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A study of vibrational spectra of zwitterionic 3-Aminobutanoic acid, as supported by density functional calculations

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Dedicated to Prof J R Durig

Zwitterionic form of solid unnatural amino acid, 3-Aminobutanoic acid, is apparent both as an individual species and in dimeric form as the vibrational modes in the observed IR and Raman spectra near 3030 – 2990 cm^{-1} and 1685 – 1540 cm^{-1}. The IR region 3500 – 2000 cm^{-1} marked by an intense broad band with sub-band structure, as is true of many amino acids, is presumably due to hydrogen bonding. A weak Raman band at 1682 cm^{-1}, two very intense doublet at 1663, 1634 cm^{-1}, two more intense doublet at 1557, 1552 cm^{-1} are assigned to the carbonyl (C=O) stretching, asymmetric/symmetric stretching of carboxylate (CO_2^-) and asymmetric/symmetric deformation vibrations of ammonium (NH_3^+). The assignments are consistent with the assumption that the solid sample of 3-Aminobutanoic acid is composed of both zwitterionic and its hydrogen bonded dimer species. Further, DFT calculations at B3LYP/6-31G* level of theory for the neutral free 3-Aminobutanoic acid that has produced a vibration spectrum at variance with the measured modes due to carboxylic acid (–COOH) and amine (–NH2) moieties but it indirectly supports analysis. A linkage between NH_2 group and H atom from COOH as shown in the optimized geometry is a signature of the tendency of the molecule to form zwitterionic species.

Keywords: Zwitterionic form, amino acid, 3-Aminobutanoic acid, IR and Raman spectra, DFT calculations, hydrogen bonded dimer

1 Introduction

Design, synthesis and applications of inter-molecularly built structures that self-assemble into supramolecular nanostructures is of enormous current interest covering the fields of crystal engineering, soft matter and drug design [1]. Contemporary research has shown that new kind of hydrogels as soft nanomaterials can be designed by using small molecules consisting of nucleobases, amino acids and glycosides. The resultant soft nanomaterials exhibit remarkable biological properties such as transporter of DNA, biostability and biocompatibility. Hydrogen bonding is one of the factors involved in the formation and stabilization of structures, reactivity and molecular networks. Its role in molecular recognition by nucleic acids, proteins and other small molecules is now established [2]. Therefore, characterizing hydrogen bonding in unnatural amino acids with respect to its structure and spectroscopy is of great significance.

The structure of an amino acid has carboxylic acid moiety (–COOH) as acidic center and amine moiety (–NH_2) as basic center and as a result, it is a zwitterionic structure consisting of ammonium (NH_3^+) and carboxylate (–CO_2^-) moieties [3]. While the zwitterionic structure of the amino acids and other molecules is apparent in condensed phase as has been demonstrated by a number of experiments, it is not uncommon in gas phase [4]. In the present work, both experimental vibrational spectral analysis and DFT calculations have pointed to the possible existence of both zwitterionic and its hydrogen bonded dimeric forms of 3-Aminobutanoic acid (3ABA for short, Fig 1) in condensed phase. Further, the IR and Raman spectral features including some broad bands are indicative of intra- and/or inter-molecular associations in 3ABA. A weak Raman band at 1682 cm^{-1} followed by intense absorption bands near 1663, 1634, 1577 and 1552 cm^{-1} and three weak to medium Raman bands at 1682, 1643 and 1548 cm^{-1} are characteristically associated with NH_3+ and CO_2^- moieties in free zwitterionic species and also hydrogen-bonded zwitterionic dimer species. While these bands are not predicted by the DFT calculations at B3LYP/6-31G* level of theory, the predicted bands for free neutral 3ABA are used as a limiting case to the assignments of experimental IR

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and Raman band spectra. Further, a linkage between $–NH_2$ and –COOH groups predicted in the optimized geometry has been interpreted as a tendency to form a zwitterion of an amine moiety ($–NH_2$) as basic center, NH_3^+ with carboxylic acid moiety (–COOH) as acidic center, CO_2^- .

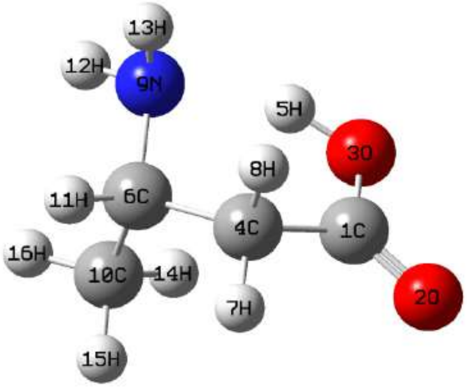

Fig 1. Molecular structure of 3-Aminobutanoic acid with numbering

2 Experimental and Computational details

Experimental

The solid sample of 3-Aminobutanoic acid was purchased from Aldrich Chemical Co. The IR spectral measurements were carried out on a Nicolet 6700 FTIR spectrometer. The spectrometer consisted of an Alum standard ETC Ever-Glo IR source, DTGS detector with KBr window. The sample preparation was made using KBr pellete technique and the spectrum was recorded in the region 4000-400 cm^{-1} for 50 scans with the resolution of 4 cm^{-1}. The Raman spectrum was recorded on a Nicolet NXR-FT-Raman spectrometer. The spectrometer consisted of a Nd:YVO4 laser source, CaF_2 beam splitter and Ge detector. Laser power around 500 mW was applied for excitation and spectrum for 500 scans with the resolution of 4 cm^{-1} was obtained.

Computational

The electronic structure calculations have been performed using quantum chemical density functional theory (DFT) methods in the Gaussian 09W and GaussView5 programs [5,6]. Optimization and vibrational frequency analyses were carried out at DFT B3LYP/6-31G* level. Optimized geometrical parameters, vibrational frequencies, IR and Raman intensities and normal modes were computed. The frequencies are scaled with a scaling factor of 0.9613 [7]. Further, normal coordinate and potential energy distribution (PED) calculations have been carried out using normal mode analysis [8].

3 Result and Discussions

The experimental IR absorption and Raman spectra of 3ABA are presented in Figs 2 and 3, respectively. The IR absorption spectrum typical of carboxylic acid (–COOH) is characteristically marked by a series of sub-bands over an intense broad absorption from 3500-2000 cm^{-1} followed by a smaller group of rather broad to sharp bands centred around 1550 cm^{-1} and sharp bands up to 450 cm^{-1}. The region 3500 – 2000 cm^{-1}, as is true of many amino acids, is due to hydrogen bonding. The Raman spectrum, on the other hand, contrasts with sharp bands throughout the spectral region except in the 600– 400 cm^{-1} region, where the bands are somewhat broader. The occurrence of some bands in both IR and Raman spectra for which there are no predicted bands is strongly indicative of the zwitterionic form of 3ABA, as is true of natural amino acids [4].

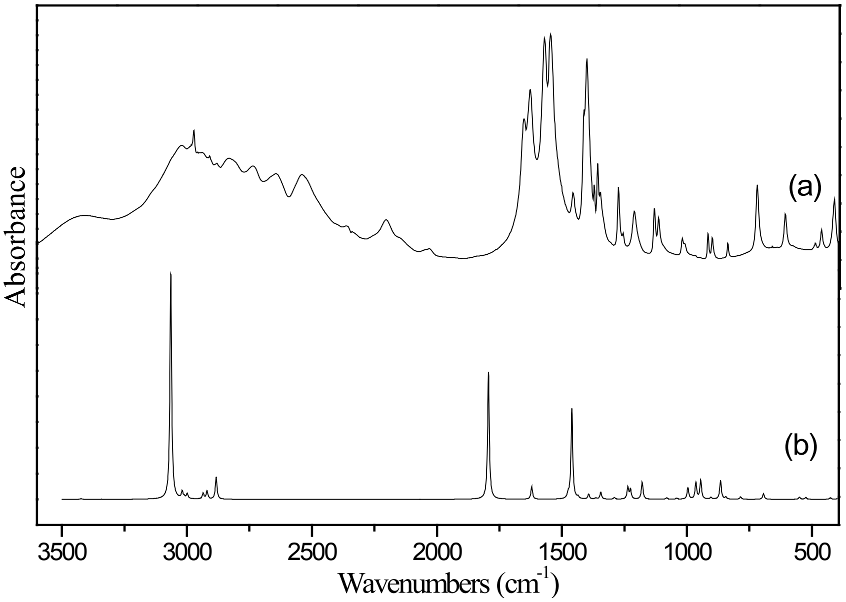

Fig 2. Experimental (a) and computed (b) IR absorption spectra of 3ABA. The spectrum (b) is thinly spread with main bands since it is like a vapor spectrum (see text for more discussion) compared to the spectrum (a).

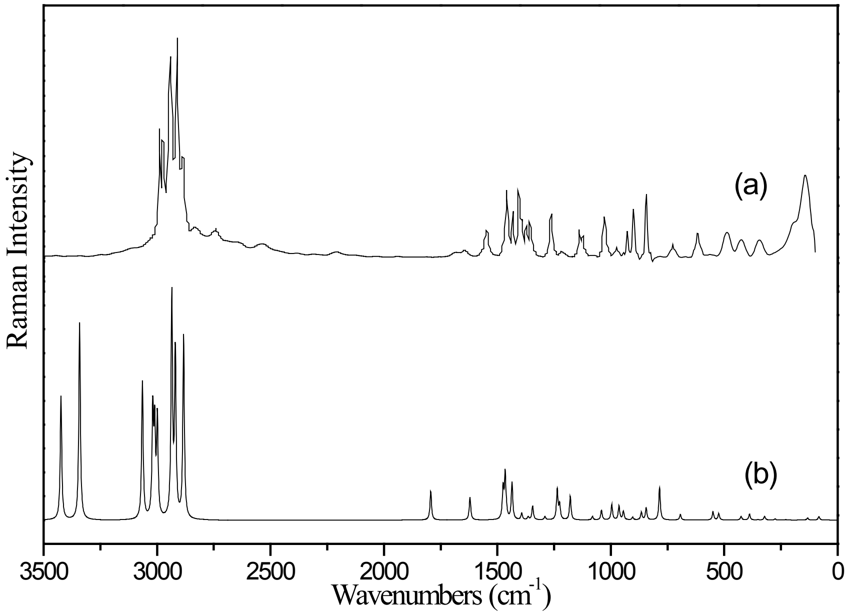

Fig 3. Experimental (a) and Computed (b) Raman spectra of 3ABA. The spectrum (b) shows main bands near 3400 – 2880 cm^{-1} due to NH_2 and CH, CH_2, CH_3 stretchings since it is like a vapor spectrum (see text for more discussion) compared to the spectrum (a) in which NH_2 stretching bands do not appear near 3500 – 3000 cm^{-1}.

It will be seen that the assignment of bands would be greatly aided if we regarded the B3LYP/6-31G* vibrational spectra as if it were vapor spectra for a neutral 3ABA (say, M^0). There are no absorptions in the 3500 – 3300 cm^{-1} region due to NH_2 vibrations but a down-shifted medium strong absorption band near 3029 cm^{-1} for which there is no predicted band is the first evidence of zwitterionic 3ABA ($M^{\pm}$). The band is assigned to asymmetric stretching of NH^{3+}. The symmetric stretching due to NH^{3+}, which is otherwise not observable due to overlap with C-H band, is a strong Raman band at 2990 cm^{-1}. The two predicted bands at 3423 and 3341 cm^{-1} are clearly due to NH2 vibrations (Fig 3(b)). A medium weak broad IR band at 3420 cm–1 is identified as O-H stretching probably originating in a dimer species [9]. However, a stretching O-H band is computed at a lower frequency of 3065 cm^{-1} which may be the result of a linkage predicted between NH_2 and O-H groups to be discussed later. A weak Raman band at 1682 cm^{-1} with four very intense bands that have appeared near 1663, 1634, 1577 and 1552 cm^{-1} in the IR and only two corresponding weak to medium Raman bands at 1643 and 1548 cm^{-1} do not allow straightforward assignments because of overlap or shifting of bands due to zwitterionic structure consisting of ammonium (NH_3^+) and carboxylate ($-CO_2^-$) moieties. There are no computed bands corresponding to these five bands. It follows that these bands arise either in dimers or zwitterionic structure consisting of ammonium (NH_3^+) and carboxylate ($-CO_2^-$) moieties.

Table 1. Optimized parameters of 3ABA

Bond lengths (Å)		**Dihedral angles (deg)**	
1C-2O	1.20	2O-1C-3O-5H	178.29
1C-3O	1.34	4C-1C-3O-5H	–3.54
1C-4C	1.53	2O-1C-4C-6C	–144.30
3O-5H	0.99	2O-1C-4C-7H	–20.67
4C-6C	1.54	2O-1C-4C-8H	93.45
4C-7H	1.09	3O-1C-4C-6C	37.54
4C-8H	1.10	3O-1C-4C-7H	161.16
5H-9N	1.77	3O-1C-4C-8H	–84.69
6C-9N	1.48	1C-4C-6C-9N	–61.50
6C-10C	1.53	1C-4C-6C-10C	59.27
6C-11H	1.10	1C-4C-6C-11H	178.36
9N-12H	1.01	7H-4C-6C-9N	176.58
9N-13H	1.01	7H-4C-6C-10C	–62.63
10C-14H	1.09	7H-4C-6C-11H	56.46
10C-15H	1.09	8H-4C-6C-9N	59.77
10C-16H	1.09	8H-4C-6C-10C	–179.45
		8H-4C-6C-11H	-60.35
Bond angles (deg)		4C-6C-9N-12H	169.00
2O-1C-3O	122.00	4C-6C-9N-13H	–72.43
2O-1C-4C	122.11	10C-6C-9N-12H	46.17
3O-1C-4C	115.84	10C-6C-9N-13H	164.73
1C-3O-5H	108.51	11H-6C-9N-12H	–73.08
1C-4C-6C	115.96	11H-6C-9N-13H	45.47
1C-4C-7H	107.06	4C-6C-10C-14H	-62.30
1C-4C-8H	107.31	4C-6C-10C-15H	57.82
6C-4C-7H	110.33	4C-6C-10C-16H	178.12
6C-4C-8H	109.11	9N-6C-10C-14H	57.99
7H-4C-8H	106.61	9N-6C-10C-15H	178.12
4C-6C-9N	108.33	9N-6C-10C-16H	–62.42

4C-6C-10C	112.50	11H-6C-10C-14H	178.99
4C-6C-11H	107.55	11H-6C-10C-15H	–60.87
9N-6C-10C	109.16	11H-6C-10C-16H	58.57
9N-6C-11H	111.06		
10C-6C-11H	108.23		
6C-9N-12H	110.80		
6C-9N-13H	110.59		
12H-9N-13H	107.05		
6C-10C-14H	110.97		
6C-10C-15H	110.46		
6C-10C-16H	110.94		
14H-10C-15H	108.29		
14H-10C-16H	108.27		
15H-10C-16H	107.77		

We wish to refer to a detailed vapor, solvent (polar/non-polar) and temperature-dependent IR study of the structure of dibutylglycine and glycine by Denisov *et al* [9] in which they convincingly assigned an IR band at 1640 cm^{-1} to CO_2^- stretching of the ionized carboxyl moiety. The same band, in a non-polar solvent, shifts to 1770 cm^{-1} accompanied simultaneously by the appearance of a weak band near 3530 cm^{-1} attributed to the stretching vibration of a free hydroxyl moiety. When the temperature is increased, the intensity of the 1640 cm^{-1} band decreases while that of 1770 cm^{-1} band rises, eventually only the latter band survives in the spectrum corresponding to carbonyl (C = O) moiety. From these spectral behavior, they conclude that there exists an equilibrium between monomers (M^0) and dimers ($D^{\pm}$) as $2M^0 \leftrightarrow D^{\pm}$. In polar solvents such as acetonitrile, the dibutylglycine shows a doublet absorption at 1650 and 1630 cm^{-1} of which the second band goes weaker at very low concentrations while the intensity of the 1650 cm^{-1} band is given up to a band at 1760 cm^{-1} upon increasing temperature. The 1760 cm^{-1} band corresponds to free carbonyl vibration. These observations have led Denisov *et al* [9] to conclude that the concentration and temperature changes dissociate dimeric forms that produced 1630 cm^{-1} band, leading to an equilibrium between monomers M^0 and $M^{\pm}$ which are hydrogen bonded to solvent molecules. Thus, the stable zwitterionic monomeric form is stable in high dielectric-solvents where protonation occurs; dimers having zwitterionic structure are formed in non-polar solvents; in polar solvents, an equilibrium exists between amino acid and solvent molecules held together by hydrogen bonding and zwitterions; only zwitterionic species remain in aqueous and alcohols. However, in the present study, 3ABA exists as a solid at room temperature which may be approximated to a medium with high dielectric constant and is apparently in stable dimer and zwitterionic forms as evidenced by the spectral features. In their study of IR spectra of some amino acids, Leifer and Lippincott [10] have pointed out that while inter-molecular hydrogen bonding in solid phase amino acids is common, the intra-molecular hydrogen bonding is also concomitant when samples are ground and pelleted in KBr for IR measurements thereby partially breaking the inter-molecular bonding [10]. In the present study, a complicated picture is thrown up by the bands near 1685 to 1540 cm^{-1}. A computed band at 1794 cm^{-1} is due to the C=O in the neutral 3ABA and it has moved down to 1682 cm^{-1} as a weak Raman band on account of carboxylic acid moiety (-COOH) becoming carboxylate, $-CO_2^-$. The 1682 cm^{-1} band is identified as asymmetric stretching of CO_2^-. Two strong absorption doublets at 1663 and 1634 cm^{-1} correspond to 1650 and 1635 cm^{-1} in dibutylglycine [9] and the second band at 1635 cm^{-1}, according to Denisov *et al* [9], is concentration- and temperature-dependent thereby strongly demonstrating its origin in dimer species. We assign these two bands to asymmetric and symmetric stretch of CO_2^- , respectively. There are two strong absorption bands near 1577 and 1552 cm^{-1} that are assigned to asymmetric and symmetric bending due to NH_3^+, respectively. These two are split modes that correspond to the degenerate mode (ν_4(E)) of NH_3 with C_{3v} symmetry [11]. There is one strong band at 1407 cm^{-1} assigned to symmetric stretching of CO_2^-. A computed band at 1460 cm^{-1} is assigned as OH bending mode and it apparently has been up-shifted from 1410 cm^{-1}, where symmetric (CO_2^-) stretching band has occurred [3,12,13]. As for the modes of C-H, CH_2 and CH_3, they are not influenced by the zwitterionic form and all the bands are observed except the $\nu_{as}(CH_3)$ mode but is computed at 2998 cm^{-1}. The bands due to these groups are shown in the computed Raman spectrum (Fig (b)). All the remaining assignments of both observed and computed bands are presented in the Table 2.

Table 2. Measured and computed vibrational frequencies (cm^{-1}) of 3ABA with assignments

IR	Raman	DFT[1]	Assignments (%PED)
--	--	3423	ν_{as} (NH, 100)
3420 mw br	--	--	ν (OH bonded) due to Dimer
--	--	3341	ν_s (NH, 100)
--	--	3065	ν (OH, 95)
3029 w	--	--	ν_{as} (NH_3^+) due to zwitterion
--	2990 s	--	ν_s (NH_3^+) due to zwitterion
2974 w	2973 s	3018	ν_{as} (CH_3, 95)
2940 w	2942 vs	3011	ν_{as} (CH_2, 90)
--	--	2998	ν_{as} (CH_3, 98)
2910 w	2911 vs	2935	ν_s (CH_3, 99)
2884 w	2886 ms	2919	ν (CH_2, 93)
2840 mw	2837 w	2883	ν (CH, 96)
2734 mw	2740 w	--	--
2647 mw	2628 vw	--	ν_s (NH_3^+) due to zwitterion
2544 ms	2536 w	--	--
2366 vw	2377 vw	--	--
2208 w	2209 vw	--	--
2036 w	2035 vw	--	ν_s (NH_3^+) due to zwitterion
--	--	1794	ν (C=O, 80)
--	1682 vw	--	ν_s (CO_2^-) due to zwitterion
1663 s	--		ν_{as} (CO_2^-) due to zwitterionic dimer
1634 vs	1643 w	--	ν_{as} (CO_2^-) due to zwitterionic dimer
--	--	1620	β (NH, 49), β (CN, 33)
1577 vs	--	--	β_{as} (NH_3^+) due to zwitterion
1552 vs	1548 mw	--	β_s (NH_3^+) due to zwitterion
1463 ms	1459 ms	--	β (CH_2)
--	1431 mw	1475	β_{as} (CH_3, 57)
--	--	1465	β_{as} (CH_3, 61)
--	--	1460	β (OH, 77)
--	--	1435	β_{sc} (CH_2, 26), β (CO, 12), β (CN, 11)

1407 vs	1405 ms	--	ν_s (CO_2^-) due to zwitterion
1378 w	1371 mw	1391	β_s (CH_3, 17), β (CC, 40), $\boldsymbol{\nu}$ (CC, 21)
1364 s	--	1364	β (NH, 16), β (CC, 23)
1355 w	1355 mw	1345	β (CN, 13), β (CC, 23)
1282 ms	--	1290	ν (CC, 26), β (CC, 34)
1264 vw	1261 mw	1236	ν (CO, 28), β (CC, 10)
1218 ms	1215 vw	1225	ν (CO, 33), β_r (NH_2, 25)
1138 ms	1138 mw	1178	ν (CO, 17), ν (CN, 14), β (CC, 20)
1122 ms	1124 w	1080	ν (CN, 19), β (CC, 32)
1027 mw	1028 mw	1041	ν (CN, 12), β (CC, 24), β (NH, 18)
--	974 w	996	ν (CC, 46), β_r (NH_2, 14)
--	--	964	β_w (NH, 31), ν (CN, 12), ν (CC, 10)
924 mw	927 mw	945	ν (CC, 26), β (COOH, 20), ν (CN, 17), β (CO, 10)
907 mw	900 ms	904	β (CC, 21), β (COOH, 10), β_w (NH, 10)
--	--	865	β_w (NH, 26), ν (CN, 15)
845 mw	843 ms	844	ν (OH, 31), ν (CO, 19), ν (CN, 10)
--	782 vw	785	ν (CC, 44), ν (CN, 26)
728 s	727 w	--	β_w (NH) due to zwitterion
--	673 vw	693	β (OCO, 18)
616 ms	617 mw	--	β (CN), β (CO)
--	564 vw	550	β (OCO, 17), ν (CC, 16)
497 vw	487 mw	524	β (CO, 19), ν (CC, 12), β (CC, 12)
472 mw	--	--	NH_3^+ mode due to zwitterion
421 ms	425 mw	426	β (CN, 29), β (CO, 25)
--	--	388	τ (CN, 52), τ (CN, 21)
--	344 mw	351	τ (CO, 19), β (CC, 17), ν (NH, 11)
--	--	322	τ (CN, 53), τ (CN, 17)
--	--	276	ν (NH, 23), τ (CN, 19), τ (CC, 12)
--	204 vw	229	τ (CC, 36), τ (CN, 33)
--	142 s	133	τ (CC, 25), τ (CN, 24)
--	--	83	τ (CO, 35), τ (C=O, 22), τ (COOH, 10)

Note. The Greek symbols used above,*ν, 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. [1] DFT = B3LYP/6-31G*

As noted above, a linkage between NH_2 and COOH groups is predicted in the optimized geometry of 3ABA at B3LYP/6-31G* calculations which we interpret as follows. The linkage distance between 5H and 9N atoms (Fig 1) is computed at 1.77 Å (Table 1) as against the normal N-H bond length of 1.00 Å. As a result, the 5H atom has moved away from the 3O atom in COOH, increasing the 5H-3O length by ~ 3%; the 1C-3O and 1C-2O bond lengths have shortened by 6 and 5 % , respectively. The sum of van der Waals radii of 5H and 9N atoms, 2.75 Å, is longer than the computed 5H...9N length, indicating a chemical structure consistent with the previous discussion on the formation of zwitterion from NH_2 and COOH groups though the structure is not predicted to be independent zwitterionic species (or rather quasi-zwitterions). However, the observed spectral features seem to favour zwitterionic species and hydrogen-bonded dimers formed between zwitterionic species of 3ABA. A series of sub-bands over an intense broad absorption from 3500 to 2000 cm^{-1} is a complex structure to explain, and the structure may be attributable to coupling between O-H stretching and low frequency dimer modes in the anharmonic potential [14]. On account of this reason, the bands from 2600 – 2000 cm^{-1} (excepting symmetric stretching mode of NH_3^+) are not assigned.

4 Conclusions

The vibrational structure of 3-Aminobutanoic acid, unlike in the natural amino acids, appear to originate from both zwitterionic species and hydrogen bonded dimer species. This is borne out by a weak Raman band at 1682 cm^{-1} and four intense absorptions near 1663, 1634, 1577 and 1552 cm^{-1}, all of which seem to arise from vibrations of carboxylate and ammonium moieties in zwitterions and zwitterionic dimer species. The B3LYP/6-31G* spectrum served as a vapor spectrum of the neutral molecule with a predicted linkage between NH_2 and COOH in the optimized geometry. This geometry partly lent support to the assignments of the observed bands. However, solvent studies would provide a definitive role of zwitterions, hydrogen bonding and dimer species, making assignments more certain than tentative as in the present study. Further, DFT calculations on 3-Aminobutanoic acid for a zwitterion and associated hydrogen bonded dimer would produce a vibrational structure in good agreement with experiment. Both these studies are in progress.

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