

# RAMAN SPECTRUM OF *l*-ASPARAGINE MONOHYDRATE

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## 1. INTRODUCTION

ASPARAGINE belongs to the class of organic compounds known as amino-acids which are characterized by exceptional properties. It is the acid amide of aspartic acid and can be easily crystallized from aqueous solutions. The crystal of asparagine monohydrate  $\text{NH}_2\text{COCH}_2\text{CH}(\text{NH}_2)\text{COOH}\cdot\text{H}_2\text{O}$  obtained thereby belongs to the orthorhombic system and is found to be laevorotatory. A systematic investigation of the Raman spectra of some of the amino-acids using  $\lambda$  2537 excitation was undertaken in this laboratory a few years ago. The Raman spectra of  $\alpha$ -glycine, triglycine sulfate (Krishnan and Balasubramanian, 1958) and diglycine hydrobromide and diglycine nitrate (Balasubramanian, 1961) have already been reported in these *Proceedings*. *l*-Asparagine monohydrate is found to be transparent and its Raman spectrum has therefore been recorded and the results are presented below.

## 2. EXPERIMENTAL DETAILS

Single crystals of *l*-asparagine monohydrate in the form of colourless rhombic prisms were grown from aqueous solutions of the pure substance. The biggest crystal grown had roughly the size 5 mm.<sup>3</sup> Using mercury  $\lambda$  2537 excitation and a Hilger medium quartz spectrograph the Raman spectrum of the crystal was photographed. With Ilford Zenith Astronomical plates an exposure of one day was found to be necessary. Due to exposure to the ultra-violet radiation, the face of the crystal adjacent to the arc progressively got translucent thus reducing the efficiency of its transmission to the exciting light. During long exposures one had therefore to use a fresh crystal every few hours.

## 3. RESULTS

An enlarged photograph of the Raman spectrum of *l*-asparagine monohydrate is reproduced in Fig. 1, along with its microphotometer record. A blank mercury spectrum is also included for purposes of comparison. The positions and frequency shifts of the Raman lines are marked on the micro-

photometer tracing. They are also listed in Table I. The figures given in brackets represent the relative intensities of the Raman lines estimated

TABLE I  
*Raman spectrum of l-asparagine monohydrate*

No.	Frequency shifts in $\text{cm.}^{-1}$	I.R. absorption maxima in $\text{cm.}^{-1}$	Assignments
1	45 (4)		Lattice line
2	58 (4)		"
3	85 (4)		"
4	100 (4)		"
5	118 (4)		"
6	135 (10)		"
7	150 (4)		"
8	163 (4)		"
9	194 (4)	}	O—H...O and N—H...O oscillations
10	245 (2)		
11	296 (2)		
12	341 (4)	}	C—C torsion
13	354 (2)		
14	379 (3)		
15	398 (2)		
16	500 (2)	}	C—N torsion
17	522 (2)		
18	544 (2)	}	$\text{NH}_3^+$ torsion
19	570 (2)		
20	668 (2)		$\text{H}_2\text{O}$ rocking
21	801 (6)	800	C—C stretching
22	825 (6)	805	
23	842 (6)	836	
24	889 (2)	886	
25	913 (2)	908	$\text{CH}_2$ rocking
		923	
		943	

TABLE I (Contd.)

No.	Frequency shifts in $\text{cm.}^{-1}$	I.R. absorption maxima in $\text{cm.}^{-1}$	Assignments
26	1077 (3)	1076	C—N stretching
27	1104 (10)	1105	NH <sub>3</sub> <sup>+</sup> rocking
28	1140 (8)	1123	
29	1150 (8)	1150	
30	1238 (4)	1233	NH <sub>2</sub> rocking
31	1301 (4)	1309	CH <sub>2</sub> wagging
32	1313 (4)		
33	1360 (8)	1357	CH bending
34	1402 (4)	1398	C—N stretching
35	1430 (10)	1431	COO <sup>-</sup> sym. stretching
36	1440 (10)		CH <sub>2</sub> bending
		1525	
37	1595 (7)		NH <sub>2</sub> bending
38	1629 (4)	1633	COO <sup>-</sup> antisym. stretching
39	1642 (8)		NH <sub>3</sub> <sup>+</sup> deformation
40	2480 (0)	}	N—H hydrogen bonded
41	2588 (0)		
42	2614 (0)		
43	2693 (0)		
44	2750 (0)		
45	2838 (0)		
46	2883 (0)		
47	2934 (10)	}	C—H stretching
48	2957 (5)		
49	2968 (10)		
50	3120 (3 <i>b</i> )	}	NH <sub>3</sub> <sup>+</sup> stretching
51	3240 (0 <i>b</i> )		
52	3384 (9)		NH <sub>2</sub> stretching
53	3405 (8 <i>b</i> )		O—H stretching

visually. The crystal was illuminated perpendicular to the  $c$ -axis and the scattered light was taken along the  $c$ -axis. Fifty-three distinct Raman lines have been recorded. Of these, the first eight lines belong to the lattice spectrum while the remaining ones arise from the internal oscillations. It is interesting to note that most of the lattice lines are fairly sharp and intense. In the region between 2400 and 2900  $\text{cm}^{-1}$  there are seven Raman lines which can be clearly seen in the microphotometer record. They can also be seen with some difficulty in the photographs. The infra-red absorption spectrum of asparagine has been studied by Lenormant (1946), Kuratani (1949), Davies and Evans (1952) and Duval (1957). The values obtained from Duval's measurements which are more extensive are given in Table I. There is very good agreement between the Raman and infra-red frequencies in the region investigated. The frequency corresponding to the infra-red absorption at 1525  $\text{cm}^{-1}$  could not be identified in the Raman spectrum as it falls close to an intense mercury line.

#### 4. DISCUSSION

*Structure.*—The space group of *l*-asparagine monohydrate was first determined by Bernal (1931). It belongs to the orthorhombic system with space group  $P2_12_12_1$ . The complete structure analysis of this compound has been carried out recently by Kartha (1961). Using three-dimensional sharpened Patterson projection, it has been established by Kartha's analysis that the asparagine molecule in the crystal has a chain configuration and not a ring one. The unit cell dimensions are  $a = 5.582 \text{ \AA}$ ;  $b = 9.812 \text{ \AA}$  and  $c = 11.796 \text{ \AA}$ . The unit cell contains four molecules. The structure as projected on the  $bc$ -plane is shown in Fig. 2. The respective atoms of a single molecule of asparagine monohydrate are marked in the figure. The molecules are held together in the structure by a three-dimensional network of hydrogen bonds. Starting from each molecule of asparagine monohydrate there are seven hydrogen bonds and a representative set of seven such hydrogen bonds is indicated in the figure by broken lines.

The dash sign (') given to some of the oxygen atoms in Fig. 2 and Table II indicates that they belong to the neighbouring molecules. The oxygen atoms  $O_3$  and  $O_3'$  are actually one above the other, but in order to show the hydrogen bond  $N_1 \dots O_3'$  clearly  $O_3'$  has been slightly displaced in Fig. 2. The oxygen atom  $O_4$  of every water molecule forms two hydrogen bonds with  $O_1$  and  $O_1'$  of the  $\text{COO}^-$  groups.  $O_4$  should therefore serve as the negative end for two hydrogen bonds. In fact,  $\text{N—H} \dots \text{O}$  bond from  $N_1$  ends on this oxygen atom. It has also got another contact with the  $\text{CH}_2$  group of the same molecule at 3.6  $\text{\AA}$ .

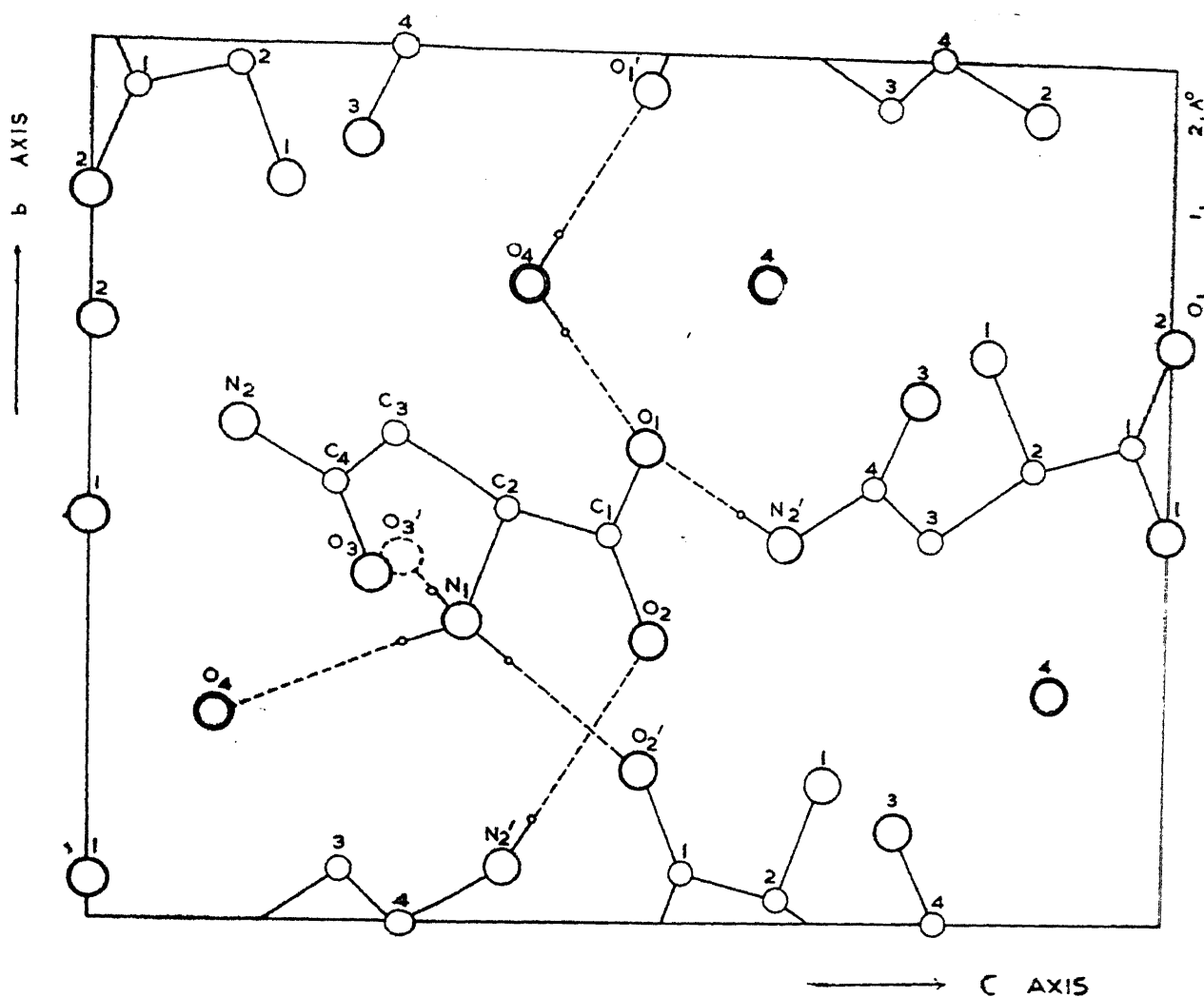


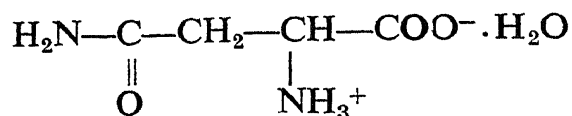
FIG. 2. Projection of the crystal structure of Asparagine Monohydrate on the *be* plane.

-  Water Oxygen
-  Nitrogen
-  Oxygen
-  Carbon
-  Hydrogen

TABLE II

Hydrogen bond type	Bond lengths in A.U.
$O_4-H \cdots O_1$	2.84
$O_4-H \cdots O_1'$	2.80
$N_1-H \cdots O_2$	2.81
$N_1-H \cdots O_3$	2.80
$N_1-H \cdots O_4$	2.85
$N_2-H \cdots O_1'$	2.92
$N_2-H \cdots O_2'$	3.02

*Internal frequencies.*—Of the fifty-three Raman lines recorded forty-two are due to internal oscillations of the asparagine molecule. From the structure it is evident that the asparagine molecule exists as a zwitter ion with the structural formula



Unlike glycine, asparagine has got apart from a  $\text{NH}_3$  group, a  $\text{NH}_2$  group also. It is also necessary to remember that the  $\text{NH}_3$  group, the  $\text{NH}_2$  group and the water molecule are hydrogen-bonded. With this background knowledge of its structure, it is easy to assign the observed Raman frequencies to the oscillations of the various functional groups.

The O—H stretching oscillation being hydrogen-bonded appears as a diffuse band with its centre at about  $3405 \text{ cm.}^{-1}$ . The intense and fairly sharp line at  $3384 \text{ cm.}^{-1}$  should be assigned to the  $\text{NH}_2$  stretching vibration being slightly displaced towards lower frequency due to hydrogen-bonding. The appearance of the broad band at  $3120 \text{ cm.}^{-1}$  which can only be due to the  $\text{NH}_3$  stretching vibration confirms the zwitter ion structure of the molecule. The two intense lines at  $2934$  and  $2968 \text{ cm.}^{-1}$  are assigned to the symmetric and antisymmetric C—H stretching vibrations of the  $-\text{CH}_2$  group, while the satellite at  $2957 \text{ cm.}^{-1}$  may be attributed to the stretching vibration of the CH group. The seven comparatively weaker Raman lines appearing in the region from  $2883$  to  $2480 \text{ cm.}^{-1}$  with intensity decreasing with decreasing frequency, should be attributed to hydrogen bonded N—H oscillations. Similar Raman lines with approximately the same frequency shifts are observed in highly hydrogen-bonded crystals like glycine and its addition compounds (Krishnan and Balasubramanian, 1958). The assignments for the remaining Raman lines appearing in the region  $340$  to  $1640 \text{ cm.}^{-1}$  have been indicated in Table I. One finds a broad band covering the region from  $1590$  to  $1650 \text{ cm.}^{-1}$ . This may be attributed to the bending vibration of the hydrogen-bonded water molecule. The rocking motion of the water molecule has been assigned to the broad and weak Raman line at  $668 \text{ cm.}^{-1}$ . There are two C—N bonds of lengths  $1.33$  and  $1.50 \text{ \AA}$ . The corresponding frequencies have been identified with the Raman lines appearing with shifts  $1402$  and  $1077 \text{ cm.}^{-1}$ .

There are three broad lines with mean frequency shifts  $194$ ,  $245$  and  $298 \text{ cm.}^{-1}$ . They are of the same structure but of different intensities. They stand out clearly from the lattice spectrum. They have been attributed to the vibrations of the hydrogen bonds  $\text{NH} \dots \text{O}$  and  $\text{OH} \dots \text{O}$ . Similar low-frequency shifts due to hydrogen bond oscillations have been observed

by Gross (1959) and Balasubramanian and Krishnan (1962) in hydrogen-bonded crystals.

*External oscillations.*—Only eight Raman lines could be identified as belonging to the lattice spectrum. All of them are quite sharp and intense and are nearly of the same width. Below  $40 \text{ cm.}^{-1}$  there may be some lattice lines. Even if they are present they will be masked by the bogus band accompanying the  $\lambda 2537$  mercury line. According to group theoretical analysis excluding the three translations of the unit cell as a whole, there are twelve rotatory and nine translatory modes of lattice oscillations which should be active in Raman effect. In organic crystals it is a fact of observation that the translatory modes rarely appear with any appreciable intensity in Raman spectra. The observed Raman lines in asparagine should therefore be attributed to the rotatory type of oscillations. Although on theoretical grounds twelve are expected to appear, only eight are recorded.

## 5. SUMMARY

The Raman spectrum of *l*-asparagine monohydrate in the form of a single crystal has been recorded for the first time.  $\lambda 2537$  excitation has been used. Fifty-three Raman frequency shifts have been recorded. They are grouped as follows: Eight Raman lines coming under the lattice spectrum, three Raman lines arising from low-frequency vibrations of the hydrogen bonds and the remaining forty-two arising from the internal oscillations of the asparagine molecule. Appropriate assignments have been given for the observed Raman lines.

## 6. ACKNOWLEDGEMENT

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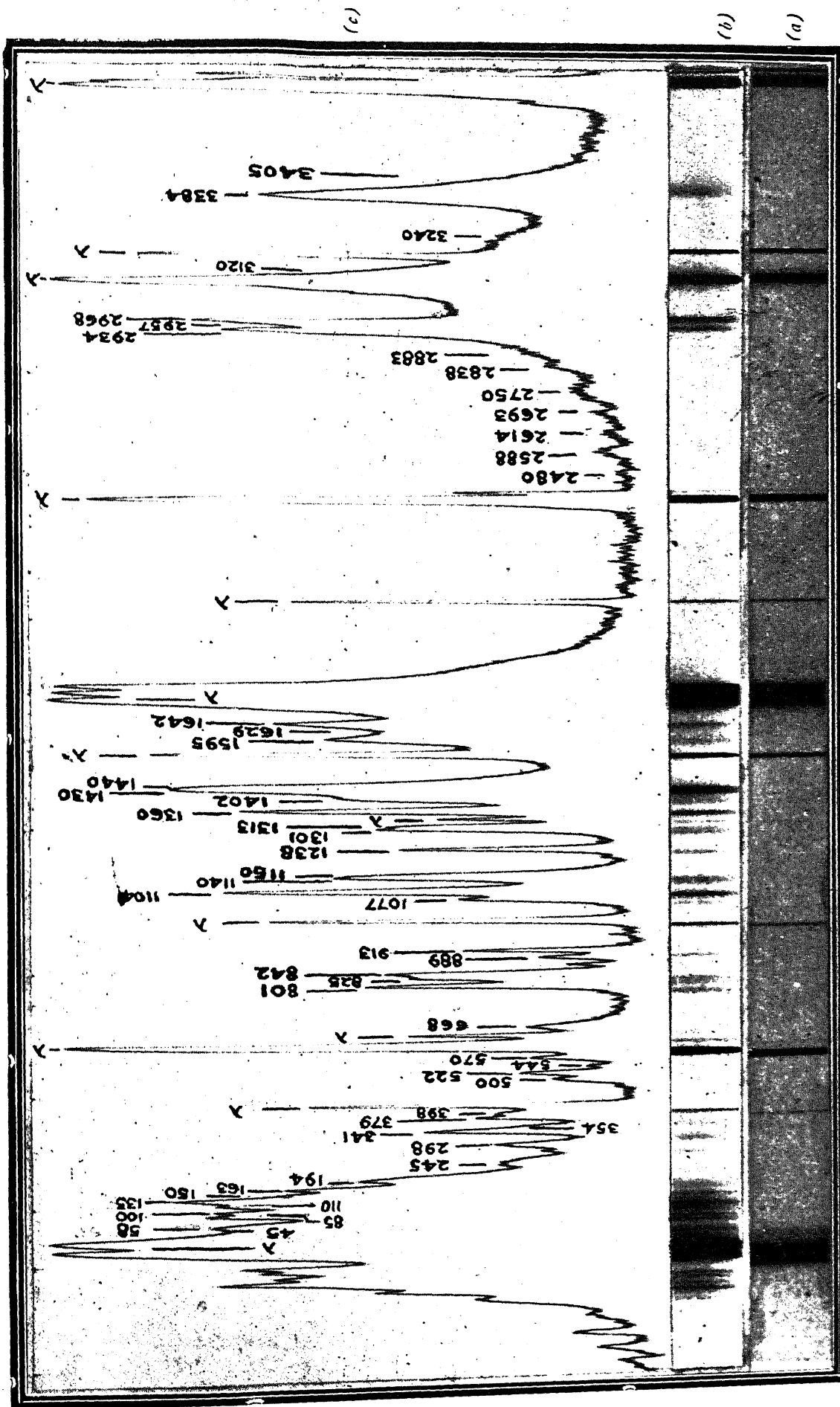


FIG. 1. (a) Mercury spectrum. (b) Raman spectrum of *l*-asparagine-monohydrate taken with Hilger medium quartz spectrograph. (c) Its microphotometer record.