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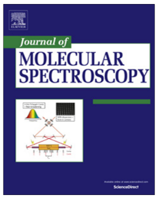

FTIR spectra and conformational structure of deutero-β-alanine isolated in argon matrices

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ABSTRACT

Low temperature FTIR spectra of β-alanine-d_3 isolated in argon matrices are used to determine the conformational composition of this compound. UV irradiation of the matrix samples is found to change the relative populations of the β-alanine-d_3 conformers. The populations of conformers **I** and **II** with an N—D···O intramolecular H-bond decrease after the UV irradiation while the populations of conformer **V** with an N···D—O H-bond and conformer **IV** which has no intramolecular H-bonds increase. This behavior of the β-alanine-d_3 conformers are used to separate the bands of the different conformers. The analysis of the experimental FTIR spectra is based on the calculated harmonic B3LYP/6-311++G(df,pd) frequencies and on the MP2/aug-cc-pVDZ frequencies calculated with a method that includes anharmonic effects. Polynomial scaling of the calculated frequencies is used to achieve better agreement with the experimental data. The observation of the wide band of the OD stretching vibration at 2201 cm^{-1} is a direct evidence of the presence of the β-alanine-d_3 conformer **V** in the Ar matrix. In total ten bands of conformer **V** are detected. The influence of the matrix environment on the structures and the IR spectra of the β-alanine and β-alanine-d_3 conformers is investigated. This involves performing calculations of the β-alanine conformers embedded in argon clusters containing from 163 to 166 argon atoms using the M06-2X and B3LYP(GD3BJ) density-functional methods. Good agreement between the calculated and the experimental matrix splitting is demonstrated.

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1. Introduction

Elucidation of the molecular structure of non-ionized β-alanine is important for two reasons. First, β-alanine is the only naturally occurring β-amino acid with a significant biological [1–4] and pharmacological [5–7] importance related to its being a part of natural or synthesized peptides. Inclusion of a β-amino acid in a peptide results in appearance of an additional rotational degree of freedom (one more single C—C bond) which increases the flexibility of the peptide backbone. The second reason is related to the origin of life. β-alanine was found in many carbonaceous meteorites, where it was one of the most abundant amino acid [8–11], and in several comet samples studied during the past decade [12].

The conformational structure of β-alanine has been continuously investigated starting from the first computational study by Ramek [13] and from the first experimental observation of non-ionized β-alanine by McGlone and Godfrey [14]. Ramek located 20 β-alanine conformers using the HF/4-31G level of theory and introduced a nomenclature for identifying the conformers [13] which has been since used in most papers on β-alanine including this work. During the following years numerous computational studies [13–19] were performed at increasingly higher levels of theory and they provided increasingly more accurate relative stabilities of the β-alanine conformers. A brief review of the studies may be found in Ref. [19]. In their study McGlone and Godfrey [14] identified two conformers, **I** and **V**, based on the analysis of the rotational spectra of gas-phase β-alanine. Later two more conformers (**II** and **III**) were detected by Sanz et al. using the Fourier transform microwave spectroscopy and a pulsed supersonic jet [20].

Matrix isolation IR spectroscopy has been successfully applied to study the conformational composition of amino acids [21–37]. Using this method Dobrowolski et al. located conformers **I**, **II** and **IV** of β-alanine isolated in Ar matrices [38]. They also suggested the presence of several other β-alanine conformers. Later we reinvestigated the conformational structure of β-alanine isolated in Ar matrices using UV irradiation of the matrix samples as a mean to alter the relative population of the different conformers [19]. We

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demonstrated that under UV irradiation the band intensities of conformers **I** and **II** decrease while the ones of conformers **IV** and **V** increase. It allowed us to separate the bands of these conformers in the matrix IR spectra and, as a result, the bands assigned to β-alanine conformer **I**, **II**, **IV**, and **V** were identified. Some spectral signatures of minor conformer **VII** were also detected [19]. We also performed a detailed investigation of the potential energy surface (PES) of β-alanine. Using the calculated relative stabilities of the conformers and the corresponding conformational interconversion barriers we determined which conformers may exist in Ar matrices and which conformers should interconvert to lower-energy conformers due to low energy barriers separating them. It was demonstrated that the conformer interconversion significantly alters the matrix populations of the conformers as compared to the gas-phase populations.

Very recently Wong et al. investigated β-alanine isolated in solid parahydrogen and Ar matrices [34] also using UV irradiation to separate bands due to different conformers. As a result five conformers (**I**, **II**, **III**, **IV**, and **VII**) were detected in parahydrogen matrices and four conformers (**I**, **II**, **IV** and **VII**) were detected in Ar matrices [34]. It is interesting that Wong et al. did not detect conformer **V** either in parahydrogen or Ar matrices. Conformer **V** is the only low energy β-alanine conformer with a N···HO intramolecular H-bond. Similar conformers were found for all α-amino acids [24–33,35–37]. Due to the formation of the N···HO H-bond the frequencies of the OH stretching vibration in these conformers are significantly downshifted (by 360–390 cm^{-1}) with respect to the OH stretching frequencies of the conformers with a free OH group which are observed in the 3200–3170 cm^{-1} spectral range. In the case of β-alanine conformer **V** the chain of atoms separating the interacting nitrogen and the hydrogen is longer than in α-amino acids. This creates more preferred steric conditions for an H bonding to form and, as a result, the N···HO H-bond in β-alanine conformer **V** should be stronger than in the corresponding conformers of α-amino acids. As a consequence, a larger low-frequency shift of the OH stretching vibration should be observed. Frequency calculations predicted that the OH stretching vibration of β-alanine conformer **V** should be observed in the region below 3000 cm^{-1} [19]. It hampered the identification of this band because in this spectral range bands due to CH stretching vibrations are observed. Similar overlapping of the CH and OH stretching vibrations were earlier observed for the proline conformer with an N···HO H-bond [25]. The band of this conformer was identified in the spectra of N,O-dideuterated proline [25]. The deuteration allowed for separating bands of the CH and OD stretching vibrations. The latter was observed at 2295 cm^{-1}.

In the present work we study the FTIR spectra of the matrix-isolated N,N,O-trideutero-β-alanine (β-alanine-d_3) to confirm the conformational composition of non-deuterated β-alanine and, in particular, to confirm the presence of conformer **V** in Ar matrices. The deuteration significantly affects the IR spectra but only very slightly changes the relative stability and therefore the population of the conformers (by changing the zero-point vibrational energies). Particular attention is paid in this work to the search for bands of minor conformers. We use UV irradiation to alter the matrix populations of the conformers and thus to assist the separation of their bands in the experimental spectra.

In many respects the vibrational frequencies of the amino acid conformers are very close. Thus a correct assignment of the observed bands requires the highest possible accuracy in calculating the frequencies. To achieve it we test the accuracy of various computational methods and basis sets employed in predicting the frequencies. We also use a polynomial scaling of the calculated frequencies in the fingerprint region of the matrix IR spectra of β-alanine-d_3 (1400–200 cm^{-1}) instead of applying the conventional constant scaling factors. This procedure allows us to improve the agreement between the calculated and the observed data. Another issue addressed in this work is the influence of the matrix environment on the vibrational spectra of the β-alanine and β-alanine-d_3 conformers. The matrix effects are studied by comparing the calculated IR spectra of the gas-phase β-alanine and β-alanine embedded in argon clusters containing between 163 and 166 argon atoms (these clusters are denoted as BA@Ar163 to BA@Ar166). The matrix frequency shifts are shown to be significant for many vibrations. This information helps to determine the conformational composition of β-alanine-d_3 in Ar matrices. In particular, the presence of minor conformer **V** with an intramolecular H-bond N···DO in Ar matrices, which was not detected by Wong et al. [34], is established. For this conformer we identify not only the band due to the OD stretching vibration but also a number of other bands which differ from the bands of the other more populated conformers.

2. Experiment

The major features of the low temperature FTIR matrix isolation setup used in this work were described previously [22,39–42]. The FTIR spectra of β-alanine-d_3 in the Ar matrices are registered in the range of 3800–200 cm^{-1} with the apodized resolution of 0.35 cm^{-1}. N,N,O-d_3-β-alanine denoted as β-alanine-d_3 is obtained by recrystallization of the commercial β-alanine (Sigma, purity >99%) from heavy-water solution followed by vacuum drying using a nitrogen ($T = 77$ K) cryopump. After the recrystallization the relative ratio of the non-deuterated and partly-deuterated molecules is less than 10%. The process of β-alanine-d_3 evaporation, which is performed in the temperature range of 365–375 K, is monitored for thermal decomposition and no thermodesctrucion products of β-alanine-d_3 are found. The typical intensities of the molecular beams of β-alanine-d_3 are 30–40 ng/(s·cm^2), while the matrix-to-sample ratio (M/S) is 700:1. The low-temperature differential quartz crystal microbalance (QCM) [40,43] is used to measure the absolute intensity of the molecular beam and the M/S ratio. The matrices are deposited on a polished copper mirror at temperature of 6 K. The purity of matrix gas (Ar) is better than 99.99%. The UV irradiation is performed using an optical apparatus comprising a mirror focused at the quartz window in the cryostat and a deuterium H4141SV lamp (Hitachi) [22,39]. We did not observe any fragmentation of β-alanine-d_3 upon the UV irradiation. Each experimental spectrum is fitted with an approximation function (a Gaussian or a Lorentzian). In the fitting the program *Fityk* is used [44].

3. Computational details

The equilibrium geometries of all β-alanine conformers were calculated earlier at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels of theory [19]. The relative stabilities and the relative Gibbs free energies of the β-alanine-d_3 conformers are recalculated in this work at those levels of theory. The calculations involve accounting for the zero-point vibrational energy (ZPVE) corrections to the total energies and for the thermal corrections to the Gibbs free energies. The relative populations of the β-alanine-d3 conformers are determined based on their Gibbs free energies calculated at the CCSD(T)/CBS (complete basis set) level. The Gibbs free energy of a conformer is calculated using its MP2/aug-cc-pVDZ geometries as $\text{GFE}_{(\text{CCSD(T)/CBS})} = E_{\text{MP2/CBS}} + \Delta(E_{\text{CCSD(T)/aug-cc-pVDZ}} - E_{\text{MP2/aug-cc-pVDZ}}) + \text{TC-GFE}_{\text{MP2}}$, where $E_{\text{MP2/CBS}}$ is the MP2 energy of the conformer extrapolated to CBS using the 2-point procedure introduced by Truhlar [45], $\Delta(E_{\text{CCSD(T)/aug-cc-pVDZ}} - E_{\text{MP2/aug-cc-pVDZ}})$ is the difference between the CCSD(T)/aug-cc-pVDZ and MP2/aug-cc-pVDZ energies of the conformer, and $\text{TC-GFE}_{\text{MP2}}$ is a thermal correction to the Gibbs free energy calculated at a certain

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