

RAMAN SPECTRA OF FERRO-ELECTRIC CRYSTALS

Part IV. Lithium Hydrazinium Sulphate ($\text{LiN}_2\text{H}_5\text{SO}_4$)

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1. INTRODUCTION

SINCE 1958 investigations on the Raman spectra of ferro-electric crystals have been initiated in a systematic way from this Laboratory. In this series the Raman spectra of triglycine sulphate (Krishnan and Balasubramanian, 1958), triglycine nitrate (Balasubramanian, 1961) and triglycine selenate (Balasubramanian and Krishnan, 1963) have so far been reported in these *Proceedings*. These three papers will henceforth be referred to as Parts I, II and III of this series. The Raman spectrum of lithium hydrazinium sulphate has now been investigated and the results are given in this part.

Lithium hydrazinium sulphate (LiHzS) crystallises in the orthorhombic system and exhibits ferro-electric properties from about 20–2050 C. (Pepinsky, Vedam, Okaya and Hoshino, 1958). X-ray structure analysis of this substance carried out by Brown (1964) and by Van den Hende and Boutin (1963 and 1964) and the magnetic resonance study carried out by Cuthbert and Petch (1963) have indicated the existence of strong hydrogen bonds and the rotation of the NH_4 group in the crystalline form at room temperature. Spectroscopic methods of study such as Raman effect and infra-red absorption LiHzS are expected to throw considerable light on the nature of the hydrogen bonds in LiHzS . Such investigations have not been carried out so far. The authors have recorded the Raman spectrum of LiHzS at room temperature and the results are presented in this paper.

2. EXPERIMENTAL DETAILS

Lithium hydrazinium sulphate was prepared by double decomposition of a mixture of equimolecular solutions of pure lithium carbonate and hydrazine sulphate and from the resulting solution single crystals of LiHzS were grown by the method of slow evaporation. Clear and transparent crystals of size $10 \times 8 \times 5$ mm. were easily obtained. They were elongated along the *c*-axis with prominent (100), (110) and (101) faces. Since LiHzS was found

to be transparent to the ultra-violet, λ 2536.5 resonance radiation of mercury was employed for exciting the Raman spectrum. Exposure extending over a period of two days were necessary to record all the essential details of its Raman spectrum. The specimen was illuminated normal to the *c*-axis and the scattered light was taken along the *c*-axis. As the specimen got fostered due to exposure to intense ultra-violet radiation, its faces had to be ground and polished once in every three hours. The Raman spectrum of an aqueous solution of LiHzS was also recorded for comparison purposes.

3. RESULTS

An enlarged photograph of the Raman spectrum of LiHzS is reproduced in Figure 1 (*c*) and the corresponding microphotometer record in Fig. 1 (*d*). Figures 1 (*a*) and (*b*) are the comparison mercury spectrum and the Raman spectrum of aqueous solution of LiHzS respectively. The positions and the frequency shifts of the Raman lines of crystalline LiHzS are marked in the microphotometer record. Thirty-eight Raman lines have been identified. They are tabulated in Table I. Because of the feeble intensity of some of the lines, they could be identified only on the microphotometer record. The Raman lines at 610 and 630 cm^{-1} fall on mercury lines on the Stokes side. Their frequency shifts have been measured from the appearance on the anti-Stokes side. The frequency shifts of the aqueous solution of LiHzS are also entered in Table I. The water bands are not included.

4. CRYSTAL STRUCTURE DATA

The structure of lithium hydrazinium sulphate has been analyzed independently by Brown (1964) and Van den Hende and Boutin (1964). According to their analysis, LiHzS crystallises in the orthorhombic system with space group $Pna\ 2_1 - C_{2v}^9$. The unit cell which has the dimensions, $a = 8.99 \text{ \AA}$, $b = 9.94 \text{ \AA}$ and $c = 5.18 \text{ \AA}$, has four molecules. Both the Li and S atoms are tetrahedrally surrounded by oxygen atoms. According to Brown the SO_4 tetrahedra are regular, while Van den Hende and Boutin claim that they are distorted. The hydrazinium ions, N_2H_5 , are linked together by infinite number of hydrogen bonds along the *c*-axis. The N atom of the NH_2 group of an N_2H_5 ion is linked to the O atom of SO_4 and the N atom of NH_2 of the neighbouring N_2H_5 ion by hydrogen bonds and the corresponding distances are 2.98 \AA and 3.01 \AA respectively. The N atom of the NH_3 group is hydrogen-bonded to 3 of the five oxygen atoms present at distances 2.82, 2.91, 2.96, 2.99 and 3.02 \AA . The two possible arrangements of the hydrazinium ions running along the *c*-axis as given by Brown are indicated in

TABLE I

Raman frequency shifts in cm.⁻¹ of LiHzS

Sl. No.	Crystal	Solution	Assignment
1	52	wing	} Lattice vibration
2	70		
3	104		
4	146		
5	174		
6	220	180	} NH...O, NH...N
7	260		
8	302		
9	350	..	Li—O
10	454	452	} ν_2 —SO ₄
11	470		
12	610	..	} ν_4 —SO ₄
13	630		
14	715	..	Li—O
15	977	980	ν_1 —SO ₄
16	1094	1050–	} ν_3 —SO ₄
17	1115		
18	1132		
19	1177		
20	1191		
21	1260	1260	NH ₃ rocking
22	1444	1425	N—N stretching
23	1493	..	NH ₂ rocking
24	1577	1570	N ₂ H ₅ ⁺ deformation
25	1630	..	NH ₃ sym. deformation
26	1670	..	NH ₃ asym. deformation
27	2205	..	NH ₂ sym. deformation
28	2484	..	NH ₂ asym. deformation
29	2553	..	Combination of $\nu_3 + \nu_1$ or $2\nu_3$ of SO ₄
30	2655
31	2734
32	2848
33	2894	..	} N—H of NH ₃ , hydrogen-bonded
34	2939	..	
35	3028	..	Sym. N—H stretching of NH ₃ ⁺
36	3132	..	Asym. N—H stretching of NH ₃ ⁺
37	3290	..	N—H stretching of N—H...N
38	3330	..	N—H stretching of N—H...O

Fig. 2 (a) and (b). From the smear of the electron density in the difference synthesis, Brown concluded that the NH_3 groups are rotating at room temperature.

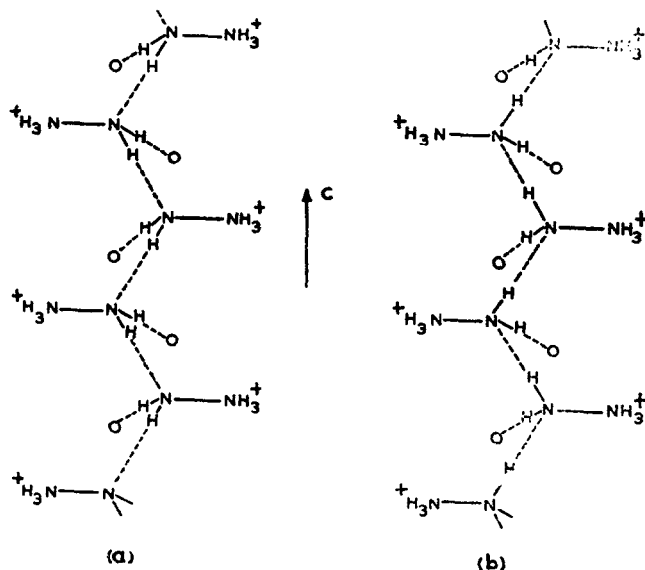


FIG. 2. The two possible arrangements (a) and (b) of the hydrogen-bonded chain if the hydrogen bonds are ordered. The arrangement of hydrazinium ions alone turning along the C-axis in lithium hydrazinium sulphate has been shown in figure.

5. DISCUSSION

The observed Raman lines in crystalline LiHzS could be classified under five different categories and these will be discussed one by one.

(a) SO_4 group.—The SO_4 group has not the tetrahedral symmetry according to Van den Hende and Boutin. Even if it had, since it is situated inside the anisotropic crystalline field and the oxygen atoms are hydrogen-bonded to varying extent, its vibrations should give rise to at least nine distinct Raman lines, i.e., 2 of ν_2 , 3 of ν_4 , 1 of ν_1 and 3 of ν_3 . (ν_1 , ν_2 , ν_3 , ν_4 refer to the frequencies of the free SO_4 ion.) Most of these have been identified and are indicated in the column on assignments in Table I. Since the symmetrical vibration of the SO_4 ion in LiHzS has nearly the same frequency as the SO_4 ion in the free state, it can be concluded that the SO_4 ion has the tetrahedral symmetry inside the crystal. This supports the conclusions of Brown from X-ray analysis. A broad faint line appearing at 2205 cm.^{-1} which appears generally in heavily exposed Raman spectra of crystalline sulphates is assigned as the combination of ν_1 and one of the ν_3 's or the octave of one of the ν_3 's.

(b) *The vibrations of the hydrazinium ion.*—Since the hydrazinium ion $N_2H_6^+$ has the structural formula $NH_2 \cdot NH_3^+$, the Raman spectrum of $LiHzS$ should exhibit two types of N—H stretching vibrations, one belonging to the NH_2 or amide group and the other to the NH_3^+ of the ammonia group. Both the vibrations are hydrogen-bonded and hence their frequencies will be lowered. The most intense line at 3330 cm.^{-1} is attributed to the N—H vibration of the NH_2 group which is hydrogen-bonded to the oxygen atom (2.98 \AA), while the weaker line at 3290 cm.^{-1} is attributed to the NH vibration of the same group hydrogen-bonded to N atom (3.01 \AA). They are in accordance with the Nakamoto curve (1955). N—H stretching vibrations of NH_3 group appear with frequency shifts less than 3200 cm.^{-1} . The intense broad line at 3028 is assigned to the symmetric N—H stretching frequency of the NH_3 , while the line at 3132 to the asymmetric stretching mode. The three Raman lines at 2848 , 2894 and 2939 cm.^{-1} have been assigned to the hydrogen-bonded N—H...O vibrations of the NH_3 group. These frequencies when plotted against the corresponding N...O distances fall into the correlation curve for $N^+—H...O$ given by Krishnan and Krishnan (1964), thereby confirming the assignments. Unlike in the case of glycine and its addition compounds, these three lines appear very weakly in the Raman spectrum of $LiHzS$. This is a very striking feature and is explained as follows. From X-ray analysis, Brown has concluded that the NH_3^+ group is rotating at room temperature and as such the NH...O bonds are formed for short duration for every cycle, *i.e.*, only when the H atoms fall on the N...O direction. So the hydrogen-bonded N—H—O vibrations appear weakly in the Raman spectrum, whereas the non-bonded N—H vibrations appear strongly in the spectrum of $LiHzS$.

The fairly intense line at 1191 cm.^{-1} is assigned to the N—N stretching vibration. In the aqueous solution the N—N stretching mode of the hydrazinium ion is not seen separated from the broad band arising from the ν_3 mode of the SO_4 ion, comparing the spectrum of $LiHzS$ with that of hydroxyl amine hydrochloride (Krishnan and Balasubramanian, 1964), the Raman lines at 1493 and 1577 have been assigned to the symmetric and asymmetric NH_3 deformation vibrations respectively. The corresponding NH_2 deformation vibrations appear at 1630 and 1670 cm.^{-1} . The rocking modes of the NH_3 and NH_2 groups have also been identified.

(c) *(Li—O₄) group.*—The lithium atom is surrounded more or less tetrahedrally by four oxygen atoms and are strongly bound and as such one may expect to observe the Li—O stretching mode. For the Li—O distance of 1.95 \AA according to Badger's rule the stretching mode should have a frequency of

about 650 cm.^{-1} . There is a faint Raman line at 715 cm.^{-1} which may be assigned to this mode. The line at 350 cm.^{-1} may be attributed to the Li—O torsional mode.

(d) *Vibrations of the hydrogen bond.*—The Raman lines at 220, 260 and 302 cm.^{-1} should be attributed to the stretching vibrations of the hydrogen bonds N—H...O and N—H...N. In the spectra of glycine compounds similar Raman lines are also observed.

(e) *Lattice spectrum.*—A group theoretical analysis of the lattice spectrum of LiHzS has been carried out taking the whole molecule as one unit. In Raman effect one should expect to observe 12 rotatory type and 9 translatory type of lattice oscillations. But, on the recorded spectrum 5 lattice lines have been identified. It has not been possible to give individual assignments.

Four faint Raman lines have been recorded in the region from 2480 to 2740 cm.^{-1} . It is often observed that the H bond stretching mode due to N—H...O vibration combines with the N—H stretching vibration giving rise to summations and differentials. The four weaker lines could be assigned to the differentials and the corresponding summations fall on the intense N—H vibrations of NH_3 and NH_2 groups.

SUMMARY

The Raman spectrum of lithium hydrazinium sulphate has been recorded both in the single crystal form and in aqueous solutions. The crystal exhibits thirty-eight Raman lines having the frequency shifts 52, 70, 104, 146, 174, 220, 260, 302, 350, 454, 470, 610, 630, 715, 977, 1094, 1115, 1132, 1177, 1191, 1260, 1444, 1493, 1577, 1630, 1670, 2205, 2484, 2553, 2655, 2734, 2848, 2894, 2939, 3028, 3132, 3290 and 3330 cm.^{-1} . The aqueous solution gave rise to six Raman lines at 452, 980, 1050–1200, 1260, 1425 and 1570 cm.^{-1} apart from a maximum at 180 cm.^{-1} in the 'wing' accompanying the Rayleigh line. The observed Raman lines have been assigned as arising from the vibrations of the SO_4 ion, N_2H_5^+ ion, Li— O_4 group, hydrogen bond and the lattice. The influence of the hydrogen bond on the N—H stretching vibrations has been pointed out. The various features of the observed spectrum strongly support the hypothesis that the NH_3 group in the crystal is rotating around the N—N axis at room temperature.

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EXPLANATION OF PLATE X

FIG. 1. Raman spectrum of lithium hydrozinium sulphate, $\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$.

- (a) Mercury spectrum.
- (b) Raman spectrum of aqueous solution.
- (c) Raman spectrum of single crystal.
- (d) Its microphotometer record.

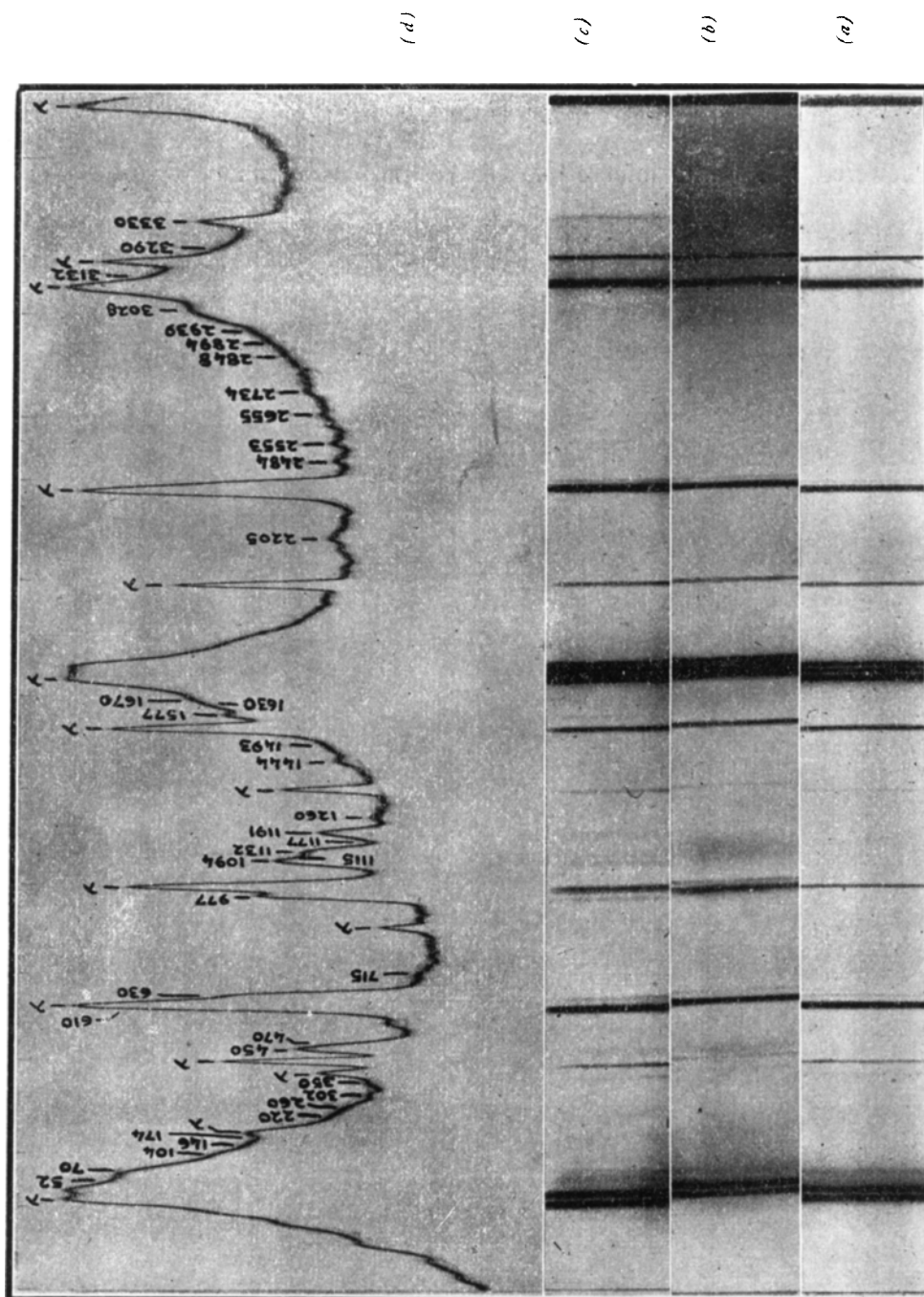


FIG. 1