

RAMAN SPECTRUM OF CRYSTALLINE AMINOSULPHONIC ACID

BY N. KRISHNAMURTHY

(*Department of Physics,
Indian Institute of Science, Bangalore-12*)

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1. INTRODUCTION

AMINOSULPHONIC ACID or sulphamic acid $\text{NH}_3^+ \text{SO}_3^-$ is the simplest derivative of sulphuric acid and has been known to be an interesting compound from the point of view of spectroscopic and structural studies (Vuagnant and Wagner, 1957; Gupta and Majumdar, 1941). At present, only an incomplete study of its Raman spectrum by Gupta and Majumdar (1941) is available. As large single crystals of sulphamic acid can be easily grown from aqueous solution, it was thought desirable to reinvestigate its Raman spectrum and to assess the nature and symmetry of these molecules in the crystal. The more detailed study of the infra-red absorption spectrum of sulphamic acid over a wide range of temperatures by Vuagnant and Wagner (1957) has been used in the assignment of the observed frequencies.

2. EXPERIMENTAL DETAILS

Single crystals of sulphamic acid exhibiting well-defined faces could be easily grown from aqueous solutions of the pure substance. The biggest crystal grown had roughly the size $20 \times 10 \times 5$ mm. As the crystals were found to be transparent to the ultra-violet, the resonance radiation $\lambda 2537$ of mercury was used for the excitation of the Raman spectra. Preliminary experiments revealed the presence of very closely spaced lattice lines and therefore in the final intense spectra a fine slit of 0.015 mm. was used. With the Hilger medium quartz spectrograph and Zenith Astronomical plates, exposures of about six hours were found to be necessary to record intense spectra.

3. RESULTS

Figure 1 *b* is an enlargement of the Raman spectrum of a single crystal of sulphamic acid with its microphotometer record in Fig. 1 *c*. Figure 1 *a*

is the comparison mercury spectrum in the ultra-violet region. The positions and frequency shifts of the Raman lines are marked on the microphotometer record. They are also listed in Table I. The figures given in brackets represent the relative intensities of the Raman lines estimated visually. Thirty-eight distinct Raman lines have been recorded. Of these, the first seven belong to the lattice spectrum while the remaining ones arise from the internal oscillations. The infra-red data are also included in the same table. There is good agreement between the Raman and infra-red frequencies in the region investigated.

4. DISCUSSION

Crystal structure data.—The crystal structure of sulphamic acid was determined by Kanda and King (1951) and by Osaki, Tadokoro and Nitta (1955) who found that sulphamic acid crystallises in the orthorhombic system with the space group $V_h^{15} - Pbc_a$. The unit cell dimensions are $a = 8.115 \pm 0.001 \text{ \AA}$, $b = 8.066 \pm 0.001 \text{ \AA}$ and $c = 9.255 \pm 0.003 \text{ \AA}$. There are eight molecules in the unit cell. The acid crystallises as Zwitter ion molecules $\text{NH}_3^+ \text{SO}_3^-$ of a distorted tetrahedral form with the existence of extensive hydrogen bonding of the type $\text{N}^+ - \text{H} \dots \text{O}$ with each NH_3^+ group entering into five bridging systems. The hydrogen bond distances vary from 2.82 \AA to 3.07 \AA , which has been confirmed by neutron diffraction studies by Sass (1960). The five hydrogen bond distances are 2.82 \AA , 2.83 \AA , 2.94 \AA , 3.02 \AA and 3.07 \AA .

External oscillations.—The conventional group theoretical methods of Bhagavantam and Venkatarayudu (1948) can be applied to find the $(3p - 6)$ internal molecular modes each q fold degenerate and $3q$ lattice rocking and $(3q - 3)$ lattice translational modes of a unit cell with q, p -atomic molecules. Such a calculation was performed treating the Zwitter ion as a unit and showed that twelve rotatory type and twelve translatory type of lattice oscillations can be expected to appear in Raman effect. The discrepancy between the observed and the calculated number of lattice lines appears to be due to the overcrowding of all these lines in a region of small frequency shifts. On account of their high intensities, the lines at $110, 120, 140$ and 158 cm^{-1} can be attributed to rotatory type of lattice oscillations. The lines at 170 and 240 cm^{-1} stand out clearly from the rest of the lattice lines in their breadth and structure even though their intensities are different. These two lines have been attributed to the vibrations of the hydrogen bonds $\text{NH}-\text{O}$. Similar low-frequency shifts due to hydrogen bond oscillations have been observed by Gross (1959) and Balasubramanian and Krishnan (1958).

TABLE I
Vibration spectrum of sulphamic acid (frequency shifts in cm.^{-1})

Sl. No.	Raman effect present	Infra-red Vuagnant and Wagner	Assignment
1	50 (2)	..	Lattice
2	68 (1)	..	"
3	80 (3)	..	"
4	110 (3)	..	"
5	125 (4)	..	"
6	140 (4)	...	"
7	155 (4)	...	"
8	170 (2)	..	NH....O
9	240 (5)	...	NH....O
10	357 (10)		
11	378 (10)	352	$\nu_{11}(e)$
12	535 (10)	526}	
13	550 (10)	540}	$\nu_{10}(e)$
14	678 (10)	682	$\nu_8(a_1)$
15	697 (10)	695	..
16	862 (?)
17	905 (5)
18	1010 (—)	1000}	
19	1020 (8)	1015}	$\nu_9(e)$
20	1057 (20)	1064	$\nu_4(a_1)$
21	1080 (10)
22	1265 (10)	1262	$\nu_3(a_1)$
23	1280 (10)
24	1302 (8)	1312	$\nu_8(e)$
25	1319 (10)
26	1440 (6)	1446	$\nu_2(a_1)$
27	1534 (5)	1542 }	
28	1571 (8)	1570 }	$\nu_7(e)$
		1786	
		2044	
		2152	
		2345	
29	2460 (5)	2465	$\nu_2(a_1) + \nu_9(e)^*$
30	2476 (4)	...	$\nu_2(a_1) + \nu_9(e)^*$
31	2539 (3)	...	$\nu_7(e) + \nu_3(e)^{-*}$
32	2553 (2)	...	$\nu_7(e) + \nu_3(e)^*$
33	2579 (3)	2569	$\nu_7(e) + \nu_3(e)^*$
34	2876 (8)	2893	N—H....O bonded
35	2906 (2)
36	3050 (5)	3055	N—H....O bonded
37	3142 (5)	3140	N—H....O bonded
38	3260 to 3450	...	Band

* Combinations with the various components into which the degenerate mode is split up.

Internal oscillations.—The free sulphamic acid molecule exists as a Zwitter ion having C_{3v} symmetry and hence its fundamental vibrations are distributed under the different symmetry types as below: $5 a_1 + a_2 + 6 e$. The torsional vibration about the N—S bond (ν_{12}) belonging to the a_2 type is forbidden to appear in the vibrational spectrum. All the remaining vibrations are active in both Raman effect and infra-red absorption. The vibrational assignments of the various modes of the free sulphamic acid are as follows:

- $\nu_1 (a_1)$ —symmetric stretching NH_3^+
- $\nu_2 (a_1)$ —symmetric deformation NH_3^+
- $\nu_3 (a_1)$ —symmetric stretching SO_3^-
- $\nu_4 (a_1)$ —symmetric deformation SO_3^-
- $\nu_5 (a_1)$ —N—S stretching
- $\nu_6 (e)$ —degenerate stretching NH_3^+
- $\nu_7 (e)$ —degenerate deformation NH_3^+
- $\nu_8 (e)$ —degenerate stretching SO_3^-
- $\nu_9 (e)$ —degenerate rocking NH_3^+
- $\nu_{10} (e)$ —degenerate deformation SO_3^-
- $\nu_{11} (e)$ —degenerate rocking SO_3^-
- $\nu_{12} (a_2)$ —N—S torsion.

But in the crystal, the site symmetry of the Zwitter ion is C_1 and hence the degeneracies of the doubly degenerate modes are removed and also the torsional mode becomes active. Assuming that the site symmetry is not far from C_s due to the coupling of the modes of the eight molecules in the unit cell, one should have a total of one hundred and forty-four modes distributed among the various species as follows: $22 A_{1g} + 22 B_{1g} + 14 B_{2g} + 14 B_{3g} + 14 A_{1u} + 14 B_{1u} + 22 B_{2u} + 22 B_{3u}$ wherein the first four species are Raman active and the last three are infra-red active. The modes coming under A_{1u} are forbidden in both. Since the actual site symmetry is C_1 and there are eight molecules in the unit cell each mode coming under the species A' and A'' split into eight modes corresponding to all the eight species of the point group of the crystal and we arrive at the result that in the crystal one can expect 54 fundamental components in infra-red absorption and 72 in Raman effect.

In the observed Raman spectrum, we find that all the degenerate modes are split up (see Table I). The $\nu_9 (e)$ mode falls near the mercury line at $\lambda 2603 \cdot 20 \text{ \AA}$ and its appearance is verified by considering the relative intensity of the mercury line. The splitting of the degenerate modes varies from

15 to 36 cm^{-1} and indicates that the distortion of the Zwitter ion from the C_{3v} symmetry is not very large. The coupling of the modes may give rise to closely spaced lines and have therefore escaped detection due to the dispersion of the spectrograph.

An interesting feature of the observed spectrum is the high intensity of the $\nu_4(a_1)$ symmetric SO_3^- deformation vibration at 1057 cm^{-1} . It is found to be excited even by the mercury lines $\lambda 2652.04 \text{ \AA}$, $\lambda 2653.68 \text{ \AA}$ and $\lambda 2655.10 \text{ \AA}$ and these are marked in the microphotometer record with shifts 2773, 2796 and 2820 cm^{-1} . The doubly degenerate SO_3 deformation modes ν_{11} and ν_{10} appear with considerable intensity on the anti-Stokes side also. In the region of the NH_3^+ stretching, there are four lines at 2876, 2908, 3050 and 3142 cm^{-1} . The latter two are actually maxima in the band while the first is a very strong line. Its frequency shift is consistent with the reported N—H...O hydrogen bond length of 2.82 \AA while the second may be the N—H...O bonded oscillation corresponding to the N—H...O distance of 2.83 \AA . The 3050 cm^{-1} line can be assigned to the hydrogen-bonded vibration for N—H...O distance of 2.94 \AA . These conclusions have been arrived at from the N—H frequency and N—H...O distance curve reported by Krishnan and Krishnan (1964). The five broad and weak lines in the region of $2460\text{--}2579 \text{ cm}^{-1}$ cannot be explained as due to hydrogen bonds of lengths $2.82\text{--}3.07 \text{ \AA}$, and are therefore overtones and combinations of the fundamentals. The band extending from 3260 to 3450 cm^{-1} has been assigned as due to the combinations involving the low frequency NH—O vibrations and the N—H...O hydrogen-bonded stretching vibrations. The absence of bands corresponding to N—H stretching vibrations occurring beyond 3150 cm^{-1} and the smaller splitting of the degenerate modes confirm the presence of Zwitter ions $\text{NH}_3^+ \text{SO}_3^-$ and only the slight distortion of the molecular symmetry C_{3v} of the free acid. It will be interesting to study the Raman spectra at low temperatures for understanding the related phenomena such as free rotation and the low-frequency hydrogen bond transitions.

5. SUMMARY

The Raman spectrum of a single crystal of sulphamic acid has been recorded with $\lambda 2537$ excitation. Thirty-eight lines have been observed, of which twenty-nine have been recorded for the first time. Seven Raman lines with shifts in the region $50\text{--}155 \text{ cm}^{-1}$ have been assigned to the lattice oscillations, two at 177 and 240 cm^{-1} have been attributed to the low-frequency hydrogen bond vibrations. The splitting of the degenerate modes and the appearance of N—H...O bonded stretching vibrations are consistent with

the structural data which expect the presence of the free molecule as a Zwitter ion with only slight distortion from C_{3v} symmetry.

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EXPLANATION OF PLATE XI

- FIG. 1. (a) Mercury spectrum.
(b) Raman spectrum of Sulphamic Acid.
(c) Microphotometer record.

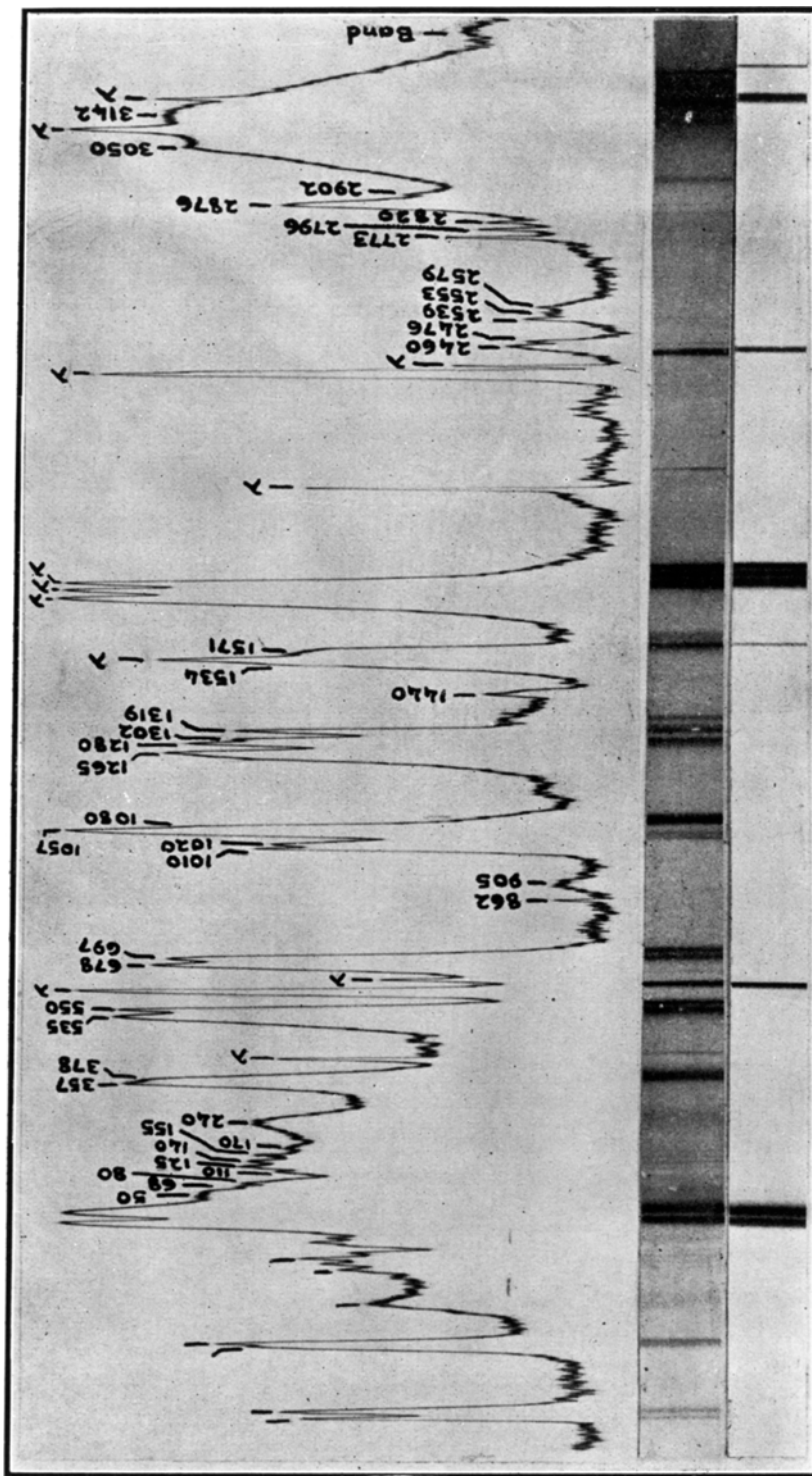


FIG. 1

(a) (b) (c)