

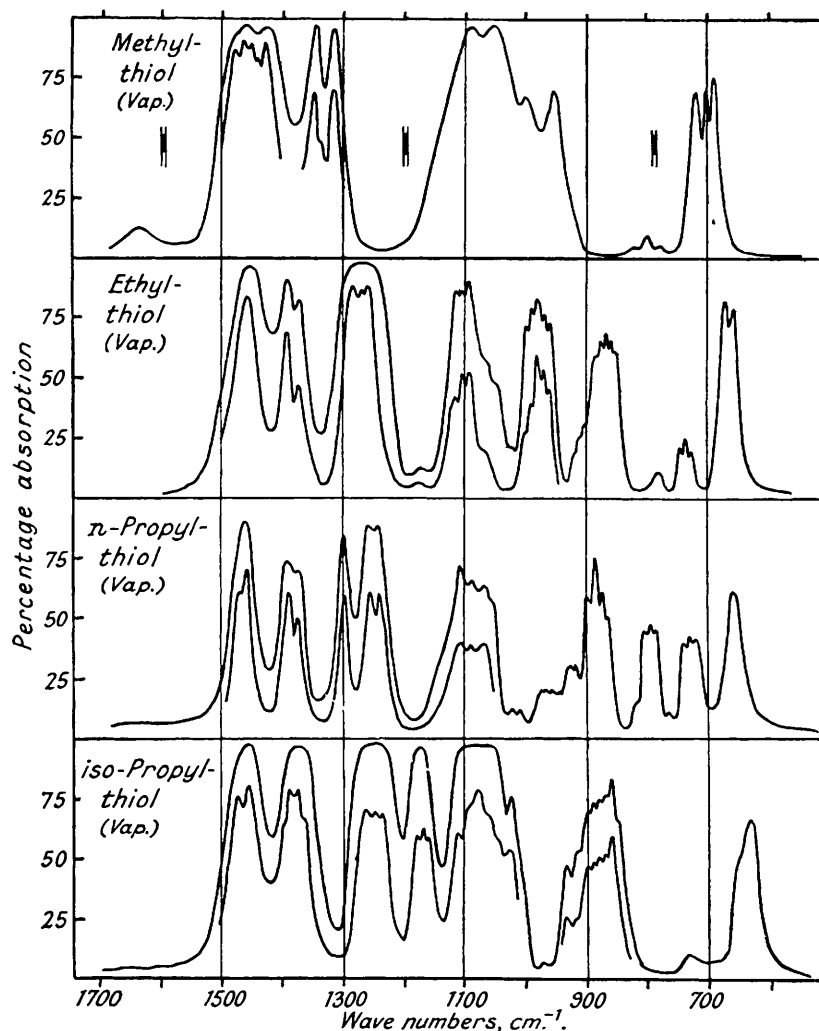
94. *The Infra-red Spectra of Thiols, Sulphides, and Disulphides.*

By I. F. TROTTER and H. W. THOMPSON.

The infra-red absorption spectra of a number of alkylthiols, alkyl sulphides, and alkyl and aryl disulphides have been measured. The results have been correlated with the Raman spectra, and in some cases a partial assignment of normal vibration frequencies has been made. The derivation of frequencies which are characteristic of vibrations of C-S and S-S linkages has been discussed. Some of the infra-red bands show a partially resolved rotational structure.

In some recent papers from this laboratory attempts have been made to correlate the infra-red spectra of complex molecules with the presence of particular atomic groupings. It has been emphasised that if such structural diagnosis is to be successful, it must be based upon a preliminary survey of the spectra of series of related simpler molecules, from which vibration bands can be found which are characteristic of particular groups in the skeleton. In connexion with infra-red measurements on vulcanised rubbers and the mechanism of vulcanisation by means of sulphur chloride (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 276) we have recently measured the spectra of a number of thiols, alkyl and aryl sulphides and disulphides, from which it was hoped to discover key vibration frequencies for the C-S and S-S bonds. The spectra of

FIG. 1.



Methylthiol, 27 cm. path with pressures 200—300 mm.
 Ethylthiol, 20 cm. path with pressures 100—200 mm.
 n-Propylthiol, 27 cm. path with pressures 100—150 mm.
 iso-Propylthiol, 27 cm. path with pressures 100—200 mm.

methylthiol and dimethyl sulphide were examined in this laboratory some years ago (*ibid.*, 1940, **36**, 812; 1941, **37**, 1), but in view of the greater resolving power now available these measurements have been repeated.

Although the work has so far failed to give an unequivocal decision on the points for which it was originally planned, the spectra were useful for general purposes of reference, and in providing data upon which analyses could be based if required. Further, the resolution of the rotational fine structure and band contour of some of the vibration bands is not without value in the assignment of the frequencies to normal modes of these molecules.

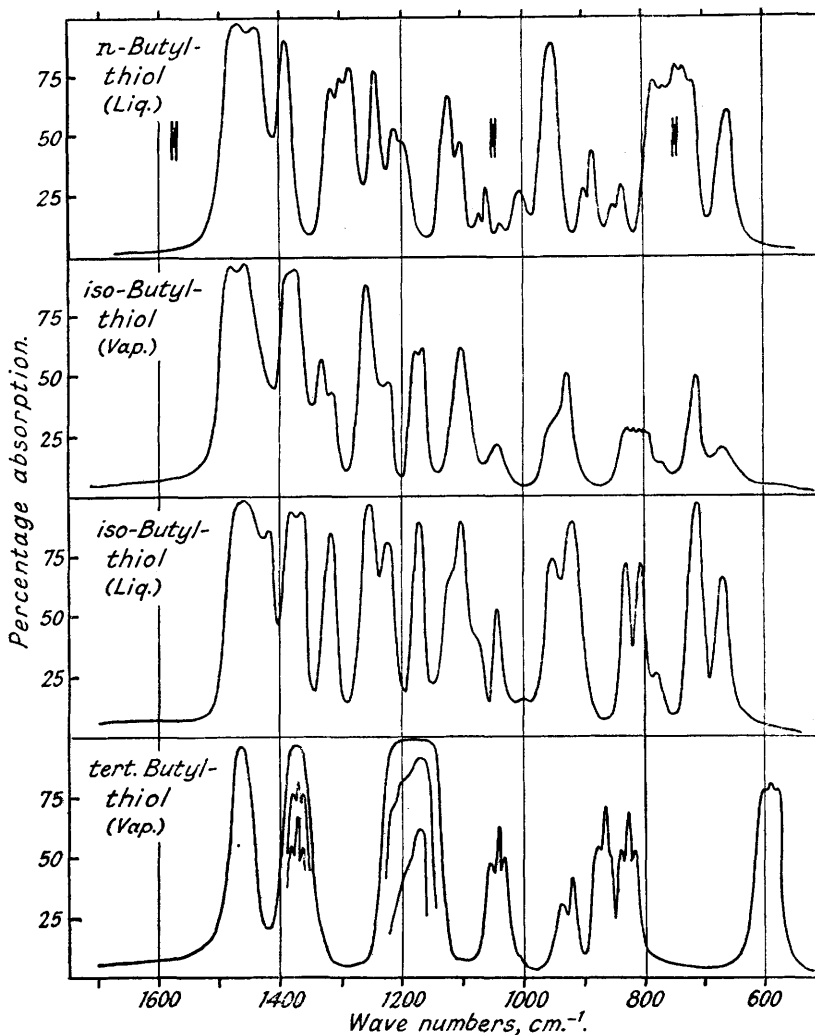
EXPERIMENTAL.

For the range 2—14 μ an automatically recording spectrometer built in this laboratory was used, with a rock-salt prism (Whiffen and Thompson, J., 1945, 268). For the range 14—20 μ a survey was made on this recorder by using a

prism of potassium bromide, but owing to the irregular background in this region resulting from absorption by atmospheric water vapour and carbon dioxide, better results were obtained by using a manually operated Hilger D 88 spectrometer with sylvine prism. "False energy" was minimised by the use of either quartz or rock-salt shutters in front of the entrance slit. The effective slit widths used are shown on the diagrams.

The vapours were contained in cylindrical glass tubes with flanged ends, on to which plates of rock-salt or potassium bromide were sealed with a hard stop-cock grease. Liquids were examined in conventional cells made by separating a pair of rock-salt or bromide plates with a suitable washer.

FIG. 2.



n-Butylthiol and isobutylthiol, approx. 0.1 mm. layer.
*iso*Butylthiol (vap.), 27 cm. path with 100 mm. pressure.
tert.-Butylthiol (vap.), 27 cm. path with 40—150 mm. pressures.

The compounds used were commercial samples, purified by careful fractionation. As a rule the middle fraction was taken, but in some cases the spectra of other fractions were also measured as a check on purity. Methylthiol was purified by fractionation of a large sample in a vacuum. The b. p.'s (uncorr.) of the other samples finally used were as follows:

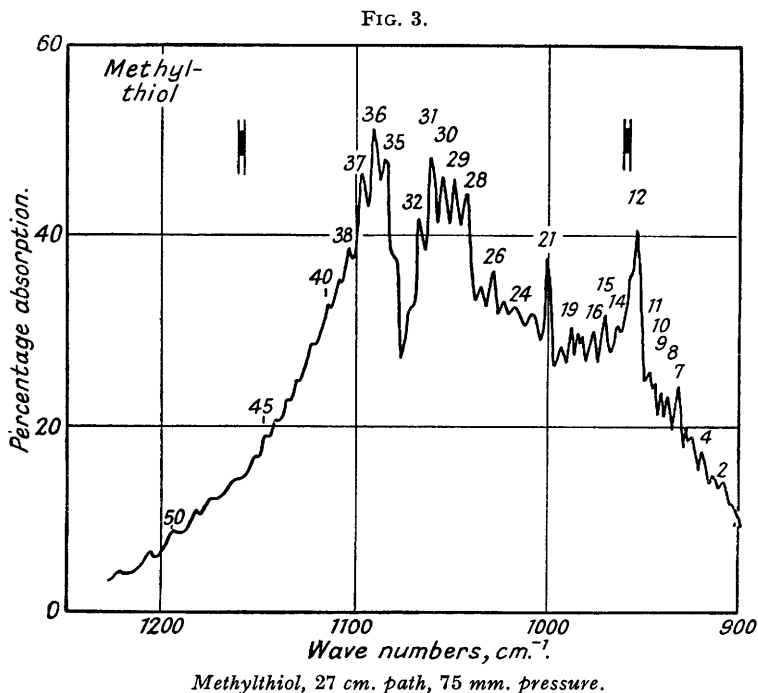
Ethylthiol	35.5°	Dimethyl sulphide	43.0°
<i>n</i> -Propylthiol	67.5—68	Methyl ethyl sulphide	62.5—63.5
<i>iso</i> Propylthiol	51—51.5	Diethyl sulphide	90.0
<i>n</i> -Butylthiol	97.5	Dimethyl disulphide	108—109/753 mm.
<i>iso</i> Butylthiol	88—88.5	Diethyl disulphide	65/40 mm.
<i>tert.</i> -Butylthiol	64.5	Di- <i>n</i> -propyl disulphide	99/40 mm.

Solid dibenzyl disulphide was recrystallised from carbon disulphide; m. p. 69°. This substance was measured both as a solid layer melted on to a rock-salt plate, and also as a powder after being ground with medicinal paraffin.

RESULTS AND DISCUSSIONS.

(1) *Thiols*.—The spectra of the thiols between 6 and 20 μ are shown in Figs. 1 and 2. The curves for the region 2—6 μ are not shown, since they do not contribute materially to the interpretations, although it may

be noted that a few minor differences in the positions of overtones and combination bands in this spectral range might be useful for analytical work. In the range 2—6 μ the only significant bands arise from the fundamentals associated with C—H stretching (2800—3000 cm^{-1}), and with S—H stretching (about 2580 cm^{-1}). The spectrum of methylthiol vapour agrees in all essentials with that given previously, but the improved resolution provides additional confirmation of the assignment of frequencies to the different types of mode. Thus the bands at 708, 800, 1330, and 2580 have the expected "parallel" type contour, with a spacing between *P* and *R* branches of about 33 cm^{-1} . The absorption in the region 900—1200 cm^{-1} previously attributed to a pair of perpendicular type vibrations, is now seen to be resolved into a galaxy of *Q* branches, confirming this assignment. This region is shown on an enlarged scale in Fig. 3, and the frequencies of the peaks observed



are given in Table I. It is seen that the distribution of intensities in these bands is so complex as to give no clue to a detailed interpretation, but about 950 and 1060 seem reasonably probable values for the centres of the two perpendicular bands. Methylthiol is very nearly a symmetrical rotator, having $I_A \sim I_B \sim 60 \times 10^{-40}$ and $I_C \sim 5.4 \times 10^{-40}$ g. cm^2 . For a symmetrical top the "normal" spacing of *Q* branches in a perpendicular type band will be $(h/4\pi^2)(1/I_C - 1/I_A)$, which is about 9 cm^{-1} . The spacing actually observed is much less than this, and shows that the perpendicular type bands have a complex structure. Such undue complexity is surprising in view of the close approximation to a symmetrical rotator. It seems probable that complex vibrational rotational interaction is occurring. If these bands can be measured with the much higher resolving power of a grating spectrometer, a more precise analysis might be profitable.

The bands at 1430 and 1475 cm^{-1} also have signs of the perpendicular type structure, as expected.

TABLE I.

Number of line.	Position, cm^{-1} .	Number of line.	Position, cm^{-1} .	Number of line.	Position, cm^{-1} .	Number of line.	Position, cm^{-1} .	Number of line.	Position, cm^{-1} .
1	902	12	953	23	1009	33	1071	43	1135
2	908	13	957	24	1017	34	1080	44	1141
3	913	14	962	25	1023	35	1084	45	1146
4	920	15	970	26	1029	36	1090	46	1152
5	924	16	976	27	1035	37	1096	47	1160
6	927	17	982	28	1042	38	1103	48	1174
7	931	18	984	29	1048	39	1109	49	1183
8	937	19	988	30	1054	40	1114	50	1195
9	940	20	993	31	1060	41	1122	51	1207
10	944	21	1000	32	1066	42	1130	52	1222
11	947	22	1006						

The results for ethylthiol agree substantially with those of Coblenz ("Investigations of Infra-red Spectra," 1905, Vol. 1), but show more detail. Also there is very close agreement between the infra-red frequencies and those obtained from the Raman spectrum, from which Venkateswaran (*Indian J. Physics*, 1930, 5, 219)

deduced the following intervals : 333(2), 659(10), 739(0*d*), 874(0), 965(0), 1054(1*b*), 1263(1*b*), 1449(3*b*), 2573(10), 2872(5*b*), 2933(10*b*), 2968(7*b*). The strong infra-red bands near 1100 and 1400 cm^{-1} have no analogues in the Raman spectrum. Many of the infra-red bands show a partially resolved and rather complex rotational contour, but it is impossible to correlate it with the molecular structure.

A rough measurement of the infra-red spectrum of *n*-propylthiol has been reported by Bell (*Ber.*, 1927, 60, 1749) and by Ellis (*J. Amer. Chem. Soc.*, 1928, 50, 2113). The present results agree satisfactorily, but again show more detail. Here, too, many infra-red frequencies agree with the Raman intervals found by Venkateswaran, namely : 367(3), 652(4), 695(1*d*), 730(0*d*), 883(0), 964(0), 1033(2*b*), 1299(1*b*), 1441(2*b*), 2575(8*d*), 2874(4*b*), 2930(8*b*), 2966(5*b*). As might be expected with the increase in molecular complexity, however, the coincidences are less complete than with methyl- or ethyl-thiol.

The results for *isopropylthiol* agree closely with the Raman spectrum recorded by Kohlrausch, Dadiou, and Pongratz (*Wien. Ber.*, 1932, 141, II*a*, 276), who found the following displacements : 261(2), 335(4), 414(2), 488(4), 626(8*b*), 855(2*b*), 886(3*b*), 1050(1), 1145(1), 1251(1*b*), 1307(1), 1450(5*b*), 2567(3), 2866(4), 2915(5*b*), 2962(3*b*). With *n*-butylthiol there is similar concordance with the infra-red measurements of Bell (*loc. cit.*) and with the Raman intervals deduced by Venkateswaran, namely, 298(1), 333(2), 437(0), 656(6), 707(0*b*), 843(0), 951(1), 1049(1*b*), 1106(0), 1296(2*b*), 1361(0*b*), 1438(8*b*), 2574(10), 2869(8*b*), 2905(7*b*), 2934(10*b*), 2964(6*b*).

In Fig. 2 the spectrum of *isobutylthiol* is shown both for the vapour and for the liquid. There is very close agreement with the Raman data of Venkateswaran (*loc. cit.*) and of Kopper, Seka, and Kohlrausch (*Wien. Ber.*, 1932, 141, II*a*, 465), the latter giving the following intervals : 224(1), 339(4), 402(2), 427(3), 668(3), 708(5), 770(2), 801(2), 824(2), 924(1), 955(3), 1108(2), 1216(2), 1250(1), 1319(1), 1336(1), 1370(1), 1423(2*b*), 1452(4*b*), 2573(8*b*), 2829(0), 2872(8), 2919(5), 2958(10). It can be seen that marked changes of intensity and to a less extent of wave-length occur in the infra-red spectrum on passing from the liquid to the vapour. Such alterations of intensity with change of state are neither uncommon nor inexplicable, and are at present being examined in greater detail with various polar and non-polar compounds. It is usually found that with the liquid or solid phase the bands tend to be sharper than with the vapour.

The infra-red spectrum given in Fig. 2 for *tert*-butylthiol agrees well with the Raman data of Köppl and Kohlrausch (*Wien. Ber.*, 1933, 142, II*b*, 477) who found the following intervals : 295(3), 368(5), 395(1), 445(1), 587(10), 819(6), 866(2), 930(2), 1030(1), 1103(0), 1160(4), 1177(3), 1218(3*b*), 1449(5*b*), 2570(7), 2714(2), 2775(1), 2864(4), 2898(6), 2924(8). With this molecule many of the infra-red bands found for the vapour show a well-marked contour of the *P-Q-R* branch type which might well arise owing to the close approximation of this molecule to a symmetrical rotator. Rough calculation of the separation of the *P* and *R* maxima using the expression of Dennison and Gerhard $[S(\beta)/\pi]\sqrt{kT/I_A}$ gives a value of about 18 cm^{-1} , which agrees with that observed within the error of measurement.

All the above thiols show an infra-red band at about 2580 cm^{-1} which is connected with a stretching vibration of the S-H bond. The intensity of this band is comparatively low. Also, each of the compounds shows bands between 2800 and 3000 cm^{-1} which are associated with the C-H bond stretching modes, but we have not attempted to explore them with high resolving power.

The main point of general interest is whether the frequency associated with a stretching vibration of the C-S bond remains approximately constant throughout the series of thiols. In methylthiol this lies at 705 cm^{-1} and in the ethyl derivative the corresponding band lies at 660 cm^{-1} , the intense Raman interval being 659. With some of the higher homologues there are several infra-red bands in the range 550—750 cm^{-1} , but in deciding which is due to the C-S stretching mode the Raman data are helpful in that the C-S stretching frequency is strong in the Raman effect. Inspection of the data shows that in all cases except that of *isobutylthiol* the assignment given in Table II is convincing. With *isobutylthiol* the infra-red bands at 672 and 708 correspond to Raman intervals 668(3) and 708(5), and it is not clear which of the two frequencies should be assigned to the C-S stretching mode.

TABLE II.

Thiol.	Infra-red, cm^{-1} .	Raman, cm^{-1} .	Thiol.	Infra-red, cm^{-1} .	Raman, cm^{-1} .
Methyl	705	702	<i>n</i> -Butyl	658	656
Ethyl	660	659	<i>iso</i> Butyl	672 or 708	668 or 708
<i>n</i> -Propyl	553	652	<i>tert</i> -Butyl	587	587
<i>iso</i> Propyl	630	626			

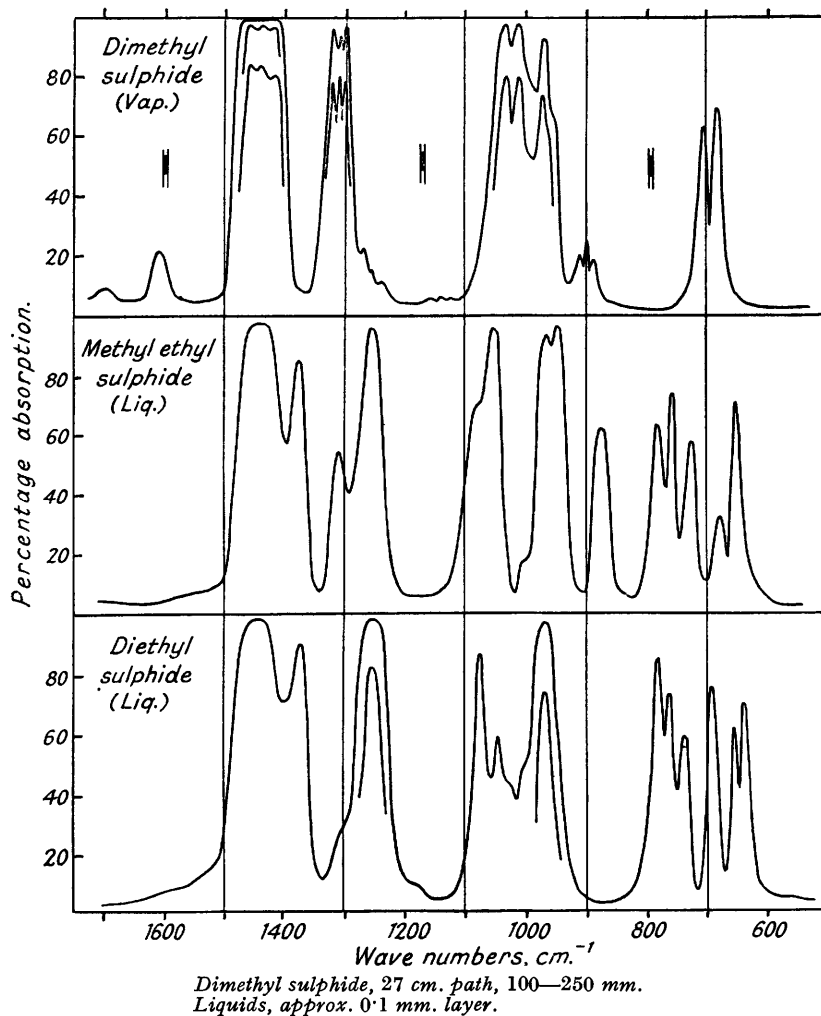
Whatever the correct assignment may be in this case, it is clear that whilst the C-S stretching frequency lies in the region of 600—700 cm^{-1} , it varies appreciably in different cases. If it is to be used in diagnosis with such structures as vulcanised rubber, the identification will have to be made with caution.

(2) *Alkyl Sulphides*.—The spectra of three alkyl sulphides are shown in Fig. 4. Although the results for dimethyl sulphide do not disagree with those given previously (*Trans. Faraday Soc.*, 1941, 37, 1), some of the bands are now much better resolved. Thus the shoulders previously found at 917 and 976 cm^{-1} now appear as definite bands at 900 and 970 cm^{-1} , and the band at 1310 has a clear three-branch contour. There seem to be three types of band contour, corresponding in principle to *A*, *B*, and *C* type bands. Although the present measurements do not directly invalidate any of the previous tentative assignments, some apparent discrepancies with the Raman data probably require further examination. There is little doubt that the

infra-red band at about 694 cm.^{-1} is connected with the symmetrical stretching mode of the C-S-C skeleton. The corresponding C-S-C antisymmetrical mode has a frequency 742 found as a depolarised Raman interval.

The Raman spectra of diethyl and methyl ethyl sulphides have been measured by Matossi and Aderhold (*Z. Physik*, 1931, **68**, 683) and by Venkateswaran (*Indian J. Physics*, 1931, **6**, 51), and the intervals found agree well with the positions of many of the infra-red bands. With these compounds some changes of relative intensity of certain bands occur on passing from the vapour to the liquid, and in several cases there is a small but definite change in the frequency of the band. There is little doubt that the vibrations mainly determined by stretching of the C-S bonds give rise to bands in the region $600\text{--}750\text{ cm.}^{-1}$, and while it is impossible to make a definite assignment, it seems probable that the "symmetrical" C-S-C stretching frequency lies at

FIG. 4.



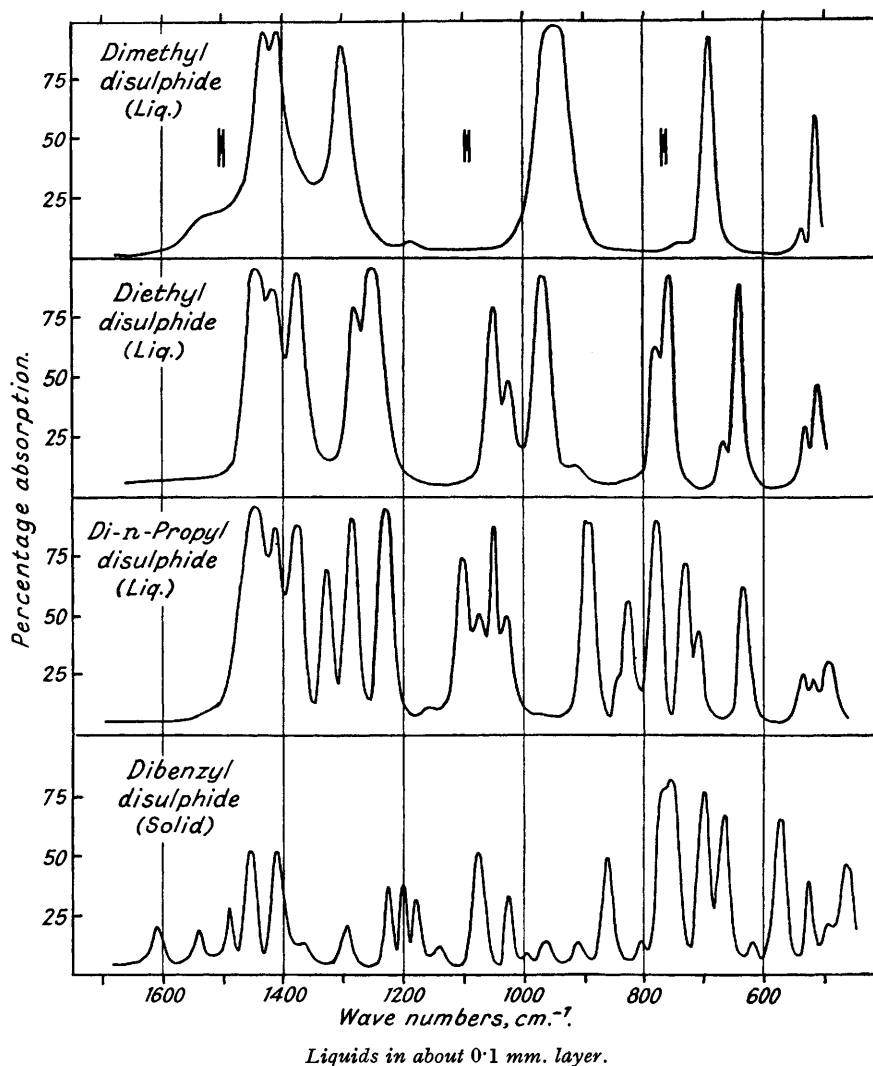
652 cm.^{-1} with methyl ethyl sulphide and at 640 cm.^{-1} with the diethyl derivative, corresponding to 694 with dimethyl sulphide. In ethylene disulphide (Thompson and Dupré, *Trans. Faraday Soc.*, 1940, **36**, 805) this mode has a value of 625 cm.^{-1} .

Another point of interest is the frequency of the symmetrical deformation mode of the CH_3 groups. This is usually found near 1375 cm.^{-1} in hydrocarbons. In methyl ethyl and diethyl sulphides there is a band at about this value, but in dimethyl sulphide where the methyl groups are attached to sulphur instead of carbon, the band is displaced. Originally, the band at 1310 with dimethyl sulphide was attributed to the deformation of the methyl group. The bands at about $1450\text{--}1460\text{ cm.}^{-1}$ with all the compounds are connected with other deformations of C-H links.

(3) *Alkyl and Aryl Disulphides.*—The spectra of dimethyl, diethyl, di-*n*-propyl, and dibenzyl sulphides are shown in Fig. 5. The Raman spectra of the first two have been recorded by Venkateswaran (*Indian J. Physics*, 1931, **6**, 51), by Venkateswaran and Paridga (*J. Indian Acad. Sci.*, 1942, *A*, **15**, 396) and by Douzelait and Chaix (*Compt. rend.*, 1936, **202**, 851). A recent paper by Gerding and Westrick (*Rec. Trav. chim.*, 1942,

61, 412) is not yet obtainable. The results are collated with the present infra-red data in Tables III and IV. Only frequencies below 1500 cm.^{-1} are included since the only fundamentals above this value will be due to C-H stretching vibrations near 2900 cm.^{-1} . Stevenson and Beach (*J. Amer. Chem. Soc.*, 1938, **60**, 2872) have determined the structural parameters of dimethyl disulphide by electron diffraction. Their results suggest a non-linear arrangement of the skeleton C-S-S-C. If rotation about the S-S bond is restricted, *cis*- and *trans*-forms may therefore exist. In this event, the *trans*-form may have a centre of symmetry, and if only the *trans*-form were present no coincidences should be found between the Raman and the infra-red

FIG. 5.



fundamentals. Coincidences certainly occur, as shown in Table III. Hence the sample examined cannot be solely *trans*- in structure. On the other hand, molecular distortions in the liquid might lead to violation of the normal selection rules.

TABLE III.

Dimethyl Disulphide.

Raman.	Infra-red.	Raman.	Infra-red.
243 (1d)	—	948 (1)	950 (s.)
284 (0d)	—	—	1192 (v.w.)
512 (6s)	517 (m.)	1305 (0)	1298 (s.)
—	533 (v.w.)	1337 (0)	—
695 (6s)	690 (s.)	—	1410 (s.)
740 (0d)	741 (?)	1425 (0d)	1432 (s.)

It seems likely that the infra-red band at 690 cm.^{-1} is connected with the stretching of C-S bonds, and that at 517 cm.^{-1} may be associated with the stretching of S-S links. The vibration frequency of chlorine is 536 cm.^{-1} , and according to Raman measurements by Venkateswaran on liquid sulphur (*Proc. Indian Acad. Sci.*, 1936, A, 4, 34) an interval of 470 cm.^{-1} is attributed to the S-S stretching mode. Morino and Mizushima (*Sci. Papers Inst. Res. Tokyo*, 1937, 32, 220) also attribute a Raman interval of 536 in disulphur dichloride to the S-S stretching vibration.

As in the case of dimethyl sulphide (above), the symmetrical deformation frequency of the methyl groups, usually found near 1375 cm.^{-1} , is displaced in dimethyl disulphide, whereas with the diethyl and the dipropyl derivative, in which methyl groups are attached directly to carbon, a band appears at 1375 .

The Raman and infra-red results with diethyl disulphide show good concordance.

TABLE IV.

Diethyl Disulphide.

Raman intervals, cm.^{-1} .*			Infra-red	Raman intervals, cm.^{-1} .*			Infra-red
V. (1942).	V. (1931).	D. (1936).	bands, cm.^{-1} .	V. (1942).	V. (1931).	D. (1936).	bands, cm.^{-1} .
115 (4) D	—	—	—	756 (2) P	764 (0d)	—	758 (s.)
189 (7) 0.71	—	179 (w.)	—	—	—	—	778 (s.)
197 (3) 0.80	—	—	—	—	—	—	925 (v.w.)
259 (1d) D	—	—	—	969 (4b) 0.79	967 (4d)	964 (w.)	966 (v.s.)
295 (1d) D	—	—	—	1033 (2) D	1033 (0)	—	1025 (m.)
324 (1d) 0.60	333 (0)	—	—	1052 (5) 0.45	1052 (4)	1045 (v.w.)	1049 (s.)
357 (2d) D	384 (0)	—	—	1125 (1) D	—	1142 (w.)	—
400 (1) D	—	—	—	—	—	1187 (w.)	—
458 (1) P	—	—	—	1257 (3) 0.57	1260 (1b)	—	1255 (s.)
506 (7) 0.32	509 (6)	507 (w.)	509 (w.)	1294 (1)	—	—	1280 (s.)
520 (4) 0.25	525 (3)	522 (w.)	527 (v.w.)	—	—	—	1375 (s.)
578 (1)	—	—	—	1417 (3) 0.84	1422 (2)	1420 (w.)	1416 (m.)
648 (10) 0.57	641 (8)	639 (s.)	642 (m.)	1444 (3) 0.86	1454 (2d)	1446 (w.)	1445 (v.s.)
668 (5) 0.48	667 (4)	663 (w.)	668 (v.w.)	—	—	—	—

* V. = Venkateswaran; D. = Douzelait and Chaix (*loc. cit.*).

The array of plausible fundamentals seems larger than could be accounted for by a single *cis*- or *trans*-structure. The infra-red bands at 642 and 509 cm.^{-1} are probably connected with the stretching of C-S and S-S bonds, but the other frequencies cannot be definitely assigned. It is noteworthy that many of the infra-red bands (and also Raman intervals) are accompanied by satellites, which may be connected with the existence of *cis*- and *trans*-forms.

No Raman data are available for the other disulphides. With the di-*n*-propyl derivative there is a band at 631 cm.^{-1} which may be connected with the stretching of a C-S bond, and there is a feeble group of bands near 500 cm.^{-1} which may be connected with motions of the S-S part of the skeleton. With dibenzyl sulphide many of the infra-red bands are common to aromatic compounds, and that at 570 cm.^{-1} may be associated with stretching of C-S bonds.

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