

# INFRARED SPECTRUM OF FERROELECTRIC LITHIUM HYDRAZINIUM SULPHATE [Li (N<sub>2</sub>H<sub>5</sub>) SO<sub>4</sub>]

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## ABSTRACT

Dielectric observations on lithium hydrazinium sulphate have shown earlier that it is ferroelectric over a range of temperatures from below  $-15^{\circ}\text{C}$ . to above  $80^{\circ}\text{C}$ . and a new type of hydrogen bond rearrangement which would allow the protons to migrate along the chain has also been suggested by others. The infrared spectrum of  $\text{LiH}_2\text{S}$  in the form of mull and as single crystal sections parallel and perpendicular to the 'C' axis exhibit about 21 well-defined absorption maxima. The position and the width of the maxima agree with the known structure of the crystal according to which the hydrazine group exists in the form of the hydrazinium ion,  $\text{NH}_2\cdot\text{NH}_3^+$  and the observed  $\text{N}^+\text{-H}$  frequencies agree better with the new correlation curve given by R. S. Krishnan and K. Krishnan (1964). However it has been pointed out that from a comparative study of the new infrared spectra of hydrazonium sulphate and lithium ammonium sulphate that the absorption band at  $969\text{ cm}^{-1}$  is due to N-N stretching vibration and that the fairly intense band between  $2050\text{-}2170\text{ cm}^{-1}$  is due to the bending vibrations of the  $\text{NH}_3^+$  group.

## INTRODUCTION

THE interesting electrical properties of lithium hydrazinium sulphate [Li (N<sub>2</sub>H<sub>5</sub>) SO<sub>4</sub>] was first reported by R. Pepinsky, K. Vedam, Y. Okaya and S. Hoshino (1958) and their observations showed that this crystal ( $\text{LiH}_2\text{S}$ ) is ferroelectric at room temperature and over a range of temperatures from below  $-15^{\circ}\text{C}$ . to above  $80^{\circ}\text{C}$ . The structure analysis of this crystal by I. D. Brown (1964) and by Van den Hende and H. Boutin (1964) and the proton magnetic resonance study by J. D. Cuthbert and H. E. Petch (1963) reveal that the hydrazine group may be in the form of hydrazinium ions  $\text{NH}_2\cdot\text{NH}_3^+$  and that at room temperature the  $-\text{NH}_3^+$  group 'rotates' about the N-N axis. The structure exhibits also infinite chains

of hydrogen bonds which run through the crystal in the direction of the C-axis and the possibility of two types of configurations of the chain and a proton migration along the chain at higher temperatures have been used to give a possible mechanism for the ferroelectric behaviour. A study of the Raman spectrum of lithium hydrazinium sulphate has recently been reported by R. S. Krishnan and K. Krishnan (1965) in this journal. We discuss below, therefore, our observations on the infrared spectrum of lithium hydrazinium sulphate.

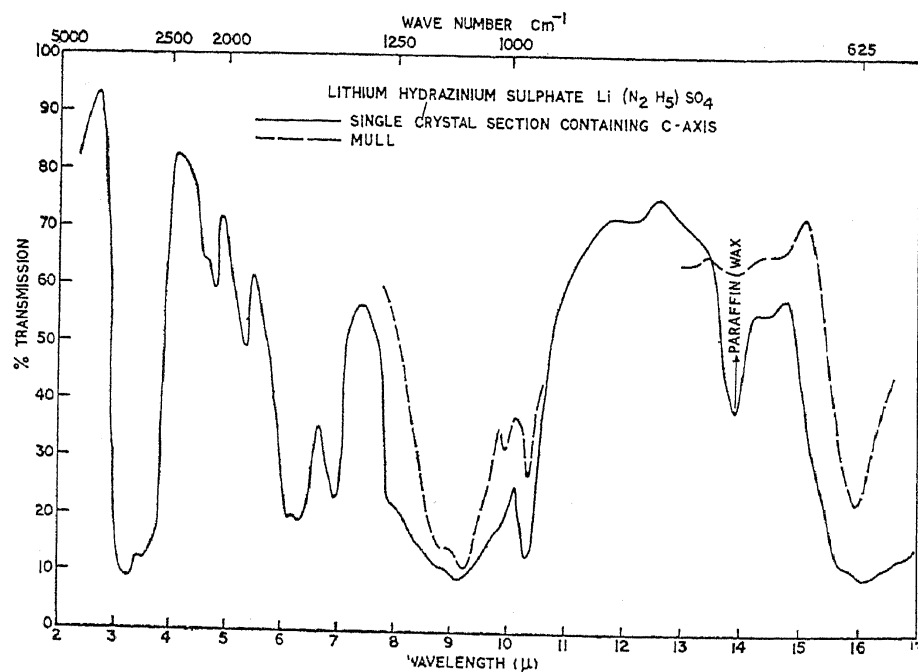
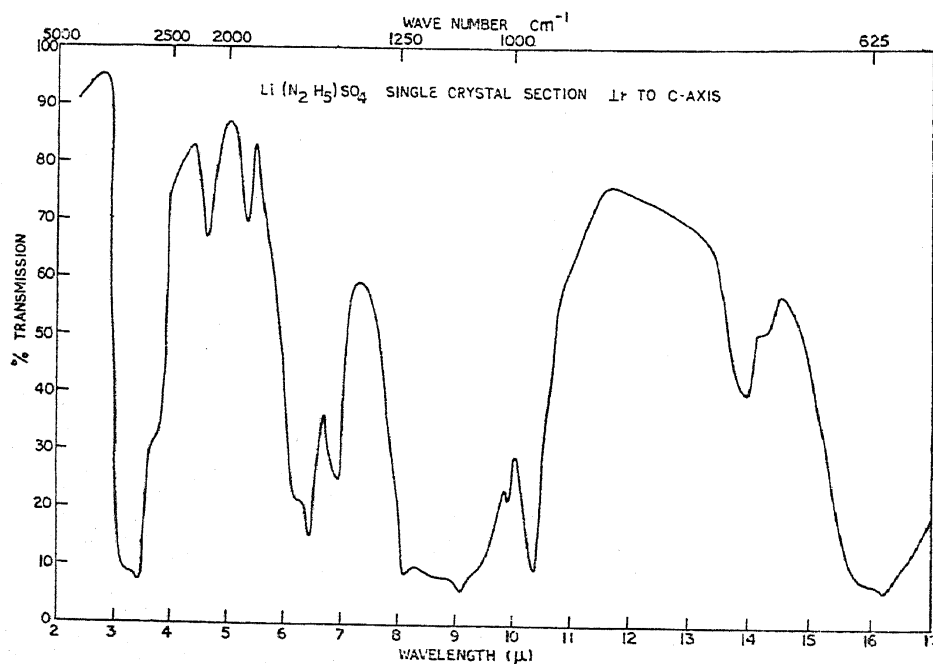
#### EXPERIMENTAL DETAILS

$\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$  was prepared by the action of  $\text{Li}_2\text{CO}_3$  with  $\text{N}_2\text{H}_4 : \text{H}_2\text{SO}_4$ . Single crystals of  $\text{LiH}_2\text{S}$  with well-developed faces were prepared by a slow evaporation of the saturated aqueous solution. The infrared spectra were recorded in the form of a mull of the crystal powder in paraffin oil and also in the form of single crystals. A Perkin-Elmer model 112 single beam infrared spectrometer with KBr prism was used to record the spectra. Two single crystal sections, one containing the C-axis and the other perpendicular to the C-axis were used to observe the effect of orientation. In order to obtain extremely thin sections the following method was used. One face of the section of the crystal was well polished and this face of the crystal was then stuck on to a polished KBr plate using a trace of paraffin wax. The exposed face of the specimen was then ground and polished till optimum transmission was obtained giving the most satisfactory spectrum possible.

#### RESULTS AND DISCUSSION

The infrared spectrum of  $\text{LiH}_2\text{S}$  is shown in Figs. 1 and 2 and the frequencies of the absorption maxima along with the most probable assignment are listed in Table I. Since the infrared spectrum of hydrazonium sulphate ( $\text{N}_2\text{H}_6\text{SO}_4$ ) will be helpful in analysing the spectrum of  $\text{LiH}_2\text{S}$  the infrared absorption maxima of hydrazonium sulphate for the mull are also indicated in the same table. The Raman frequencies reported by R. S. Krishnan and K. Krishnan have also been included for purposes of comparison.

According to Brown (*loc. cit.*) and Van den Hende and Boutin (*loc. cit.*) lithium hydrazinium sulphate is orthorhombic and has the space group  $\text{Pbn}2_1$  with  $a = 8.99$ ,  $b = 9.94$ ,  $c = 5.18 \text{ \AA}$  and  $Z = 4$ . The S-O distances observed indicated that one of the bonds may have a considerable amount of double bond character and that in the crystal the  $\text{SO}_4$  ion is distorted from the tetrahedral symmetry which it has in the free ion state. Therefore one may expect all the degeneracies of the free ion to be removed and all

FIG. 1. Infrared spectra of  $\text{LiH}_2\text{S}$ .FIG. 2. Infrared Spectra of  $\text{LiH}_2\text{S}$ .

the nine frequencies of the  $\text{SO}_4$  ion to be active in infrared absorption due to the low site symmetry. In addition, as there are four formula units in the unit cell, by a coupling of the individual vibrations there can be a further

increase in the number of active frequencies. However in the first approximation this effect will not be as prominent as the effect due to lower site symmetry. The weak absorption band at  $1003\text{ cm.}^{-1}$  is therefore assigned to the symmetric vibration  $\nu_1 (a_1)$  of the  $\text{SO}_4$  groups. Krishnan and Krishnan, on the other hand, have identified the line at  $977\text{ cm.}^{-1}$  with this mode. This we believe is incorrect because the corresponding infrared absorption at  $969\text{ cm.}^{-1}$  is quite strong and is therefore more probably due to N-N stretching vibration. Further evidence for this revised assignment is the fact that in  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Li}(\text{NH}_4)\text{SO}_4$ , the symmetric vibration of the  $\text{SO}_4$  has a value around  $1000\text{ cm.}^{-1}$ . It is quite possible that the presence of a mercury line in this region prevented R.S. Krishnan and K. Krishnan from observing the  $\nu_1 (a_1)$  of the  $\text{SO}_4$  ion and led them to the erroneous identification. The present investigation does not extend to the frequency  $\nu_2 (e)$  of the doubly degenerate mode of the  $\text{SO}_4$  ion. But in the region of the two triply degenerate frequencies  $\nu_3 (\sim 1100\text{ cm.}^{-1})$  and  $\nu_4 (\sim 620\text{ cm.}^{-1})$  we find two broad bands with clear peaks at  $1127\text{ cm.}^{-1}$ ,  $1087\text{ cm.}^{-1}$  and  $623\text{ cm.}^{-1}$ . Though the width of these bands indicate a partial removal of the degeneracy due to lower symmetry, no striking alteration in the relative intensities of the bands or shift in the frequencies is found to justify the conclusion of Van den Hende and Boutin that one of the S-O bonds has a large amount of double bond character in the crystal.

In crystals of  $\text{LiH}_2\text{S}$  each lithium and sulphur atom is surrounded tetrahedrally by oxygen atoms and these tetrahedra share corner oxygen atoms to form a three-dimensional network. In the channels which exist in the crystal running parallel to the C-axis the hydrizinium ions lie with their N-N bond axis perpendicular to the C-axis. The  $\text{NH}_2$  groups of the hydrizinium ions are linked into infinite chains by hydrogen bonds of the type  $\text{N-H}\cdots\text{N}$ . It is also hydrogen-bonded to one of the oxygens of the sulphate group with the corresponding  $\text{N-H}\cdots\text{O}$  distance as  $2.98\text{ \AA}$ . The positively charged  $\text{NH}_3^+$  group on the other hand can be hydrogen-bonded to three of the five oxygen atoms present at distances of  $2.91$ ,  $2.99$ ,  $2.96$ ,  $3.02$  and  $2.82\text{ \AA}$ . According to the proton magnetic resonance investigations of Cuthbert and Petch (*loc. cit.*) at room temperature, the  $\text{NH}_3^+$  group is capable of "rotation" about the N-N axis. Therefore one may hope to find a considerable broadening of the absorption due to N-H vibrations and a striking dependence of their width on temperature. From the new correlation curve given by Krishnan and Krishnan for  $\text{N}^+-\text{H}\cdots\text{O}$  vibration with N-O distance, one finds for the above distances that corresponding frequencies lie in the range  $3050\text{--}3350\text{ cm.}^{-1}$  except for the  $2.82\text{ \AA}$  bond distance.

In fact the observed absorption in this region has the expected width and the assignments are indicated in Table I. In Raman effect the weak band occurring in the region of  $2205\text{ cm.}^{-1}$  has been attributed to a combination of  $\nu_3$  and  $\nu_1$  or  $2\nu_3$  of the  $\text{SO}_4$  ion. But in infrared the absorption band around  $2100\text{ cm.}^{-1}$  cannot arise from such a combination for the following. This band as well as the band around  $3000\text{ cm.}^{-1}$  show a similar behaviour when the orientation of the crystal is changed (see Figs. 1 and 2). Also the band at  $2100\text{ cm.}^{-1}$  has an intensity comparable with the band at  $1900\text{ cm.}^{-1}$ . It is therefore more likely that both these bands arise from the deformation vibrations of the hydrogen-bonded  $\text{NH}_3^+$  groups and possibly a combination of the torsional vibration around the N-N axis, which may have a value of about  $500\text{ cm.}^{-1}$  with other modes.

The absorption spectrum of  $\text{LiH}_2\text{S}$  will show not only features characteristic of the  $\text{NH}_3^+$  and  $\text{NH}_2$  modified to a certain extent but may exhibit a strong interaction in the hydrazinium ion with the torsion around N-N axis and also N-N stretch. Taking these facts into account the assignment of the absorption maxima have been indicated in Table I; those given for the bands in the region  $1440\text{--}2000\text{ cm.}^{-1}$  should be regarded as provisional.

The assignment of the Raman line of shift  $1191\text{ cm.}^{-1}$  to the N-N stretching vibration by R. S. Krishnan and K. Krishnan (*loc. cit.*) also calls for a revision in the light of our infrared data. According to Raman effect data, the values of the N-N stretching frequency for  $\text{N}_2\text{H}_4$  in the liquid state (K. W. F. Kohlrausch, 1936) and for  $\text{N}_2\text{H}_5^+$  and  $\text{N}_2\text{H}_6^{++}$  ions in aqueous solution (J. T. Edsall, 1937) are 876, 965 and  $1036\text{ cm.}^{-1}$  respectively. The N-N vibrations for crystalline  $\text{N}_2\text{H}_6\text{Cl}_2$  and  $\text{N}_2\text{H}_6\text{SO}_4$  are at 1024 and  $1050\text{ cm.}^{-1}$ . R. Ananthakrishnan (1937), J. C. Decius and D. P. Pearson (1953) showed that the N-N stretching vibrations in crystalline  $\text{N}_2\text{H}_5\text{Cl}$  and  $\text{N}_2\text{H}_5\text{Br}$  are at 965 and  $973\text{ cm.}^{-1}$  respectively. In view of the above facts we have to assign the  $969\text{ cm.}^{-1}$  band now to the N-N stretching vibration. It is possible that in their study of the Raman spectrum of an aqueous solution of  $\text{LiH}_2\text{S}$ , R. S. Krishnan and K. Krishnan (*loc. cit.*) could have mistaken this  $970\text{ cm.}^{-1}$  line as due to the  $\nu_1$  of  $\text{SO}_4$  ion, as the salt gets completely ionised and the  $\nu_1$  of the free  $\text{SO}_4$  ion and the N-N valence vibration appear at the same position. In the infrared spectrum of hydrazonium sulphate ( $\text{N}_2\text{H}_6\text{SO}_4$ ) taken by us we find an absorption at  $1034\text{ cm.}^{-1}$  which is in good agreement with the Raman frequency reported by Ananthakrishnan for the N-N stretching vibration.

TABLE I  
Absorption maxima and Raman shifts of Li (N<sub>2</sub>H<sub>5</sub>) SO<sub>4</sub>

Li (N <sub>2</sub> H <sub>5</sub> )SO <sub>4</sub>		Hydrazonium sulphate (N <sub>2</sub> H <sub>6</sub> ) SO <sub>4</sub> /mull	Assignment
Infrared	Raman		
..	3330	..	N-H... O
3263	3290	..	N-H... N
3140	3132	..	Asym. N-H stretch of NH <sub>3</sub> <sup>+</sup>
3059	3028	3059	Sym. N-H stretch of NH <sub>3</sub> <sup>+</sup>
	2939	..	(2820 to 3350) N-H...O of different NH... O distances
2874	2894	..	..
	2734	..	..
2684	2655	2604	..
	2553	..	..
	2484	..	..
2168	2205	2049	} NH <sub>3</sub> <sup>+</sup> bending—(hydrogen-bonded) (see Text)
2086	..	..	
1880	..	1946	} N <sub>2</sub> H <sub>5</sub> <sup>+</sup> deformation + torsion about N-N
..	..	1818	
1639	1670	1639	} NH <sub>3</sub> <sup>+</sup> and NH <sub>2</sub> deformation vibrations
	1630	..	
1621	1577	1523	
1560	1493	..	
1481	..	..	
1444	1444	..	} NH <sub>2</sub> rocking
1256	1260	..	
	1191	1154	} ν <sub>3</sub> - SO <sub>4</sub>
	1171	..	
1127	1132	..	
	1115	..	
1087	1094	..	} N-N stretch
	..	1034	
1003	..	969	ν <sub>1</sub> - SO <sub>4</sub>
969	979	..	N-N stretch
..	715	..	..
684	..	..	..
623	630	633	ν <sub>4</sub> - SO <sub>4</sub>
	610	623	
	470	..	ν <sub>2</sub> - SO <sub>4</sub>
	454	..	

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