualized. Obtained results have been applied for interpretation of experimental spectra of selected zeolites. The most significant changes have been determined in the region of pseudolattice vibrations (800–500 cm^{-1}). On the other hand, an introduction of heavy metal cations into the structure of zeolites has caused the considerable modification of bands due to Me-O vibrations in FIR spectra (below 400 cm^{-1}). In both cases systematic changes connected with the type of cation (its chemical character) have been revealed.

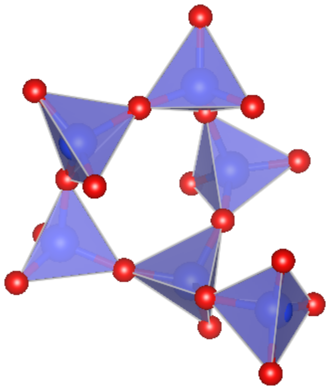

Fig.1 Cluster for calculation.

It was proven those cations' sorption causes changes in the experimental spectra of zeolites. Sorption has been conducted on monoionic forms of mordenite (MOR) and ferrierite (FER). Based on results of atomic absorption spectroscopy (AAS), the proportion of ion-exchange to chemisorption in the process and the effective cation exchange capacity of the individual samples have been estimated. Results of AAS studies have been compared with those obtained by vibrational (IR and Raman) spectroscopy. Changes in intensities and positions of the bands corresponding to the characteristic ring vibrations, due to the immobilization of heavy metal ions, have been observed.

Keywords: infrared spectra; 5-1 structural units; zeolites; sorption; heavy metals; DFT calculations

Po1.72 HYDOTHERMAL SYNTHESIS OF ZEOLITE A FROM EXPANDED PERLITE WASTE

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Zeolites are aluminosilicates characterized by unique physical and chemical properties, which show a very wide range of applications [1]. Zeolites are produced in a large scale since a mid of recent century. The natural or waste aluminosilicates (kaolin, volcanic tuffs, perlite, fly ashes, etc.) are often applied as starting reagents. However, due to the variable composition of raw materials, and thus formed products, the syntheses of zeolites from waste materials are difficult to control and describe. Infrared spectroscopy is a method widely used in the investigation of aluminosilicates and can be successfully used for the analysis of the zeolites [2, 3].

The results of the synthesis of zeolite A from expanded perlite waste using hydrothermal method under autogenous pressure were presented. The resulting materials were analyzed regarding phase composition. In particular, the structures of materials were examined using FT-IR spectroscopy in the mid and far infrared range. This method is particularly useful for following the progress in a crystallization process. The results were compared to the XRD measurements, as well as SEM observations.

The effects of synthesis temperature and time, as well as Si/Al and Na/Si ratios on the obtained products were determined. It has been found that by using a sufficiently high concentration of NaOH is possible to efficiently zeolite synthesis at temperatures above 50°C. The presence of crystalline phases (long-range order) was confirmed by the measurement of spectra in the far infrared. The type of resulting zeolite structure was identified based on XRD measurements and confirmed by analysis of the mid infrared spectra. Pseudolattice range, i.e. 800–400 cm^{-1}, was detailed analyzed. In this range, there are bands associated with the ring vibrations, which are characteristic for secondary building units (SBU) occurred in zeolite structure [2–4]. Depending on the composition of the reaction system, temperature and time, zeolite X, A, Na-P1 and hydroxysodalite have been identified as synthesis products.

Financial support this work was provided by The National Centre for Research and Development under grant no. PBS1 177 206.

Keywords: zeolites; sorption; hydrothermal synthesis

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Po1.73 SPECIATION OF CHROMIUM(III) IN MODERATELY ACIDIC SOLUTIONS

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The existing Cr(III)-containing species were thoroughly investigated by Marty et al. by mainly ion exchange chromatographic techniques in the pH range of 2–4.5 [1],[2]. Several oligomer species (from dimer up to hexamer ones) were reported forming during weeks. Later, this speciation was used as an analogy of polymerization to explain some behavior of Cr(III) in highly alkaline solutions [3]. Our recent UV-Vis study confirmed that only one Cr(III)-containing species is necessary to characterize the alkaline solutions so it was plausible to reinvestigate the equilibrium of Cr(III) solutions in the above defined pH range.

Several experimental series were carried out by varying the total concentrations of Cr(III) and hydroxide added. The slow reactions were followed up to two months by X-ray absorption and UV-Vis spectroscopy, as well as, *p*H-metric measurements. Fig. 1 represents a typical *p*H-metric study to illustrate the changes. The following conclusions can be derived:

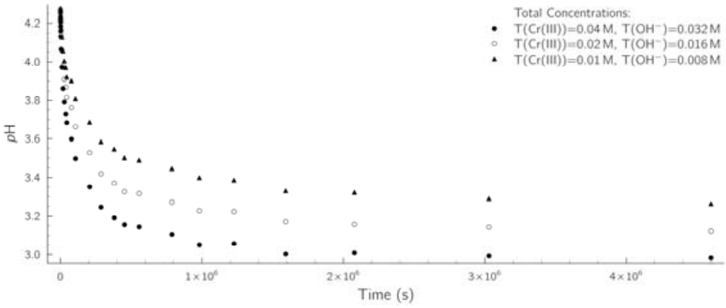

Fig.1 Typical pH-metric kinetic curves with varying total concentrations.

- The EXAFS measurements confirmed that there are not several chemically different environments around Cr(III). Only a slight change can be noticed in the spectra of the one month old, one week old, one day old and freshly prepared solutions.
- The matrix rank analysis of UV-Vis measurements proved that up to three linearly independent Cr(III)-species are enough to describe the absorbances.
- The kinetic curves of the *p*H-metric study strongly suggest that only dimer formation happens and the formation of more complex species should not be supposed.

The poster presentation details the measurements carried out and the consequences of their evaluation.

Keywords: chromium(III); EXAFS; formation of Cr(III)-dimer

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Po1.74 MOLECULAR STRUCTURE, SPECTROSCOPIC AND DFT COMPUTATIONAL STUDIES ON 4,5-BIS(TERT-BUTYLSULFANYL)PHTHALONITRILE

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The molecular geometry, vibrational frequencies and gauge including atomic orbital (GIAO) ^{1}H and ^{13}C-NMR chemical shift values of 4,5-bis(tert-butylsulfanyl)phthalonitrile (Fig. 1) in the ground state have been calculated using the density functional method (B3LYP) with 6-311++G(d,p) basis set. The calculated results show that the optimized geometry can well reproduce the crystal structure, and the theoretical vibrational frequencies and chemical shift values show good agreement with experimental values. To investigate the NLO properties of the title compound, the electric dipole moment (μ), the polarizability (α) and the first hyperpolarizability (β) were calculated using the density functional B3LYP method with the 6-311++G(d,p) basis set. According to results, the title compound exhibits nonzero (β) value revealing second order NLO behavior. To predict reactive sites for electrophilic or nucleophilic attack for the investigated molecule, the molecular electrostatic potential (MEP) at the B3LYP/6-311++G(d,p) basis optimized geometry was also calculated.

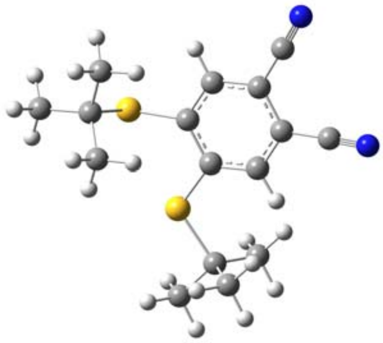

Fig.1. *The molecular structure of 4,5-bis(tert-butylsulfanyl)phthalonitrile*

Keywords: Phthalonitrile; DFT; FTIR; NMR; NLO; MEP.

Acknowledgements
This study was supported financially by the Research Centre of Amasya University (Project No: FMB-BAP 13-045).

Po 1.75 CHLOROPHYLL FLUORESCENCE QUENCHING INDUCED BY SILVER NANOPARTICLES

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Nanotechnology is an emerging field in science and technology, with significant impacts on the economy, society, and environment. Nowadays, nanoscale materials are used in different areas such as electronics, biomedical, pharmaceutical, cosmetics, energy, environment, products and materials applications. Silver nanoparticles (AgNPs) are among the most widely produced and used nanomaterial due to their antimicrobial and antibacterial properties, allowing a wide range of commercial applications. The production, use and disposal of Ag NPs will inevitably lead to their release to the atmosphere, water and soil and there are still several uncertainties about the effects and impacts of these materials into the environment.

The increasing use of AgNPs should inevitably lead to the release and accumulation of these NPs into the environment, resulting in adverse effects on plants, animals and humans. Chlorophyll fluorescence (ChlF) has been proposed as a non-destructive and accurate tool for detecting the impacts of environmental stress on plants. Little is known about the photophysical behavior of plants when exposed to a metal NPs-containing environment.

In the present study, we evaluated the interaction between Chlorophyll and AgNPs by monitoring the ChlF. Our results revealed that ChlF is quenched in the presence of AgNPs, as a result of the static and dynamic quenching processes. Additionally, a ChlF quenching was observed for soybean plants submitted to the AgNPs treatment. The results also suggest that AgNPs were able to translocate and accumulate in the soybean plants after seed inoculation.

Keywords: Chlorophyll; Fluorescence; Silver nanoparticle

Po1.76 TERAHERTZ TIME-DOMAIN SPECTROSCOPIC STUDY ON FORM II PVDF AND PVDF-TRFE

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We investigated the complex dielectric constants of form II polyvinylidene fluoride (PVDF) and polyvinylidene fluoride-trifluoroethylene copolymer (PVDF-TrFE) by a terahertz time-domain spectroscopy (THz-TDS) with transmission configuration in a frequency range of 0.2 – 4.5 THz and a temperature range of 6 – 300 K.

PVDF has a repeat unit of -CH_2-CF_2- and shows four structural phases. The form II PVDF is monoclinic with the space group $P2_1/c$ and has a chain conformation of trans-gauche-trans-gauche' [1-3]. On the other hand, PVDF-TrFE has a unit of -CHF-CF_2- and shows ferroelectric phase at room temperature with the space group *Cm2m* [4].

Figure 1 shows the imaginary part of the complex dielectric constants of PVDF and PVDF-TrFE at room temperature. In the PVDF spectrum, two clear phonon peaks are observed at 1.6 and 3.0 THz, which have been assigned as an intermolecular rotatory vibration mode and an intramolecular vibration mode, respectively [3]. In addition, for both materials, Debye like broad absorption bands which have a peak around 1.5 THz were observed.

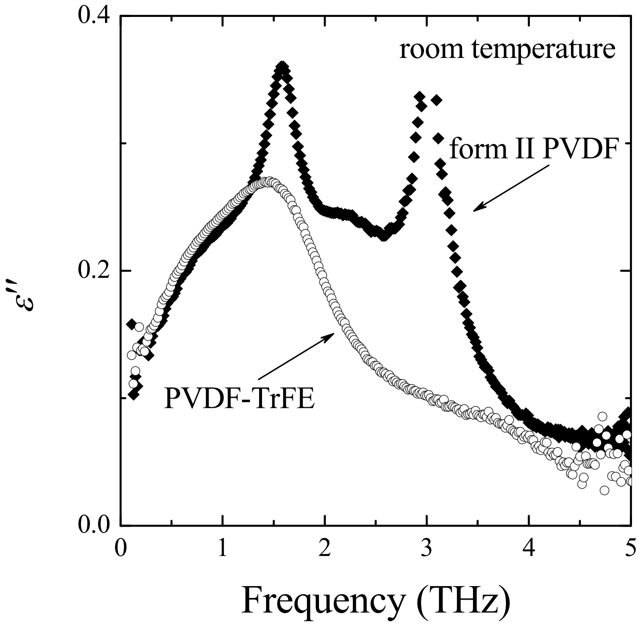

Fig. 1. Imaginary parts of the dielectric constants of form II PVDF and PVDF-TrFE at room temperature.

Keywords: THz-TDS; PVDF; PVDF-TrFE

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1.77 POLYMORPHIC TRANSITIONS AND IR SPECTROSCOPY OF SEMICRYSTALLINE POLYMERS FROM PERIODIC FIRST-PRINCIPLES CALCULATIONS: PBT AND PTT

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The development of new nanostructured polymer systems and their applications in many fields require a detailed understanding of the structural features at the nanoscale and their influence on the physicochemical properties. Vibrational spectroscopy has been widely used to this aim. However, due to the lack of reliable softwares, the analysis of the IR spectra of semicrystalline polymers for practical and analytical purposes were mainly based on experimental works. Due to the complexity of the intra/intermolecular effects involved in polymorphism phenomena, different and contrasting interpretations can be found in the past literature. Only in the last years, high level quantum chemical tools, that allow to study the spectroscopic properties of crystalline polymers, became available: their potentialities still need to be fully explored [1-4]. Using the CRYSTAL09 code [5], we performed a Density Functional Theory investigation of two polyesters, poly(trimethylene terephthalate) (PTT) [6] and poly(butylene terephthalate) (PBT) [7], to clarify the ambiguities in the interpretation of their crystalline structure and IR spectra.

In particular, the conformation and solid state structure of the two α and β polymorphs of PBT have been studied: focusing on the debated β form, induced by mechanical deformation, the setting on of an all-trans conformation have been predicted; the comparison between the simulated IR spectra of the different polymorphs and the available experimental spectra confirm this result. The transition from the α to the β form and the evolution of the intramolecular structure has been also simulated, showing a transition from the GTG' conformation found for the α form to the TTT conformation of the strained β form. In the case of PTT, the crystal structure and the IR spectrum have been investigated and the results showed a very good agreement with the experimental data taken from the literature. Furthermore, spectroscopic markers of crystallinity or regularity can be proposed.

These works demonstrates that state of the art computational methods can provide an unambiguous description of the structural and vibrational properties of crystalline polymers on the basis of the peculiar intra and intermolecular interactions occurring in different macromolecular materials.

Keywords: IR spectroscopy; polyester; ab initio calculations

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Po1.78 BROADBAND TERAHERTZ TIME-DOMAIN SPECTROSCOPY OF AQUEOUS SUGAR SOLUTIONS

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The complex dielectric constants of aqueous sugar solutions, glucose, maltose, fructose and sucrose were investigated by a broadband terahertz time-domain spectroscopy (THz-TDS) with transmission configuration in a frequency range of 0.5 – 5 THz at room temperature.

We used an ultrafast THz-TDS which employs a measurement technique of high-speed asynchronous optical sampling (AOS) method [1]. The AOS technique uses two femtosecond lasers in substitution for mechanical delay stage, and the repetition rates of those lasers are slightly modulated. This technique drastically decreases measurement time down to about 10 milliseconds for one shot of THz pulse. In addition, we can use widely tunable monochromatic Cherenkov phase-matched THz wave generator, which was developed using nonlinear optic crystals of ferroelectric MgO doped $LiNbO_3$ [2].
Figure 1 shows the absorbance spectra of aqueous glucose solutions whose concentrations are 0, 10, 30, 50 %. The absorbance increases toward higher frequency showing a kink around about 2 THz, and decreases with higher glucose concentration. Using the absorbance and phase shift spectra, we successfully extracted the complex dielectric constants.

Keywords: THz-TDS; aqueous sugar solution

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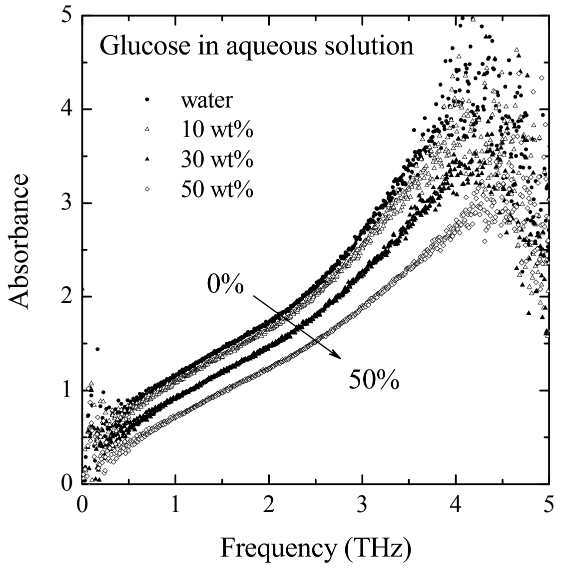

Fig. 1. THz absorbance spectra of aqueous glucose solutions with concentration 0, 10, 30, 50 % at room temperature.

Po1.79 SpIM 2.4 GEOMETRY CHANGE OF 5-CYANOINDOLE UPON ELECTRONIC S_1←S_0 EXCITATION

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The geometry of a molecule is defined by ist nuclear and electronic framework. This framework in different electronic states of the molecule can be investigated by different techniques. One method to determine the electronic structure of electronically excited states is the analysis of fluorescence spectra via the Franck-Condon principle. The fluorescence intensities of Franck-Condon allowed vibronic transitions depend on the geometry change during the underlying electronic transition.[1]

In proteins, the fluorescence properties of the tryptophan moieties are used for the investigation of the protein structure.[2] These spectra are influenced by the chemical surrounding of the indole chromophore in each tryptophan unit. The energetic order of its two lowest lying electronically excited singlet states and the S_1-S_0 gap depend on the polarity of the the surrounding and can also be influenced by the introduction of different substituents.

One of those indole derivatives is 5-cyanoindole, which has an electron withdrawing substituent. The geometry change of 5-cyanoindole between the electronic ground state and first electronically excited singlet state has been determined with a combined Franck-Condon analysis using the fluorescence intensities from single vibronic level fluorescence spectroscopy and the changes of rotational constants from high resolution laser induced fluorescence spectroscopy.[3,4]

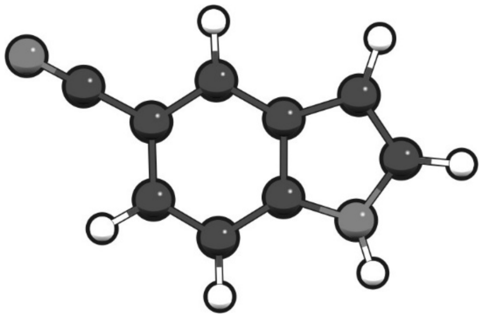

Fig. 2: Structure of 5-cyanoindole

The Franck-Condon analysis was compared to the results from ab initio calculations and points to an excited state structure which is L_a-like in the nomenclature of Platt. Additionally, the effects of mode selective coupling of vibronic bands were observed in the fluorescence emission spectra.

Keywords: 5-Cyanoindole, Franck-Condon, Rotational Constants, Dispersed Fluorescence, High Resolution Laser Induced Fluorescence, Geometry, Electronic Spectroscopy

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Po1.80 CHARACTERISTICS OF PAINTING TECHNIQUES USED FOR CERAMICS IN PAKISTAN DURING THE PERIODS 4TH TO 2ND MILLENIUM B.C.

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This study is part of the archaeological ANR-DFG project "ROXIANA" which seeks to use archaeometric studies of pottery and metal to explore the interrelations between the Indus Basin (Pakistan) and Central Asia during the protohistoric period. In the project, specific questions are addressed on the characteristics and evolution of the painting techniques (raw materials, fabrics and painting processes) used by the potters from these two regions since the beginning of the 4th millennium BCE until the end of the 2nd millennium BCE.

Continuing work which focussed on polychrome painted pottery manufactured in Pakistani Balochistan, a region known to be an important center of pyrotechnological craft innovation during the Chalcolithic and Bronze Age periods (5th-3rd millennia BCE), the present project focuses on extending the study to the monochrome painted pottery and to enlarge the chrono-geographical window. Besides characterizing the composition of the paintings (of various colors: black, brown, red, white and yellow), the issue is also to define if specific technologies were displayed in distinctive craft areas and if technical changes can be observed in time[1].

Focusing on samples from sites (Mehrgarh, Nausharo and Pirak) in the Kachi Bolan and Makran regions, results from studies using a combination of experimental methods will be presented: PIXE analyses with the AGLAE 2MV ion accelerator (giving the elementary chemical composition of the paints), optical microscopy and SEM -EDX (for stratigraphic observations of the paint layers), X-ray diffraction (XRD)(to identify the mineral phases) and Raman spectroscopy (giving the molecular composition of the paints).

Results show the presence of enstatite, quartz and traces of cristobalite in the white paints, an assemblage typical of steatite fired at around 950°C. However, the dark brown to black paintings are much more diversified and complex. Four different black pigments have been identified, the first of which corresponds to an Fe-enriched material with very low amounts of Mn. While a second group is characterized by a Mn-Fe mixture with variable proportions of these two elements, the third type contains only very high amounts of carbon. A fourth group with only hematite was identified. Studies of the complex phases has made it possible to identify several spinel structures[2]. These minerals neoformed during the baking process are all of variable structural formulas, and hence, can help determine the baking procedures used.

Pakistan painted pottery; Raman spectroscopy; PIXE analyses

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Postersession II

Po2.1 DICHROISM OF POLYMER FOILS CONTAINING DYES MOLECULES

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Poly (vinyl) alcohol foils containing dye molecules become dichroic in the stretching process [1], [2]. The dichroic ratio emphasizes the process of the polymer chains alignment in the stretching process [2],[3]. Some electro-optical properties of the long dye molecules can be obtained by the study of the dichroism induced in the stretched foils. As dyes were used Congo red and some azo-benzene derivatives.

The degree of order of the spectrally molecules in polymer foils was established on the basis of the dichroic ratio established using linearly polarized radiations with electric field intensity acting parallel and perpendicular on the foil stretching direction [4].

The characteristics of the electronic transition responsible for the visible band appearance were also established.

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Keywords: Polymer foils; dichroic ratio; degree of order of polymeric chains

Po2.2 INHIBITION OF BIOFILM DEVELOPMENT OF PATHOGENS BY USING GREEN BIOSYNTHESIS OF SILVER NANOPARTICLES FROM *CURCUMA LONGA L.*

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Synthesis of metal nanoparticles is developing area of research. Metallic nanoparticles have used different area such as chemistry, physicist and biology. Most scientist used metallic nanoparticles for the development of a new-generation of nanodevices. Mostly plant's extracts have antifungal, antibacterial and antitumoral activity. These proporties, commonly be used in medical area. In recent years, *Curcuma longa* attract attention with antifungal and antibacterial activity extracts[1].

In this study, silver nanoparticles were biosynthesized from 1mM aqueous silver nitrate solution and *Curcuma longa* extracts, which acted as a reductant and stabilizer simultaneously. Characterizations and analization of nanoparticles were carried out by different methods, which included ultraviolet-visible spectroscopy, Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy. For biofilm development assay, *Pseudomonas aeruginosa PA01, Staphylococcus aureus, E.coli, Proteus mirabilis, ESBL(+) Klebsiella pneumoniae* bacteria and extract were inoculated and incubated at Tryptic Soy Broth(TSB) medium at 37 ^{0}C for 24h.Overnight culture were diluted optical density OD600 nm Mc Farland 0,5. Then, biofilm assay was performed in 24 well polystrene plate.These plate incubated at 37 ^{0}C for 48h. After incubation, plates were washed three times in sterile 1xPBS and dried 65 ^{0}C.Crystal violet was used for staining. Measuring of biofilm inhibition was performed at 595λ nm.

As a results, The ultraviolet-visible spectrum of the silver nanoparticles showed an absorption peak at around 415 nm. To use a combination of FTIR/SEM, in order to analyse biofilm chemistry. Inhibiton of biofilm formation was determinated relatively % 30 -%40.

We suggest that Silver nanoparticle which produces from *Curcuma longa* extract, impress to form biofilm in different *Pseudomonas aeruginosa PA01, Staphylococcus aureus, E.coli, Proteus mirabilis, ESBL(+) Klebsiella pneumoniae* bacteria. These nanoparticles can be used new approach production of silver nanoparticles[2].This study will be the development of value-added products from C. longa for biomedical and nanotechnology-based industries.

Keywords: FT-IR,UV-Visible spectrofotometer, Silver nanoparticles,

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Po2.3 AN UPS/IPS STUDY OF BAND LEVEL ALIGNMENT OF A QUANTUM DOT BASED SENSOR

Ghazal Tofighi [1], Martin Möbius[2], Francisc Haidu[1], Jörg Martin[3], Volodymyr Dzhagan[1], Christian Spudat[3], Thomas Otto[2], Thomas Gessner[2,3], Ovidiu D. Gordan [1] , Dietrich R.T. Zahn[1]

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Over the last decade, nanocrystalline semiconductor materials called quantum dots (QDs) have received a lot of attention due to their unique electronic and optical properties. Therefore, they can be used in a wide range of application such as optoelectronics, photovoltaics, biological labelling and many others. In our studies, we use QDs in a layered structure as an extremely thin film-based sensor integrated with a piezoelectric layer. Under mechanical stress, electrical charges are produced within the piezoelectric film and injected into the QDs thus quenching their photoluminescence (PL).
CdSe QDs passivated with hexadecylamine (HDA) and trioctylphophine oxide (TOPO) as well as CdSe/ZnS QDs passivated with TOPO purchased from SIGMA ALDRICH were deposited from a water surface onto a gold substrate by the Langmuir-Blodgett (LB) method. The QDs were chosen due to their bright PL, narrow emission band, size tunable PL and good photostability. Moreover, the composite layer structure includes besides QDs, Poly(9-vinylcarbazole) (PVK) and a layer of poly (3,4- ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT:PSS) which are sandwiched between a conductive layer of Indium Tin Oxide (ITO) and Aluminum (Al) as electrodes. On such layers UV-photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPS) were performed. The electronic structure and the alignment of the band levels were determined in order to investigate the charge transfer efficiency through the layered system. Therefore the suitability for charge injection into QDs can be assessed, *e.g.* it should allow only one type of charges to be trapped in the QDs. One possibility would be created when the HOMO level of the adjacent layer of QDs is at the same level as the valence band maximum of QDs, while the LUMO level should be at higher energies than the conduction minimum of QDs to make a potential well for trapping electrons and therefore leading to an increased efficiency of charge injection and quenching the PL in the sensor.

Po2.4 SYNTHESIS AND CHARACTERIZATION OF NOVEL PHOSPHAZENE COMPOUNDS CONTAINING OLEFINE GROUPS USING SPECTROSCOPIC TECHNIQUES

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Phosphazenes are a remarkable class of inorganic molecules in which the phosphorus and nitrogen repeat units can form cyclic compounds or chains [1]. In addition, phosphazenes exhibit very different physical and chemical characteristics depending on the type and properties of the attached substrates. Both phosphazenes and Schiff bases have a variety of applications in fields such as flame resistance, biomedicine, semi-conductors, dyes and catalysis. Antiproliferative activity of phosphazenes containing Schiff bases was observed to be much higher against cancer cells than the normal cells [2]. In this study, we synthesized three Schiff bases from condensation reactions of 4-aminobenzylamine and some salicylaldehyde derivatives. Then we reacted this Schiff bases with hexachlorocylotriphosphazene. So, we obtained new phosphazene compounds containing olefin groups **(I-III)**. The structures of compounds were confirmed on the basis of FTIR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy.

Keywords: phosphazene; Schiff base; antiproliferative activity; hexachlorocyclotriphosphazene.

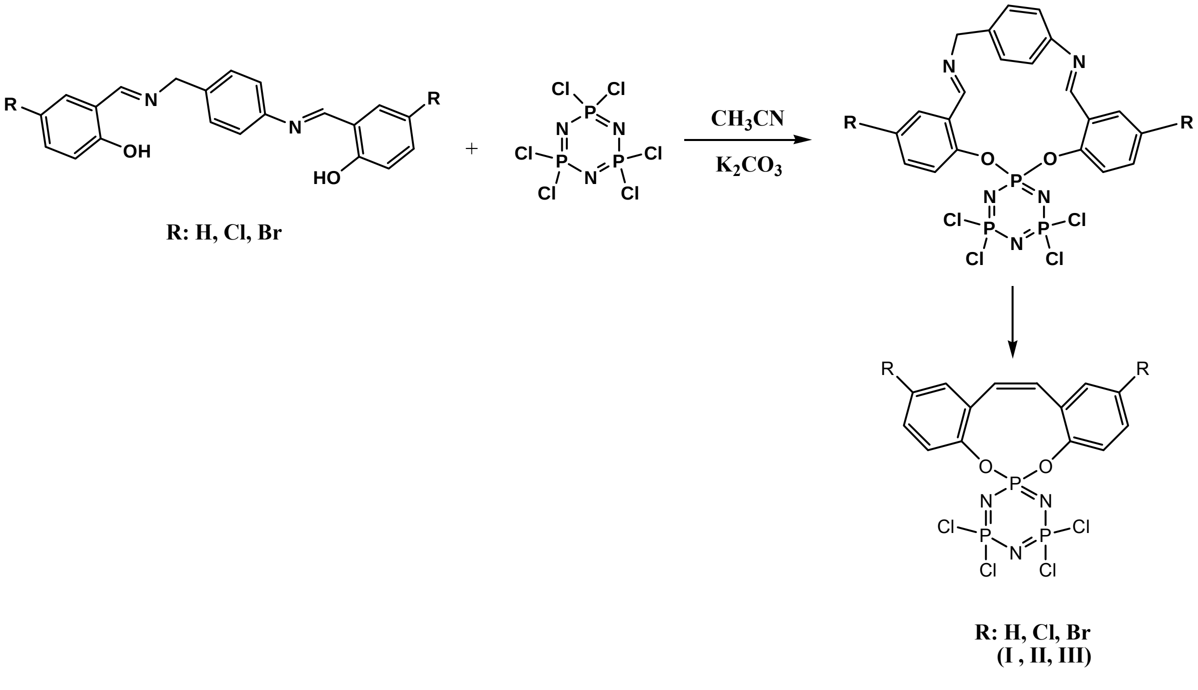

Fig.1 Synthesis reaction of (I-III) compounds

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Postersession II

Po2.5 LO-RAY-LIGH® DIFFRACTION GRATINGS IN UV-VIS SPECTROSCOPY

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It has been more than half a century since the release of the first Shimadzu UV-VIS spectro-photometer QB-50 in 1952 and during this time more than 160.000 UV-VIS spectrometers have been produced and installed in a wide variety of different applications. A lot of technical innovations have been implemented to improve the performance and significantly reduce the stray light levels. The latest innovation during development of sophisticated spectrophotometers is based on a new holographic exposure method and optimized etching process which has made it possible to produce both high-efficient and exceptionally low stray light gratings.

These LO-RAY-LIGH® gratings have guaranteed values of stray light at the intermediate position between zero- order and first-order lights. The values are measured by Shimadzu's laser stray-light-measuring system. The latest development in the series of UV-VIS spectrophotometers is the UV-2700 which is a true double beam double monochromator system in a compact design for high-precision spectral analysis of a wide range of samples including organic and inorganic compounds, biological samples, optical materials and photovoltaics. The high performance optical system is designed with “LO-RAY-LIGH®” diffraction gratings, featuring highest efficiency and exceptionally low stray light. The spectrophotometer operates in the wavelength range of 185 to 900 nm and allows highly sophisticated applications such as direct measurement of high density samples up to 8 absorbance units without dilution.

A typical example for high density measurements are $KMnO_4$ solutions in different concentrations which show an excellent linearity of up to 8 absorbance units. A variety of possible system configurations will be discussed on recent application examples and advantages of the new spectrophotometer series will be explained.

Keywords: LO-RAY-LIGH®, stray light, diffraction grating, spectrophotometer, single monochromator, holographic grating, high efficiency, double monochromator

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Po2.6 THE ELECTRONIC DONATION AND FREQUENCY SHIFTS ON THE YCCH···BH_4^- BORON-BONDED COMPLEXES (Y = H, CH_3, CF_3 AND CCl_3)

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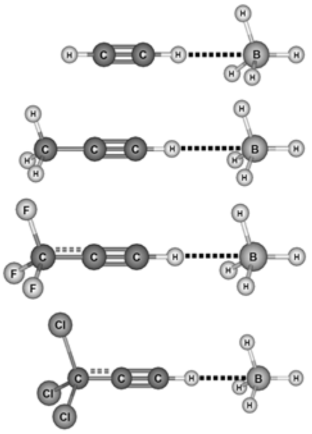
Besides the hydrogen bond, in recent years several alternative forms of intermolecular interactions have been studied either on the basis of experimental procedures or theoretical methods [1]. In this context, the great insight is the proton acceptor in whose charge concentration should be fairly high for binding with acid entities. In the best of our knowledge, the ionic character of the tetrahydroborate (BH_4^-) was used as proton acceptor upon the formation of the YCC–H···BH_4^- boron-bonded complexes (Y = H, CH_3, CCl_3 and CF_3). At the B3LYP/6-311++G(d,p) level of theory, the changes on the bond lengths are in good agreement with the frequency shifts of the proton donors HCC–H, H_3CCC–H, Cl_3CCC–H and F_3CCC–H [2]. The reductions of electronic density computed through the Quantum Theory of Atoms in Molecules (QTAIM) corroborate with the red-shifts of the C–H bond, wherein the contribution of the *s*-orbital diminishes while the *p*-orbital is increased, what reflect a polarization of the C–H bond [3]. In line with this, the variations on the atomic radii computed via QTAIM calculations show the following profile ΔrC > ΔrH. This scenario is indirectly supported by the Bent`s rule of the chemical bonding [4]. Although the interaction energies (corrected with BSSE and ZPE) vary between -19 and -67 kJ.mol^{-1}, these complexes are bound without covalence character.



Keywords: Boron bond; QTAIM; NBO

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Po2.7 SILVER COMPOUNDS INTERACTION WITH YEAST, BACTERIAL AND ANIMAL CELLS

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Silver compounds are toxic for fungi and bacteria but do not destroy mammalian cells. These properties make silver compounds prospective agents in a drug design. In the present work, the antibacterial effects and mechanism of action of silver were investigated for bacteria (*E.coli*) and yeast (*S. cerevisce).* We have analyzed the morphology and ultra structure of the cells treated with Ag(I) complexes of amino- and hydroxyacids, Ag(I) salts, and Ag nanoparticles. Release of the Ag^+ ions and Ag(0) nanoparticles and their interactions with the cells and the cell components were studied by combination of molecular spectroscopy techniques (circular dichroism, IR absorption and fluorescence) and transmission electron microscopy. The obtained results showed considerable changes in both the cell membranes and intracellular structures. The degradation of the cell wall and silver interaction with cell organelles were tested as the possible ways of the antimicrobial activity of the Ag compounds.

The work was supported by the Grant agency of the Czech Republic (P205/12/P584)

Keywords: silver, antibacterial, coordination polymer, circular dichroism ,fluorescence, microscopy

Po2.8 ELECTRON-β-NUCLEAR SPECTROSCOPY OF MOLECULES AND CHEMICAL BOND EFFECT ON THE β-DECAY PARAMETERS

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We develop relatively new direction in molecular spectroscopy, namely, electron-beta-nuclear spectroscopy of molecules and discuss the cooperative electron β-nuclear processes in molecules, including the excitation, ionization, electronic rearrangement, induced by the nuclear reactions and β-decay [1,2]. The many-body perturbation theory (PT) with the optimized Kohn-Sham (DKS) zeroth approximation [1] is used to calculate the β-decay parameters for a number of allowed (superallowed) transitions (^{33}P-^{33}S, ^{241}Pu-^{241}Am etc) and study a chemical bond effect on β-decay parameters. There are taken into account the following effects: i) Changing the electron wave functions because of the changing molecular electric field; changing the valence shell occupation numbers in different chemical substances; ii) The integration limits (calculating the Fermi integral function) are also changed in a case of the different chemical substances; as a rule, β-particle and neutrino take away the difference between the initial and transmuted final nuclei, provided by the nuclear and electronic rearrangement. One must also mention the additional channel, when β-electron occupies a free state in the bound molecular spectrum and other decay channels. We calculated the final-state probability distribution for excitations to the electronic continuum of $^3HeT^+$ resulting from the β-decay of T_2. The energy approach (non-relativistic version) is used to obtain a geometry dependant treatment of the resonance states of $^3HeT^+$ allowing for nuclear motion effects of these states to be accounted for explicitly in the determination of the final-state distribution. We studied the electronic rearrangement induced by nuclear transmutation in the β-decay ${}^6_2He_4 \rightarrow ({}^6_3Li_3^+)^* + e^- + \bar{\nu}_e$. The half-life period $T_{1/2}$ for β-decay of tritium atom (molecule) has been estimated while taking into account the bound β-decay channel and some other accompanying effects. The estimated values of $T_{1/2}$ for the tritium β-decay and free triton decay are: $(T_{1/2})_a$=12.26 years (correction due to the electron-atomic-molecular effects $(\Delta T_{1/2}/T_{1/2})_a$=0.8%) for the tritium atom and $(T_{1/2})_t$ =12.36 years for the triton decay. These data are in physically reasonable agreement with experimental data [2]. We firstly present the value $T_{1/2}$ in a case of the β-decay in the halogen-containing molecular tritium (^3HCl): $(T_{1/2})_m$=12.28 years (^3HCl); the correction due to the chemical bond effect is $(\Delta T_{1/2})_{am}$=0.024 (i.e. 0.20%).

Keywords: Molecular spectroscopy; Electron-beta-nuclear spectroscopy; Chemical bond effect

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Po2.9 MULTI-PHOTON EXCITATION AND DISSOCIATION FOR MOLECULES: EFFECT OF THE ROTATIONAL AND V-T RELAXATION AND CHAOS

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Phenomenological approach to description uncollisional excitation of a number of the molecules (CF_3I, SF_6, OsO_4 etc.) has been realized in papers of Letokhov, Stown etal [1]. At the same time a problem of correct influence of collisions on dynamics of multi-photon processes, selectivity of dissociation, absorption and energy transfer etc. requires a further studying. Here we present an advanced stochastic, quantum-kinetical approach to multi-photon excitation and dissociation of molecules in a laser field and quantitatively study effects of the rotational and V-T relaxation and chaos. It is studied a link between the integral characteristics of the multi-photon excitation and dissociation with parameters of relaxation in a medium of the buffer gas (N_2) within new stochastic-kinetical model [2]. It is calculated the output of multi-photon dissociation and absorbed energy for molecules of $^{12}CF_3Br$, $^{13}CF_3Br$. We describe a process of excitation into continuum within generalized kinetical equations model. A key moment is connected with account of the stochastic diffusion mechanism in quasi-continuum. Within it, the lowest levels system is described by two velocities: radiative velocity of excitation of some separated levels, which is proportional to pressure, and the rotational relaxation velocity. We calculate a dependence of the absorbed energy $^{13}\varepsilon$ and dissociation output $^{12}\beta$, $^{13}\beta$ upon a summarized pressure $p_\Sigma = p(N_2) + p(CF_3Br)$ [$p(CF_3Br) = 0{,}5$ Torr] for a number of laser lines of the CO_2 laser (1048,66; 1043,16; 1035.47 cm^{-1}). It is carried out an analysis of absorption by molecules in the quasi continuum, molecules on the lowest levels, contribution of the V-T relaxation. It is shown that in the pressure interval p<50-100Torr a dissociation output is mainly determined by influence of the rotational relaxation and the V-T relaxation is not significant. Above 200Torr the dissociation output is mainly determined by concurrence of two processes: the V-T relaxation and involving the molecules from the lowest levels. Stochastic model block is manifested in more correct description of the excitation dynamics in the quasi continuum. Elements of a chaos in dynamics are definitely stated and analyzed by means of the complex uniform approach, which combines together our versions of different non-linear analysis methods to dynamics, such as an advanced wavelet analysis, multi-fractal formalism, mutual information approach, correlation integral analysis, false nearest neighbour algorithm, the Lyapunov exponent's analysis, surrogate data method, memory matrix formalism [3].

Keywords: Multi-photon spectroscopy; Excitation and dissociation; Rotational and V-T relaxation and chaos

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Po2.10 INTERATOMIC POTENTIALS, COLLISIONAL HYPERFINE LINE SHIFT AND BROADENING FOR HEAVY ATOMS IN AN ATMOSPHERE OF THE BUFFER INERT GAS

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Studying collisional shifts and broadening the hyperfine lines for heavy elements (alkali, alkali-earth, lanthanides and others) in an atmosphere of inert gases is one of the important and actual topics of collision theory and spectral lines theory. Especial interest attracts the corresponding phenomenon for alkali and lanthanides atom [1,2]. Besides, these atoms are very interested from the point of view of studying a role of the weak interactions in an atomic physics. At last, calculating the hyperfine line shift allows to detect an quality of the wave functions and study a contribution of the relativistic and correlation effects. To calculate the hyperfine spectral lines collision shift one should use the expression from kinetical theory of the spectral lines [1]:

$$f_p = \frac{D}{p} = \frac{4\pi w_0}{kT} \int_0^{\infty} dw(R) \exp(-U(R)/kT) R^2 dR$$

where $U(R)$ is an effective potential of the inter atomic interaction, which has a central symmetry in a case of the pairs A-B (for example, A=Rb; B=He); T is temperature, w_0 is a frequency of the hyperfine transition in the isolated active atom; $d\omega (R)=Dw (R)/w_0$ is the relative local shift of the hyperfine lines, which is arisen due to the disposition of atoms of the A and B on a distance R. The relativistic many-body perturbation theory [3] is used to determine the relativistic Dirac functions for studied atoms.

We present new data on the interatomic potentials, local and observed collisional f_p shifts and widths for pairs: A-B (A=Rb,Cs,Tl,Yb; B=He,Ar, Kr,Xe) in dependence on temperature T. Our results are compared with the available experimental data and other theoretical results (see Refs. in [1, 2]), which are obtained within a perturbation theory with the Hartree-Fock or Dirac-Fock zeroth approximation. The feature of our scheme is a precise accounting for the correlation effects with using effective potentials [2]. Analysis shows that our data for studied systems are in the reasonable agreement with available experimental data (at least for available T). Very interesting features are found for the collisional broadening Γ_a parameter, namely, violation of the known Folly law ($\Gamma_a \sim f_p$) for lines in optical part of a spectrum [3]

Keywords: Hyperfine spectral lines; Collisional shift and broadening; Interatomic potentials.

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Po2.11 OPTIMAL SCHEMES OF LASER IONIZATION AND DISSOCIATION OF MOLECULES AND THEIR APPLICATION TO OPTIMIZATION OF ISOTOPE SEPARATION METHOD

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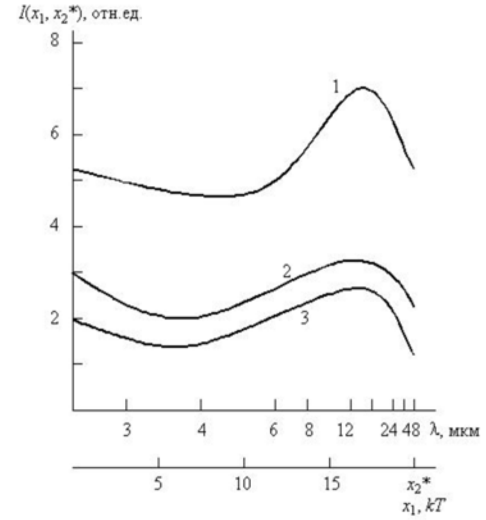
A majority of tasks, connected with action of powerful laser field and high energy particles sources on molecular gases, are more less adequately described by multi-level models, that leads to necessity of consideration of the high dimension differential equations systems or the Focker-Plank differential equations in the partial derivatives for density of molecules with the vibration energy *x* on a chosen vibrational level and operators, describing the RT relaxation and action of external radiation correspondingly [1,2].

We present a new multi-level optimized model for definition of the optimal real form of laser pulse to reach maximal effectiveness of laser action in process of ionization (dissociation) of molecules. Model is based on differential equation of the Focker-Plank type for density of molecules with the vibration energy x on some vibration level and operators, describing RT relaxation and laser field [2]. The conditions and parameters for optimal excitation for molecules of HCl (PH_3,CF_3Br, SiH_4) are given.



As illustration, in figure we give the dependence (number of particles) of functional: $I(u)=\int f(x_1,t_1;x_2,t_2)h(x)dx$ in the interval x_c~ {15,21} on x_1 and laser wavelength, corresponding to rotational transition x_1-x_2 (T=300 K). Here h(x) is the function, corresponding to required form of the final distribution f(x,t,u), i.e. density of molecules with vibration energy x at moment t~[0,R]. We also consider advanced optimal scheme of laser photo-ionization and photo-dissociation method for the isotopes separation and give the corresponding optimal parameters of laser and electric fields, quantum transitions etc are given.

Keywords: Laser ionization and dissociation; Optimal schemes; Isotope separation;

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PO2.12 HYDROGEN-BONDED CLUSTERS IN MONOHYDRIC ALCOHOLS

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Clusters, by definition, are aggregates of atoms/molecules with more or less regular and arbitrarily scalable repetition of basic building blocks. Their size is intermediate between atoms/molecule and the bulk. The growing interest to the clustering phenomena that produce partially ordered atomic or molecular structures is due to the recent developments and challenges in nanotechnologies, smart materials, heterogeneous systems, basic biochemical research, etc [1, 2].

The processes of molecular cluster formation in monohydric alcohols were investigated using FTIR and a matrix isolation technique. The methods of cluster isolation in low-temperature matrixes provide the possibility to study individual clusters of different sizes. FTIR spectra of monohydric alcohols (from methanol to decanol) in argon and nitrogen matrices were registered in the frequency range from 500 cm^{-1} to 4000 cm^{-1}. The gradual transformation of the spectral bands assigned to different vibrations was observed with matrix heating from 10 to 50 K, indicating the transformation of the structure of the isolated clusters. Main changes with the temperature increasing were observed in the spectral regions of stretch O-H and C-O vibrations.

The observed temperature dependence of the registered spectra may be considered as the model of structural transformations in alcohols during the phase transition from gas to liquid state.

The work was supported by the State Fund for Fundamental Researches of Ukraine (grant F54.1/008) and by Swedish Research Council (grant 348-2013-6720).

Keywords: alcohol; matrix isolation; hydrogen bond

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PO2.13 ROTATIONALLY RESOLVED ELECTRONIC SPECTROSCOPY OF TOLUNITRILES AND METHOXYPHENOLS IN SUPERSONIC JETS

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The electronic excitation results in numerous dynamical and structural properties of molecular systems in both the ground and excited electronic states can be studied using the high resolution spectroscopy technique. The analysis of the experimental spectra supplemented by *ab-initio* calculations, provides a rich knowledge of the fine rotational structure of polyatomic molecules and helps to their conformational assignment of *the* electronic origin and several *vibronic bands of* the potential barriers for the hindered methyl group torsional motion and the determination of the ground and excited state dipole moments of several molecules. Among others, these particular spectral details are related to crucial dynamical information occurring in the molecules upon excitation. Through this work, the electronic origin and some vibronic transitions have been investigated where such phenomena are manifested.

The origin bands of 2-, 3- y 4-tolunitrile[1]; and the origin and the most intense bands of 2-, 3- y 4-methoxyphenol[2] are studied using rotationally resolved electronic spectroscopy. Our interest in the tolunitrile family is on learning about the effect due to the presence of an electron withdrawing group (nitrile) on the torsional barrier height of the hindered CH_3 group in 2-, 3- y 4-TN, in both S_0 and S_1 states. In the case of the methoxyphenol family, the rotational constants provide a precise description of the structure of the molecule. By the knowledge of the inertial parameters of these molecules, we are able to assign the vibronic bands of the molecules in the S_1 state to their corresponding low frequency vibrational modes.

Keywords: Molecular spectroscopy; High resolution; Laser Induced Fluorescence

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Po2.14 CRYSTAL STRUCTURE DETERMINATION OF DOUBLE-ARMED [3-({16-[(4-AMİNOPHENOXY)METHYL]-2,3,5,6,8,9,11,12-OCTAHYDRO-1,4,7,10,13-BENZOPENTA OXACYCLOPENTADECİN-15-YL}METHOXY)PHENYL]AMİNEO-AMİNBENZO-15-CROWN-5

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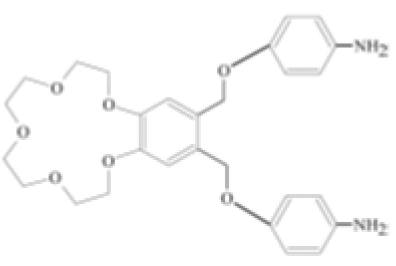
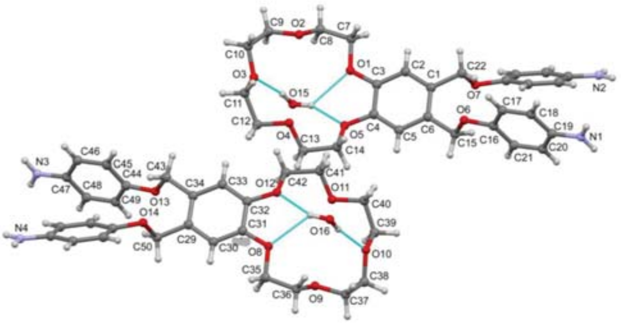
Macrocycles are the most important building blocks in supramolecular chemistry, since their discovery in 1967 [1–3]. Crown ethers have a central cavity structure, medium polarity, and strong electronegative effects of heteroatoms on the crown ether ring. The crown ethers have been found to be powerful extracting agents for the alkali and alkali–earth metals [4,5]. Crown ether compounds having reactive nitro or amine substituent in the aromatic ring are considered to be interesting starting materials for the synthesis of the new crown ether molecules [6,7].

This work describes the syntheses and crystal structure determination of double-armed benzo-15-crown-5 containing amine groups with single crystal X-ray diffraction technique. The compound crystallizes in triclinic, space group p-1 with a=9.1420(3), b=14.9580(4), c=20.4110(5), and Z = 4 [8].





Keywords: Crown ethers, Double armed macrocyclic ligands, Single crystal X-ray diffraction

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Po2.15 NEW SERS APPROACHES FOR DYES IDENTIFICATION ON TEXTILES

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The identification of natural dyes in ancient textile fibers is quite challenging as often the samples are valuable materials coming from a museum and containing a mixture of different colored molecules in minute amounts. Therefore high sensitivity methods that preserve the original sample are needed. At the same time, it is required to use methods that are possibly capable to distinguish between molecules that differ only by small structural details. Under this respect surface enhanced Raman scattering measurements represent a suitable approach to the problem. In order to avoid contamination of the sample we use specific solvent/reagents for the micro-extraction of the dye molecules from the textile. By the use of appropriate solvents/reagents dissolved in a small hydrogel bead we can remove from the textile a very limited amount of dye without any detectable discoloration and contamination[1]. The differences between the different dyes in the extraction yield and in the spectroscopic signature they give in Surface Enhanced Resonance Raman Scattering experiments while experiencing different chemical environments give us the potential to recognize all the different colored molecules present even in complex natural dyes. The spectroscopic data are supported by DFT calculations on the different chemical species involved.

Keywords: SERS; dyes; Resonance Raman

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Po2.16 THE EFFECT OF ZIRCONIA THICKNESS ON THE DEGREE OF CONVERSION AND MICROHARDNESS OF RESIN CEMENTS

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Resin cements have become popular clinically because of their ability to bond both the tooth structure and restoration. It is known that to reach optimum physical properties of resin cements for ceramic restorations; monomer to polymer conversion should be as high as possible. Degree of conversion (DC) is defined as conversion of carbon-carbon double bonds (C=C) present in the monomers to single bonds (C-C) during the process of polymerization. Thickness, translucency of the ceramic, composition and shade of the cement might have an influence on polymerization on the resin cement and therefore on its mechanical properties [1].

Zirconia based restorations have been widely used in dentistry due to their superior mechanical properties. Optical opacity of zirconia led to use of veneering ceramics to obtain esthetic result. Recently developed zirconia with increased translucency namely monolithic zirconia is used without veneering ceramic. The objective of this study was to evaluate the effect of zirconia thickness on the degree of conversion and was to compare microhardness of resin cements polymerized with different thicknesses of zirconia.

Three resin cements (Variolink II light-cure, Variolink II dual-cure and Zirconite dual-cure) were tested in order to evaluate the degree of conversion (DC) and microhardness. The specimens were prepared into 5 groups: monolithic zirconia (thickness; 2 mm, 1.5 mm and 1 mm), 1 mm zirconia substructure veneered with 1 mm ceramic, and 2 mm thick lithium disilicate ceramic (n=6 each subgroup). Infrared spectra were recorded using Attenuated Total Reflectance-Fourier Transform Infrared Spectrometer (ATR-FTIR). The DC % was calculated by the ratio of the infrared absorbance values of aliphatic and aromatic peaks for uncured and cured states. The data were statistically analyzed by ANOVA and TUKEY's post hoc tests.

The highest degree of conversion was obtained with Zirconite dual cured under 1 mm monolithic zirconia. The highest surface hardness Zirconite dual polymerized with 2 mm zirconia ceramic dental resin cement was found.

Keywords: Monolithic zirconia, resin cement, degree of conversion, ATR-FTIR, microhardness,

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This research was partially supported by grant, No: 03/2013-06 from Scientific Research Project of the Rectorship of Gazi University.

Po2.17 IN VITRO STUDY ON THE DEMINERALIZATION/REMINERALIZATION OF TOOTH ENAMEL SURFACES BY RAMAN SPECTROSCOPY AND SAXS

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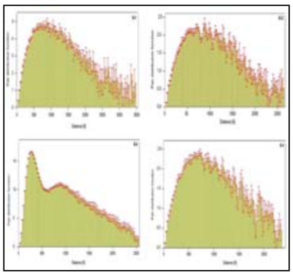
Enamel is the hardest and most highly mineralized substance of the human body. Dental erosion is the situation of a loss of dental hard tissue by a chemical process that does not involve bacteria. **Remineralization** is the process of replacing the essential minerals lost from teeth by **demineralization**.

The aim of this study was to determine the effect of two remineralizing agents CPP-ACP (Casein-Phosphopeptide Amorphous Calcium Phosphate, Tooth mousse®) and ROCS® (Remineralizing Oral Care Systems) on the demineralized human enamel surface.

Freshly extracted 20 human central teeth without caries and defects were used for this study. After extraction the teeth were cleaned with steril saline solution for removing tissue debris, and then the teeth were sterilized with %5 NaOCl for 1 hour and stored in artifical saliva during the whole experimentation. The teeth were cut transversely from cervical side and roots of the teeth were removed. Then the crowns of the teeth-labial portions to remain outside-were embedded in acrylic resin blocks. Labial surfaces of the teeth were assigned to four groups and are marked; Group 1: Normal enamel, Group 2: Demineralization solition Group 3: Demineralization solition + **Remineralization** agent (Rocs for 10 teeth, CPP-ACP for 10 teeth) and Group 4: **Remineralization** agent (ROCS for 10 teeth, CPP-ACP for 10 teeth).



The enamel surfaces of groups were investigated by Raman spectroscopy and Small Angle X-ray scattering (SAXS). To describe the changes of tooth enamel, phosphate group concentration within enamel is a good indicator of the degree of mineralization. The phosphate and carbonate bands in the Raman spectra were used to investigate of the structural changes in the demineralized and remineralized enamel. Nanosize surface morphologies of the samples were compared by using PDDs (Pais Distance Distributions) obtained by SAXS analyses (Fig. 1). The repair effects of the agents were determined for Groups 3 and 4.

Keywords: Keywords: Eenamel, demineralization, remineralization, Raman Spectroscopy, SAXS

This study was supported by Hacettepe University Research Fund. No 013D03 704001

Po2.18 2D STUDY OF THE BENDING VIBRATIONS IN NONRIGID UO_3 MOLECULE USING EXACT KINETIC ENERGY OPERATOR

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According to calculations [1] UO_3 has two equilibrium planar structures. Introducing bending coordinates φ,δ and γ one can specify both configurations as $\gamma_0 \approx 90^0$ (Y-form) and $\gamma_0 \approx 156^0$ (T-form). In both cases $\varphi_0 = \delta_0$ and $\varphi_0 + \delta_0 = 2\pi - \gamma_0$: $\varphi + \delta + \gamma = 0$: Y-form seems energetically preferable. 2D PES in φ,δ coordinates was calculated. Exact kinetic energy operator $\widehat{K}$ for two bending coplanar coordinates (A-B-C and C-B-D) having common bond B-C can be represented as:

$$\widehat{K} = h_\varphi \frac{\partial}{\partial\varphi} + h_\delta \frac{\partial}{\partial\delta} + G_{\varphi\varphi}\frac{\partial^2}{\partial\varphi^2} + G_{\delta\delta}\frac{\partial^2}{\partial\delta^2} + G_{\varphi\delta}\frac{\partial^2}{\partial\varphi\partial\delta} \quad (1)$$

where $h_\varphi = -\frac{\hbar^2}{2M_A} div_{\vec{r}_A}(\vec{s}^{\,\varphi}_{r_A}) - \frac{\hbar^2}{2M_B} div_{\vec{r}_B}(\vec{s}^{\,\varphi}_{r_B}) - \frac{\hbar^2}{2M_C} div_{\vec{r}_C}(\vec{s}^{\,\varphi}_{r_C})$

$$h_\delta = -\frac{\hbar^2}{2M_C} div_{\vec{r}_C}(\vec{s}^{\,\delta}_{r_C}) - \frac{\hbar^2}{2M_B} div_{\vec{r}_B}(\vec{s}^{\,\delta}_{r_B}) - \frac{\hbar^2}{2M_D} div_{\vec{r}_D}(\vec{s}^{\,\delta}_{r_D})$$

$$G_{\varphi\varphi} = -\frac{\hbar^2}{2M_A}\left(\vec{s}^{\,\varphi}_{r_A}\right)^2 - \frac{\hbar^2}{2M_B}\left(\vec{s}^{\,\varphi}_{r_B}\right)^2 - \frac{\hbar^2}{2M_C}\left(\vec{s}^{\,\varphi}_{r_C}\right)^2; G_{\delta\delta} = -\frac{\hbar^2}{2M_C}\left(\vec{s}^{\,\delta}_{r_C}\right)^2 - \frac{\hbar^2}{2M_B}\left(\vec{s}^{\,\delta}_{r_B}\right)^2 - \frac{\hbar^2}{2M_D}\left(\vec{s}^{\,\delta}_{r_D}\right)^2$$

$$G_{\varphi\delta} = -\frac{\hbar^2}{M_B}\left(\vec{s}^{\,\varphi}_{r_B}\cdot\vec{s}^{\,\delta}_{r_B}\right) - \frac{\hbar^2}{M_B}\left(\vec{s}^{\,\varphi}_{r_C}\cdot\vec{s}^{\,\delta}_{r_C}\right)$$

Here were used Wilsons $\vec{s}^{\,\varphi}_r$ vectors and masses of A, B,C, D atoms (M_A, M_B, M_C, M_D). For UO_3 molecule one can simplify (1) assuming additionally that the lengths of all U-O bonds equals (l):

$$h_\varphi = -\frac{\hbar^2 ctg\varphi}{\mu_{UO} l^2} + \frac{\hbar^2}{M_U l^2 \sin\varphi}; \quad h_\delta = -\frac{\hbar^2 ctg\delta}{\mu_{UO} l^2} + \frac{\hbar^2}{M_U l^2 \sin\delta}$$

$$G_{\varphi\varphi} = \frac{\hbar^2}{\mu_{UO} l^2} - \frac{\hbar^2\cos\varphi}{M_U l^2}; G_{\delta\delta} = \frac{\hbar^2}{\mu_{UO} l^2} - \frac{\hbar^2\cos\delta}{M_U l^2}; G_{\varphi\delta} = -\frac{\hbar^2}{\mu_{UO} l^2} + \frac{\hbar^2(\cos\varphi + \cos\delta - \cos(\varphi+\delta))}{M_U l^2}$$

where μ_{UO} - reduce mass of U and O atoms. Schrödinger equation with this kinetic energy operator and calculated PES was solved numerically according with [2, 3]. The results are compared with experimental data [4].

Keywords: Nonrigid molecules, exact form of kinetic energy operator, UO_3.

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Po2.19 MİCRO-RAMAN, MİD-IR, FAR-IR AND DFT STUDİES ON2-[4-(4-FLUOROBENZAMİDO) PHENYL] BENZOTHİAZOLE

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Molecular structure of 2-[4-(4-Fluorobenzamido)phenyl]benzothiazole (BSN) was determined by quantum chemical calculations (Fig. 1). MidIR and FarIR spectra were recorded at room temperature, with 4 cm^{-1} resolution in the 4000–400 cm^{-1} and 700–30 cm^{-1} regions, respectively for the first time. Raman spectrum was recorded in the 4000–100 cm^{-1} range. Optimized molecular structure and vibrational wavenumbers of the compound in its ground state have been calculated by using Density Functional Theory using B3LYP functional with 6-311++G(d,p) basis set. Vibrational wavenumbers were seen to be in good agreement with the experimental IR data. Furthermore, assignments of each vibrational mode were interpreted in terms of potential energy distributions in detail [1].

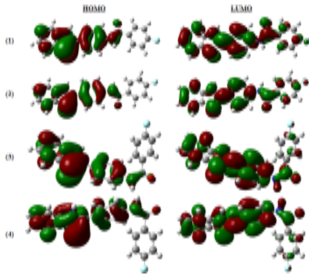

Fig.1 HOMO's and LUMO's of BSN

Keywords: 2-[4-(4-Fluorobenzamido)phenyl]benzothiazole; Micro-Raman, Far-infrared, Mid-Infrared, DFT, PED, benzothiazole

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Po2.20 INVESTIGATING THE APPLICATION OF SPECTROSCOPY IN THE DEVELOPMENT OF NOVEL ORAL DRUG TECHNOLOGIES AND PRODUCTS

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Development of a characterization technique for Sigmoid Pharma's proprietary SmPill® drug delivery platform will enable the spectral identification of the constituent components of a specific drug product and its subsequent location within the SmPill® mini-capsule, consequently leading to formulation optimisation. This project will contribute to optimal formulation activity in the gastrointestinal tract, including the development of improved treatments for gastrointestinal and immunological diseases using known or novel APIs incorporated into a proprietary drug delivery technology. Through the use of spectroscopic techniques such as Raman and IR spectroscopy, changes within the SmPill® emulsion can be tracked, allowing for the identification of chemical constituents. The use of particle sizing techniques such as Dynamic Light Scattering (DLS) allows for the determination of the optimal formulation as well as the oil phase to aqueous phase ratios by measuring the droplet size of the dispersed oil phase. These ratios, coupled with the knowledge of the distribution of each component at the molecular level, will allow for formulation development optimisation in a knowledge based approach.

Keywords: Drug Delivery, Formulation Optimisation, Spectroscopy, Dynamic Light Scattering (DLS),

Po2.21 MATRIX ISOLATION FTIR AND DFT STUDIES ON PHOTOCHEMISTRY OF 5-METHYLTETRAZOLE

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Tetrazole derivatives exhibit a large number of practical applications such as environmentally friendly energetic materials, stabilizing substituents in drug design, metal coordination compounds including spin-crossover materials and peptides components in metal chelating agents. They are also very stimulating heterocycles from an academic viewpoint due to their tautomeric and conformational properties and very interesting photochemistry.[1-3]

The most interesting compounds containing tetrazole moieties are 5-substituted tetrazoles. One of the simplest of them is 5-methyltetrazole (MT). MT exists in two tautomeric forms: 1H- and 2H-tautomers. According to the theoretical prediction, the 2H-tautomer is the predominating form in the gas phase but various physicochemical methods revealed that in solutions and in the solid state the more polar 1H-tautomer prevails. The infrared spectrum of the MT/Ar sample shows that both 1H-MT and 2H-MT tautomers are present in an argon matrix. The theoretically predicted population of MT tautomers at the sublimation temperature (ca. 305 K) equals 4 and 96%, for 1H- and 2H-forms, respectively.

In situ photolysis of 5-methyltetrazole isolated in low temperature argon matrices was induced by tunable UV laser radiation. The progress of the reactions was followed by FTIR spectroscopy that allowed for spectroscopic identification of three photoproducts resulting from the MT ring cleavage, namely C-methylnitrilimine CH_3CNNH, N-methylcarbodiimide CH_3NCNH, methylcyanamide CH_3NHCN. The kinetic profiles obtained for these products show different behavior of the species in the course of irradiation. The N-methylcarbodiimide molecules were found to decompose further into two HCN or HNC molecules that interact in the matrix cages to form different hydrogen bonded dimers.

Keywords: Tetrazoles; Matrix-isolation; Infrared spectroscopy; Tunable laser photochemistry

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Po2.22 SPECTRAL PROPERTIES OF BILIVERDIN IN SOLUTION AND IN NEAR-INFRARED FLUORESCENT PROTEIN IRFP

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Current interest to biliverdin (BV) is caused by its use in the new near-infrared fluorescent probes developed from bacterial phytochrome photoreceptors (BphPs), in which BV is a natural chromophore. Being a heme derivative, BV is abundant in mammalian cells. BV absorbs and fluoresces in a near-infrared “optical window” (650-900 nm) where mammalian tissues are the most transparent. The fluorescent probes developed on the basis of BphPs provide an opportunity for non-invasive imaging of deep tissues and whole organs in living animals [1, 2, 3]. Naturally, BV binding occurs in the chromophore-binding part of BphPs, which consists of so called PAS and GAF domains. The PAS domain in BphPs contains at an N-terminal patch a conserved cysteine residue, which covalently attaches the BV, while the chromophore itself fits into the cleft in the GAF domain. The N-terminal region of 35 residues upstream of the PAS domain and the loop contributed by the GAF domain (residues 225-257) create a figure-of-eight knot structure, which bridges the PAS and GAF domains [4], so that BV pierces through this structure. At the same time it was shown that apoform of iRFP has native structure. Apoprotein correctly binds BV as proved by recovery of near-infrared absorption, fluorescence and CD. Experiments on iRFP mutant with a substitution of Cys15 with Ser allowed us determining the BV binding constant by equilibrium microdialysis. The denaturation of iRFP and its apoform (BV-free form) induced by guanidine hydrochloride imply that the chromophore significantly stabilizes iRFP and makes the denaturation transition more cooperative. Moreover, in contrast to the apoform, the denaturation of iRFP with bound BV is irreversible, and its renaturation is complicated by the aggregation of protein molecules. [5]. To clear the spectral properties of BV incorporated in proteins we examined its microenvironment in iRFP and studied spectral properties of the free chromophore in solutions with different polarity, viscosity, dielectric constant and pH.

This work was supported by the MCB Program of RAS, RFBP grant (13-04-01842) and Scholarships of the President of the RF (SP-65.2012.4).

Keywords: heme oxygenase, near-infrared fluorescence, bacterial phytochrome, protein structure

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Po2.23 APPLICATION OF MULTIVARIATE CURVE RESOLUTION-ALTERNATING LEAST SQUARES METHOD TO SPECTROPHOTOMETRIC TITRATIONS FOR QUANTIFICATION OF VANILLIN, P-HYDROXYBENZALDEHYDE AND MALTOL

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In this study the application of multivariate curve resolution alternating least squares (MCR-ALS) [1], for the quantitative determination of mixtures of vanillin, p-hydroxybenzaldehyde and maltol using spectrophotometric acid-base titrations has been reported. The quantitative determination of these compounds in different synthetic mixtures and in some real samples has been performed using only a synthetic external standard solution of the analyte of interest. The spectra of the samples and standards were disposed in a column-wise augmented data matrix. This kind of data structure led to an accurate quantitation in the rank deficient data systems. Initial estimates of spectral profiles of different analytes were built using ortogonal projection approach (OPA). The method was applied to the determination of these compounds in some foodstuffs with satisfactory results. Good recoveries were obtained in the range of 98–108%. Applying this method in routine testing can be valuable in food analysis, where rapid identification of forbidden additives is important in detecting adulterations in food.

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Po2.24 INTERACTION OF ASYMMETRIC FS LASER FIELD WITH MOLECULES: A TOOL FOR INDEFICATION OF MOLECULAR DISSOCIATION CHANNELS

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The last few years it has been shown that selective molecular ionization/dissociation in gas phase can be achieved by utilizing ultrashort asymmetric laser field. This kind of field can be easily tailored by combining the fundamental laser frequency (800 nm) of a Ti: Sapphire laser and its second harmonic (400 nm).

Experimentally the orientation selectivity is verified by recording the dependence on the phase φ between the 800 and 400 nm laser beams of the intensity ratio of the ions ejected toward and backward to the detector of a TOF mass spectrometer. Nevertheless, in many cases fragment ions with the same mass (m/z ratio) are released with similar kinetic energy, although they are products of different dissociation channels. The identification of the dissociation channels involved in these cases is difficult on the ground of the TOF mass spectra data.

Recently, we have shown that this identification could be achieved by studying the dependence of the integrated signal of one peak component (e.g. the forward one) on the phase φ. In the case of N_2O molecule, it is found that albeit the majority of the ions exhibit a ω dependence on phase φ, one of them (NO^+) exhibits, along with the ω, a 2ω dependence too. Based on this finding we have proposed that two different dissociation routes were involved in this ion production [1]. This observation has been verified for the case of the $^{15}N^{14}NO$ too.

Moreover, by extending the study for the CH_3OH molecule, we have observed a 2ω dependence for the H_3^+, OH^+ and HOH^+ fragments. For the interpretation of above findings we suggest that in the signal of OH^+ and HOH^+ ions exists contribution from dissociation channels taking place in the singlet and the triplet state of doubly charged methanol ion [2]. As far as the H_3^+ ejection is concerned the existence of a slow and a fast dissociation route is discussed.

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Acknowledgment: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program:**THALES** (ISEPUMA). Investing in knowledge society through the ESF.

Po2.25 EXPERIMENTAL AND THEORITICAL GROUP VELOCITY DELAY CONPENSATION AND PHASE CONTROL IN ω/2ω EXPERIMENTS

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The superposition of the fundamental laser frequency and its second harmonic creates an asymmetric electromagnetic field () that can be used in orientation studies of gas phase molecular samples. A temporal separation of the two colors is introduced while passing through the various optics of the experimental setup. Uniaxial birefringent crystals like calcite, which have large birefringence, with the optic axis in the plane of incidence and asymmetrically cut, exhibit a wide temporal compensation of two perpendicular polarization modes (800 nm ordinary and 400 nm extraordinary) of different color as a function of the angle of incidence. Furthermore, fine tuning the angle of incidence offers the ability to control the phase of the asymmetric laser field. [1].

A complete geometrical analysis of the beam paths within the calcite for the two laser fields, allows us to generate theoretical time delay versus angle of incidence graphs for two calcite crystals (of different thickness and cut). We compare these with the experimental graphs obtained by recording the H_2O^+ signal as a function of the delay between the ω/2ω pump and the ω probe [Fig.1]. In order to experimentally identify the ω/2ω phase dependence on the rotation angle of the calcite crystal we have employed a Mach-Zehnder type interferometer and recorded the ordinary ω/ω and extraordinary 2ω/2ω fringe pattern intensity. This is also compared with the corresponding theoretical calculations. In both cases we have found good agreement between theory and experiment. We are therefore optimistic that we can extend our theoretical calculations towards longer wavelengths, available using an optical parametric amplifier (OPA), where an enhanced efficiency in the control of electron localization is theoretically predicted [2].

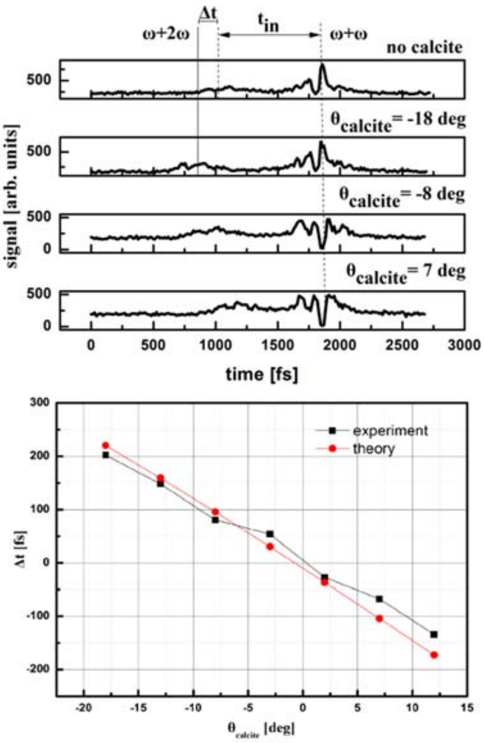

Fig.1 Time delays comparison.

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Po2.26 THEORETICAL STUDIES ON THE MOLECULAR STRUCTURE AND VIBRATIONAL SPECTRA OF 2-PYRIDINEETHYLAMINE

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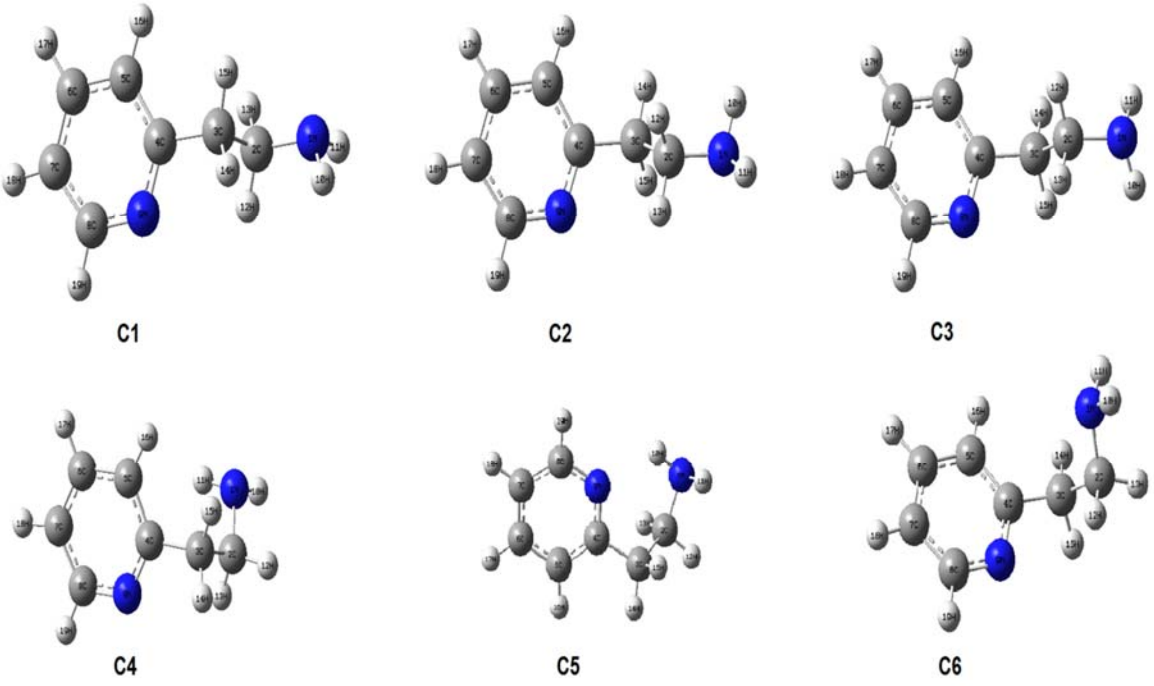
In this study, the structural and spectroscopic investigations of 2-pyridineethylamine (abbreviated as aepy) have been experimentally and theoretically investigated. The optimized geometric parameters, conformational equilibria, normal mode frequencies and corresponding vibrational assignments of aepy are examined by means of B3LYP hybrid density functional theory (DFT) method together with 6-31G(d) basis set. Moreover, reliable vibrational assignments have been made on the basis of potential energy distribution (PED). Calculated wavenumbers and intensities are compared with FT-IR and Raman spectra of aepy in the range of 4000-250 cm^{-1}. Time depended density functional theory (TD-DFT) method using 6-31G(d) basis set is used to determine the minimum energy structure of aepy. Additionally, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of aepy are predicted with time depended density functional theory (TD-DFT) method using 6-31G(d) basis set. Calculations are carried out employed for different conformations of aepy in gas phase. According to the calculated results, the vibrational wavenumbers and excitation energies show an excellent agreement with the experimental data.



C1 C2 C3

C4 C5 C6

Fig. 1. Six different conformations and numbering of aepy

Keywords: 2-Pyridineethylamine; FT-IR spectra; Raman spectra; DFT; B3LYP; PED

Po2.27 ULTRAFAST DYNAMICS OF TOLUENE EXCITED AT 160 nm

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Using the 5th harmonic (λ=160 nm, pump beam) of a 30 fs Ti:Sapphire laser, toluene ($C_6H_6CH_3$) and its deuterated derivative ($C_6D_6CD_3$) are excited to Rydberg states. The dynamics of these states are probed by the controlled delayed fundamental laser pulse (λ=800 nm) using a Time-of-Flight mass spectrometer in order to detect the generated ions. In particular, the decay of the parent $[P]^+$ ions and that of the $[P\text{-}H]^+$ and $[P\text{-}D]^+$ fragment ions are studied.

The structures of $[P\text{-}H]^+$ and $[P\text{-}D]^+$ ions have been an issue of dichotomy, i.e. whether the six-membered ring (benzyl) is preserved or a seven-membered (tropyl) structure is formed [1],[2],[3].

From the comparative analysis of the recorded data (Fig. 1) it is suggested that the tropyl radical is formed, following molecular rearrangement after excitation. The rates of the involved decays have been estimated for each molecule. Furthermore, the oscillations observed on the $[P\text{-}H]^+$ and $[P\text{-}D]^+$ signals have been determined and their values found to support the above made assignment for their structure [4].

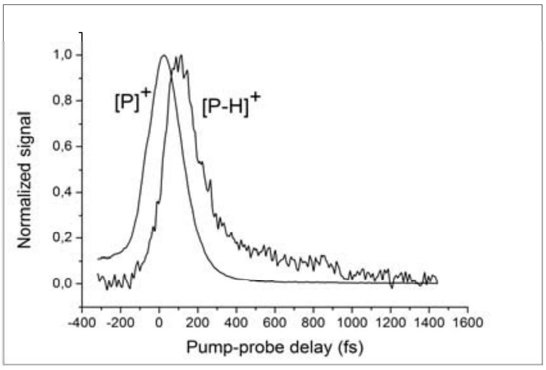

Fig. 1 Pump-probe normalized signal of $[P]^+$ and $[P\text{-}H]^+$ ions

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Po2.28 VIBRATIONAL SPECTROSCOPIC INVESTIGATION OF GLYCYLPROLYLGLYCYLGLUTAMYLGLUTAMINE (GPGQQ) AS A PART OF SPIDER SILK PROTEIN

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Silk from spiders have also generated considerable scientific potential in recent years. Over the past two decades, scientists have been attempting to unravel the molecular details of spider silks. Spider silk fibers have remarkable mechanical properties and certain threads are superior to Nylon, Kevlar and high-tensile steel [1].

Spiders that spin orb webs secrete seven types of silk. Silk proteins are composed almost entirely of repetitive elements [2-5]. Furthermore, the amino acid sequences of each silk can be generalized as sets of consensus repeats. Comparison of the consensus repeats from the various silk proteins reveals four types of shared amino acid motifs: (a) GPGGX/GPGQQ; (b) GGX; (c) poly-Ala/poly-Gly-Ala; and (d) a 'spacer' sequence. The GPGGX repeat unit (in many cases, GPGQQ is the major form) has been suggested to be involved in a β-turn spiral. Major ampullate and flagelliform silks share the GPGGX /GPGQQ motif, and are the only silks with elasticity 5–10%. [6].

Conformer analysis, geometry optimization and vibrational (IR and Raman) analysis have been carried out in gas for GPGQQ part of the spider silk chain and calculated by DFT/B3LYP with 6-31G(d) basis set. All computational studies had been performed with the Gaussian 09 program package [7]. Potential Energy Distributions of normal modes have been calculated using the VEDA4 program [8].

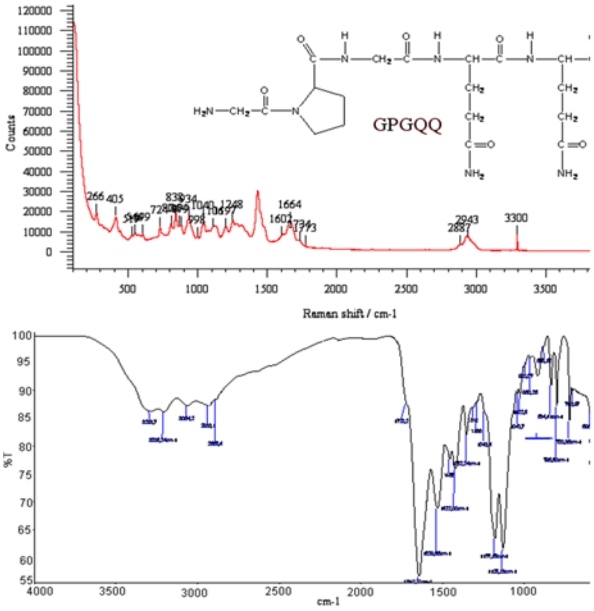

Fig. 1 The structure of GPGQQ and Raman & IR Spectra

This study was supported by Erciyes University Scientific Research Project (Project no: FDK-2013-4543).

Keywords: Spider silk; GPGQQ; IR - Raman, DFT

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Po2.29 THEORETICAL APPROACH TO KETO-ENOL TAUTOMERISM IN METHYL 2-(4-METHOXYBENZOYL)-3-(4-METHOXYPHENYL)-3-OXOPROPANOYLCARBAMATE

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Keto-enol tautomerism is critical for the biological effect of carbamates in most cases. Examination of tautomeric equilibrium in carbonyl compounds can be very important to rationalize their biological activity [1-3]. A carbamate compound having tricarbonyl groups, methyl 2-(4-methoxybenzoyl)-3-(4-methoxyphenyl)-3-oxopropanoylcarbamate (BPOC) indicates keto enol tautomerism. The two carbonyl group are similar that have aromatic rings and connected the same carbon. Therefore, the two enol and one keto tautomers which have several conformers can be considered for BPOC. The keto form (KF), enol-1 form (EF-1), transition state for keto form to enol-1 form (TS-1), enol-2 form (EF-2), transition state for keto form to enol-2 form (TS-2) and transition state for enol-1 form to enol-2 form (TS-3) were all given in Fig.1.

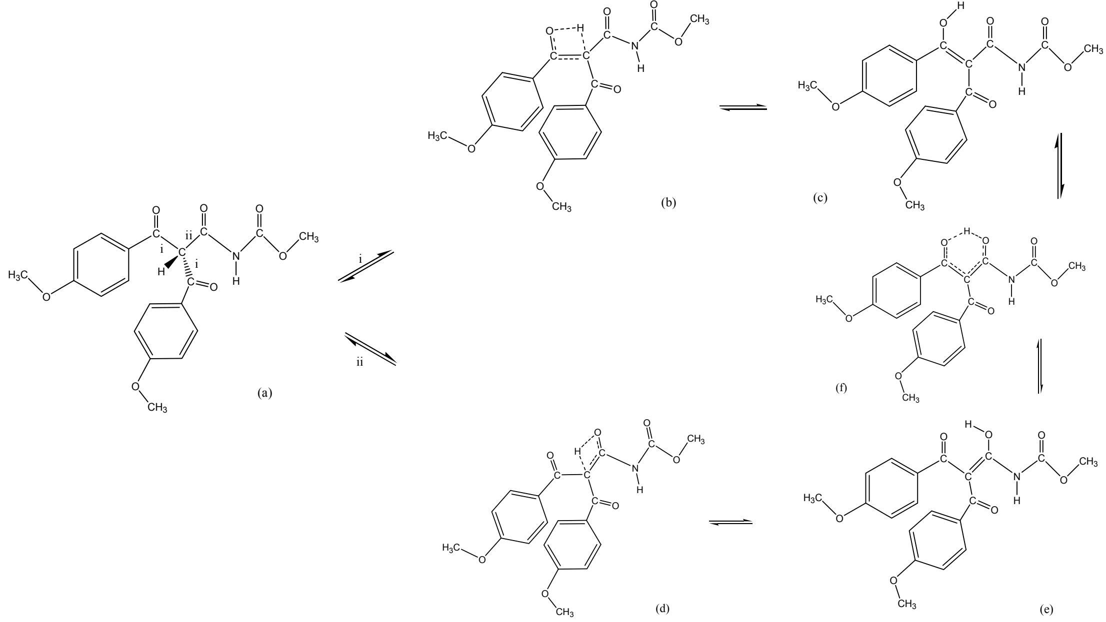

Fig.1 (a) KF, (b) TS-1, (c) EF-1, (d) TS-2, (e) EF-2 and (f) TS-3 of BPOC.

DFT (B3LYP, X3LYP and B3PW91) methods employing 6-311 G(d,p) basis set were used for the calculations in Gaussian 09 program package [4]. Rotational barriers and conformational analyses were performed to find the most stable conformer of keto and enol isomerization of the molecule. The transition state for keto-enol isomerization was obtained. The results of the calculations showed that enol-1 form of BPOC was more stable than keto and enol-2 forms.

Keywords: Keto-enol tautomerism; Carbamate; Transition state; DFT

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Po2.30 THEORETICAL AND VIBRATONAL ANALYSIS OF N-METHYL-2-[[3-[(E)-2-PYRIDIN-2-YLETHENYL]-1H-INDAZOL-6-YL]SULFANYL]BENZAMIDE(AXITINIB)

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Recent estimates show that the number of people suffered from cancer will increase from 1.6 million to 2.3 million during the period 2010-2030 in the United States[**1**]. Although significant advances have been made in cancer researches, discovery of new target molecules and development of novel therapeutic techniques are still needed. The protein kinase family, consisting of more than 500 members, is an important therapeutic target for drug developers[**2**]. Axitinib is a small molecule tyrosine kinase inhibitor that inhibits growth of breast cancer[**3**] and plays important role in clinical trials with Renal cell carcinoma(RCC)[**4**] and several other tumour types[**5**]. Although axitinib is investigated in medical chemistry[5], a detailed theoretical and spectroscopic characterization of this compound has not been studied yet. In this study, conformer analysis of the molecule has been carried out to find the most stable conformer. NBO analysis has been performed to characterize intra-molecular interactions and possible H bondings. The vibrational spectra have been measured and interpreted by theoretical calculation. All the calculations have been performed with Gaussian 09 program package[**6**] using several hybrid functionals of Density Functional Theory(DFT/6-31G*). VEDA4 program[**7**] is employed to obtain Potential Energy Distribution(PED). The calculated results are in good agreement with the experimental ones.

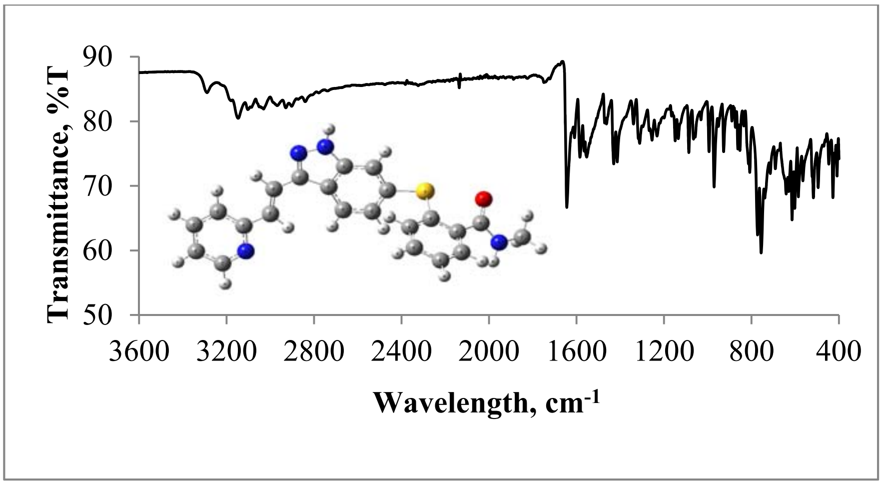

Figure 1. Experimental IR Spectum of AXITINIB

This study was supported by Erciyes University Scientific Research Project (Project no: FDK-2013-4586)

Keywords: *tyrosine kinase inhibitor (axitinib), theoretical - vibrational analysis, DFT*

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Po2.31 SPECTRAL PROPERTIES OF BADAN IN SOLUTIONS WITH DIFFERENT POLARITIES

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[1]Laboratory of Structural Dynamics, Stability and Folding of Proteins, Institute of Cytology, Russian Academy of Science, 194064, Tikhoretsky av.,4, St. Petersburg, Russian Federation
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Fluorescent solvatochromic dye BADAN (6-bromo-acetyl-2-dimethylamino-naphtalene) is used for studying of the phase transitions in biological membranes, protein conformational changes induced by different factors, proteins interactions with their partners and ligands [1-3]. Furthermore, fluorescence of this dye is used as a recorded signal in biosensor systems [4, 5].

In this work spectral characteristics BADAN in a nonpolar (hexane) and (acetonitrile) solvents were examined. The ratio of the intensity of short-wavelength absorption band to the long-wavelength absorption band of the dye significantly changes with polarity increasing. It was shown that the BADAN fluorescent characteristics in hexane do not depend of excitation wavelength. In acetonitrile the fluorescence spectrum of BADAN can be described by log-normal function with maximum around 475 nm when the dye is excited in the long-wavelength absorption band (387 nm). The shape of fluorescence spectra of BADAN in acetonitrile excited in the short-wavelength absorption band (220 - 300 nm) is not log-normal and is significantly extended. The fluorescence excitation spectra of BADAN in acetonitrile after correction for the inner filter effect does not coincide with its absorption spectrum.

By chemometrics methods we divided the BADAN fluorescence spectra and fluorescence excitation spectra in acetonitrile into two components. One component of BADAN fluorescence (which has maximum of fluorescence spectrum about 475 nm) is present at the excitation when the dye is excited both in the long-wavelength and in short-wavelength absorption bands. Another component of BADAN fluorescence (which has maximum of fluorescence spectrum about 435 nm) appears only when the excitation is in the short-wavelength absorption band. The BADAN fluorescence excitation spectra in acetonitrile were separated into two components also.

Taken together, the experimentally obtained data show that in low-polarity solvent (acetonitrile) BADAN solution is two components which differ both in fluorescence and fluorescence excitation spectra.

Keywords: fluorescence, BADAN, excitation and emission spectra, chemometrics, inner-filter effect

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PO2.32 VIBRATIONAL-THEORETICAL INVESTIGATION OF THE GLYCYLPROLYLGLYCYLGLYCYLALANINE (GPGGA) PART OF THE SPIDER SILK CHAIN

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The spider uses as many as seven different kinds of silk fiber (major ampullate dragline, minor ampullate dragline, flagelliform, aggregate, cylindrical, aciniform and pyriform) for various functions. Each type of spider silk fiber exhibits a distinctive combination of mechanical properties [1]. All silks are chains of iterated peptide motifs. The peptide motifs can be grouped into four categories: (1) GPGX$_a$X$_b$ (X$_a$X$_b$= GA, GS, GY, or QQ); (2) GGX (X: X=L, Q, R, or Y); (3) poly-Ala, poly-Gly-Ala; and (4) a 'spacer' sequence [2]. The GPGX$_a$X$_b$ pentapeptide repeat has been suggested to conform to a spiral that is similar to the β-turn spiral of elastin [3-5]. This β-spiral spring could easily serve as the elastic mechanism of the fiber. Only the major ampullate and flagelliform silks contain the GPGX$_a$X$_b$ motif they are also the stretchiest of spider silks [6].

Raman and IR spectra have been recorded for GPGGA. The calculations including conformer analysis, geometry optimization, vibrational analysis, NBO analysis and HOMO-LUMO analysis of GPGGA part of the spider silk chain had been performed in the ground state by using the DFT/B3LYP with 6-31G(d) basis set. Potential Energy Distribution (PED) of normal frequencies was calculated using the VEDA4 program [7]. All calculations were carried out using Gaussian 09 program package [8].

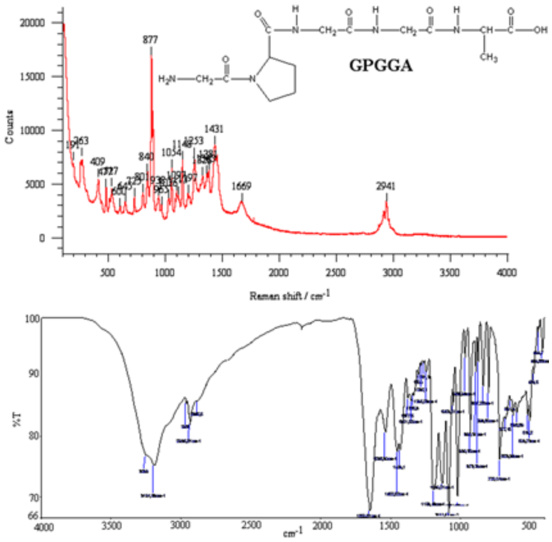

Fig. 1 The structure of GPGGA and Raman & IR

This study was supported by Erciyes University Scientific Research Project (Project no: FDK-2013-4543).

Keywords: Spider silk; GPGGA; Vibrational Analysis, DFT

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Po2.33 SUPRAMOLECULAR COMPLEXES OF DNA WITH LINKER CHROMOSOMAL PROTEINS: THE ROLE OF PROTEIN-PROTEIN INTERACTIONS REVEALED BY FTIR SPECTROSCOPY.

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Structural organization of the chromatin at the post nucleosomal level strongly depends on the DNA-protein interactions within the linker regions. The most abundant proteins, which interact with linker DNA, are linker histone H1 and non-histone chromosomal proteins HMGB1/2. The investigation of the interactions between these proteins and DNA are complicated due to the supramolecular nature of the complexes being formed. Earlier we have shown [1,2] that vibrational spectroscopy provided valuable information about the DNA-protein interactions in large DNA/H1/HMGB1 complexes. Besides, the data obtained indicated that the interactions between the protein molecules were likely involved in the complex formation. However, the details of the protein-protein interactions, which occurred in the system, remained unknown.

Our present study is primarily devoted to the investigation of the individual binary protein-protein and DNA-protein complexes using FTIR spectroscopy in H_2O/D_2O solutions. We have analyzed the secondary structure of the H1 and HMGB1 molecules and attempted to estimate its changes in the complexes: (1) – HMGB1/H1; (2) – DNA/H1 and (3) – DNA/HMGB1. We have also analyzed spectra of DNA in the complexes, using the vibrations in carbonyl region and sugar-phosphate backbone. We have studied complexes of the proteins with plasmid DNA using analytical ultracentrifugation and gel mobility shift assay. The experiments revealed different affinity of the proteins to the supercoiled, relaxed and linear forms of the DNA. Similar experiments with proteins revealed that HMGB1/H1 preferentially form 1:1 complexes. Dynamic light scattering demonstrated that a small fraction of large clustered complexes of pure protein also presented in the solution. Each of such clusters contained ~80 protein molecules.

The authors are grateful to the Russian Foundation for Basic Research (RFBR) for the financial support (grant 12-08-01134). Part of the research was performed at the “Center for optical and laser materials research” and “Center for diagnosis of functional materials for medicine, pharmacology and nanoelectronics” of St.Petersburg State University.

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Po2.34 DFT STUDY OF SUBSTITUENT EFFECT ON THE BAND STRUCTURE OF BICYCLIC CONJUGATED POLYMER

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Some important developments on polyselenophenes, related to the potential applications for high technology materials, have been achieved during the last years [1]. In one of recent studies, polyphosphole has been synthesized and very low band gap and a high electron-accepting ability have been observed for this compound [2].

Substituents alter the electronic properties of conjugated oligomers [3]. In this study, substituent effect on the band structure of novel polymer which is composed of phosphole and thiophene rings (Fig. 1.) has been studied employing B3PW91 functional[4,5] within Periodic Boundary Conditions [6]. 6-31G(d,p) basis set has been used for all the elements with the exception of Se which LanL2DZ(d) has been used. Gaussian 09 program package [7] has been used for all the calculations.

As seen from the Fig. 1., monomer has four open positions to make bond with another one, leading four different connections for polymerization in linear direction. So it is possible to make substitution into open positions other than positions oligomerization take place. As a result, in this study we have three parameters which may be varied to obtain conducting polymers with different band properties. These paramaters are connection positions, substituent positions and substituent type. It is imporant to tune electronic properties via different parameters for applications. We have performed DFT calculations on the polymers with different functional groups substituted to different positions. As a result, we have theoretically obtained many conducting polymers which may be used for several applications. For example, unsubstituted form of polymer with 2-4 connection has band gap with the value of 1.81 eV (E_{HOCO}= -4.82 eV and E_{LUCO}= -3.01 eV). When $-NO_2$ group was substituted into sixth positions (Fig 1.), we have calculated band gap of polymer as 1,69 eV (E_{HOCO}= -6.09 eV and E_{LUCO}= -4.40 eV). Due to this substitution, band gap value is shifted to relatively smaller value, E_{HOCO} and E_{LUCO} were shifted to lower values.

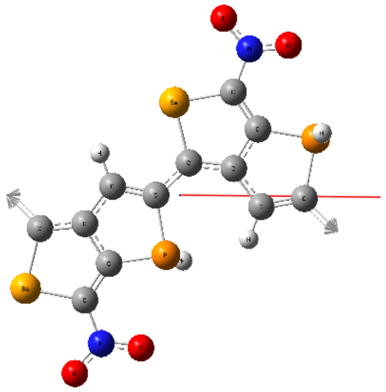

Fig.1 Optimized geometry of $-NO_2$ substituted polymer.

Acknowledgements: This study has been supported by The Scientific and Technological Research Council of Turkey (TUBITAK) (Project no: 212T051). The numerical calculations reported in this paper were performed at TUBITAK ULAKBIM (Turkey), High Performance and Grid Computing Center.

Keywords: DFT; Band Structure; Substituent Effect; Conducting Polymers

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Po2.35 QM CALCULATIONS OF IR AND UV-VIS SPECTRA OF SOME PUSH-PULL MOLECULES

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Some Push-pull molecules (Fig. 1) with NLO properties have been first studied from a structural point of view using B3LYP/6-31+g(d,p) level of Theory. Structures have been optimized for a variety of electron donors and attractors groups. The donors groups are different in molecules A and B and the attractors are varied in the two cases from NO2, CN, COOet , COCH3. In the second stage, the exited states as well as UV-vis spectra have been performed using TD-DFT method [1].

For this aim different functional have been employed such as TD-M06, TD-M06l, TD-M062x and TD-M06hf combined with the 6-31g+(d,p) basis set. The solvent effect has been included using the Continuum Polarisable Model (PCM) [2]. The IR spectra have been also computed, compared with the experimental ones and discussed.

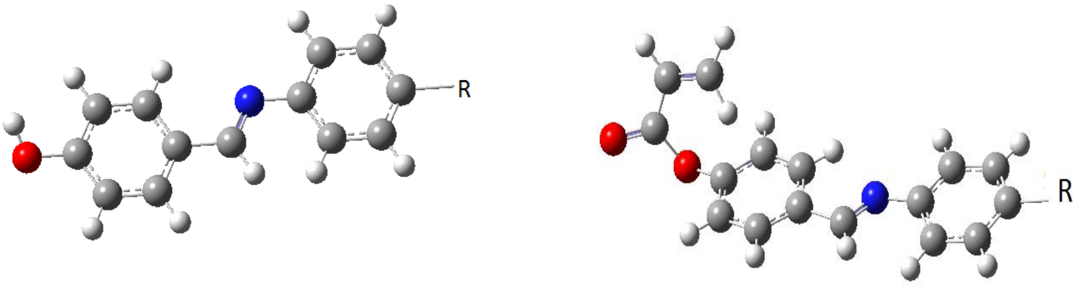

Fig. 1 Structures of A,B molecules having as substituent R : NO2, CN, COOet , COCH3,H.

Keywords: Push-pull molecules; DFt and TD-DFT; IR spectra, UV-vis spectra

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Po2.36 SPECTRAL STUDY OF DIPOLAR MOLECULES ORIENTATION

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The polymer side chains can be oriented by etiration determining the alignment of dipolar spectral active molecules in this process.

In the case of known directions of electronic transition one can establish the degree of orientation of these molecules along this polymer chains.

The spectral analyze of the polymer foils in which cycloimmonium ilids are included has led to the conclusion that about 60% of the spectrally active molecules can be oriented along the polymer chains. The dipole moments and the directions of electronic transition were established by Hyper Chem. 8.60.

The degree of order of the polymer chains depends of the magnitude of dipole moment of the spectral active molecules.

Keywords: polymer foils, degree of order, dipole moment

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Po2.37 UNAMBIGUOUS DETERMINATION OF THE MONOMER ALTERNATION IN STYRENE AND 2,3,4,5,6-PENTAFLUOROSTYRENE COPOLYMER

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The heteronuclear multiple bond correlation (HMBC) NMR spectra have been collected for a group of styrene (St) and 2,3,4,5,6-pentafluorostyrene (FSt) copolymers (St-*co*-FSt), which were copolymerized with different St and FSt monomer ratios (St:FSt). The sequential structure information of these St-*co*-FSt copolymers has been achieved by analyzing the 13C projection of specific area (1H chemical shift range from 6.2~7.5 ppm, while 13C chemical shift range from 37.0~46.5 ppm) on the HMBC spectra. Comparing with the sequential structure identification by the chemical shift change, our method determined the alternative structure of St-*co*-FSt (St:FSt=1:1) copolymer unambiguously and also the degree of monomer alternation for St-*co*-FSt copolymers with different monomer ratios[1].

Keywords: HMBC; copolymer; alternation

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Po2.38 CHARACTERISATION OF SURFACE MODIFICATIONS OF POLYETHYLENE FROM PLASMA POLYMERISATION USING SILICON-OXYGEN CONTAINING PRECURSOR COMPOUNDS BY FTIR-ATR SPECTROSCOPY

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Plasma polymerization is a method widely used for the fabrication of thin coatings for modifying the physico-chemical surface properties of various polymers. We are interested in the hydrophilisation of polyethylene (LDPE), which is used for harvesting atmospheric water (dew) by radiation exchange through the atmospheric window at wavelengths between 8 to 13 µm with the cold upper atmosphere [1]. Here, we report on results from plasma enhanced chemical vapour deposition (PECVD) at low pressure using tetraethoxysilane (TEOS) as well as hexamethyldisiloxane (HMDSO) as monomers. In addition to the infrared spectroscopic surface characterisation, also contact angle measurements were carried out over a time period of 60 days with untreated and surface-modified PE-foils under different storage conditions, i.e. either under normal laboratory air conditions, using a climatic chamber or under UV-radiation exposure.

The chemical composition of the fabricated surface layers was studied by Fourier-transform infrared (FTIR) spectroscopy by employing the attenuated total reflection (ATR) technique. We used a trapezoidal crystal of ZnSe with a reflection angle of 45°. For better comparison of the vibrational absorption bands resulting from the Si moieties, difference spectra versus the spectrum of an untreated LDPE film were calculated. We compared the surface layer spectra with that of silicone oil, i.e., a liquid polymerized siloxane with organic side chains. A recent publication on polydimethylsiloxane (PDMS) based polymers provides a band assignment to Si-group vibrations [2].Our results are also discussed with those of recent studies, by which polypropylene was surface-modified by PECVD using either TEOS [3] or HMDSO as precursor compounds [4]. The spectral characterisation of their obtained surface layers was also carried out by means of the ATR-technique.

Keywords: plasma enhanced chemical vapour deposition; polyethylene surface modification; ATR-FTIR spectroscopy, contact angle measurement, TEOS, HMDSO

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Po2.39 COMPILATION AND COMPARISON OF MID- AND NEAR-INFRARED SPECTRAL LIBRARIES OF PHARMACEUTICALS AND DRUGS FOR FORENSIC ANALYSIS

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In forensics and criminology, the abuse of pharmaceuticals available without prescription as well as prescription medicaments has often been reported. However, their chemical identity is not always known when those substances are found and forensic investigations are needed. Spectra of such compounds are usually compared to those of a data bank consisting of a large number of spectra of the respective substances. For this study, high-quality transmission mid-infrared (MIR) and transflection near-infrared (NIR) spectra were recorded from µg amounts of many pharmaceuticals including drugs.

As measurement technique for the MIR-spectra, KBr-micropellets had been manually prepared, whereas for the NIR-spectra the diffuse reflection technique was applied using an ellipsoidal mirror-based accessory and gold-coated abrasive paper substrates. For library testing, qualitative analyses were carried out by means of the OPUS-IDENT programme (Bruker Optics). The respective results of an identity test based on library search and a cluster analysis are exemplarily discussed for pure and laced drugs (2 and 3 component mixtures).

As a conclusion, both-spectral methods show certain advantages and disadvantages. Especially, the laborious sample preparation for the MIR-spectra catches the eye as a disadvantage, although nowadays more frequently attenuated total reflection (ATR) measurements have been suggested [1]. Powdered substance masses required for recording either MIR or NIR spectra with a large signal-to-noise ratio were similar (≈ 100 µg and less). Although the obtained results from the identity test using MIR-spectra were better than those results from the NIR, however, in both cases the results were unequivocal. Finally the statement is allowed that NIR spectroscopy, despite the probably higher costs in instrumentation is an alternative to MIR-measurements, especially because of short measurement times without any sample preparation for spectral recording.

Keywords: forensics; drug analysis; infrared spectroscopy; KBr-micropellets; near-infrared spectroscopy: identity test; library search; cluster analysis

References

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Po2.40 ANALYSIS OF MINERAL OIL PRODUCTS AND FATTY ACID ESTERS IN SOIL USING DIFFUSE REFLECTION NIR SPECTROSCOPY

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The production of crude oil is still an important industry. With lack of alternatives, it can be expected that this scenario would not be changed in the foreseeable future. These technologies, storage and transport entail risks for the environment due to accidents and sabotage causing huge ecological damage. In case of such accidents, a fast detection and quantification of contaminations is important to start countermeasures in due time. Therefore, the development of new methods of analyzing hydrocarbons in environmental compartments is still a relevant issue. For this study, a characterization of different types of soil, their chemical and dispersive properties concerning their distribution of particle sizes are described.

An analysis of contaminated soils with diffuse reflection near-infrared spectroscopy was frequently revisited over the past few years [1-4]. Inspired by the results of different workgroups, the possibility of analyzing soil by diffuse reflection is discussed in detail. Therefore, different soils were contaminated with different concentrations of engine and vegetable oil. The correct preparation and measurement method were important topics. The own results and those from other workgroups show that a further investigation is worthwhile and needed. Diffuse reflection measurements directly on soil-samples are an interesting topic, especially, since an expensive preparation of the samples is not necessary. Nevertheless, it could be shown that this preparation effort must not be underestimated. Also the correct processing and normalization of the spectra is important to achieve comparable results. The concept must be developed further even with the use of mobile devices, which could be used for field analyses.

Keywords: environmental assay; hydrocarbons; near-infrared spectroscopy; soil analysis;

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Po2.41 EXCITED STATE POLARIZABILITY OF SOME NON-POLAR SPECTRALLY ACTIVE MOLECULES FROM SOLVATOCHROMIC ANALYSIS

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Dispersive forces are predominant in non-polar solvents containing spectrally active molecules with small dipole moments in their ground electronic state.

Solvatochromic studies offer information about the strength of the dispersive interactions by the spectral shifts measured in non-polar solutions.

A series of isolated benzene derivative molecules in the ground electronic were analyzed from quantum-mechanical point of view and their electro-optical parameters were computed. The results obtained by HyperChem and those corresponding to the solvatochromic studies permitted us to estimate the molecular polarizability in the excited state of the spectrally active molecules based on the theories describing the solvent influence on the electronic absorption spectra.

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Keywords: electronic absorption spectra; universal interactions in non-polar solutions; molecular polarizability in excited state

Po2.42 ISOMERIZATIONAL AND CONFORMATIONAL STUDY OF 3-FLUOROPHENYLAMINO-2-ACETYL PROPENENITRILE (FPAAPN)

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Heteroarylaminoethylene compounds substituted with fluorine are excellent precursors for the synthesis of biologically active 4-quinolones, and some of them are also biologically active themselves as they show, for example, photobleaching activity towards cells of Nicotiana tabacum, and fungicidal, germicidal or herbicidal properties.

3-fluorophenylamino-2-acetyl propenenitrile (FH_4C_6)-NH-CH=C(CN)$(COCH_3)$ (FPA-APN) belongs to the push-pull ethylenes intensively used in synthetic organic chemistry. The electron donor fluorophenylamino group in the investigated compound seems to have a special influence on their conformational and configurational equilibria perhaps due to the possibility to create an intramolecular hydrogen bond.

Using ab initio MP2 and DFT B3LYP calculations in different basis sets eight conformers of FPAAPN have been found, four for *Z*-isomer and four for *E*-isomer (the first letter denotes *cis* and *trans* position of fluorophenylamino and acetyl groups, the second *Z* or *E* and the third *s* or *a* letters denote the conformational orientation of carbonyl oxygen and fluorophenylamino group towards or from double C=C bond, respectively). However, as shown by calculations, they significantly differ in energy. The most stable conformer is the *ZZa* one that enables an intramolecular hydrogen bond. In the synthetic process the pure *Z*-isomer has been obtained and *ZZa* conformer has been confirmed by X-ray diffraction [1] and by NMR in chloroform. Due to the high energy the *ZZa* cannot pass to other *Z*-isomer conformers and no isomerization process occurs as has been confirmed by NMR spectra after 4 weeks. Nevertheless, in more polar DMSO the process of isomerization takes place practically immediately and the next conformer of *E*-isomer with *anti* orientation of fluorophenylamino group has been confirmed.

In DMSO the presence of both *Z*-isomer and *E*-isomer conformers has been proven both by NMR and vibrational spectroscopy with *EZa* conformer as the more stable one. In order to explain such behavior, solvent effect calculations using PCM model with solvents of various polarity have been done.

Table 1: B3LYP calculated relative energies ΔE of FPAAP conformers in cc-pVDZ basis set.

FPAAPN	*EZa*	*EZs*	*EEa*	*EEs*	*ZZa*	*ZZs*	*ZEa*	*ZEs*
ΔE (kJ/mol)	15.29	44.81	33.75	67.46	0.00	66.26	57.03	89.23

Keywords: Conformational analysis; Vibrational and NMR spectra; Push-pull compounds

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Po2.43 PROPERTIES OF ZnO PARTICLES PRECIPITATED BY RAPID HYDROLYSIS OF ZINC ACETYLACETONATE

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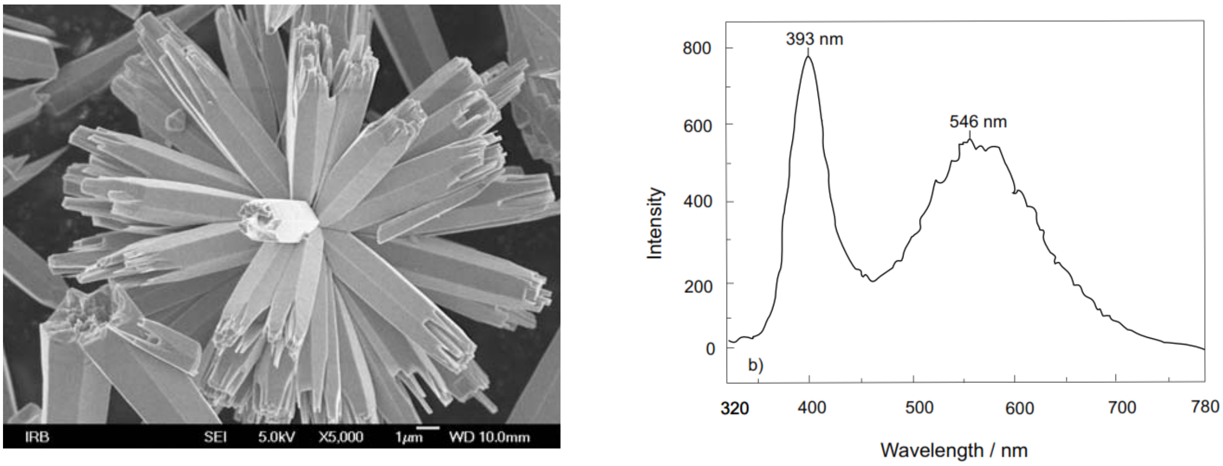
The precipitation chemistry of zinc oxide (ZnO) has been extensively investigated, primarily because ZnO has found important applications, both in the traditional technologies such as paints, catalysts, rubbers, cosmetics and in advanced technologies as sensors, photodetectors, LEDs and transistors. The nano/microstructure of ZnO in the form of powders or films is an important property of specific applications of this material. ZnO can be synthesized to possess various nano/microstructures and other properties by varying the chemistry and physical parameters in a corresponding synthesis. In the present work we have investigated the influence of experimental conditions on the nano/microstructure and optical properties of ZnO particles produced by rapid hydrolysis of zinc acetylacetonate at 160 °C. The samples were characterized with XRD, FE scanning electron microscopy, FT-IR, UV/Vis/NIR and photoluminiscence (PL) spectroscopies. XRD patterns of all samples were assigned to the hexagonal ZnO phase (wurtzite-type), as well as the corresponding FT-IR spectra. FE-SEM inspection showed high dependence of ZnO microstructure on the chemical composition of the reaction mixture and time of ageing during the rapid hydrolysis of zinc acetylacetonate. Microstructural differences were noticed between C_2H_5OH/H_2O and H_2O media, as well as under the influence of NH_4OH adding. Aggregation of ZnO nanoparticles into much bigger ZnO particles (micron size) and dissolution/recrystallization are found to be also important factors in the formation of different ZnO nano/microstructures. The band gap values for prepared ZnO samples were calculated on the basis of UV/Vis spectra recorded. PL spectra were recorded for ZnO samples in powder form and their suspensions in pure ethanol. A differences noticed will be discussed.



Hollow ZnO particles (multipod) and their PL spectrum

Po2.44 INFLUENCE OF EXPERIMENTAL CONDITIONS ON THE PRECIPITATION OF 1D α-FeOOH in HIGHLY ALKALINE MEDIUM

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α-FeOOH (goethite) particles are characterized with excellent acid-base surface properties which can be utilized for decontamination of radioisotopes as well as for removal of toxic elements (arsenic, lead, cadmium and some others) from waste waters. The colour of α-FeOOH particles may vary from lemon yellow to dark brown and this property can be utilized in pigment applications. 1D α-FeOOH particles can be used as precursor in the synthesis of 1D magnetic oxide (γ-Fe_2O_3). In the present work we have investigated the influence of CTAB (cetyl trimethylammonium bromide) and gum arabic on the precipitation of 1D α-FeOOH particles in highly alkaline medium and properties of these particles. Objective of this work is to obtain more data about the factors which influence the microstructure of 1D α-FeOOH particles and corresponding phase transformations. The precipitates were characterized with XRD, FE-SEM, ^{57}Fe Mössbauer, FT-IR and UV/Vis/NIR techniques. 1D α-FeOOH particles were precipitated by adding concentrated NaOH solution into $FeCl_3$ or $Fe(ClO_4)_3$ solution at pH ~ 12.3-12.8, followed by heating the precipitation systems at 90 or 160 °C. Precipitation from $FeCl_3$ solution containing 1-2 % CTAB also yielded a small fraction of α-Fe_2O_3 (hematite). This effect can be related with the adsorption of positively charged surfactant onto 1D α-FeOOH crystallites. Advantage of ^{57}Fe Mössbauer spectroscopy in determination of small α-Fe_2O_3 fraction in these precipitates is shown. A strong influence of gum arabic on the precipitation of 1D α-FeOOH from $Fe(ClO_4)_3$ solution in highly alkaline medium was noticed. The steric effect played also important role for observed phase and microstructural changes. The abilities of XRD, ^{57}Fe Mössbauer and FT-IR spectroscopies in determination of the phase composition of the precipitates will be discussed. UV/Vis spectra of prepared samples were also sensitive on the changes in the precipitates investigated.

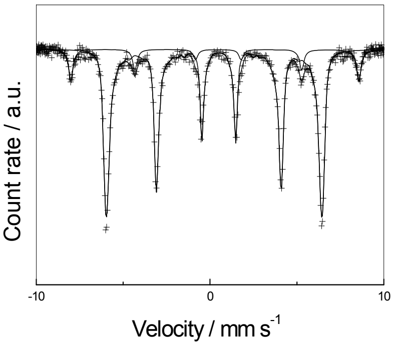

Fig.1 ^{57}Fe Mössbauer spectrum shows the presence of 1D α-FeOOH and small fraction of α-Fe_2O_3 in the precipitate produced in the presence of 2% (wt) of

Po2.45 INVESTIGATION ON NEW Ni(II) AND Co(II) DITHIOPHOSPHINATE COMPLEXES

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Long-alkyl-chain dithiophosphinate (DTP) anions $[R_2PS_2]^-$ have long been under investigation for the solvent extractions of metals. Dithiophosphinic acids (DTPA) and their derivates are of interest for their excellent metal complexing abilities, such as Au^+, Ag^+, Cu^{2+}, Co^{2+}, Ni^{2+} [1]. Several patents describe the potential industrial use of DTPA–metal salts as additives in lubricating oils, plastics, and rubber [2]. Some DTPA– ^{99}Tc complexes have been introduced as brain imaging agents in radiography [3].6 Cephalosporin-type chemicals containing DTPA moieties have been suggested as antibiotics in clinical medicine [4].

In this study, bis[iso-butyl(4- methoxyphenyl) dithiophosphinato]nickel(II), $[Ni(L^1)_2]$, bis[sec-butyl(4-methoxy-phenyl) dithiophosphinato] nickel (II), $[Ni(L^2)_2]$; bis[iso-butyl(4- methoxyphenyl)-dithiophosphinato] cobalt(II), $[Co(L^1)_2]_2$, and bis[sec-butyl(4-methoxy phenyl)dithio-phosphinato]cobalt(II), $[Co(L^2)_2]_2$ were characterized by elemental analysis, ^1H, ^{13}C, and ^{31}P NMR (Figure 1). Also, we report on the crystal structure of the $[Ni(L^2)_2]$ suitable for X-ray analysis.

Keywords: dithiophosphinic acids ; phosphinodithioates ; Dithiophosphinato complexes

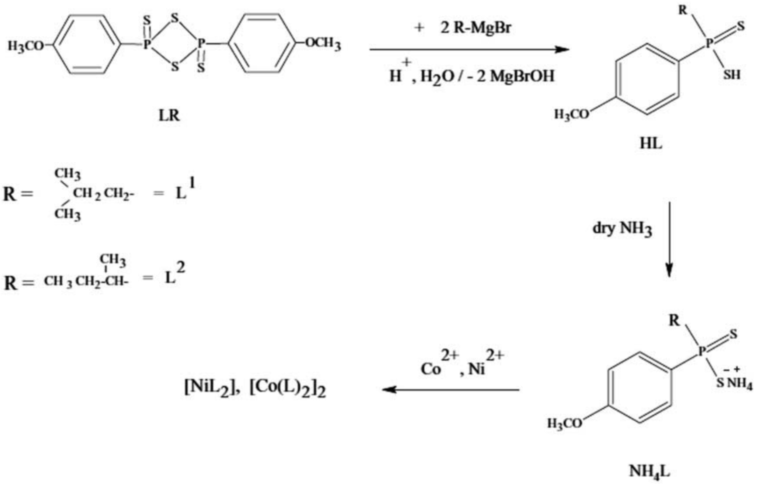

Figure 1. The preparation of some new DTPAs and their complexes

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Po2.46 BUILDING, CHARACTERISING AND CATALYTIC ACTIVITY TESTING OF CO–C-PROTECTED AMINO ACID COMPLEXES COVALENTLY GRAFTED ONTO CHLOROPROPYLATED SILICA GEL

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Homogeneous catalysts are most often complexes comprising of a metal or metal ion and various organic compounds. They can be very active and, occasionally, extremely selective, however, during work-up their separation from the reaction mixture is usually difficult; therefore, their recovery and reuse seldom can be solved efficiently.

Metal ions are cofactors in many enzymes, most frequently in oxidoreductases. The ions there are capable of altering their redox states as well as their coordination number. The ligands are amino acid residues of various kinds. The cofactor together with the proteomic skeleton forms the most selective of all catalysts, the enzymes. They are semi-solid materials capable of working at near atmospheric pressure, in a limited temperature range and physiological aqueous solution. However, if metal ion–amino acid complexes inspired by the metal ion containing enzymes are prepared and immobilised on various supports, then, we may be able to produce catalysts with activities and selectivities resembling those of the enzymes. This widens the range of conditions under which the heterogenised complexes are capable of working and at the same time facilitates easy recovery and recycling.

In order to approach these goals, Co–C-protected amino acid (C-protected L-histidine, L-cysteine and L-cystine) complexes were covalently grafted onto chloropropylated silica gel, and the materials thus obtained were structurally characterised by mid and far IR as well as X-ray absorption spectroscopies and their catalytic activities were also tested.

Even visual inspection of the sample revealed the success of building the complex on the surface of the support, since the products were all coloured – they were all blue. The blue colour even indicated that the coordination of the Co(II) ion in the surface-grafted complexes was four. Analysis of the mid and far IR and X-ray absorption spectra allowed to determine the coordinating groups and if both amino acids were in the coordination sphere when a 1:1 mixture of amino acids were used for surface grafting and ligation. Generally, when protected histidine was present as ligand, it coordinated through the imidazole nitrogen, and very often through the carbonyl oxygen too. Protected cysteine was coordinated through the thiolate or thiol sulfur and the carbonyl group. The sulfur atoms of the disulfide bridge were always coordinated when protected cystine was in the coordination sphere. Here also, the carbonyl oxygens were often binding sites as well.

All materials displayed catalytic activity, although catalytic activities differed widely. As a tendency, it was found that the complexes prepared under ligand-poor conditions (surface-anchored amino acids were only available for ligation) were more active than those made in the presence of excess amino acids. Surface complexes with mixed amino acid ligands were more active than those having uniform amino acids in their coordination environment, although there were some exceptions.

Keywords: Co–C-protected amino acid complexes, structural characterisation, catalytic activities

Po2.47 THE EVOLUTION OF RAMAN SPECTRA OF POLY(p-PHENYLENEDIAMINE) DURING CARBONIZATON

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Poly(*p*-phenylenediamines) synthesized by the oxidation of *p*-phenylenediamine with ammonium peroxydisulfate at two oxidation levels (Fig. 1; equimolar and double amounts of the oxidant were used), were heated to 200–800 °C in inert nitrogen atmosphere. The changes of the structure of the material during heating were followed by Raman spectroscopy, thermo-gravimetric analysis and scanning electron microscopy [1].

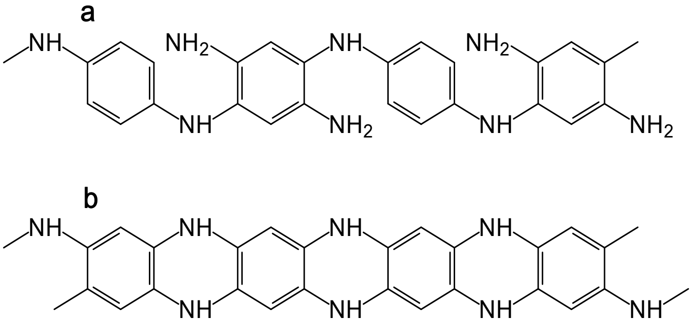

Fig. 1. The idealized structure of lowly (a) and highly (b) oxidized form of poly(*p*-phenylenediamine).

The poly(*p*-phenylenediamine) prepared in lower oxidation state is more thermally stable. Both forms were converted to nitrogen-containing carbon material.

The molecular structure of low- and high-oxidized poly(*p*-phenylenediamine) and the products of their heating are discussed in the context of polyaniline and aniline oligomers. Two idealized structures proposed for poly(*p*-phenylenediamine) (Fig. 1) reflect the observation of basic constitutional units, but the true structure of these polymers is believed to be more disordered.

*Keywords: Raman spectroscopy; poly(*p*-phenylenediamine); carbonization*

References

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