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LOW-TEMPERATURE OPTICAL SPECTROSCOPY

Effect of low-temperature argon matrices on the IR spectra and structure of flexible N-acetylglycine molecules

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A study of how the matrix environment impacts the structure and IR spectra of N-acetylglycine conformers. The conformational composition of this compound is determined according to an analysis of the FTIR spectra of N-acetylglycine isolated in low temperature argon matrices. Bands of three N-acetylglycine conformers are identified based on the spectra: one major and two minor. The structure of all observed conformers is stabilized by different intramolecular hydrogen bonds. The Gibbs free energies of the conformers were calculated (CCSD(T)/CBS method), and these energy values were used to calculate conformer population at a temperature of 360 K, of which 85.3% belonged to the main conformer, and 9.6% and 5.1% to the minor conformers. We also determined the size and shape of the cavities that form when the N-acetylglycine conformers are embedded in the argon crystal during matrix deposition. It is established that the most energetically favorable cavity for the planar main conformer is the cavity that forms when 7 argon atoms are replaced. At the same time, bulky minor conformers were embedded into cavities that correspond to 8 removed argon atoms. We calculated the complexation energy between argon clusters and conformers, and the deformation energy of the argon crystal and the N-acetylglycine conformers. The matrix-induced shifts to the conformer oscillation frequency are calculated. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4973702]

1. Introduction

The method of low-temperature matrix isolation in combination with IR spectroscopy is an effective instrument for studying the structures of many different types of molecules.[1,2] It is actively used to determine the detailed structural features of the most important biological molecules, particularly of nucleic acid bases (DNA and RNA components), and amino acids (peptides and protein components). One of the advantages to isolating molecules in inert gas matrices is the weak interaction of the test molecule with that matrix environment. In many cases, especially in the study of rigid molecules, this interaction can be neglected. However, for molecules that are incredibly flexible, the interaction with the matrix can exert a significant impact on their structure. A feature of such molecules is that very little energy is required in order for their intramolecular structure to be altered—up to 10 kJ/mol. This energy is comparable to both the interaction energy between a molecule and an inert matrix, and the interaction energy between the atoms of inert gas crystals. Consequently, when flexible molecules are embedded in a matrix, they assume the shape that causes the minimum amount of perturbation in the inert gas crystal structure. As a result, the structure of the molecule inside the matrix can differ from the unperturbed molecule in the gas phase. Obviously these types of structural changes must also lead to changes in the oscillation frequency of the molecule. It should be noted that yet another reason for changes in the oscillation frequency is the interaction between the isolated molecule and the matrix environment. In this case, if changes to the frequency are not associated with significant changes to the molecular structure, then it will be observed for both rigid and flexible molecules. As such, there are two reasons by which oscillation frequencies of flexible molecules in inert gas matrices will change, in comparison to the oscillation frequencies of these molecules in the gas phase. These are the interaction with the matrix environment and changes to the structure during embedding.

At present, records of such effects are particularly relevant due to the significant improvements in the precision of quantum-mechanical calculations of the normal vibration frequencies[3] that are used to analyze experimental IR spectra. Comparing vibrational spectra calculated for single molecules to the experimental spectra of matrix-isolated molecules gives us the difference between the calculated and experimental frequencies. This difference cannot be reduced to less than 5–10 cm^{-1} even when using the most accurate calculation methods, including those that account for the anharmonicity of the vibrations and the polynomial scaling of the calculated frequencies.[4–6] In order to solve this problem, it is necessary to use the results from calculations obtained for a model system that includes both the test molecule and the inert gas atoms, when analyzing the experimental IR spectra. First, the

calculations were conducted for the simplest model systems that included only one inert gas atom. Studies pertaining to complexes of pentahydric formic acid molecules (HCOOH) with argon, krypton, and xenon gases[7–10] allowed us to qualitatively explain the difference between some vibrational frequencies of formic acid isolated in different inert gas matrices. However, such a simplified approach does not allow us to account for the spectral effects associated with embedding the molecule into the matrix. A more complex model of accounting for matrix effects was recently used in order to analyze the vibrational spectra of small (two and three-atom) linear molecules.[11–13] In this model, the test molecule is surrounded by a monolayer of inert gas atoms (10–20 atoms per molecule). The scope of this model is limited to molecules that occupy only one or two vacancies in the inert gas crystal. For larger molecules, the shell made of one layer of inert gas atoms becomes unstable and does not correspond to the structure of the crystal. It is obvious that in order to model the effects the matrix has on the structure of the IR spectra of polyatomic molecules, much larger fragments of inert gas crystals must be used.

The goal of this study is to determine the molecular structure of N-acetylglycine, which is the simplest molecule containing a peptide bond, and therefore, is the model of the protein peptide chain. The study of the conformational behavior of N-acetylglycine is important to the understanding of the structural organization of protein molecules and short peptides. Low-temperature FTIR spectroscopy in an argon matrix is used to solve this problem, as well as quantum-mechanical calculations for the structure, relative stability, populations, and vibrational spectra of N-acetylglycine conformers. Due to the large number of single bonds, the N-acetylglycine molecules are very flexible. In order to define the matrix effects on the structure and vibrational spectra of N-acetylglycine using the DFT/M06–2X method, we performed quantum-mechanical modeling of this compound, embedded into the fcc argon crystal made of 163–167 atoms.

2. Experimental methods and calculations

Low-temperature FTIR spectra of N-acetylglycine in an argon matrix were recorded in the frequency range 3600–200 cm^{-1} using the matrix isolation spectroscopy described in detail earlier in Refs. 14–17. The apodized resolution was 2.5 cm^{-1}. During matrix deposition the molecular flows of N-acetylglycine (Sigma-Aldrich, USA) were monitored using low-temperature quartz microbalances[17] and were 10–20 ng/s cm^2) with a precision of ±1%. The concentration of N-acetylglycine molecules in the matrix (M/S, matrix-to-sample ratio) was 700:1. The matrices were deposited onto a polished copper mirror at a temperature of 6 K. The purity of the matrix gas (Ar) was >99.99%. The evaporation of N-acetylglycine from the Knudsen cell occurred at a temperature of 360 K. Fityk software was used to expand the experimental bands into their constituent approximating functions (Guassians or Lorentzians).[18]

Calculations of the equilibrium geometry, relative energies, relative Gibbs free energies, and vibrational spectra of N-acetylglycine conformers were carried out via second order perturbation theory (MP2) and density functional theory (DFT) using the correlation-consistent basis sets aug-cc-pVDZ and aug-cc-pVTZ.[19] The density functionals B3LYP[20] and M06–2X[21] were used in the DFT calculations. All calculations of N-acetylglycine conformer energies were conducted after adjusting for zero-point vibrational energy (ZPVE). The populations of N-acetylglycine conformers were determined based on their Gibbs free energies using the CCSD(T)/CBS method (complete basis set). The Gibbs free energy of each conformer was calculated for the geometry defined according to the MP2/aug-cc-pVDZ method. The calculations were consistent with the following formula: $GFE_{(CCSD(T)/CBS)} = E_{MP2/CBS} + \Delta(E_{CCSD(T)/aug\text{-}cc\text{-}pVDZ} - E_{MP2/aug\text{-}cc\text{-}pVDZ}) + TC\text{-}GFE_{MP2}$, wherein $E_{MP2/CBS}$-MP2 is the conformer energy, extrapolated to the CBS limit using the 2-point Truhlar procedure,[22] $\Delta(E_{CCSD(T)/aug\text{-}cc\text{-}pVDZ} - E_{MP2/aug\text{-}cc\text{-}pVDZ})$ is the difference between CCSD(T)/aug-cc-pVDZ and MP2/aug-cc-pVDZ conformer energies, and $TC\text{-}GFE_{MP2}$ is the thermal correction to the Gibbs free energy, calculated using the MP2/aug-cc-pVDZ method at evaporation temperature from the Knudsen cell in the experiment.

The simulation of N-acetylglycine conformers embedded into an argon matrix was conducted using the DFT method, with the M06–2X[21] density functional. The basis set aug-cc-pVDZ was used for N-acetylglycine atoms (C,N,O,H). The effective core potential (ECP) basis set GRENBL ECP[23] was used for the argon atoms. The resulting combined basis set is denoted as BS1 (aug-cc-pVDZ(C, N, O, H)/GRENBL ECP (Ar)). Initially, the M06-2X method was used to optimize the geometry of the fcc argon crystal fragment composed of 171 atoms. The resulting structure is then used as a model of an argon matrix. Different cavities for N-acetylglycine conformers embedded into the argon lattice were obtained by removing some of the argon atoms (4–8) from the center of the crystal fragment. The size and shape of the cavities were determined by the results of simulating different methods of embedding N-acetylglycine conformers into the argon crystal. This simulation was conducted using the molecular dynamics method of the NAMD program.[24] The geometries of all complexes ($NAG@Ar_x$ ($x = 163–168$)) were fully optimized using the M06–2X/BS1 method. After this, the calculations of the harmonic vibrational frequencies were conducted. The energies of interaction between the embedded N-acetylglycine molecules and the argon crystal were calculated considering the basis set superposition error (BSSE). At the same time, the counterpoise correction procedure was implemented.[25] All quantum-mechanical calculations were conducted using the Gaussian 09 program package.[26]

3. Results and discussion

3.1. Conformer population in FTIR spectra of N-acetylglycine in an argon matrix

The spatial structure of the N-acetylglycine molecule (Fig. 1) is defined by five dihedral angles, corresponding to the rotation of molecule fragments around the bonds C_m–C_p, C_p–N, N–C_α, C_α–C_c and C_c–O(H). The existence of these rotational degrees of freedom is what determines the high flexibility of N-acetylglycine molecules. Using the MP2/aug-cc-pVDZ method we were able to conduct a detailed investigation of the potential energy surface (PES) of N-acetylglycine. The total energy of the molecule was calculated as a function of dihedral angles. Each minimum along

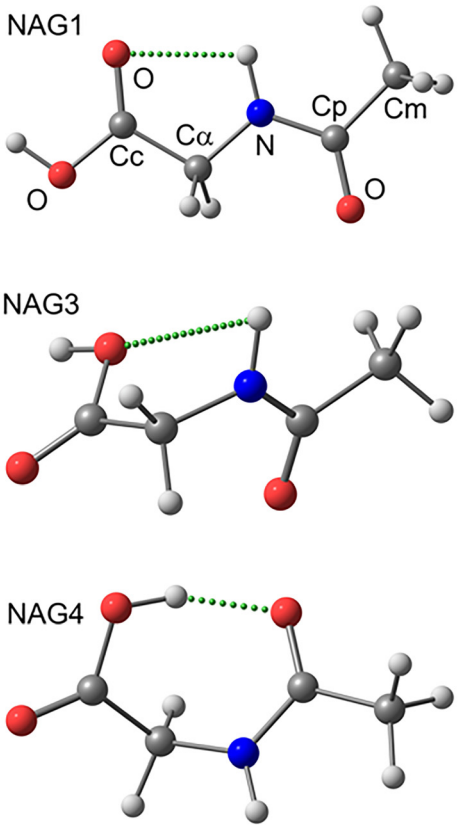

Fig. 1. Structure of N-acetylglycine conformers, calculated using MP2/aug-cc-pVDZ.

the PES corresponds to a particular conformation of N-acetylglycine. In contrast to the previous studies of the N-acetylglycine conformation structure,[27,28] we identified a full set of conformers, comprised of 15 structures. An analysis of the relative energies (MP2/aug-cc-pVTZ) and relative Gibbs free energies (CCSD(T)/CBS) has shown that at evaporation temperature only three conformers have populations in excess of 1%. The main conformer-NAG1 (we used the standard notations for N-acetylglycine conformers[27,28]) is stabilized by the strong intramolecular hydrogen bond C_c = O•••H–N and has a flat frame of heavy atoms (Fig. 1). The population of the conformer NAG1 is 85.3%, at a temperature of 360 K. Gibbs free energies (CCSD(T)/CBS method) of two minor conformers NAG3 and NAG4 are 9.7 and 10.1 kJ/mol higher than that of the NAG1 conformer, but their populations are 9.6% and 5.1%, respectively. The structure of NAG3 and NAG4 conformers is stabilized by intramolecular hydrogen bonds C_c–O•••H-N and O–H•••O = C_p, respectively. The presence of three different hydrogen bonds in conformers NAG1, NAG3 and NAG4 is important for their identification using IR spectroscopy. This is due to the high sensitivity of vibrational frequencies to the formation of hydrogen bonds, which usually makes it possible to identify minor conformers with populations less than 10%.

The FTIR spectrum of N-acetylglycine isolated in an argon matrix is shown in Fig. 2. The experimental spectrum is in good agreement with the calculated conformer populations. The most intense spectrum bands correspond to the vibrations of the main conformer, NAG1. In addition to the bands of this conformer, in all regions of the IR spectra of N-acetylglycine, we have identified weak bands of two minor conformers. In

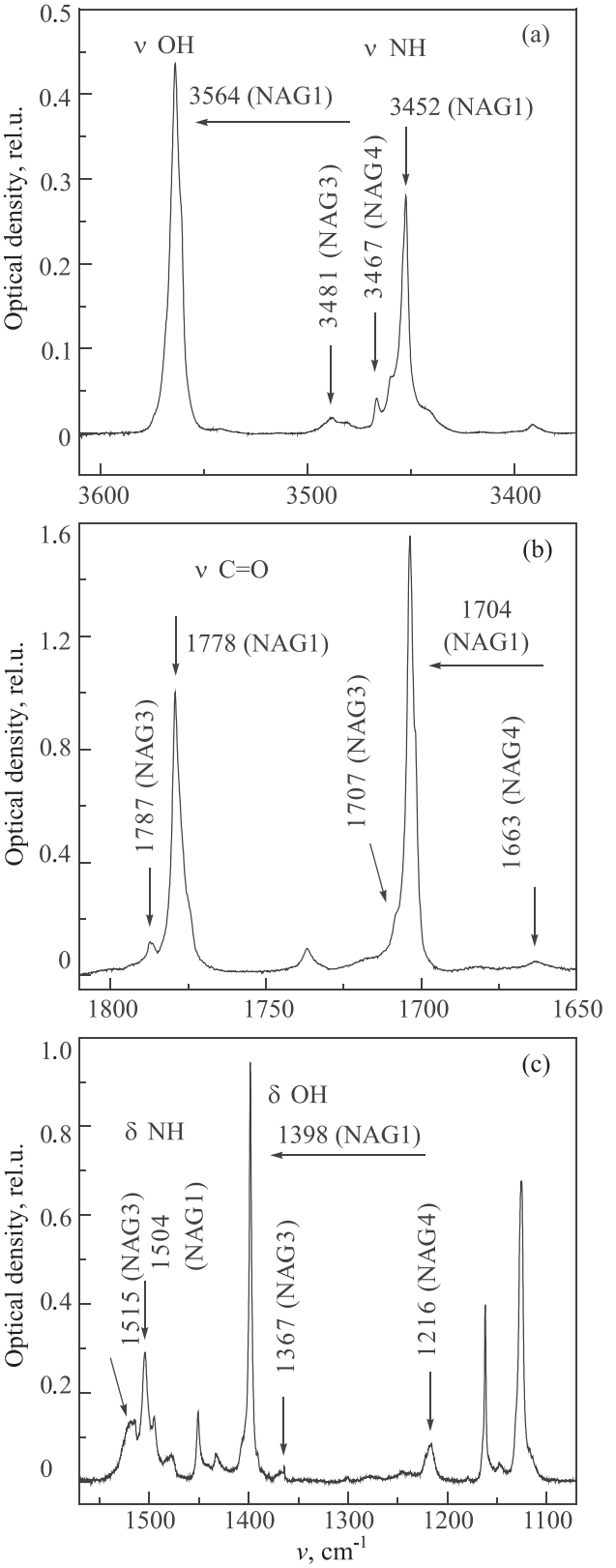

Fig. 2. FTIR spectra of N-acetylglycine in an argon matrix (T = 6 K, M/S = 700).

the high-frequency range 3600–3400 cm^{-1} (Fig. 2(a)) two intense bands are observed: OH and NH stretching vibrations of NAG1 at 3564 and 3452 cm^{-1}, respectively. As can be seen from Fig. 2(a), in this range NH stretching vibrations of NAG3 and NAG4 conformers are also identifiable. The integrated intensities of the experimental NH stretching vibration bands of the three conformers are in good agreement with their

calculated populations. The frequencies of the OH stretching vibrations of NAG1 and NAG3, calculated using the B3LYP/aug-cc-pVTZ method, are practically the same. This explains why the corresponding band of the minor conformer NAG3 was not observed in the IR spectra. Due to the formation of an intramolecular hydrogen bond O–H•••O=C_p the OH band of stretching vibrations of NAG4 is shifted into the low-frequency region by about 600 cm^{-1}, and is covered by the bands of CH stretching vibrations belonging to the main conformer.

The bands of C=O stretching vibrations of N-acetylglycine conformers are located in the region 1800–1650 cm^{-1} (Fig. 2(b)). Two of the more intense bands are attributed to the stretching vibrations of the C=O bonds of the carboxyl (1778 cm^{-1}) and peptide (1704 cm^{-1}) groups of the main conformer NAG1. In this area there are also bands of similar vibrations belonging to the minor conformer NAG3, which are shifted into the high-frequency region by several inverse centimeters, in comparison to the bands of the main conformer. This shift is associated with the variety of intramolecular hydrogen bonds in conformers NAG1 and NAG3, and is entirely consistent with the calculated data. The formation of the relatively strong intramolecular hydrogen bond O–H•••O=C_p in conformer NAG4 leads to a significant (by 41 cm^{-1}) low-frequency shift of the C=O stretching vibrations band of this conformer's peptide group. As a result, the corresponding band is observed at 1663 cm^{-1}. The spectrum also contains a weak band at 1738 cm^{-1} (Fig. 2(b)), which cannot be attributed to the main fluctuations of N-acetylglycine conformers. Based on calculations of the anharmonic frequencies and intensities of the vibrations, conducted using the MP2/aug-cc-pVDZ method, it is shown that this band corresponds to the Raman vibration υOH_{def} (1112 cm^{-1}) + υOH tor. (631 cm^{-1}) of NAG1. The bands of the three N-acetylglycine conformers are also identified in the region below 1600 cm^{-1} (Fig. 2(c)). In general, all vibrational bands of the main conformer NAG1, as well as the more intense bands of the two minor conformers NAG3 and NAG4 are identified in the IR spectrum.

The identification of the conformer bands was conducted using the results of calculated frequencies and intensities of the vibrations, implemented by the DFT method with the B3LYP density functional. Currently, this method ensures the greatest possible accuracy of the calculated vibrational frequencies.[3] However, the average difference between the experimental and theoretical conformer frequencies of flexible molecules is about 10 cm^{-1}.[4,29,30] At the same time, for many types of vibrations the differences between the frequencies of several conformers do not exceed 5 cm^{-1}, which makes it difficult to form a reliable interpretation of the experimental spectra. In the case of using the method of isolating the molecules in inert gas matrices, the reason behind the divergence of the experimental and theoretical vibration frequencies is the influence the matrix environment has on the structure and spectra of the isolated molecules. The results of studying these effects are presented in the next section.

3.2. The influence of the matrix environment on the structure and spectra of N-acetylglycine conformers

At the first stage of studying N-acetylglycine inside argon clusters, we determined the size and shape of the cavity that forms via the insertion of N-acetylglycine molecules into the argon crystal during matrix deposition. Initially we calculated the volume of the N-acetylglycine conformers. The conformer volume was defined as the volume bounded by the surface in which the conformer is located, and the appropriate 0.001 a.u. electron density (according to the DFT/M06–2X/aug-cc-pVDZ method). The calculation results showed that the amount of N-acetylglycine conformers is about 140 $Å^3$. The amount of argon atom was determined using the same method, and came to 36 $Å^3$. This suggests that the N-acetylglycine molecule replaces at least 4 argon atoms in the crystal lattice ($4 \times 36\ Å^3 = 144\ Å^3$). However, considering the complex spatial form of the N-acetylglycine molecule, we can assume that when it is embedded into the crystal it can replace more than 4 argon atoms. This fact was taken into account during computer simulation. The determination of the cavity shapes inside the argon crystal that form when the N-acetylglycine molecules are embedded, was implemented using the molecular dynamics method, wherein the Charmm27force field was used.[31,32] The N-acetylglycine conformer force field parameters were determined using the VMD program.[33] A fragment of the fcc lattice comprised of 6912 argon atoms was used as a model of the argon crystal. The N-acetylglycine molecule was located in the center of the lattice fragment, and then 4–7 argon atoms were removed (in order to simulate different sizes of cavities), located at a minimum distance from the atoms of the molecule. The total energy of the resulting complex was first minimized during the first 10 000 cycles, at which point the system was equilibrated using the method of molecular dynamics. The duration of the simulation was 1 ns, and 1 fs was the simulation increment. The calculations were performed for three conformers, earlier identified based on analysis of the experimental IR spectra. For each conformer there were 8 start geometries generated, which differed by the initial orientation of the N-acetylglycine molecules relative to the argon crystal.

As a result of this simulation, more energetically favorable methods for embedding the N-acetylglycine conformers into the argon crystal were identified. Fig. 3 shows the shape of the matrix sites with various sizes, upon insertion of the NAG1 conformer into the crystal and the resulting substitution of 4–7 argon atoms. As we can see in Fig. 3, when the NAG1 conformer is embedded, and the substitution of 4–6 argon atoms takes place, the molecule is located within one {111} crystal lattice layer. This can be explained by the fact that the heavy atom frame of the NAG1 conformer has a planar structure (Fig. 1). At the same time, the total thickness of the molecule does not exceed the thickness of the layer composed of argon atoms, with the exception of the methyl group, the size of which just slightly (by 0.2–0.3 Å) exceeds the size of the argon atom. This makes it more energetically favorable to embed the NAG1 conformer into one layer of the matrix. At the same time, the frame of conformers NAG3 and NAG4 is bulky (Fig. 1). As a result, the matrix sites of these conformers, which are shown in Fig. 4, have a complex shape. Conformers NAG3 and NAG4 substitute the argon atoms that are located in two adjacent {111} crystal lattice layers, upon insertion in the matrix.

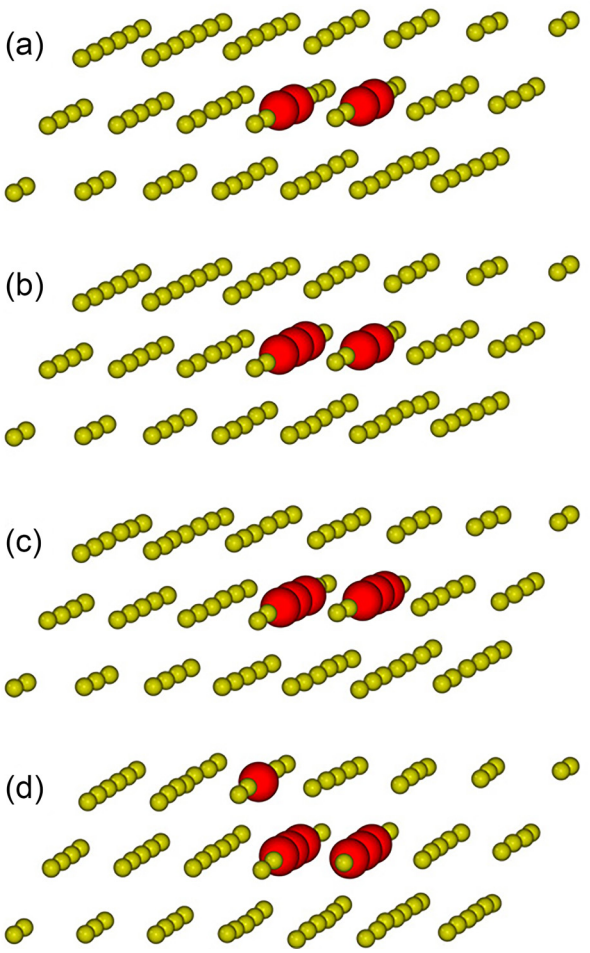

Fig. 3. The shape of the matrix sites that form when the NAG1 conformers are embedded and substitute 4 (a), 5 (b), 6 (c), and 7 (d) argon atoms. We show a fragment of the lattice that includes three {111} layers of the argon fcc crystal lattice. The replaceable argon atoms are shown in red.

The structures of the matrix sites, obtained using the molecular dynamics method, were used as the start geometries for quantum-mechanical calculations, which were carried out using DFT/M06-2X. The choice of the M06-2X functional of electron density for the DFT calculations is justified by the fact that this functional was specially designed for calculating systems with non-bonded interactions, including those systems that contain inert gas atoms.[21] Quantum-mechanical calculations were conducted for an fcc lattice fragment consisting of 171 argon atoms, containing one N-acetylglycine molecule. The shape of the matrix site was taken from the results of molecular dynamics simulations. The calculations were performed for three conformers inside the argon cluster, consisting of 164–167 atoms (depending on the size of the cavity). Full geometry optimization was carried out for each system, after which the vibrational spectrum was calculated. First we analyzed the complexation energy, the interaction energy between N-acetylglycine conformer molecules, as well as the deformation energies of both the argon cluster and conformers. These data are shown in Table 1.

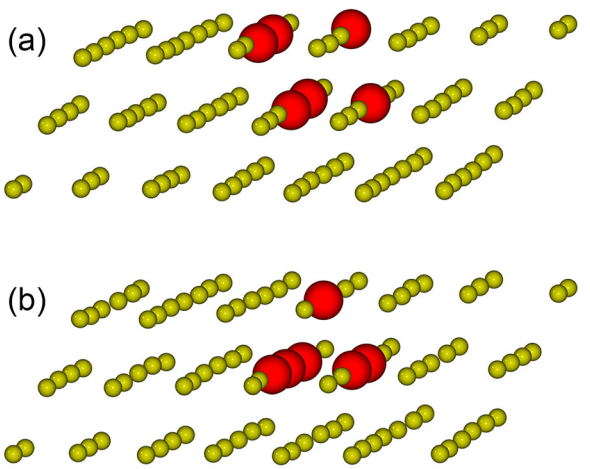

Fig. 4. The shape of the matrix sites that form during the insertion of NAG3 (a) and NAG4 (b) conformers, with the replacement of 6 argon atoms. We show a fragment of the lattice that includes three {111} layers of the argon fcc crystal lattice. The replaceable argon atoms are shown in red.

For the minimum size of the matrix site (NAG1@Ar167, 4 argon atoms substituted), the strain energy for the matrix environment is significant (34.0 kJ/mol) and the formation energy for the whole complex is at its lowest value (−15.3 kJ/mol). This suggests that the size of this site is insufficient to accommodate the NAG1 conformer. As can be seen in Table 1, given a step-by-step increase in the size of the cavity (up to NAG1@Ar164) there is an observable decrease in the deformation energy, down to 8.0 kJ/mol, and an increase in the absolute value of the complex formation energy. This suggests that it is energetically preferable to place NAG1 in the cavity that forms by the replacement of 7 argon atoms. The calculated structure of the NAG1@Ar164 complex is shown in Fig. 5. Further increases in the size of the cavity (NAG1@Ar163) lead to a decrease in the complex formation energy. Moreover, this is accompanied by an increase in the strain in the matrix deformation energy to 13.5 kJ/mol. As such, we can conclude that the matrix site

TABLE 1. The energies of cluster formation NAG@Ar_N (E_{form}), the deformation energies of the matrix ($E_{def}(Ar_N)$) and the N-acetylglycine molecule (E_{def}(NAG)), and the interaction energy between the N-acetylglycine molecule and the matrix environment (E_{int}), calculated using M06-2X. All energies are given in kJ/mol. The energies E_{form} and E_{int} are calculated using BSSE. The formation energies are calculated as the difference between the energy of the entire cluster NAG@Ar_N and the sum of the N-acetylglycine and ArN subsystem energies (all energies are calculated for fully optimized geometries). The deformation energies $E_{def}(Ar_N)$ and E_{def}(NAG) were calculated as the difference between the subsystem energies with fully optimized geometries and the subsystems energies with non-optimized geometries that were extracted from the cluster structure. The interaction energies were calculated as the difference between the energy of the cluster and the sum of the N-acetylglycine and ArN subsystem energies in non-optimized geometries, extracted from the cluster structure. N is the number of argon atoms removed during the formation of the cavity in the matrix.

Cluster	N	E_{form}	E_{def} (ArN)	E_{def} (NAG)	E_{int}
NAG1@Ar167	4	−15.3	34.0	1.1	−50.4
NAG1@Ar166	5	−27.1	15.8	1.9	−44.8
NAG1@Ar165	6	−34.2	13.2	1.3	−48.7
NAG3@Ar165	6	−30.6	17.6	3.2	−51.4
NAG4@Ar165	6	−21.3	17.6	3.2	−42.1
NAG1@Ar164	7	−35.9	8.0	0.8	−44.7
NAG3@Ar164	7	−33.5	15.1	3.1	−51.7
NAG4@Ar164	7	−35.3	9.8	2.8	−47.9
NAG1@Ar163	8	−29.7	13.6	0.6	−43.9
NAG3@Ar163	8	−35.9	8.4	2.1	−46.4
NAG4@Ar163	8	−37.3	4.2	1.7	−43.2

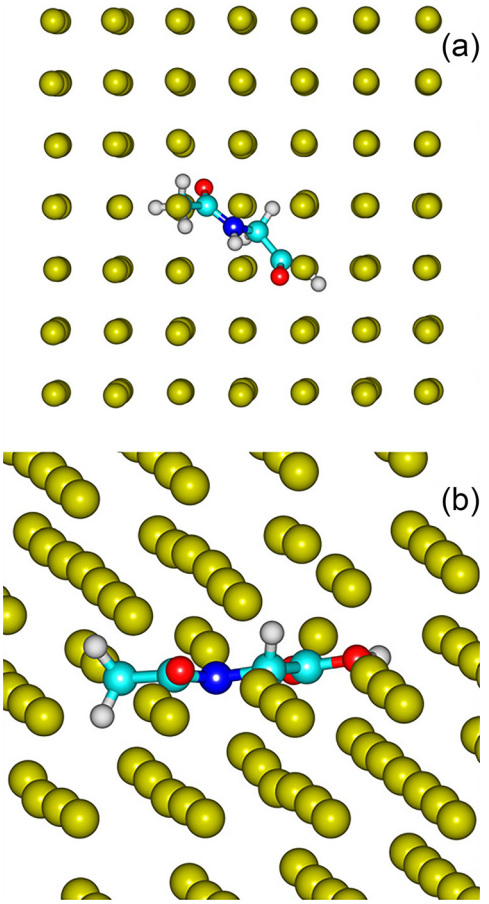

Fig. 5. The structure of the NAG1@Ar164 cluster, calculated using M06-2X/BS1. The shape along plane {100} (a), NAG1 conformer insertion into plane {111} (b).

corresponding to the removal of 8 atoms is too large to accommodate conformer NAG1. Therefore, during the optimization of the complex NAG1@Ar163 structure there is a significant deformation of the matrix structure. At the same time, for conformers NAG3 and NAG4, it is more energetically favorable to embed into a crystal composed of 163 argon atoms. As can be seen from Table 1, minimum matrix deformation energies are observed for complexes NAG3@Ar163 and NAG4@Ar163. This behavior is associated with the sophisticated spatial shape of the NAG3 and NAG4 conformers, in comparison to NAG1 that has, as noted above, a flat frame (Fig. 1).

Vibrational spectra were calculated for each N-acetylglycine conformer embedded into a cluster or argon atoms. The comparison of these data with the vibrational spectra of single molecules allows us to determine how the interaction with the matrix environment will impact the frequencies of N-acetylglycine conformer vibrations. The calculated vibration frequencies of the most energetically favorable complexes (NAG1@Ar164, NAG3@Ar163 and NAG4@Ar163), as well as the experimental data, are summarized in Table 2 for the main (most intense) vibrations. Table 2 also shows the matrix displacements of the oscillation frequencies ($\Delta\upsilon$), which were defined as the difference between the calculated frequencies of the single and argon-matrix-embedded conformers. As we can wee, the values of the matrix displacements for the majority of the vibrations range from several to 20 cm^{-1}, even though for some vibrations we do observe strong changes in frequency. The largest low-frequency matrix shift by 75 cm^{-1} is registered for the OH stretching vibration of the NAG4 conformer. In this conformer the OH group participates in the formation of a strong intramolecular O–H•••O=C_p bond. The strong matrix shift is a characteristic feature of this vibration and is observed earlier for those amino acid conformers in which the OH bond was also involved in the formation of an intramolecular hydrogen bond.[34] It should be noted that for stretching vibrations of N-acetylglycine conformers low-frequency displacements are observed, but for deformation and torsional vibrations, the displacements are in the high frequency range. Additionally, for each vibration we determined the difference between the scaled frequency calculated for each single molecule, and the experimental frequency of the corresponding vibration of the matrix-isolated conformer. These data (shown in Table 2 in brackets) are in good agreement with the values of the matrix displacements. Although in some cases there are observed differences in the magnitude of these shifts, the predicted directions of the displacements are always the same. This demonstrates that the influence of the matrix environment is the main reason behind the divergence of the experimental frequencies registered for matrix-isolated molecules, and the theoretical frequencies that are calculated for single molecules.

The interaction with the matrix manifests itself in changes to the structure of N-acetylglycine conformers. The

TABLE 2. Vibration (υ, cm^{-1}) frequencies of single N-acetylglycine conformers and the matrix displacements ($\Delta\upsilon$, cm^{-1}) of conformer frequencies inside argon clusters, calculated using M06-2X/BS1. Experimentally determined values of oscillation frequencies of N-acetylglycine conformers isolated in an argon matrix are shown in parentheses. The square brackets show the difference between the frequencies calculated for single molecules and those that are experimentally derived. The calculated values of the frequency are scaled using scaling factors 0.945 for frequencies above 2000 cm^{-1} and 0.960 for frequencies less than 2000 cm^{-1}.

Vibration	NAG1 υ	NAG1@Ar164 $\Delta\upsilon$	NAG3 υ	NAG3@Ar163 $\Delta\upsilon$	NAG4 υ	NAG4@Ar163 $\Delta\upsilon$
OH_{str}	3592 (3564) [−28]	−23	3600(3559) [−41]	−32	3286	−75
NH_{str}	3467(3452) [−15]	−21	3489 (3481) [−8]	−4	3480(3467) [−13]	−13
C_c=O_{str}	1790(1779) [−11]	−8	1801(1787) [−14]	−11	1809(1793)[−16]	−11
C_p=O_{str}	1712(1704) [−8]	−3	1714 (1707) [−7]	−3	1671(1663) [−8]	−5
NH_{def}	1501 (1504) [+3]	+2	1484(1515) [+31]	+18	1511(1521) [+10]	+6
C_c-O_{str}	1407(1398) [−9]	−7	1387(1367) [−20]	−14	1384	−9
OH_{def}	1164 (1162) [−2]	−5	1167	−3	1398(1419) [+21]	+11
OH_{tor}	628 (643) [+15]	+7	643	+3	840(892) [+52]	+27
NH_{tor}	446 (455) [+9]	+13	431 (446) [+15]	+19	424	−17

TABLE 3. A comparison of the most important structural parameters of single and matrix-isolated N-acetylglycine conformers (r is the bond length in Å; α is the angle in degrees; and ψ is the dihedral angle in degrees) calculated by M06-2X/BS1. The atom designations are shown in Fig. 1.

Parameter	NAG1 single	NAG1@Ar164	NAG1@Ar165	NAG1@Ar166	NAG1@Ar167	NAG4 single	NAG4@Ar163
$\psi_{Cm–Cp–N–C\alpha}$	180.0	174.8	172.8	171.7	170.5	−174.4	−164.6
$\psi_{Cp–N–C\alpha–Cc}$	180.0	−172.2	−163.4	−163.6	−163.9	−77.3	−76.3
$\psi_{N–C\alpha–Cc=O}$	0.0	0.7	−3.8	−5.4	6.2	−121.4	−126.2
$\psi_{O=Cc–O–H}$	0.0	−0.1	−0.2	−0.4	0.2	−178.6	−179.1
$\psi_{O=Cp–N–H}$	180.0	−176.0	−175.0	−175.1	−173.1	−175.5	−177.2
r_{OH}	0.969	0.970	0.970	0.971	0.970	0.982	0.988
r_{NH}	1.011	1.012	1.011	1.012	1.011	1.008	1.009
$r_{Cp=O}$	1.221	1.221	1.222	1.222	1.222	1.231	1.232
$r_{Cc=O}$	1.206	1.206	1.207	1.207	1.206	1.203	1.203
α_{COH}	107.4	108.0	107.7	107.9	107.7	110.1	109.8
$\alpha_{O–Cc=O}$	123.4	123.5	123.3	123.2	123.7	122.4	122.5
$r_{OH\cdots OCp}$	…	…	…	…	…	1.778	1.763
$\alpha_{O–H\cdots O}$	…	…	…	…	…	158.8	161.3

flexibility of this compound is determined primarily by the presence of single bonds N–C_α and C_α–C_c. The rotation around these bonds corresponds to changes in the dihedral angles $\psi_{Cp–N–C\alpha–Cc}$ and $\psi_{N–C\alpha–Cc=O}$. In amino acid molecules the energy barriers around these bonds are usually within 3–8 kJ/mol. At the same time a change to the dihedral angles of 10°–20° increases the energy of a single molecule by only 1–2 kJ/mol. This behavior is a characteristic feature of flexible molecules. Table 3 shows the values of the main structural parameters calculated for single N-acetylglycine conformers NAG1 and NAG4, as well as for the conformers that are part of the argon cluster. Analysis of the given data shows that the argon matrix has the greatest impact on dihedral angles that define the structure of the molecular skeleton. At the same time, the biggest difference between dihedral angles in matrix-isolated conformers from the values of the single molecules is observed, as expected, for the angles $\psi_{Cp–N–C\alpha–Cc}$ and $\psi_{N–C\alpha–Cc=O}$, corresponding to the rotation around single bonds of the N-acetylglycine molecule. It should also be noted that as the size of the matrix cavity decreases, in the series NAG1@Ar164 → NAG1@Ar167 there are observed systematic increases in the distortion of the structure of conformer NAG1, in comparison to a single molecule. Changes in bond lengths for all complexes do not exceed 0.001 Å. The only exception is the bond length OH in conformer NAG4. As can be seen in Table 3, when this conformer is embedded into the matrix there is an increase in this bond length by 0.006 Å. This change is consistent with the anomalous (75 cm^{-1}) low-frequency shift of the stretching vibrations frequency in this group. The bond OH in conformer NAG4 participates in the formation of a strong intramolecular hydrogen bond. The data in Table 3 are the structural parameters (length and angle) of the hydrogen bonds that demonstrate the strong distortion that occurs as a result of inserting NAG4 conformers into the argon matrix.

4. Conclusion

The conformational composition of the compound is defined according to an analysis of FTIR spectra of the simplest peptide N-acetylglycine isolated in a low-temperature argon matrix. Three N-acetylglycine conformers are identified: the main conformer NAG1, stabilized by intramolecular hydrogen bond C_c=O•••H-N, and two minor conformers NAG3 and NAG4 with intermolecular hydrogen bonds C_c–O•••H-N and O–H•••O=C_p, respectively. The conformational structure of N-acetylglycine, defined on the basis of experimental data, is in agreement with the results of *ab initio* Gibbs free energy calculations for conformers, conducted by CCSD(T)/CBS. The estimated population of conformer NAG1 is 5.3% at a temperature of 360 K, and the populations of the minor conformers NAG3 and NAG4 come to 9.6% and 5.1%, respectively. The FTIR spectra show all bands of the main conformer, as well as the most intense bands of the minor conformers.

The DFT/M06-2X method is used to study the impact the matrix environment has on the structure and IR spectra of N-acetylglycine conformers. The size and shape of the cavities that form during N-acetylglycine conformer insertion in the argon crystal during matrix deposition are determined. It is found that for conformers NAG1 insertion into cavities that form by substituting 7 argon atoms is more energetically favorable. At the same time, for conformers NAG3 and NAG4, it is more energetically favorable to be inserted into a cavity that corresponds to the removal of 8 argon atoms. The calculated conformer complex formation energies of N-acetylglycine with argon clusters range from −35 to −38 kJ/mol. At the same time the deformation energies of the argon crystal do not exceed 10 kJ/mol. Calculations of IR spectra of single conformers and conformers inserted into argon clusters have shown that the values of the matrix shifts for the majority of the vibrations are within several to 20 cm^{-1}. For OH and NH stretching vibrations stronger changes to the frequency are observed. The maximum low-frequency matrix shift by 75 cm^{-1} is registered for OH stretching vibrations of conformer NAG4, which is consistent with changes to the structure of this conformer during its insertion into the argon matrix. Overall, the structural changes analysis has shown that the argon matrix has the greatest impact on the dihedral angles that define the structure of the molecular frame. The maximum difference in values of the dihedral angles in matrix-isolated and single molecules was observed for angles $\psi_{Cp–N–C\alpha–Cc}$ and $\psi_{N–C\alpha–Cc=O}$. These angles correspond to the rotation around single bonds and are what define the high flexibility of the N-acetylglycine molecule.

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