ON THE RAMAN SPECTRA OF A FEW ALKYL SULPHIDES IN THE SOLID STATE.

By S. C. SIRKAR, *D.Sc., F.N.I. and* B. M. BISHUI, *M.Sc.*

(Received September 16, 1943.)

ABSTRACT.

The Raman spectra of methyl, ethyl, propyl and butyl sulphide have been studied in the liquid state and in the solid state at the temperature of liquid oxygen. The polarisation of the lines in the liquid state has also been studied in the present investigation. Disappearance of some prominent Raman lines and changes in the relative intensities of the lines with the solidification of the substance have been observed in each case. The causes of these changes have been discussed and the changes have been correlated in the cases of methyl, ethyl and propyl sulphide to strong association of the molecules in the solid state through hydrogen bond in the first case and probably through a sulphur bond in the other two cases. In the case of butyl sulphide the disappearance of the lines is attributed to the absence of free rotation about the C-C bond in the solid state.

INTRODUCTION.

The Raman spectra of a large number of organic compounds have been investigated in the solid state at low temperatures by many workers previously. It was first observed by Gross and Vuks (1935) that in the case of some aromatic compounds some new Raman lines appear in the low frequency region when the substances are solidified. The origin of the lines was attributed to lattice oscillations. Such intense new lines were also observed later by Sirkar (1936) in the case of simple centro-symmetric molecules such as CS_2, naphthalene and *p*-dichlorobenzene and it was pointed out by him (Sirkar, 1937) that in the case of naphthalene and *p*-dichlorobenzene large changes in the polarisabilities cannot be produced by intermolecular oscillations in the unit cell of the crystal. Although a different hypothesis has been put forward (Venkateswaran, 1938) regarding the nature of these lattice oscillations, the large intensities of the new lines observed in the case of centro-symmetrical crystals cannot be accounted for by such a hypothesis.

A second type of change in the Raman spectra was observed by Mizushima *et al.* (1936) in the case of a few organic compounds when these substances were solidified. In the liquid state each of these substances gives a large number of Raman lines, but when it is solidified some of the prominent lines disappear. This fact has been explained by the said authors on the assumption that owing to free rotation about single bonds the liquid state contains two types of molecules, one of the trans form and the other either of the cis or of the gauche form, and in the solid state the molecules exist only in one of these forms. It is true that this hypothesis can explain the number of lines observed in the case of a few substances in the solid state quite satisfactorily, but from a closer examination of the results reported by the said authors in the case of a few other substances it appears that all the lines observed in the liquid and solid states cannot be accounted for by such a hypothesis. The free rotation about the single bond might exist in many other aliphatic compounds and it would be of interest to investigate whether the Raman spectra undergo any such changes as observed by Mizushima *et al.* (1936) when these substances are solidified and whether the hypothesis put forward by them can account for all the lines observed in these cases. Also from a comparison of the Raman spectra of a large number of aliphatic and aromatic compounds in the solid state with those for the liquid state, it might be possible to obtain some information regarding the general laws which govern the intensities of the new lines appearing in the low frequency region in the solid state. With this object in view investigations on the Raman spectra of aliphatic and aromatic compounds in the solid and liquid states have been undertaken

and the results obtained for methyl, ethyl, propyl and butyl sulphide are discussed in the present paper.

Experimental.

The investigation of Raman spectra in the solid state of substances which are in the liquid state at the room temperature is beset with the difficulty that if the liquid is solidified by immersing the glass tube containing it in a refrigerant such as liquid oxygen, a translucent white mass is obtained in most cases. Stray light is so intense in comparison with the light scattered by molecules in these cases that it is difficult to get the Raman lines photographed with any clear background. To overcome this difficulty, Mizushima *et al.* (1938) used a liquid bath which was cooled by immersion in liquid oxygen, so that the solid mass obtained was sufficiently transparent. In the present investigation a slightly different method has been used so that the substances having freezing points, which are slightly higher than the boiling point of liquid oxygen, as well as those solidifying at temperatures only a few degrees below the freezing point of water, can be investigated with this arrangement.

The liquid distilled in vacuum is put in a double-walled cylindrical vessel, and in order to evacuate the volume between the two walls a side tube is connected through a stop-cock to a pumping system. Dry air can be introduced at any desired pressure through another stop-cock connected to the side tube. When initially the double-walled vessel is inserted in liquid oxygen contained in a larger Dewar vessel, the pressure inside the annular space between the two walls is made very low and so the rate of cooling of the liquid becomes very slow. When the substance is solidified, the pressure inside the annular space is raised slowly by introducing small quantities of dry air through the second stop-cock mentioned above and finally the pressure is made equal to the atmospheric pressure so that the temperature of the substance approaches very nearly that of the liquid oxygen. Suitable portions of the outer Dewar vessel are blackened and the substance is illuminated with the two vertical quartz mercury arcs, the light being focussed with the help of two six-inch glass condensers. The scattered light emerges through a window on one side. A short glass tube provided with a side tube is attached to the outer Dewar vessel against the window with sealing wax and its mouth is closed by a glass plate attached with sealing wax. The side tube is connected to a pump and the tube is evacuated. This prevents the moisture from being deposited on the window. It was observed in the preliminary tests that in the case of any liquid the solid mass, obtained with the help of this apparatus, was much more transparent than that obtained by immersing an ordinary pyrex tube containing the liquid in liquid oxygen.

A Fuess spectrograph having optical parts of glass was used in the present investigation. It has a dispersion of about 14 A.U. per mm. in the region of 4046 A.U. A blue glass filter was placed in the path of the incident light in order to diminish the intensity of the continuous background in the region on the long wave-length side of 4500 A.U. and to cut off the line 5460 A.U. The polarisation of the Raman lines due to the liquid state was studied in each case by photographing simultaneously spectra of the vertical and horizontal components of the scattered light with the help of a double image prism. Light from a mercury arc focussed with the help of a condenser was used as the incident light in this case also. The spectrograms, therefore, only indicated whether any Raman line was partially polarised or completely depolarised and no attempt has been made to measure the absolute values of factor of depolarisation accurately.

Results and Discussion.

The results obtained for methyl sulphide are given in Table I. The Raman spectrum of the liquid was studied previously by Venkateswaran (1931), Kohlrausch (1936) and Medard *et al.* (1936). There were some discrepancies in the results reported by these authors and so Fonteyne (1940), while studying the infra-red absorption spectrum of methyl sulphide investigated the Raman spectrum and also the polarisation of the Raman lines. His results were compared by him with those of previous workers. The results given by

Fonteyne are included in Table I for comparison. Some weak lines reported by him are not observed in the well-exposed spectrogram due to methyl sulphide obtained in the present investigation.

TABLE I.

Methyl sulphide.

Liquid at room temp.				Solid state at about −180°C. (Present authors.)
Fonteyne.		Present authors.		
				70 (1), *k*
				84 (1), *k*
285 (*s*, P)	..	282 (2d), *e*	$\rho > 0{\cdot}6$	338 (1), *e*
480 (*vw*)	..		$< 6/7$	402 (0) *e*
690 (*vs*, P)	..	693 (8s) *k*, *e*	P	691 (3s) *k*, *e*
742 (*s*, D)	..	740 (3d) *k*, *e*	D	740 (2s) *k*, *e*
919 (*vwb*)	..			
1041 (*vw*)	..			
1224 (*vw*)	..	1335 (0d) *k*		
1325 (*w*, P)	..			
1426 (*mb*, D)	..	1424 (2) *k*, *e*	D	
		1440 (1) *k*, *e*	D	1450 (1s) *k*, *e*
1609 (*vw*)	..			
2832 (*w*, P)	..	2832 (2) *k*, *e*	P	
		2852 (1) *k*, *e*	P	
2911 (*vs*, P)	..	2915 (10s) *k*, *e*	P	2915 (2d) *k*, *e*
2980 (*s*, *b*., D)	..	2990 (5d) *k*, *e*	D	2970 (2dd), *k*, *e*

In this table and in the following tables the intensities are given in parentheses. The letters s, b and d signify sharp, broad and diffuse respectively. The letters *k*, *i* and *e* represent exciting lines in Kohlrausch's notation. P means $\rho \ll 6/7$ and D means $\rho = 6/7$.

The results given in Table I differ slightly from those reported earlier (Sirkar and Bishui, 1943) in this respect that a line 1440 has been observed later to be just resolved from the stronger line 1424 and the polarisation of the line 282 has been given more precisely. Formerly it was given as $\rho \sim 6/7$. According to Fonteyne this line is well polarised. Actually, however, the value of ρ is greater than 0·6 and less than 6/7.

In the solid state the line 282 is not observed, but two new lines 338(1) and 402(0) appear in its place. The line 1440 becomes stronger and shifts to 1450 while the line 1424 which is stronger for the liquid state becomes too weak to be observed and two new lines 70 and 84 appear in the solid state. Fonteyne (1940) assumed that the molecule of methyl sulphide possesses the symmetry of the group C_{2v} and showed that it has 21 fundamental modes of vibration. He also made assignments of some of these vibrations to the Raman lines observed. Thompson (1941) more recently studied the infra-red spectrum of this substance and revised some of the assignments made by Fonteyne. According to both of them the line 282 is due to the C-S-C deformation oscillation. According to Thompson the line 1424 is due to the CH_3 bending oscillation symmetric to the plane of C-S-C and the line 1440 to similar vibration either totally symmetric or anti-symmetric to σ_x and σ_y and symmetric to the twofold axis. The assignment of the latter line was not definite because its polarisation was not given by Fonteyne. This line is now observed to be depolarised and so it should be identified with ν_9 given by Thompson. Thus the frequencies of the C-S-C and CH_3 bending oscillations are observed to undergo changes with the solidification of the substance. There is also marked change in the relative intensities of some of the lines with the solidification. For instance, in the liquid state the line 2915 (*k*) is more intense than the line 693 (*k*, *e*), but in the solid state the intensity ratio is reversed. This change cannot be due to the absorption of the line 2915 in the solid state owing to its high degree of polarisation, because the line 693 is also

highly polarised and its intensity would also be reduced in the same proportion had such absorption taken place in the crystal. On the other hand, such a change in the relative intensities of the lines might be due to the presence of strong association of the molecules in the solid state through the hydrogen bond. This view is corroborated by the fact that the line 1426 due to the bending CH_3 oscillation symmetrical to σ_x is weakened very much in the solid state. It appears from these results that the plane of symmetry through the $\widehat{CSC}$ angle is probably not present in the solid state as far as the hydrogen atoms are concerned. The angle $\widehat{CSC}$ probably does not change with the solidification, because the lines 693 and 740 due to CS valence oscillations do not shift appreciably. The origin of the lines 70 and 84 might be traced to the intermolecular oscillations and the strong association through the hydrogen bonds mentioned above may be responsible for their appearance.

Ethyl sulphide.

The results for ethyl sulphide are given in Table II. These have been collected from a good spectrogram obtained recently after repeated trials. The polarisation of the lines given in Table II are those obtained in the present investigation. No such data were reported by previous workers. The Raman spectrum of this substance was studied previously by Venkateswaran (1931), Meyer (1931), Matossi *et al.* (1931) and Thatte and Ganesan (1933). The lines reported by these authors are all given in Table II. No special attempt has been made in the present investigation to record the very faint lines for the liquid, because it was found impossible to detect such lines in the case of the solid state owing to the presence of unavoidable stray light. Table II shows that the lines 640 and 657, which are prominent in the liquid state, disappear in the solid state, although the neighbouring line 690 is quite intense in the solid state. If it is assumed that the $\widehat{CSC}$ angle is less than 180°, the line 690 may be ascribed to the $\widehat{CSC}$ antisymmetric oscillation,

TABLE II.

Ethyl sulphide.

Liquid at room temp.		Solid at ca. −180°C. (Present authors.)
Previous authors.	Present authors.	
		88 (3d) *k*
302 (0)	302 (0) *e*; P	
336 (0)	336 (0) *e*; P	340 (1s) *k*
391 (0)	391 (0) *e*; P	
640 (3)	640 (2) *k*, *e*; P	v
657 (3)	657 (2) *k*, *e*; P	v
693 (3)	690 (2) *k*, *e*; $\rho > 6$, $< 6/7$	690 (3s) *k*, *e*
790 (0dd)		
976 (2)	976 (1) *k*, *e*; P	973 (1s) *k*, *e*
1020 (0)		
1050 (0)	1048 (0) *k*, *e*; P	
1070 (0)	1070 (0) *k*, *e*; P	
1256 (0d)		
1333 —		
1426 (1d)	1426 (2) *k*, *e*; D	1426 (1d) *k*, *e*
1456 (3d)	1456 (2) *k*, *e*; D	1456 (1d) *k*, *e*
2874 (3)	2874 (2) *k*, *e*; P	2874 (2d) *k*, *e*
2912 (0)		
2930 (8)	2930 (6) *k*, *e*; P	2930 (4d) *k*, *i*, *e*
2970 (2)	2970 (3) *k*, *e*; D	2970 (2) *k*, *e*
3010 —		

although the value of ρ appears to be less than 6/7, because there is no other depolarised line in this region. The line 640 would in that case represent the symmetric C-S valence oscillation. The disappearance of the two lines 640 and 657 is probably due to a change in the $\widehat{CSC}$ angle in the solid state. In this case the CH_3 groups do not undergo any change on solidification, because the corresponding lines do not undergo any change in intensity or in frequency with solidification. The hypothesis put forward by Mizushima *et al.* that the disappearance of such prominent lines in the solid state is due in many cases to the absence of free rotation about the C-C bond cannot explain the disappearance of the line due to C-S valence oscillation in the present case. The line 88 is due to some intermolecular oscillation and the association in this case is not through the hydrogen bond, but is probably through the sulphur bond.

TABLE III.

Propyl sulphide.

Liquid at room temp.		Solid at ca. −180°C. (Present authors.)
Previous authors.	Present authors.	
		96 (3b) *k*
		142 (1s) *e*
146 (1)		160 (1s) *e*
282 (2)	282 (2) *e*; P	272 (2b) *e*
380 (1)	378 (0b) *e*; P	
433 (0)	432 (0) *e*; ?	
650 (4)	650 (4b) *k*, *e*; P	v
712 (2)		725 (1) *k*, *e*
734 (4)	735 (3) *k*, *e*; D	735 (1) *k*, *e*
788 (3)	787 (1) *k*, *e*; P	
850 (3)	845 (1) *k*, *e*; P	
893 (5)	892 (3) *k*, *e*; P	892 (1) *k*, *e*
1032 (8)	1032 (5) *k*, *e*; P	1032 (2) *k*, *e*
1054 (0)		
1085 (1)	1088 (1) *k*, *e*; P	
1293 (3)	1295 (2) *k*; D	
1329 (2)	1326 (1) *k*; P	
1418 (4)	1420 (3) *k*, *e*; D	1420 (0s) *k*, *e*
1450 (2)	1452 (4) *k*, *e*; D	1452 (0s) *k*, *e*
2865 (8)	2868 (8) *k*, *e*; P	2862 (3s) *k*, *e*
2902 (10)	2907 (10) *k*, *e*; P	2910 (5s) *k*, *i*, *e*
2927 (10)	2930 (10) *k*, *e*; P	2920 (5s) *k*, *i*, *e*
2965 (8)	2965 (8) *k*, *e*; D	2965 (2b) *k*, *e*

Propyl sulphide.

The results for propyl sulphide are given in Table III. In this case as well as in the case of butyl sulphide only those lines for the liquid state which appeared with appreciable intensity have been entered in the tables and no attempt has been made to record the extremely feeble lines recorded by previous workers. It will be observed that in the liquid state there are three lines 282 (P), 650 (P) and 736 (D), which probably correspond respectively to the deformation, symmetric valence and antisymmetric valence oscillations of the $\widehat{CSC}$ group. In the solid state the line 650 disappears completely and the line 735 is split up into two lines 725 and 735 of the same intensity. Thus in this case also as in the case of ethyl sulphide there is some distortion of the molecule so as to restrict the symmetric C-S oscillation. The lines 892 and 1032 due probably to C-C valence oscillations appear in the solid state. There is a small diminution in the frequency 2930 of the C-H

valence oscillation in the solid state. Again, although the spectrogram due to the liquid did not indicate the presence of the line 146 reported previously by Venkateswaran (1931) but not recorded by Thatte and Ganesan (1933), the spectrogram due to the solid indicated the presence of two lines 142 and 160. A band at 96 was also observed but the corresponding anti-Stokes line was not observed by the side of λ 4046. These facts show that the molecule of propyl sulphide undergoes structural changes on solidification. The free rotation about C-C bond in the liquid state cannot account for the results in this case also. It might be possible that some association of the molecules takes place through the sulphur atom in the solid state.

TABLE IV.

Butyl sulphide.

Liquid at room temp.			Solid at ca. −180°C. (Present authors.)
Previous authors.	Present authors.		
			50 (1) *k*
142 (0)			72 (1) *k*
274 (0)	274 (0b) *e*;	P	223 (1) *e*
573 (0)	331 (0b) *e*;	P	
655 (3)	652 (2b) *k*, *e*;	P	652 (1) *k*, *e*
677 (0)			
715 (0)			
727 (0)			
753 (1d)	755 (1b) *k*, *e*;	$\rho > \cdot 6 < 6/7$	755 (1) *k*, *e*
794 (1d)	795 (1b) *k*, *e*;	P	
867 (3)	870 (2) *k*, *e*;	D	
892 (3)	892 (2) *k*, *e*;	D	906 (1) *k*, *e*
968 (1)			
1001 (1)			
1054 (4)	1050 (3) *k*, *e*;	D	1050 (1) *k*, *e*
1102 (3)	1106 (1) *k*;	P	
1298 (3)	1294 (3d) *k*;	D	1294 (1) *k*
1331 (1)			
1417 (4)	1420 (1) *k*, *e*;	D	
1454 (6d)	1454 (5d) *k*, *e*;	D	1454 (2s) *k*, *e*
2873 (5)	2864 (6) *k*, *e*;	P	2868 (2s) *k*, *e*
2914 (8)	2903 (10) *k*, *e*;	P	2898 (3s) *k*, *e*
2934 (5)	2935 (5) *k*, *e*;	P	2935 (1s) *k*
2960 (5)	2962 (5) *k*, *e*;	D	2950 (1s) *k*

Butyl sulphide.

The results for butyl sulphide are given in Table IV. The Raman scattering due to this substance is quite feeble and so the faint lines have not been recorded in the solid state. There are a large number of lines in this case and any attempt at the interpretation of the result will be a mere guess work. However, the lines 223, 652 and 755 observed in the solid state may be due to the vibrations of the CSC group as in the case of propyl sulphide. The lines 870 and 892 and 1106 which are more intense in the liquid state than the line 753 are absent in the spectrogram due to the solid. This may be due to the absence of free rotation in the solid state because these lines are most probably due to the C-C oscillations. Thus in this case in the solid state the $\widehat{CSC}$ angle remains intact and the molecule assumes one of a few configurations produced by free rotation about C-C bonds in the liquid state. The lines 50 and 72 are due to intermolecular oscillations but no direct evidence for strong association of the molecules is obtained from the results given in Table IV. The CH frequences undergo only minor changes, but the intensities of the lines 2915 and 2950 appear to diminish with the solidification of the substance.

The Raman spectra of ethers will be analogous to those of the thioethers mentioned above and so the Raman spectra of a few ethers will be studied in order to elucidate the points mentioned above more clearly.

The authors are indebted to the authorities of the Indian Association for the Cultivation of Science for kindly providing all facilities for carrying out the investigations at the laboratories of the Association.

REFERENCES.

Fonteyne, R. (1940). Infra-red and Raman spectra of polyatomic molecules. *Journ. Chem. Phys.*, **8**, 60.

Gross, E. and Vuks, M. (1933). Quasi-crystalline structure of liquids and the Raman effect. *Nature*, **135**, 100.

Kohlrausch, K. W. F. (1936). The Raman effect LVIII. *Monatsch.*, **68**, 349.

Matossi, F. and Aderhold, H. (1931). Raman effect of some sulphur compounds. *Z. f. Phys.*, **68**, 683.

Medard, L., *et al.* (1936). Raman effect of some organic sulphur compounds. *Comptes Rendus*, **203**, 1518.

Meyer, J. (1931). Raman spectra of sulphur compounds. *Z. anorg. allgem. Chem.*, **203**, 146.

Mizushima, S., *et al.* (1936). Raman effect and dipole moment in relation to free rotation III. *Sc. Papers. Int. Phys. Chem. Research*, **29**, 63.

———— (1938). Raman spectra and molecular configuration of solid ethylene dihalides. *Proc. Ind. Acad. Sc. India*, **8**, 315.

Sirkar, S. C. (1936). On the Raman spectra of solid carbon dioxide. *Science & Culture*, **1**, 587.

———— (1937). On the intensities of Raman lines due to the lattice oscillations. *Ind. J. Phys.*, **11**, 343.

Sirkar, S. C. and Bishui, B. M. (1943). On the Raman spectra of methyl and ethyl sulphide in the solid state. *Science & Culture*, **9**, 90.

Thatte, V. N. and Ganesan, A. S. (1933). The Raman effect in organic sulphides and some thio compounds. *Phil. Mag.*, **15**, 51.

Thompson, H. W. (1941). The infra-red spectrum and internal torsion of dimethyl sulphide. *Trans. Faraday Soc.*, **37**, 38.

Venkateswaran, C. S. (1938). The nature of lattice oscillations in solid carbon dioxide. *Current Science*, **6**, 378.

———— (1931). Raman spectra of some organic sulphides. *Ind. J. Phys.*, **6**, 51.