

Study of vibrational spectra of zwitterionic 3-Aminobutanoic acid, as supported by DFT calculations

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World Journal of Advanced Research and Reviews, 2022, 16(03), 1122–1131

Publication history: Received on 10 November 2022; revised on 18 December 2022; accepted on 21 December 2022

Article DOI: <https://doi.org/10.30574/wjarr.2022.16.3.1487>

Abstract

3-Aminobutanoic acid is an unnatural amino acid and by analogy with other amino acids, is represented in its zwitterionic form by $R-CH(COO^-)NH_3^+$ (where side group $R =$ aryl, alkyl or any other group) in solid phase. Experimental IR and Raman modes near 3029, 2871, 1577, 1288 cm^{-1} measured for 3ABA are strongly in favor of the zwitterionic dimer structure formed of $-N-H\cdots O-C$ bonding between $-NH_3^+$ and anion $-CO_2^-$ groups. Zwitterionic monomer and dimer structures at B3LYP/6-311++G(d,p) level are computed. It has been found that the stable zwitterionic monomer and dimer structures are possible only in a water solvent medium computed using SCRF SMD solvation model. The zwitterionic dimer vibrational structure is in good agreement with the experiment and both zwitterionic monomer and dimer models have identically predicted the frequencies of the modes that are localized and unperturbed except those that characterize the H-bonding due to the $-N-H\cdots O$ bonding. This is supported by the appearance of two characteristic medium strong Raman modes at 900 and 843 cm^{-1} that suggest unperturbed C-C skeletal structure and localized modes due to CH, CH₂ and CH₃ groups bound to it.

Keywords: 3-Aminobutanoic acid; IR; Raman; DFT; N-H \cdots O bonding

1. Introduction

β -amino acids are rare substances by comparison with α -amino acids. The tendency to use β -amino acids in drug synthesis has increased over recent years. They have shown not only therapeutic potential but also stimulated a number of studies as probes of protein structure and function [1-6]. 3-Aminobutanoic acid ($C_4H_9NO_2$) is one such β -amino acid. It is also known as 3-methyl- β -alanine which is a methyl derivative of β -alanine. 3-Aminobutanoic acid (3ABA in short) is found in cereal and cereal products and is known for its ability to induce plant disease resistance [7].

Amino acids which have their amino group ($-NH_2$) bonded to β -carbon atom are known as β -amino acids. Due to zwitterionic (ZW) nature ($-CO_2^-$ and $-NH_3^+$ groups) they form a molecular system in which van der Waals interactions and H-bonds network determine stability of crystalline structures in condensed phase or in aqueous solution. On the other hand, they exist in neutral (NE) form in a gas phase [8-9]. Several experimental and theoretical studies were carried out to understand the structure and vibrational properties of β -amino acids. In order to understand the properties of 3ABA it is convenient to consider β -alanine, the only naturally occurring β -amino acid as nearest parent molecule. β -alanine crystallized from aqueous solution is orthorhombic with space group $Pbca$ with eight molecules per unit cell. The H-bonds around the nitrogen atom indicate the ZW nature of β -alanine. The $-N-H\cdots O$ H-bonds tie the molecules into double layers and these double layers are linked to the neighbouring double layers by van der Waals bonds [10]. FT-IR, Raman spectra of crystalline β -alanine in ZW form and matrix isolation IR spectra of NE form were recorded by Rosado et al. To support the assignment of vibrational spectra, they have computed IR and Raman spectra using SCF-MO ab initio calculations. In NE form, the free OH stretching and bending bands were observed at 3560 and 1100 cm^{-1} respectively, C=O and C-O stretching bands at 1770 and 1180 cm^{-1} , NH₂ stretching and bending bands in the region 3300 - 3400 and 1600 cm^{-1} [11]. But in ZW form, $-NH_3^+$ groups are strongly H-bonded to ionized carboxyl groups,

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resulting in redshift of $-\text{NH}_3^+$ and ionized $-\text{CO}_2^-$ stretching frequencies and blueshift of $-\text{NH}_3^+$ bending frequencies. That is in ZW form, the $-\text{NH}_3^+$ stretching bands observed around $3000 - 3080 \text{ cm}^{-1}$ and bending around 1680 cm^{-1} . The bands due to ionized carboxyl group are observed at 1630 cm^{-1} (asymmetric stretch), 1410 cm^{-1} (symmetric stretch) and bending modes around 800 cm^{-1} [12-13].

This paper is concerned with the characterization of the structure and spectroscopy of 3ABA in terms of its NE and ZW monomer, dimer species in ZW form and analyses the results by comparing with different studies. As amino acids are stable in their ZW form, we have successfully modeled ZW 3ABA in water medium at B3LYP/6-311++G(d,p) level with the SCRF method. 3ABA has shown the signature of inter-molecular H-bonding as seen in its FT-IR spectrum as a broad absorption in the region $3500 - 2000 \text{ cm}^{-1}$ with fwhm $\sim 740 \text{ cm}^{-1}$. Since the $-\text{N}-\text{H}\cdots\text{O}$ bonds in β -alanine tie the molecules together into double layers; assuming the same is true for 3ABA, we modeled a ZW dimer linked by intermolecular $-\text{N}-\text{H}\cdots\text{O}$ bonding. The optimization, vibrational frequency analysis and IR and Raman spectra were computed at DFT B3LYP/6-311++G(d,p) level. The modeled ZW dimer satisfactorily explains the vibrational structure and observed vibrational spectra.

2. Material and methods

2.1. Experimental Methods

The solid sample of 3-Aminobutanoic acid was used as received (Aldrich Chemical Co). The IR spectral measurements were carried out on the *Nicolet 6700* FT-IR spectrometer. The spectrometer consisted of an Alum standard ETC Ever-Glo IR source and the signals were collected by Deuterated Triglycine Sulphate (DTGS) detector with KBr window. The sample preparation was made using KBr pellete technique and the spectra were recorded in the region $4000 - 400 \text{ cm}^{-1}$ for 50 scans with the resolution of 4 cm^{-1} . The Raman spectra ($4000 - 400 \text{ cm}^{-1}$) were recorded on the *Nicolet NXR-FT-Raman* spectrometer. The spectrometer consisted of a Nd:YVO₄ (1064 nm) laser as an excitation source, CaF₂ beam splitter and a high-performance LN₂ cooled Ge detector. Solid sample is taken in a glass tube and the spectrum is recorded. A total of 500 numbers of scans were taken for each spectral measurement with the resolution of 4 cm^{-1} .

2.2 Computational Methods

The electronic structure calculations have been performed using DFT methods in the *Gaussian 09W* and *GaussView5* programs [14-15]. The levels used for calculation include RHF/3-21G and B3LYP/6-311++G(d,p) [16]. To search for all possible conformers, the relaxed PES scan was carried out at RHF/3-21G level for NE form of 3ABA (refer Fig. 1). The dihedral angles τ_1 and τ_2 were scanned simultaneously from 0° to 350° with the interval of 10° and it resulted in several minima on the PES scan curve. The optimization for all the minimum energy points at B3LYP/6-31G(d) level yielded a single conformer with 99% Boltzmann population. Since the small 6-31G(d) basis set does not give sufficient accuracy, therefore higher basis sets suitable for amino acids should be attempted [17]. Accordingly, the conformer was optimized with basis set 6-311++G(d,p) with B3LYP method. The geometry optimization and frequency analysis were carried out and the resultant optimized geometrical structure is shown in Fig. 2(a). This resultant structure in NE form is further optimized into its ZW in water medium using self-consistent reaction field solvation model based on charge density (SCRF-SMD) implicit solvation methods at B3LYP/6-311++G(d,p) level. The optimized ZW structure is presented in Fig. 2(b). Since the FT-IR spectrum of 3ABA indicates the strong H-bonding, a ZW dimer has been modeled in water medium by the combination of two optimized ZW monomers linked by $-\text{N}-\text{H}\cdots\text{O}$ bonding. The vibrational modes are characterized in terms of potential energy distributions (PED) that were calculated using VEDA program [18]. Since, calculated spectra generally estimate higher wave number values for vibrational modes, the frequency values of monomer and dimer have been scaled with a factor of 0.9688 for the B3LYP/6-311++G(d,p) level [17].

3. Results and discussion

The NE structure of 3ABA is presented in Fig. 2(a). By examining the optimized structure and geometrical parameters of the NE structure it is found that, a linkage between NH₂ and COOH groups is predicted in the optimized geometry of 3ABA which we interpret as follows. There is intramolecular interaction between O10-H2 of carboxyl group and N1 of amine group [19]. As a result, the H2 atom has moved away from the O10 atom in COOH, increasing the O10-H2 length by $\sim 3\%$ indicating a chemical structure consistent with the formation of ZW by transferring a proton from COOH to NH₂ group. As a consequence of proton transfer, positive charge is developed on the amine group and negative charge on the carboxyl group. The IR and Raman spectra of NE 3ABA are computed and compared with the observed FT-IR and Raman spectra of 3ABA (Fig. 3 and Fig. 4). However, the observed spectral features seem to favour ZW species ($-\text{NH}_3^+$ and $-\text{CO}_2^-$ groups). Thus, to aid the assignment of observed spectra we tried to optimize the NE structure into its ZW. But the optimization of ZW in gas phase converges to NE structure. Therefore, the solvent models based on charge

density in which the solute-solvent interaction is responsible for the stabilization of ZW were used for optimization. The optimization and frequency analysis were carried out and the optimized geometrical structure of ZW is shown in Fig. 2(b).

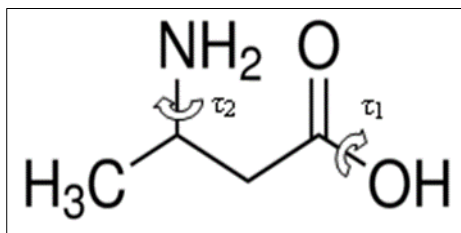


Figure 1 Molecular structure of 3-Aminobutanoic acid showing the dihedral angles τ_1 and τ_2 for conformer determination

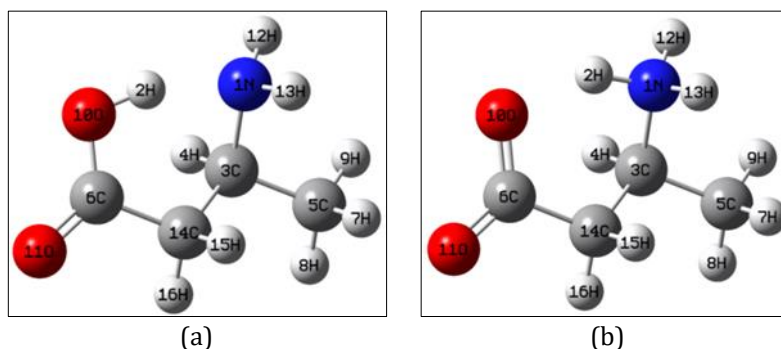


Figure 2 Optimized geometrical structures of (a) neutral and (b) zwitterionic 3-Aminobutanoic acid.

The vibrational frequencies of NE and ZW forms of 3ABA monomer are presented in Table 1. The computed frequencies of NE 3ABA are in good agreement with the matrix isolation IR results of β -alanine and the spectrum served as a vapor spectrum with the predicted linkage between COOH and NH_2 groups. On the other hand, the computed frequencies of ZW 3ABA are in close agreement with our experimental FT-IR spectrum and aid the assignments of observed vibrational frequencies. Further, the computed dipole moment values also support this argument. Higher value of the dipole moment, 16.53 D, of the ZW is in the range of values for the amino acids and therefore supports the optimized ZW structure in the water medium. The value, 6.73 D, for the NE is also comparable to its experimental values [20]. The intense broad band with fwhm $\sim 740 \text{ cm}^{-1}$ indicating the existence of possible intermolecular $\text{-N-H}\cdots\text{O}$ bonding. To understand the nature of H-bonding in the molecule, we modeled ZW dimer as a combination of two units of optimized ZW monomer structures through $\text{-N-H}\cdots\text{O}$ bonding in which N-H of -NH_3^+ coming from one ZW monomer and O atom of -CO_2^- coming from another ZW monomer. The ZW dimer is optimized using solvent models at B3LYP/6-311++G(d,p) level. The optimized parameters, vibrational frequencies, IR and Raman intensities were calculated. The optimized structure is presented in Fig. 5 and the hydrogen bonding parameters in Table 2. The N-H bond length in ZW monomer is 1.015 \AA and that in dimer is 1.049 \AA showing the elongation in bond length by 3.3%. The $\text{O}\cdots\text{H}$ bond length 1.757 \AA , is shorter than the sum of van der Waal's radii of oxygen and hydrogen (2.720 \AA) and the $\text{-N-H}\cdots\text{O}$ bond length being 2.807 \AA and the bond angle is 171.1° . These parameters suggest that the H-bonding is strong.

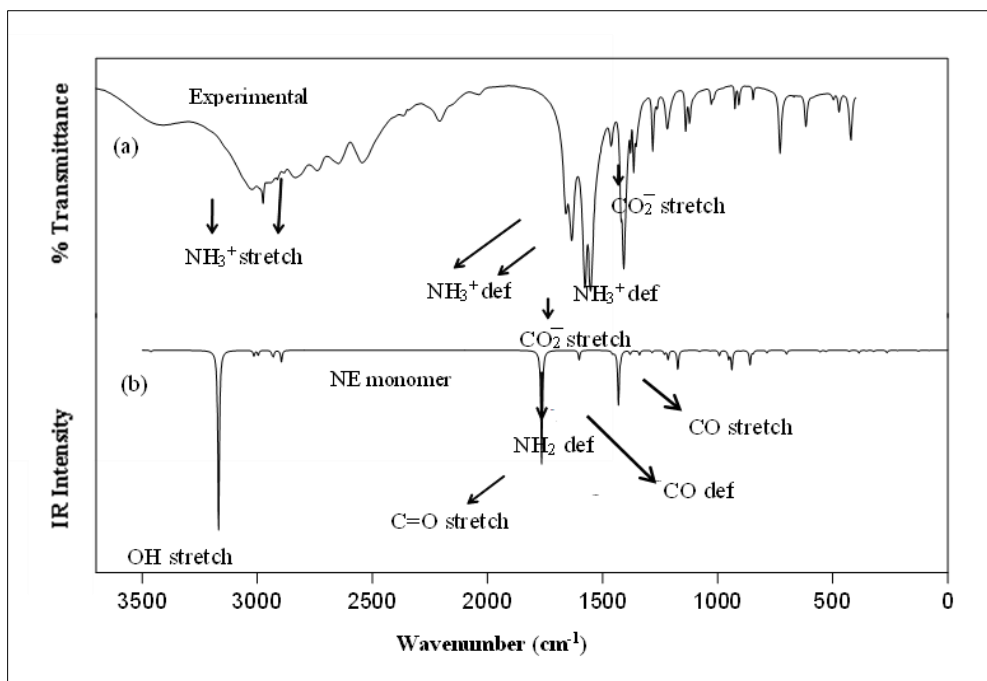


Figure 3 (a) Experimental and (b) simulated neutral monomer IR spectra of 3-Aminobutanoic acid

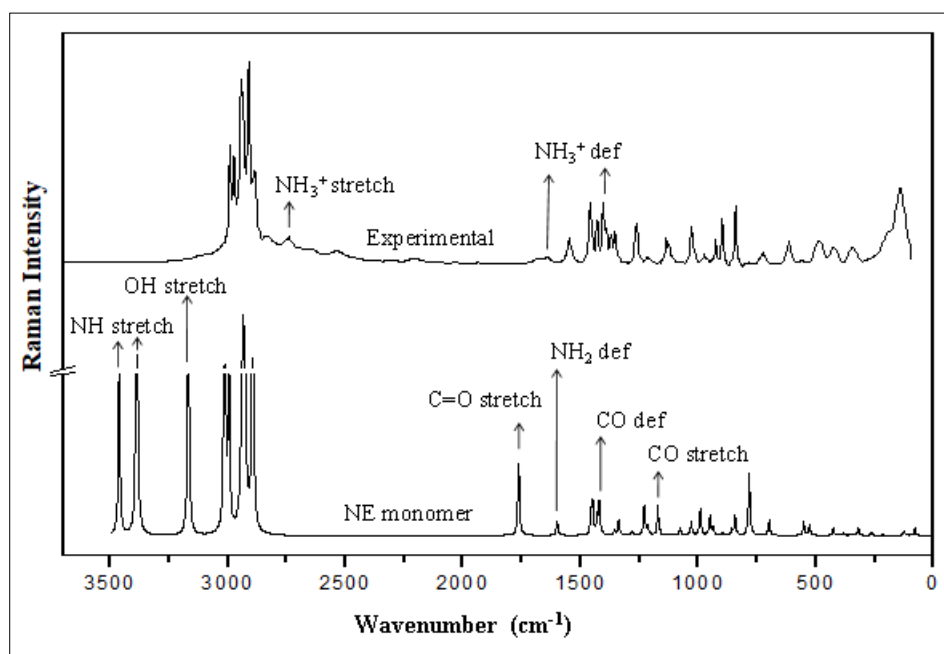
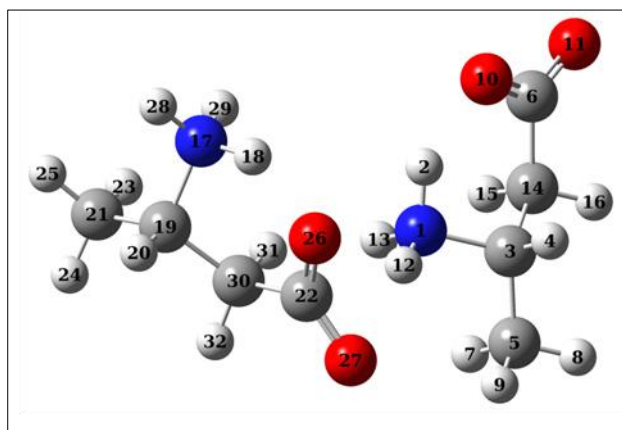


Figure 4 (a) Experimental and (b) simulated neutral monomer Raman spectra of 3-Aminobutanoic acid. (Ordinate in NE monomer is broken to adjust the bands from overshooting because of their largest intensity)

We present the measured FT-IR spectrum compared with that of simulated ZW monomer and dimer in Fig. 6 and the Raman spectrum compared with that of simulated ZW monomer and dimer in Fig. 7. In characterizing the vibrational modes of -NH_3^+ and -CO_2^- , it would be helpful to see how the intensities and frequencies of the modes of these ionic species are influenced with respect to the modes of free NH_3 and COOH molecular species. As bonded ionic species in 3ABA, the degenerate modes of NH_3 group are supposed to split into two independent modes whose frequencies either change or remain invariant as both will be demonstrated below. For a given dimer, there are two pairs of -NH_3^+ and -CO_2^- groups of which one pair of -NH_3^+ and -CO_2^- of opposite monomers, as presented in Fig. 5, are H-bonded by $\text{-N-H}\cdots\text{O}$ linkage, whereas, the other pair is free from H-bonding. Accordingly, the computed frequencies for the dimer species are sorted out into free and bound frequency values in Table 3.

Table 1 Vibrational frequencies of functional groups in NE and ZW monomers of 3-Aminobutanoic acid

Functional groups	NE monomer			ZW monomer		
	IR (cm ⁻¹)*	DFT (cm ⁻¹)	Mode	IR (cm ⁻¹)	DFT (cm ⁻¹)	Mode
COOH/ CO ₂ ⁻	1770	1764	$\nu(\text{C}=\text{O})$	1577	1479	$\nu_{\text{as}}(-\text{CO}_2^-)$
	--	1431	$\beta(\text{C}-\text{OH})$	1288	1313	$\nu_{\text{s}}(-\text{CO}_2^-)$
	1181	1215	$\nu(\text{CO})$	907	896	$\beta_{\text{sc}}(-\text{CO}_2^-)$
	516	554, 529	$\beta(\text{CO})$	728	708	$\beta_{\text{w}}(-\text{CO}_2^-)$
				616	597	$\beta_{\text{r}}(-\text{CO}_2^-)$
NH ₂ /NH ₃ ⁺	3408	3462	$\nu_{\text{as}}(\text{NH})$	--	3389	$\nu_{\text{as}}(-\text{NH}_3^+)$
	--	3387	$\nu_{\text{s}}(\text{NH})$	3029, 2734	3035, 2871	$\nu_{\text{s}}(-\text{NH}_3^+)$
	1634	1601	$\beta_{\text{as}}(\text{NH}_2)$	1663, 1634	1589, 1557	$\beta_{\text{as}}(-\text{NH}_3^+)$
	822	858	$\beta_{\text{w}}(\text{NH}_2)$	1407	1401	$\beta_{\text{s}}(-\text{NH}_3^+)$
	--	785	$\beta_{\text{t}}(\text{NH}_2)$	1138	1185	$\beta_{\text{r}}(-\text{NH}_3^+)$

**Figure 5** Optimized geometrical structure of zwitterionic dimer of 3-Aminobutanoic acid**Table 2** Hydrogen bonding parameters of zwitterionic 3ABA dimer

Parameters	3ABA	
	ZW monomer	ZW dimer
N1-H13	1.015	1.049 Å
H13...O26	--	1.757 Å
N1...O26	--	2.807 Å
N1-H13...O26	--	171.1°

NH₃⁺ and CO₂⁻ vibrations

The characteristic antisymmetric doubly degenerate mode of NH₃ is 3414 cm⁻¹ which would split into two frequency components, of which the asymmetric mode is predicted accurately at 3402 cm⁻¹ for the monomer and at 3389 cm⁻¹ for the dimer species. The corresponding free dimer mode is computed at 3400 cm⁻¹. The mode 3389 cm⁻¹ comes from the bonded -NH₃⁺ group. The second component is identified as a strong absorption at 3029 cm⁻¹. Its computed mode at 3035 cm⁻¹ agrees with the observed value whereas the computed free mode is at 3340 cm⁻¹ for the dimer and at 3345 cm⁻¹ for the monomer. This down-shifting of the frequency may be attributed to the H-bonding factor. Their absence as Raman modes strongly suggests the ZW form of 3ABA. The symmetric stretching mode is only predicted at 2871 cm⁻¹ and may be correlated to the mode at 3337 cm⁻¹ in NH₃. The down-shifting of the mode, as for the second component of

the anti-symmetric doubly degenerate mode noted above, with the difference of 466 cm^{-1} suggests that the mode being signature of the H-bonding. The frequency for the free mode is 3158 cm^{-1} for the dimer and 2983 cm^{-1} for the monomer. As for the anti-symmetric doubly degenerate bending modes, two intense absorptions near 1663 and 1634 cm^{-1} are identified corresponding to the doubly degenerate mode at 1628 cm^{-1} of NH_3 . They are weak as Raman modes because the modes are mainly due to $-\text{NH}_3^+$ group vibrations. A medium strong absorption at 1138 cm^{-1} may be correlated to the symmetric bending mode of NH_3 near 950 cm^{-1} . Two strong absorptions near 1407 and 1368 cm^{-1} may be assigned to the $-\text{NH}_3^+ - \text{X}$ modes (where X refers to the remaining molecular configuration). The two modes are coupled vibrations between $-\text{NH}_3^+$ and CH, CH_2 and CH_3 groups.

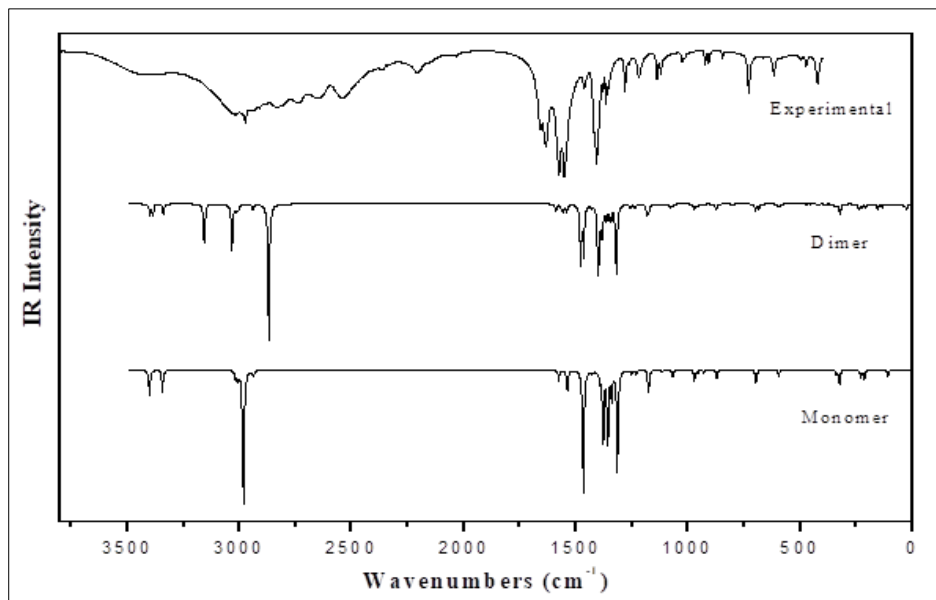


Figure 6 Experimental IR spectrum compared with simulated ZW monomer and dimer IR spectra of 3-Aminobutanoic acid

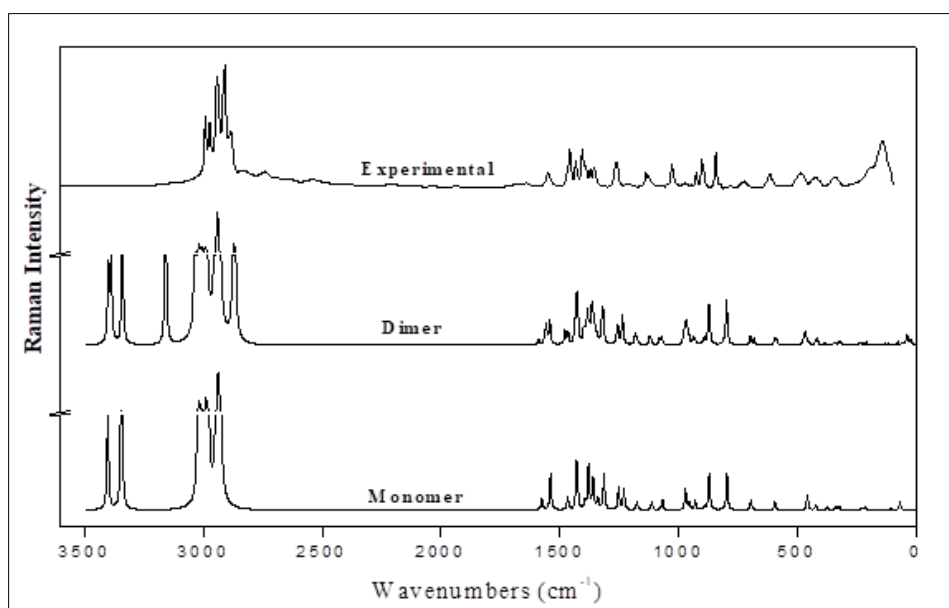


Figure 7 Experimental Raman spectrum compared with simulated ZW monomer and dimer Raman spectra of 3-Aminobutanoic acid. (Ordinate in simulated spectra is broken to adjust the bands from overshooting because of their largest intensity)

Of the modes of $-\text{CO}_2^-$, the antisymmetric stretching mode is a very strong absorption at 1577 cm^{-1} . The mode's characteristic shift from $1740 - 1720\text{ cm}^{-1}$ to 1577 cm^{-1} is the first evidence of its role in the H-bonding. The symmetric

mode is allotted to a medium absorption band at 1288 cm^{-1} with the coupling between $-\text{CO}_2^-$ and CC vibrations. Its occurrence near 1288 cm^{-1} being away from its characteristic position near $1400 - 1410\text{ cm}^{-1}$ may be attributed to partly the dominance of bending modes of NH_3^+ and CH_3 groups and partly to its strong coupling to NH_3^+ vibration. [21-22]. We have two bands for $-\text{CO}_2^-$ bending, one Raman band at 900 cm^{-1} and one medium strong absorption at 728 cm^{-1} with the coupled vibrations between $-\text{CO}_2^-$ and CC groups that may be identified as the degenerate components. However, the 900 cm^{-1} Raman band occurs along with a medium strong and weak Raman bands 843 at and 974 cm^{-1} respectively. The vibrational contributions to these modes suggest the dominant character of C-C vibration over C-C stretching and therefore, we consider the bands 900 and 843 cm^{-1} as skeletal C-C mode of 3ABA. Their relative unshifted positions may be taken to mean that the molecular C-C skeletal structure is not perturbed due to the H-bonding.

Further, the combination of asymmetric bending of $-\text{NH}_3^+$ with CN stretching or torsional modes of $-\text{NH}_3^+$ appear only in the IR spectrum in the region $2700 - 2000\text{ cm}^{-1}$ as medium weak absorptions on the broad absorption band [23]. The medium weak absorption at 2647 cm^{-1} is due to $-\text{N}-\text{H}\cdots\text{O}$ bonding [24]. The absorption bands at 2544 , 2366 and 2208 cm^{-1} are the combination of bending of $-\text{NH}_3^+$ with $-\text{NH}_3^+$ rocking mode and CN torsion respectively. The weak absorption at 2036 cm^{-1} , which is a combination of asymmetric bending of $-\text{NH}_3^+$ with CN torsional mode is identified as a marker band for the identification of charged $-\text{NH}_3^+$ moiety in amino acids [25]. It is evident that the ZW dimer frequencies are in fair agreement with the experimental values.

CH vibrations

CH stretching vibrations are observed as very strong Raman bands in the region 2990 to 2837 cm^{-1} . The 2990 and 2942 cm^{-1} bands assigned to asymmetric stretching vibration of methyl group. Of the two bands, the first band is not observed in IR and second band is observed at 2940 cm^{-1} . These two bands are predicted at 3020 and 3008 cm^{-1} . The symmetric stretching band of CH_3 group is observed at 2884 cm^{-1} (IR) and 2886 cm^{-1} (Raman) and is predicted at 2940 cm^{-1} . The asymmetric and symmetric stretching modes of CH_2 are observed at 2974 (IR), 2973 cm^{-1} (Raman) and 2840 (IR), 2837 (Raman) are predicted at 3013 and 2936 cm^{-1} respectively. CH stretching vibration is observed at 2910 (IR) and 2911 (Raman) cm^{-1} and is predicted at 2994 cm^{-1} .

Table 3 Zwitterionic monomer, dimer, experimental IR and Raman vibrational frequencies (in cm^{-1}) of 3-Aminobutanoic acid with vibrational assignments

ZW Monomer	ZW Dimer	IR	Raman	Assignments ^a
3402	3400 (f)	--	--	$\nu_{as}(\text{NH}_3^+, 76)$
	3389 (b)	(3414)*		
3345	3340 (f)	3029 s	--	$\nu_s(\text{NH}_3^+, 78)$
	3035 (b)	(3414)*		
3020	3020	--	2990 s	$\nu_{as}(\text{CH}_3, 49)$, $\nu_{as}(\text{CH}_2, 16)$
3013	3013	2974 w	2973 s	$\nu_{as}(\text{CH}_2, 35)$, $\nu_{as}(\text{CH}_3, 27)$
3007	3008	2940 w	2942 vs	$\nu_{as}(\text{CH}_3, 43)$, $\nu_{as}(\text{CH}_2, 16)$, $\nu(\text{CH}, 14)$
2991	2994	2910 w	2911 vs	$\nu_{as}(\text{CH}_3, 25)$, $\nu(\text{CH}, 22)$
2939	2940	2884 w	2886 ms	$\nu_s(\text{CH}_3, 70)$
2933	2936	2840 mw	2837 w	$\nu_s(\text{CH}_2, 52)$, $\nu_s(\text{CH}_3, 13)$
2983	3158 (f)	2734 mw	2740 w	$\nu_s(\text{NH}_3^+, 44)$
	2871 (b)	(3337)*		
--	--	2647 mw	2628 vw	$1663 + 974$ (N-H...O bonding)
--	--	2544 ms	2536 w	1577 ($\beta_{as}(\text{NH}_3^+)$) + 974 ($\beta_r(\text{NH}_3^+)$)
--	--	2366 vw	2377 vw	1407 ($\beta_s(\text{NH}_3^+)$) + 974 ($\beta_r(\text{NH}_3^+)$)
--	--	2208 ms	2209 vw	1663 ($\beta_{as}(\text{NH}_3^+)$) + 497 ($\tau(\text{CN})$)
--	--	2036 w	2035 vw	1634 ($\beta_{as}(\text{NH}_3^+)$) + 421 ($\tau(\text{CN})$)

1577	1589 (b)	1663 s	--	β_{as} (NH ₃ ⁺ , 88)
	1564 (f)	(1628)*		
1539	1557 (b)	1634 vs	1643 w	β_{as} (NH ₃ ⁺ , 76),
	1541 (f)	(1628)*		
1468	1479 (b)	1577 vs	--	β_s (NH ₃ ⁺ , 39), ν_{as} (CO ₂ ⁻ , 24)
	1466 (f)			
1429	1437	1552 vs	1548 mw	β_{as} (CH ₃ , 79)
1428	1427	1463 ms	1459 ms	β_{as} (CH ₃ , 70)
1395	1396	--	1431 mw	β_{sc} (CH ₂ , 55)
1380	1401 (b)	1407 vs	1405 ms	β_{sc} (CH ₂ , 30), β_s (CH ₃ , 23), β_s (NH ₃ ⁺ , 22)
	1384 (f)			
1361	1375	1378 w	1371 mw	β_s (CH ₃ , 43), β_s (CH ₂ , 21)
1359	1364 (b)	1368 s	--	β_s (CH ₃ , 29), β_s (NH ₃ ⁺ , 24), β (CH, 11)
	1344 (f)			
1341	1352	1355 w	1355 mw	β_w (CH ₂ , 26), β (CH, 23)
1316	1319 (f)	1288 ms	--	β (CC, 37), ν_s (CO ₂ ⁻ , 24)
	1313 (b)			
1253	1256	1264 vw	1261 mw	β_w (CH ₂ , 48), β (CH, 22)
1230	1236	1218 ms	1215 vw	β_t (CH ₂ , 39), β (CN, 17)
1177	1185 (b)	1138 ms	1138 mw	β (CC, 51), β_r (NH ₃ ⁺ , 35)
	1177 (f)	(950)*		
1114	1118	1122 ms	1124 w	β (CC, 41), β (CN, 31)
1069	1071	1027 mw	1028 mw	β (CC, 57), β (CN, 24),
971	979 (b)	--	974 w	β_r (NH ₃ ⁺ , 51), ν (CC, 17)
	974 (f)			
956	956	--	--	β (CC, 47), β (CN, 34)
931	930	924 mw	927 mw	β (CC, 43), ν (CC, 10)
891	896(b)	907 mw	900 ms	β (CC, 48), β_{sc} (CO ₂ ⁻ , 20)
	891 (f)			
872	872	845 mw	843 ms	β (CC, 47), ν (CC, 13)
797	798	--	782 vw	β (CC, 50), ν (CN, 15)
697	708 (b)	728 ms	727 w	β (CC, 36), β_w (CO ₂ ⁻ , 32)
	699 (f)			
596	597	616 ms	617 mw	τ (CC, 38), β (CCO, 27)
459	454	497 vw	487 mw	β (CCO, 25), τ (CC, 22), τ (CCN, 17)
424	424	421 ms	425 mw	τ (CC, 34), τ (CN, 29), β (CCO, 15)

Note: The Greek symbols used above α , β , τ refer to stretching, bending, torsion vibrations respectively and subscripts to them are defined as = antisymmetric; s = symmetric; r = rocking; w = wagging, sc = scissoring, t = twisting and the intensities of IR and Raman bands are defined as vs=very strong, s=strong, ms = medium strong, mw = medium weak, w = weak, vw = very weak; (f) = free, (b) = bonded.

*Free NH₃ group frequencies [22]. The quantities given in brackets are PED contribution (in %)

The bending modes of CH are observed below 1550 cm⁻¹. There are two asymmetric bending modes of CH₃ observed at 1552 and 1463 cm⁻¹ as strong IR absorptions having their counterpart in Raman at 1548 and 1459 cm⁻¹ and are predicted at 1437 and 1427 cm⁻¹ respectively. The symmetric bending mode is observed at 1378 (IR) and 1371 (Raman) cm⁻¹ and predicted accurately at 1375 cm⁻¹. The scissoring mode of CH₂ is observed as medium weak Raman band at 1431 cm⁻¹ and is predicted at 1396 cm⁻¹. The wagging modes of CH₂ are weakly observed at 1355 and 1264 cm⁻¹ both in IR and Raman and are predicted at 1352 and 1256 cm⁻¹ respectively.

CN and CC vibrations: The CN bending vibrations are observed at 1218, 1122 and CN stretching mode is observed at 782 cm⁻¹ and are predicted at 1236, 1118, and 798 cm⁻¹ respectively. There are coupled vibrations of CC stretching and bending below 1100 cm⁻¹. The CC bending modes observed at 1027, 924, 845, 782 cm⁻¹ are predicted at 1071, 930, 872, 798 cm⁻¹. The CC stretching mode is observed at 974 cm⁻¹. The torsional modes of CN are observed as weak to medium Raman bands below 500 cm⁻¹, that is at 497, 421, 344 and 142 cm⁻¹ which are predicted at 454, 424, 339 and 124 cm⁻¹ respectively.

4. Conclusions

The 3-Aminobutanoic acid has been shown to have a zwitterionic structure, R-CH(CO₂⁻)NH₃⁺ both structurally and vibrationally. Two stretching modes of -NH₃⁺ near 3029, 2871 cm⁻¹ and those of -CO₂⁻ near 1577, 1288 cm⁻¹ are chiefly in favor of -N-H...O bonding between -NH₃⁺ and -CO₂⁻ groups. The two modelings, zwitterionic monomer and zwitterionic dimer, at B3LYP/6-311++G(d,p) level of calculations have shown stable structures only in a solvent medium (water in the present case) and have predicted satisfactory structures and vibration spectra, with the dimer results in close agreement with experiment. It is shown that -N-H...O bonding characterizes the dimer structure in which the total H-bond length, H...O (1.757 Å) is lower than the sum of van der Waal's radii, suggesting fair agreement with the known H-bonding parameters. Excepting those modes that characterize the H-bonding, the frequencies of the remaining modes almost are identically predicted by both zwitterionic monomer and dimer indicating the localization of vibrational modes due to the -N-H...O bonding. This is supported by the two characteristic medium strong Raman C-C skeletal modes at 900 and 843 cm⁻¹.

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