

THE RAMAN SPECTRA OF ORGANIC COMPOUNDS: DIETHYL DISULPHIDE

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INVESTIGATIONS on the Raman spectra of organic polysulphides are comparatively few, and no attempt appears to have been made to determine the state of polarisation of the lines. Using ten grams of pure freshly distilled liquid, a very intense spectrum of diethyl disulphide and its polarisation are obtained and the results are discussed in the present paper in relation to its structure.

Results

The observed frequency shifts and their polarisation characters are given in Table 1. The values of frequencies of the intense lines are correct to $\pm 1 \text{ cm.}^{-1}$. For the weak lines which could not be observed in the measuring microscope, the shifts are estimated with reference to an iron arc comparison spectrum and are correct to $\pm 5 \text{ cm.}^{-1}$. The state of polarisation of weak lines for which the deflection in the microphotometric curve is very small is given as either polarised (P) or depolarised (D). The photographs of the spectrum and its horizontal and vertical components are reproduced in Plate XVII.

Ethyl disulphide has been investigated by Venkateswaran (1931) and by Douzelot and Chaix (1936) and their results are also given in Table I.

Discussion of Results

The discussion of the Raman spectra of organic sulphur compounds by earlier investigators is wholly confined to the determination of frequencies corresponding to C-S, S-S and S-H linkages. In the case of thioethers, there is general agreement in the assignment of a sharp and intense line at about 640 cm.^{-1} to C-S binding and the lines at 506 and 189 cm.^{-1} to S-S oscillations wherever they exist. It is significant that the Raman frequency of 506 in diethyl disulphide which is intense and highly polarised, has nearly the same value as the polarised Raman line at 470 and that at 189 corresponds to the intense depolarised line at 150 cm.^{-1} .

TABLE I
Raman frequencies of diethyl disulphide

No.	Authors $\Delta\nu$ cm. ⁻¹	Polarisation	Venkateswaran 1931	Douzelot and Chaix (1936)	Assignments
1	115 (4)	D	..		Chain
2	189 (7)	.71	..	179 (w)	„
3	197 (3)	.80	„
4	259 (1 d)	D	„
5	295 (1 d)	P	„
6	324 (1 d) (double)	.60	333 (0)	..	„
7	357 (2 d)	D	384 (0)	..	„
8	400 (1)	.71	„
9	458 (1)	P	„
10	506 (7)	.32	509 (6)	507 (w)	„
11	520 (4)	.25	525 (3)	522 (w)	„
12	578 (1)	„
13	649 (10)	.57	641 (8)	639 (st)	„
14	668 (5)	.48	667 (4)	663 (w)	„
15	756 (2)	P	764 (0 d)	..	„
16	969 (4 b)	.79	967 (4 d)	964 (w)	„
17	1033 (2)	D	1033 (0)	..	(C ₂ H ₅)
18	1052 (5)	.45	1052 (4)	1045 (v.w)	Chain
19	1125 (1)	P	..	1142 (w)	(C ₂ H ₅)
				1187	
20	1257 (3)	.57	1260 (1 b)	..	Chain
21	1294 (1)	(C ₂ H ₅)
22	1417 (3)	.84	1422 (2)	1420 (w)	„
23	1444 (3)	.86	1454 (2 d)	1446 (w)	„
24	2874 (4)	.30	2871 (4)	2873 (m)	„
25	2911 (3)	.54	2911 (4 d)	..	„
26	2931 (8)	.59	2930 (8)	2923 (m)	„
27	2973 (4)	.78	2969 (4 b)	..	„

in molten sulphur (Venkateswaran, 1936). By analogy with sulphur, these frequencies can be treated as the valence and the deformation frequencies of the S-S bond. The presence of these two lines in ethyl disulphide supports the conclusion arrived at by Venkateswaran (1931) that S-S is connected by a single bond.

The presence of this single bond in polysulphides raises the interesting question of the existence of 'free rotation' in these compounds about the S-S bond. This problem of free rotation about a single bond in liquids has been examined by several authors from the point of view of the Raman effect. Theoretically, the *trans* configuration has the minimum potential energy and is therefore the most stable. But due to thermal energy, the molecule can be rotating about the stable position or between the *cis* and *trans* forms. It is also assumed that the latter case is equivalent to free rotation about the single bond. Extensive experimental investigations on the problem have been undertaken by Kohlrausch and his collaborators

(1935) and by Mizushima, Morino and others (1934-1936) with ethane derivatives. Recently, Ananthakrishnan (1937) has also given some attention to this problem. Kohlrausch and others (1933) have observed that these compounds yield a greater number of Raman lines than is to be expected from a purely *trans* state and have come to the conclusion that there is no free rotation as such, but the *cis* and the *trans* types of molecules co-exist in them. From a series of investigations carried out by Mizushima, Morino and Higashi on the Raman effect and dipole moment of ethane derivatives, they come to the conclusion that the intra-molecular state is far from that corresponding to the 'free rotation' in its literal meaning and in some cases (solids) they have found a state corresponding to the 'frozen rotation' in which all the molecules settle themselves in a *trans* state. According to the latter authors, the greater number of Raman lines observed is to be explained as arising from the disturbance of the symmetry of the *trans* form by the interaction of the C-C bond with other valence bonds.

The only compound of sulphur which has been investigated for observing the possibility of free rotation about S-S bond is S_2Cl_2 by Morino and Mizushima (1937). These authors have used the green and the yellow radiations of the mercury arc as exciting lines. Since the scattering power of these lines is small, only the intense Raman lines have been recorded by them. The spectrum cannot, therefore, be considered as sufficiently complete to draw any definite conclusion regarding the free rotation about the S-S bond. The two compounds, $(CH_3)_2S_2$ and $(C_2H_5)_2S_2$, are more suitable for investigation as 4046 and 4358 A.U. radiations could be made use of for excitation. The structural formula of dimethyl disulphide could be written as $H_3C-S-S-CH_3$ and that of diethyl disulphide as $H_5C_2-S-S-C_2H_5$. To a first approximation, we may separate out the vibrations of the C-H bonds from the chain of carbon and sulphur atoms. The chain may be straight or symmetrical *trans* type, or it may be asymmetrical *cis* type. For methyl disulphide as the former two forms possess a centre of symmetry, only three of the six normal modes of vibrations are allowed in the Raman effect; for the *cis* form, all the six are active. Venkateswaran (1931) has reported nine lines for this compound, of which five may be assigned to the chain and four to the CH_3 group. The polarisation characters of these lines are not known. From the data available, it is not possible to draw any definite conclusion and a more exhaustive investigation appears desirable. We could not undertake this investigation as the liquid was not available.

In the case of diethyl disulphide, there are six atoms in the chain $C_2-S-S-C_2$ and we should expect six polarised Raman lines for the straight

chain and for the *trans* form. For the *cis* form, there should appear twelve Raman lines, half of which should be depolarised. If the chain is zigzag without any element of symmetry, there will be twelve Raman lines, all of them being polarised. Of the twenty-seven lines recorded for ethyl disulphide, the lines 1052, 1125, 1294, 1417, 1444, 2874, 2911, 2931 and 2973 can be easily identified as the frequencies of C_2H_5 groups, by a comparison of its spectrum with those of ethyl alcohol, diethyl ether and diethyl amine. The remaining eighteen lines are due to the chain. This total number of lines due to the chain is more than should be expected either for a pure *trans* or a pure *cis* symmetry or to the loss of symmetry of the *trans* form due to resonance as shown by Mizushima and his co-workers. The presence of five lines which are more or less completely depolarised, *viz.*, 115, 197, 259, 357 and 969 is significant, suggesting the existence of the *cis* molecule in the liquid. The *trans* configuration is, on the other hand, revealed by the presence of highly polarised lines in its spectrum. It will be observed that the intense lines due to S-S in the region of 506 and 189 and due to C-S in the region of 649 cm.^{-1} are accompanied in each case by lines of medium intensity and having nearly the same polarisation characters. We may, therefore, attribute the lines at 189, 506 and 649 to the *trans* form and those at 197, 520 and 668 to the *cis* form. Theoretically for the same mode of oscillation which is symmetric, the Raman line due to the *trans* form will be more intense than of the *cis*. Hence, from the recorded intensity of the above lines, we can conclude that the two types of the molecules co-exist in nearly equal proportions. If there is free rotation about the S-S bond in the molecule, we should expect a wing to accompany the intense lines of the chain similar to the rotation wing accompanying the Rayleigh line in liquids; but no such wing was observed in the spectrum of ethyl disulphide, indicating that free rotation as such does not exist.

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Summary

An intense Raman spectrum of diethyl disulphide and its polarisation characters are recorded. The spectrum consists of twenty-seven lines. Nine of these are observed for the first time. It is shown that nine of these lines (three of which are depolarised) belong to the ethyl group (C_2H_5), and the remaining eighteen of which six are depolarised belong to the chain $C_2-S-S-C_2$. The results are discussed in relation to the problem of 'free rotation' about the S-S bond. It is concluded that six polarised lines are due to the *trans*

and twelve due to the *cis* forms; and that these two types of molecules co-exist in the liquid in equal proportions.

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