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The rotamerization of conformers of glycine isolated in inert gas matrices. An infrared spectroscopic study

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Abstract

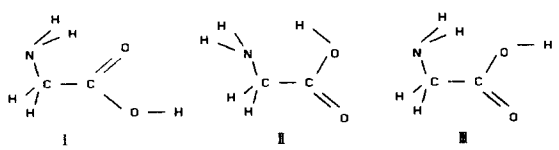
The infrared spectra of glycine isolated in Ne, Ar and Kr matrices have been measured. The matrix-isolated glycine is shown to be in the molecular form. The spectral manifestations, both conformational and site splitting, are separated. Three different conformers of glycine have been identified experimentally for the first time. It is shown that during the deposition of the samples the substrate temperature must be lowered to 13 K – this is a decisive factor permitting fixation of a complete set of glycine conformers in an inert matrix. The relative energies of the three glycine conformers are estimated to be 0, 1.3–1.6 and 0.9–1.5 kcal/mol.

1. Introduction

Glycine, the smallest among natural aminoacids, is an object of numerous studies. Depending on its environment, glycine, like all aminoacids, can exist either as a zwitterion (NH_3^+–CH_2–COO^-), which is typical for crystals [1] and solutions [2], or in the molecular form (NH_2–CH_2–COOH), which is characteristic of the gas phase [3]. The molecular form has a higher conformational mobility because rotation about three intramolecular axes, i.e. N–C, C–C and C–O bonds, is possible.

Early in the development of the ab initio glycine calculation, it was shown [4,5] that three C_s structures of possible glycine conformers (see Scheme 1) are most stable. Subsequent semiempirical [6–8] and ab initio [9–18] calculations have one finding in common: conformer I has a global energy minimum in the gaseous phase. Conformers II and III (or their non-planar counterparts) correspond to local minima on the conformational potential energy surface of glycine. Their relative energies are approximately equal and not exceed 1.8 kcal/mol in reference to conformer I [13,14]. The other local minima are far less advantageous. The zwitterion form of the gas-phase glycine has no minimum at all [12].

Experimental studies on the gas-phase glycine structure are faced with a problem. The method of microwave spectroscopy is of limited application because the transition intensities of microwave spectra



Scheme 1.

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are proportional to the squared dipole moment of the molecules. Conformer I has a considerably lower dipole moment than conformer II [14–17]. Therefore, conformer I could be identified successfully only after a considerable improvement of the spectral equipment [19,20] and was detected much later than conformer II [21,22]. Conformer III has not been yet registered.

Electron diffraction studies on gaseous glycine [23] identified conformer I as most stable. At the same time it is believed [23] that conformers II and III are indistinguishable from the standpoint of electron scattering intensity because their structures differ in the positions of the hydrogen atoms of the amine and hydroxyl groups.

It is known that conformations of organic molecules are effectively studied by the methods of vibrational spectroscopy [24]. When applied to aminoacids these methods however run into obstacles such as e.g. a low vapor pressure at temperatures most suitable for heating the sample. So, heretofore experimental vibrational spectra of the molecular glycine are scantily known.

The work objectives were to study the infrared vibrational spectra of isolated glycine molecules, to detect and identify various conformers of glycine. The method of molecule isolation in low temperature inert matrices is a unique tool for solving this problem. Since the isolated molecules do not rotate in the matrix and their interaction with the environment is weak, the width of the absorption bands in the vibrational spectra considerably decreases [25]. This permits experimental identification of the rotational conformations of the molecules, whose spectral distinctions are very slight [26–29].

2. Experimental

To prepare samples of the required quantitative composition and to measure the flux densities of the sample components, a low-temperature quartz microbalance was used. Homogeneity of the samples was ensured by careful maintenance of stable evaporation conditions for glycine and matrix gases. Commercial glycine was evaporated from the Knudsen cell at 140–165°C. The thermostatting accuracy was 0.2°C. The matrix-to-sample ratio (M/S) was controlled by selecting the matrix gas flows. The matrix gases used were Ne, Ar and Kr. Prior to evaporation, Ar was cooled down to liquid nitrogen temperature which ensured constant vapour pressure above solid Ar. The Ne and Kr pressure was stabilized with a special manostat. The matrix gas flows were controlled with fine-accuracy needle valves.

The spectra in Ne and Ar matrices were recorded by an FS-01 FTIR spectrometer with a resolution of 0.2 cm^{-1}. The cooled quartz microbalance mirror was used as the matrix substrate. The spectra in the Kr matrix were recorded with an updated Specord IR-75 grating spectrometer whose resolution was 1 cm^{-1} at 2000–400 cm^{-1}. The optic substrate for matrix was a CsI plate. The control and stabilization of the matrix deposition conditions, the recording and processing of spectra were performed using an original program package. An IBM-AT computer, the spectrometer and the cryostat were connected via the CAMAC system. To avoid the influence of atmospheric water and CO_2 vapours on the spectra, the instruments were blown through with dry nitrogen. The cryostat used for matrix IR spectroscopy is described elsewhere [30].

3. Results and discussion

The observed IR spectrum of glycine trapped in Ne matrix is shown in Fig. 1. The absorption bands at 3600–3500 cm^{-1} (OH stretching (str)), 1800–1700 cm^{-1} (C=O str) and 1650–1600 cm^{-1} (NH_2 bending (bend)) indicate that the matrix-isolated glycine is in the molecular form. This is also true for previously investigated matrix-isolated leucine [31] and proline [32].

It should be noted that some absorption bands of the matrix spectra have a complex structure. This splitting may be caused by different factors – association, different packing of the isolated molecules (site splitting), conformational effects. With the M/S increased to 1000, the formation of associates in the matrices becomes negligible and may be excluded as a factor responsible for the band splitting. Furthermore, studies on the spectra of a substance obtained in different matrices may permit separation of the matrix-induced splitting and the conformational effects [33].

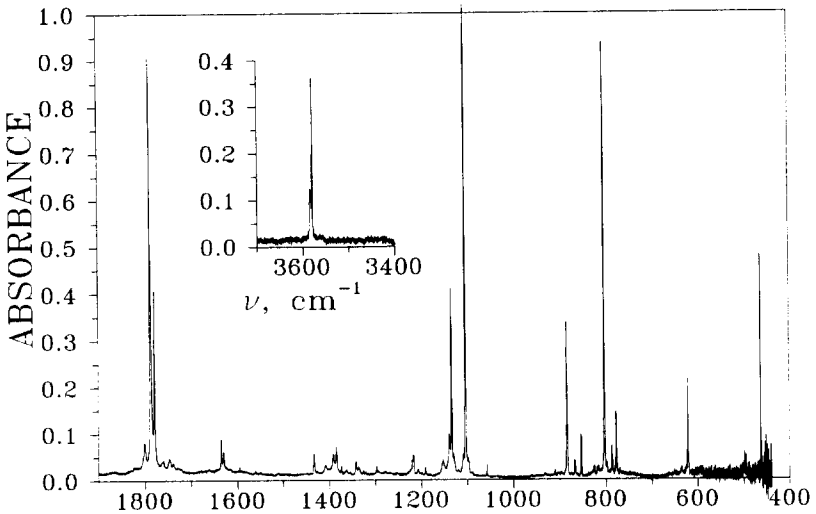

Fig. 1. IR spectrum of glycine isolated in a Ne matrix at 5.5 K. M/S=550. The 1103.6 cm^{-1} band is truncated.

The spectra of glycine isolated in Ne, Ar and Kr matrices are shown in Fig. 2. It is seen that there are at least three bands in the C=O str region whereas calculation predicts only one for each glycine conformer [14]. Comparison of the spectra (Fig. 2) shows that varying of the matrix gas does not have pronounced influence on the spectral shapes in this region. This prompts the assumption that the multiple trapping site effects cannot fully account for the band splitting in the spectra because the manifestations of this effect are hardly identical in different matrices. We may thus believe that the band splitting in the IR spectra of glycine is most probably caused by the conformational effects. This reasoning is supported by the experimental finding that gas-phase molecular glycine can have at least two conformers [19–23].

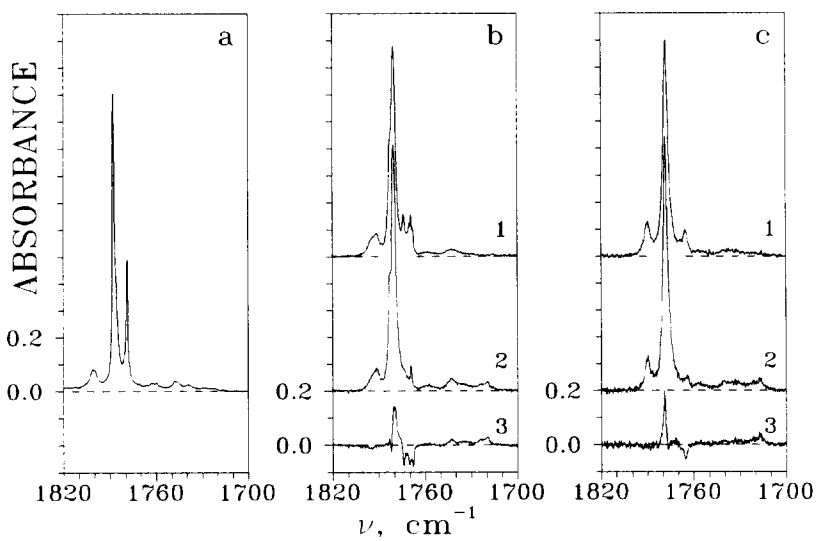

Fig. 2. C=O stretching region of matrix-isolated glycine. (a) Ne matrix, M/S=550, deposition at 5.5 K; (b) Ar matrix, M/S=850; (c) Kr matrix, M/S=500. (1) Spectra after deposition at 13 K; (2) Spectra after matrix annealing at 20 K for 15 min in Ar matrix and for 30 min in Kr matrix; (3) Difference spectra (3=2−1). The spectra are shifted for clarity.

Assuming that the equilibrium distribution of the conformers typical of the gas phase still persists in glycine trapped in an inert gas matrix, the spectral and energy characteristics of different conformers can be studied experimentally. This assumption however entails the requirement that no mutual conversion of the conformers should occur in this case. As Barnes shows [33], there is a rough correlation between the barrier to internal rotation and the lowest temperature at which interconversion was observed. The above requirement becomes important when the barriers to internal rotation are small enough. This situation can be realized in glycine. In such an event, the substrate temperature has to be maintained lower than certain level when the matrix is deposited.

To determine this level we deposited the set of samples at a range of different substrate temperatures. These temperatures were varied between 19 and 5.5 K. We have revealed that the chilling of substrate surface results in the appearance of new absorption bands starting with 16 K. In our opinion these new bands are caused by fixing in the matrix of an additional glycine conformer. On cooling down to 13 K an increase of the band intensities was found. On further cooling down to 5.5 K, the gain of intensities was stopped. By this means we have directly verified that freezing out the gas phase distribution of glycine conformers may be attained at a temperature equal to or less than 13 K.

Let us assign the bands in the C=O str region (Fig. 2) to particular conformers. According to Hu et al. [14], in the C=O str case the absolute intensities of the IR absorption bands of conformers **I**, **II**, **III** agree to within 5%. We may thus expect that in the C=O str region the relative intensities of the multiplet components are proportional to the fractions of the corresponding conformers in the matrix. On fast freezing and in the absence of interconversion in the matrix, the non-equilibrium distribution of the conformers in the low temperature matrix should correspond to their gas-phase equilibrium distribution at the sublimation temperature. These are sufficient grounds to believe that the most intensive bands refer to the most stable conformer **I**. The analysis of Table 12 in Ref. [14] suggests that the highest-frequency absorption band of carbonyl should be assigned to the glycine conformation with the trans-position of the O–H and C=O groups. Structure **II** meets this condition. The lowest-frequency stretching vibration of carbonyl corresponds to structure **III** in Scheme 1. The fact that structure **III** has, among the others, the lowest-frequency C=O absorption band is in good agreement with theoretical calculation [14]. The results of the assignment are collected in Table 1. The validity of band assignment in Table 1 to the single conformers but not to the associated species is confirmed by the fact that the bands of the last ones appeared in the 1750–1700 cm^{-1} region after matrix annealing (Figs. 2b and 2c).

The above assignment of the conformers is additionally supported by the comparison of the results of matrix annealing and the calculation of the barriers to internal rotation in glycine [13]. It is seen from Fig. 2 that there are three types of bands in the spectra – unchanged (A), increased (B) or decreased (C) – due to annealing. Since on annealing the proportion of conformer **III** decreases and that of conformer **I** increases, and this process starts at 19–20 K, then, according to Barnes [33], the barrier to this conformational rearrangement **III**→**I** should not be higher than 1.4 kcal/mol. As follows from the theoretical analysis of the conformational potential energy surface of glycine, the barrier to the transition **III**→**I** is 1.3 kcal/mol [13] (ab initio 6-31G* calculation). It should be noted that the spectra of glycine in a Ne matrix both deposited at 5.5 K (Fig. 2a) and annealed at 8.5 K are not different from each other. The band 1778.9 cm^{-1} of conformer **III** does not disappear in the Ne matrix up to 8.5 K, i.e. conformational interconversion does not happen. This fact confirms the suggestion that the results represented at Figs. 2b and 2c are caused by conformational effects but not by matrix repacking during annealing. The barriers calculated for the transitions between the non-planar analogue of conformation **II** and the conformations **I** and **III** are about 20 kcal/mol. This result agrees with the fact that the band intensity of conformer **II** does not change on annealing (Figs. 2b and 2c).

It is now clear why the only previous attempt to study the matrix-isolated glycine [34] could not answer the question about its conformational structure. The reason is that the experimental setup permitted the temperature of the optic substrate to be as low as 20 K [34], which is insufficient to fix the complete set of glycine conformers in the matrix.

Table 1
C=O stretching frequencies and intensities of glycine isolated in Ne, Ar and Kr matrices. Assignment of bands to the various conformers

Conformer [a]	IR frequencies and intensities [b]				Type of band [e]
	observed [c]			calc. [d]	
	Ne matrix	Ar matrix	Kr matrix		
II	1800.6 (950)	1791.60 (773)	1790 (794)	1842	A
I	1778.9 (2128)	1774.1 (1224)	1778 (3912)	1818	B
III	1787.8 (6008)	1769.2	1765 (603)	1814	C

[a] For the conformational forms, see Scheme 1.
[b] Frequencies in cm^{-1}, integral intensities in parenthesis (au).
[c] Evaporation temperatures are 162, 165 and 140°C for the Ne, Ar and Kr matrix, respectively.
[d] Ref. [14]. [e] (A) No changes on annealing; (B) increases on annealing; (C) decreases on annealing.

Having assigned the glycine conformers over the C=O str region, it is interesting to trace the conformations in other spectral regions. It is most likely that the vibration bands of the groups involved in the formation of intramolecular H bonds (stabilizing the structures of various conformers) will be most conformation sensitive. These, in addition to C=O, include O–H and N_2 groups. In the O–H str absorption region the splitting is slight, and the absorption frequencies calculated theoretically coincide for conformers I and III [14]. The absorption intensity of NH str vibrations is very low in IR spectra (Fig. 1), which agrees with calculation [14]. The NH_2 bend vibrations behave much like the OH str bands: the splitting is weak, the theoretical absorption frequencies of conformers I and III nearly coincide [14], the annealing does not affect the structure of the NH_2 bend band. This gives no way of estimating the conformational behaviour of these bands within our experiment (e.g., on annealing).

We have found a range sensitive to the matrix annealing in the low-frequency region of the IR spectrum of glycine (Fig. 3). Note that in the region 840–760 cm^{-1} calculation predicts only one normal vibration (ω_{17} in Table 12 of Ref. [14]) for each conformer of glycine, and the NH_2 wagging and C–C stretching vibrations make a considerable contribution to this absorption (about 20% and 30%, respectively) [35]. The structure of the IR spectrum in this region is strongly dependent on the nature of the matrix gas. The IR spectrum of glycine isolated in the Ne matrix (Fig. 3a) displays only three bands in this region but the total number of bands in the Ar matrix (Figs. 3b and 4) is twice as many as what the three conformers can produce. The origin of this may be due to superposition of the conformational effects and the spectral manifestations of various matrix packings. The band assignment to different glycine conformers in this region may be based on the reasoning used for the C=O str multiplet components.

As seen in Fig. 4, there are two multiplet bands which vary with the matrix temperature. The 776.5, 772.2 cm^{-1} doublet remains in the spectra both in the sample deposited at 5.5 K and in the one obtained at 13 K (Figs. 4a and 4b). On annealing the matrix this doublet vanishes (Figs. 4b and 4c) in the narrow temperature range between 16 and 20 K in synchronism with the C=O str band of conformer III. Thus we assigned this doublet to the conformer III.

The second temperature-dependent multiplet is bounded by 803 and 795 cm^{-1}. We assign this multiplet band to the vibration of conformer I. The considerable redistribution of the intensity in the 803–795 cm^{-1} region is observed in the wide temperature range between 5.5 and 28 K (Figs. 4a–4d). This redistribution is in our opinion caused by the matrix effects. We believe that these effects mask the slight increase in the integral intensity of the whole multiplet gained from the conformational transition.

In our opinion the contribution of the conformational and the matrix effects to the splitting of the ω_{17} bands may indicate that in low-temperature matrices the notion 'conformation' refers to the complex including the molecule and its nearest surroundings rather than to the molecule alone. That conclusion is a matter of principle: the molecule's geometries are

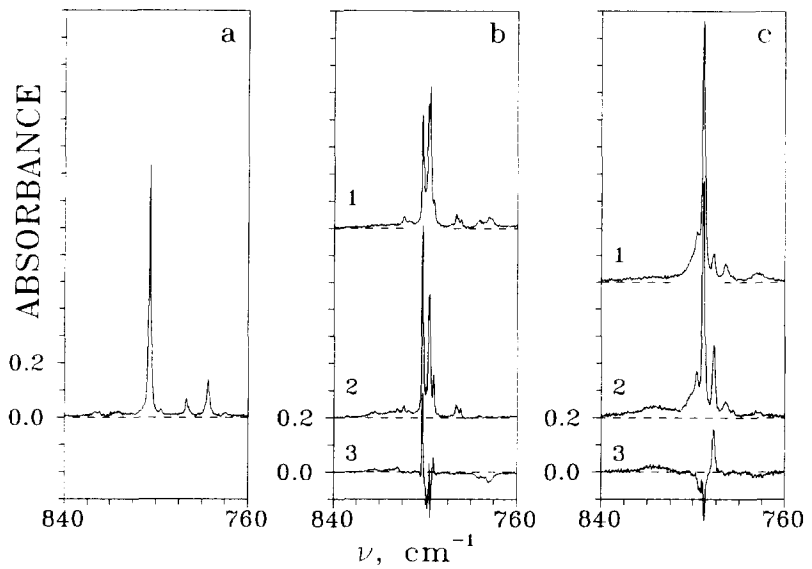

Fig. 3. The 840–760 cm^{-1} region of matrix-isolated glycine. For the comments see caption to Fig. 2.

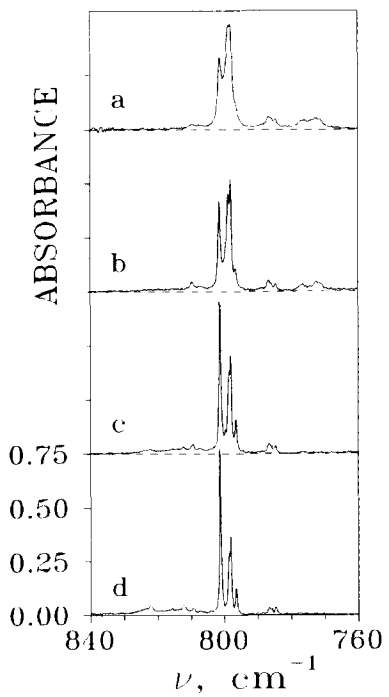

Fig. 4. IR spectra of glycine isolated in Ar matrix. (a) The sample deposited at 5.5 K; (b) the sample deposited at 13 K; (c) annealed for 15 min at 20 K; (d) annealed for 10 min at 25 K. The spectra are shifted for clarity.

slightly distorted in the low-temperature matrix and the method of matrix isolation may be unable to distinguish between molecules with slightly varying geometrical parameters. It is therefore very difficult to specify for all types of glycine conformers whether the heavy atom framework has a planar or non-planar atom arrangement. This is particularly important to conformer II for which theory predicts an energy minimum at the N–C–C=O angle of about 15° with the saddle point at 0° and the barrier below 0.15 kcal/mol [18].

The knowledge of spectral peculiarities of different glycine conformers is a significant prerequisite to the solution of another important problem – the energetics of the conformers. The most consistent approach calls for measuring the temperature trend of the bands corresponding to different conformers. This is however difficult to do with glycine because of its low thermal stability. Glycine starts to degrade heavily even at 180–200°C though without appreciable redistribution of intensity in the conformation-sensitive multiplets.

For estimating, even roughly, the difference in energy among the conformers without measuring the temperature behaviour of the bands, several preliminary assumptions are required:

(i) The whole set of conformers which are in equilibrium in the gas phase at the sublimation tempera-

ture persists on freezing in the low temperature matrix at 13 K and lower.

(ii) Only three of the above-described conformers contribute considerably to the conformational equilibrium at 140–165°C, the rest of them may be disregarded.

(iii) All the conformers are planar and contribute to the equilibrium distribution with a statistical weight of unity. If conformer **II** is not planar, this does not come into conflict with theory since its vibration ground state is above the barrier and its probability distribution has a single maximum at the planar form [18].

The spectral manifestations of different glycine conformers are most clear and simple in the C=O str absorption region. The assignment of this spectral region to C=O str vibrations is beyond question, and the energy parameters of the conformers estimated over this region seem to be reasonable. Let us recall that in this region all glycine conformers have close calculated intensities of IR absorption [14], thus we may consider that the fractions of conformers in matrix are proportional to the corresponding band intensities. Taking into account the above assumptions and comments, the calculations suggest that conformer **I** corresponds to the global energy minimum of glycine. The relative energy of conformer **II** is 1.6, 1.5 and 1.3 kcal/mol in Ne, Ar and Kr matrix, respectively. The analogous values of conformer **III** are 0.9, 1.1 and 1.5 kcal/mol (the calculation is based on Table 1).

4. Conclusions

The IR spectra at 4000–400 cm^{-1} of glycine isolated in Ne, Ar and Kr matrices have been obtained for the first time. It is shown that glycine, isolated in inert matrices is, like in the gas phase, in the molecular form. The band splitting in the IR spectra was demonstrated to have both conformational and matrix nature. The manifestations of these phenomena in the spectra were separated. Three different conformers of glycine have for the first time been identified spectrally. This assignment has been done based on (i) the predicted relative band intensities in the multiplets and their relative frequency arrangement; (ii) the predicted relative energies of the conformers and the values of the barriers to intramolecular rotation; (iii) the behaviour of the bands on matrix annealing; (iv) the shapes of spectra in various matrices. To fix the complete set of glycine conformers in the matrix, the substrate temperature must be lowered at least to 13 K. The relative energies of the **I**, **II** and **III** conformers of glycine are roughly estimated to be 0, 1.6–1.3 and 0.9–1.5 kcal/mol, respectively. The results of matrix annealing indicate that the barrier to conformational rearrangement **III**→**I** does not exceed 1.4 kcal/mol.

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