

Letter

Infrared and Raman spectra of DL-aspartic acid nitrate monohydrate

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Abstract

Infrared and Raman spectral studies of DL-aspartic acid nitrate monohydrate help to determine the influence of extensive intermolecular hydrogen bonding in the aspartic acid crystal. The presence of the carbonyl rather than the carboxylic group indicates that the molecule is ionic. The shifting of several group frequencies in the molecule confirms extensive hydrogen bonding. The anion fundamentals however continue to be degenerate. This indicates that its symmetry is unaffected in the molecule. © 1998 Elsevier Science Ireland Ltd. All rights reserved.

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1. Introduction

With the rapid development of molecular biology, understanding biological functioning based on molecular structure has become a felt need. Amino acids are an important class of organic compounds that form the building blocks for larger biological molecules like proteins. They behave as a language that writes a large sentence—the protein. Proteins are nitrogenous substances that occur in both animal and plant cells.

They yield a strong mixture of amino acids when hydrolysed by strong inorganic acids or enzymes. Enzymes themselves are proteins and are necessary for the efficient catalysis of the various reactions needed for cellular functions. The polypeptide chain making up an enzyme contains a few hundred amino acids. It functions effectively if the primary sequence is correct and if the polypeptide chain maintains its three-dimensional structure. The forces that maintain this structure are the hydrophobic interaction between hydrocarbon side chains, electrostatic forces between acidic and basic residues and hydrogen bonding. Aspartic acid, together with glutamic acid, lysine,

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arginine and histidine, belongs to the group called polar amino acids. These residues help in determining the solubility and the polyelectrolytic properties of proteins. Aspartic acid is the starting material in the synthesis of many amino acids in the bacterium *E. coli* [1,2]. Spectroscopic methods are capable of giving a detailed knowledge of any molecular framework. Infrared and Raman spectral studies give structural features and changes due to biological functioning. The disadvantage with the infrared spectra is that water, the biological medium, absorbs strongly in that region where most of the vibrational frequencies lie. Raman spectroscopy, then, becomes a powerful tool to supplement any information obtained with the infrared spectra.

Edsall [3–6] has done pioneering work in studying the ionisation of the carbonyl group through Raman spectroscopy. The vibrational studies of amino acids like glycine [7–10], alanine [11–14], serine [15,16], cysteine [16,17] and glutamic acid [18] have been reported. Most of these are of the pure or deuterated form, which exist in the zwitterion configuration with an NH_3^+ and a COO^- group. Studies on compounds of amino acids have been confined to hydrochlorides, chlorides, dichlorides and sodium salts [3,4,19–22]. These studies show that it is possible to suppress the ionisation of the carboxylic group under suitable conditions.

In this study, the analysis of the structure of DL-aspartic acid nitrate monohydrate is done with the help of its Infrared and Raman spectra. The compound has a large degree of hydrogen bonding and this is expected to modify the spectra from that of the pure amino acid. The factor group analysis of the title compound has also been done.

2. Experimental

DL-Aspartic acid nitrate monohydrate crystals were grown by slow evaporation using a 1:1 stoichiometric ratio of DL-aspartic acid and nitric acid in an aqueous medium. The crystals were plate shaped and elongated. The infrared spectrum was recorded using a BRUCKER IFS FT

IR spectrometer employing the KBr pellet technique. Raman measurements were made as described by Jeyaraj and Ramakrishnan [23] and the laser power was maintained at 200 mW.

3. Results and discussion

In DL-aspartic acid nitrate, the nitrate is planar while the aspartic acid cation has an extended trans-configuration. The water molecule of the monohydrate has its usual bent configuration. With the involvement of all potential donors, extensive intermolecular hydrogen bonding takes place in the molecule [24]. DL-Aspartic acid nitrate has a triclinic geometry, belongs to the space group P1 and has two formula units per unit cell [24]. The factor group analysis gives 141 normal modes of vibration, $\Gamma = 72\text{Ag} + 69\text{Au}$, excluding the three non-genuine acoustic modes. The Ag mode of vibration is Raman active while the Au mode is infrared active. There are no common modes.

3.1. Vibrations of the aspartic acid cation

The aspartic acid cation, $\text{C}_4\text{H}_8\text{NO}_4^+$, is itself made up of several groups. These group frequencies, however, are expected to undergo changes in their intensity and position according to their environment.

The ammonium group $-\text{NH}_3^+$, exists with a pyramidal symmetry. In the free state it has a C_{3v} symmetry and its normal modes of vibrations are v_1 (A_1), v_2 (A_2), v_3 (E), and v_4 (E). They are both infrared and Raman active [25]. The broad band at 3155 cm^{-1} in the Raman spectrum and the corresponding band at 3138 cm^{-1} in the infrared spectrum (Figs. 1 and 2) are attributed to the asymmetric N–H stretching mode v_3 . The symmetric stretching mode v_1 of the $-\text{NH}_3^+$ group is expected at 2970 cm^{-1} [26]. In the title compound, this band is considerably weaker as strong hydrogen bonds exist between the $-\text{NH}_3^+$ group and the surrounding H_2O and NO_3^- groups. The much more intense $-\text{CH}_2$ stretching mode, which lies in the same region [6], masks this band. The bending, rocking and torsional frequencies,

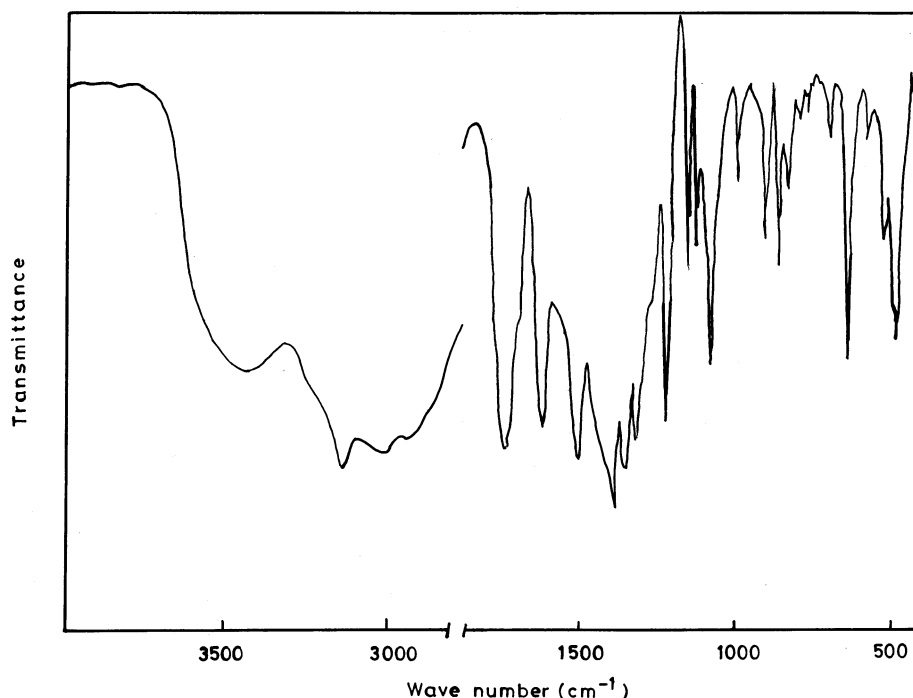


Fig. 1. Infrared spectrum of DL-aspartic acid nitrate monohydrate.

together with their combination and over tones are also assigned. As expected, the stretching frequencies are downshifted by about 100 cm^{-1} from that of the corresponding free ion. When the $-\text{NH}_3^+$ ion is attached to the rest of the molecule, the N–H bond is weakened, reducing the vibrational frequencies. Hydrogen bonding is also responsible for the lowering of the stretching frequencies. The NH_3^+ deformation modes shift to higher frequencies for precisely the same reason.

In amino acids with a zwitterion configuration, a carboxylic group is present but salts of amino acids often contain the unionised carbonyl group. The intense bands at 1736 cm^{-1} (in the infrared spectrum) and at 1731 cm^{-1} (in the Raman spectrum) confirm the presence of the carbonyl group in DL-aspartic acid nitrate monohydrate.

The frequency of the $-\text{CH}_2$ vibrational mode depends on its immediate environment. The strong band at 1452 cm^{-1} is due to its deformation mode when attached to the carbonyl group. In the Raman spectrum of L-aspartic acid nitrate hydrochloride [4], Edsall has reported a broad peak

at 2961 cm^{-1} . In this investigation, two very intense peaks occur at 2982 and 2945 cm^{-1} in the Raman spectrum. These are due to the asymmetric and symmetric stretching modes, of the methylene group respectively. The wagging, rocking, and twisting modes of the $-\text{CH}_2$ group are also identified (Table 1).

The $>\text{CH}$ group is also next to a carbonyl group. In this environment, as expected, the $>\text{CH}$ bending mode occurs as a strong band near 1400 cm^{-1} both in the infrared and the Raman spectra [27]. The $>\text{CH}$ stretching modes, which occur around 2960 cm^{-1} [18,27], are overlapped by the stronger $-\text{CH}_2$ stretching modes.

DL-Aspartic acid nitrate has a C–C–C–C skeleton, which can be considered to be made up of two coupled oscillators [27]. The bands at 418 and 285 cm^{-1} correspond to the in phase and out of phase bending vibrations. The C–C skeleton has characteristic frequencies in the 1132 – 885 cm^{-1} range. Dhamelincourt and Ramirez [18] identified three C–C bands (around 970 , 918 and 806 cm^{-1}) in the infrared and Raman spectra of L-glutamic

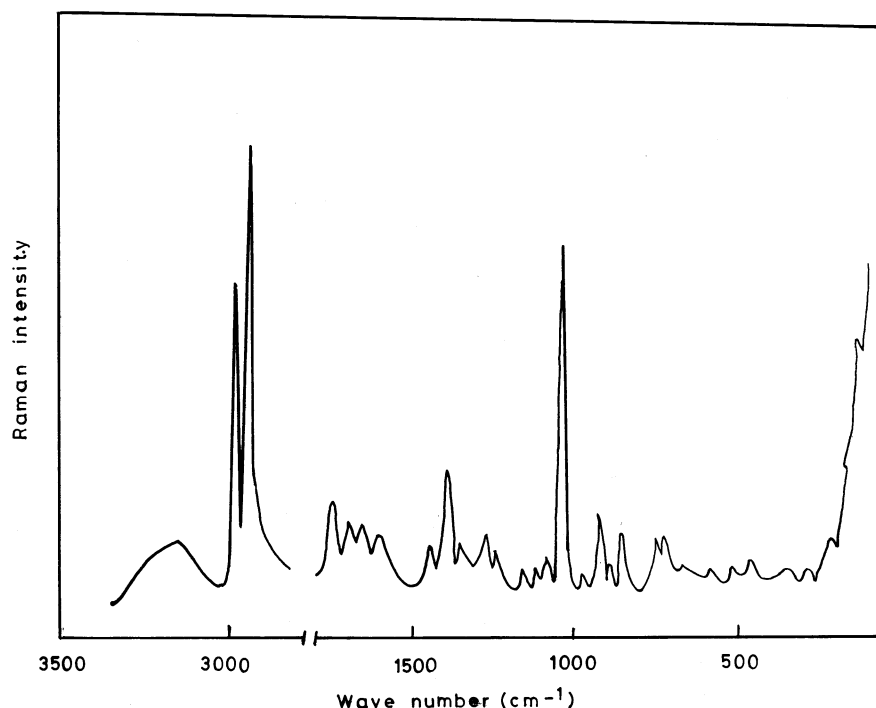


Fig. 2. Raman spectrum of DL-aspartic acid nitrate monohydrate.

acid. This indicated three different orientations of the C–C bonds in the crystal.

An inspection of the spectra shows a broad band around 3000 cm^{-1} (more prominent in the infrared spectrum). This is because of the strongly bonded O–H stretching modes, typical of carboxylic dimers [27]. The strong bands due to the N–H and CH₂ stretching mode superimpose this band. The ‘in plane’ deformation of the (C)–OH bond occurs at the same frequency (1313 cm^{-1}) as that observed for L-glutamic acid [18]. However, the ‘out of plane’ deformation frequency is higher than that observed at about 940 cm^{-1} for L-glutamic acid. This shift is attributed to hydrogen bonding. In contrast, the C–O (H) stretching frequency at about 1110 cm^{-1} , is substantially lower than the expected range ($1315\text{--}1280\text{ cm}^{-1}$) for the same reason [27].

3.2. Vibrations of the nitrate ion

The nitrate ion in this compound exists in the planar form [24]. When free it has a D_{3h} symme-

try and its normal modes of vibrations are $A_1 (v_1)$, $A_2 (v_2)$ and $E (v_3 \text{ and } v_4)$. The frequency v_1 is Raman active, v_2 is infrared active, while v_3 and v_4 are both infrared and Raman active. In its free ion state, v_1 (symmetric stretch) occurs at 1049 cm^{-1} , v_2 (symmetric bend) at 830 cm^{-1} while v_3 and v_4 (asymmetric stretch and bend) occur at 1355 and 690 cm^{-1} , respectively [28]. When attached to the cation, there is a loss of symmetry and some of the forbidden modes may be excited.

The v_1 mode at 1043 cm^{-1} is very strong in the Raman spectrum but it is missing in the infrared spectrum. The medium intensity band of v_2 at 860 cm^{-1} , is an example of the forbidden Raman vibration being excited. However, there is an increase in the frequency of this bending mode from the free ion value. The asymmetric stretching frequency at about 1350 cm^{-1} is both infrared and Raman active and has almost the same value as the free ion state. The asymmetric bending mode is also both infrared and Raman active. It occurs at a frequency near 720 cm^{-1} , which is again slightly higher than the free ion case. For any

molecule the totally symmetric stretching mode leads to a strong band in the Raman spectrum. Here, the v_1 mode creates an intense Raman line. All the fundamentals also appear within the expected regions, with the non-removal of degeneracy (for v_1 and v_2). This confirms that the symmetry of the nitrate ion is not affected in this molecule.

Table 1
Experimental data for the vibrational spectra of DL-aspartic acid nitrate monohydrate^a

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
3434 (br, s)		O–H str (H ₂ O)
3139 (vs, br)	3156 (br, m)	NH ₃ ⁺ asym str
3013 (vs, br)	2982 (vvs)	CH ₂ asym str
	2945 (vvvs)	CH ₂ sym str
1736 (vs)	1731 (s)	C=O str
	1685 (m)	NH ₃ ⁺ asym defor
	1650 (m)	H ₂ O sym bend
1618 (s)	1601 (m)	NH ₃ ⁺ sym defor
1500 (vs)		C–N asym str
	1452 (m)	CH ₂ sym defor
1384 (vs)	1401 (s)	CH bend
1349 (vs)	1357 (m)	NO ₃ ⁻ asym str
1312 (vs)	1313(sh)	OH in plane defor
	1277 (m)	CH ₂ wag
	1248 (w)	CH ₂ twist
1213 (s)		CH bend
1141 (m)	1156 (w)	NH ₃ ⁺ rock
1116 (w)	1100 (w)	C–OH str
1072 (s)	1082 (w)	C–N sym str
	1043 (vvs)	NO ₃ ⁻ sym str
986 (w)		OH out of plane def
916 (w)	930 (m)	C–C str
894 (w)	896 (w)	C–C str
854 (m)	860 (m)	NO ₃ ⁻ asym bend
694 (w)	703(w)	H ₂ O rock
643 (s)		O–C–O defor
578 (vw)	578(vw)	H ₂ O wag
525 (w)	531 (vw)	C–C–O defor
479 (m)	460 (w)	NH ₃ ⁺ tor
418 (vw)		C–C–C–C in phase vib
	343 (w)	
	286 (w)	C–C–C–C out of phase vib
	238 (m)	
	213 (w)	lattice modes
	104 (w)	

^a s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; str, stretch; sym, symmetric; asym, asymmetric; defor, deformation; tor, torsion; vib, vibration.

3.3. Vibrations of water

In the solid state, water has a C_{2v} symmetry with normal modes 2A₁ (v_1 and v_2) and B₂ (v_3), all of which are both infrared and Raman active. These modes occur at about 3400, 1620 and 3220 cm⁻¹ respectively. In the present compound, water exists as lattice water. The broad, strong band at 3434 cm⁻¹ in the infrared spectrum is assigned to the symmetric stretching frequency (v_1) of the water molecule. The corresponding frequency in the Raman spectrum is so weak that it is hardly noticeable. The symmetric bending frequency, v_2 , occurs in the Raman spectrum at 1650 cm⁻¹, whereas the asymmetric stretching frequency, v_3 , is masked by the more intense N–H stretching mode that lies in the same region.

In the low frequency regions, lattice water exhibits vibrational modes due to restricted rotations and oscillations of the water molecule [25]. The bands due to the rocking and wagging modes have also been assigned.

4. Conclusion

Vibrational assignments of bands in the infrared and Raman spectra have been done for DL-aspartic acid nitrate monohydrate. The results confirm that the compound exists in the ionic form with the positive charge residing on the –NH₃ group. The NO₃⁻ forms the anion.

The downshifting of several stretching frequencies together with an increase in many of the bending frequencies confirms the occurrence of extensive intermolecular hydrogen bonds. Additional data like isotopic substitution will probably help in confirming many of the assignments and reveal information about overlapping bands.

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