

## Raman Spectra of the Mercaptans

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### ABSTRACT.

The paper describes the results of a study of the Raman spectra of methyl, ethyl, propyl, butyl, isobutyl, iso-amyl and phenyl mercaptans. A characteristic feature of the spectra of these compounds is the appearance of a prominent line at 2573. Hydrogen sulphide has been found by Bhagavantam to show this line in the same position and this frequency is therefore attributed to the SH oscillation. The prominence with which this frequency occurs in all the mercaptans is in marked contrast to the behaviour of the OH group which appears only in water and methyl alcohol but not in the higher alcohols. Two strong frequencies at about 659 and 739 also appear with all the mercaptans and are evidently due to the oscillation of the CS group. Differences in the nature of the oscillations between the CO and CS groups are pointed out. A definite decrease in the magnitude of the CS frequencies is noticed from methyl to ethyl mercaptan. In the higher members these frequencies attain a more or less steady value. The spectra of ethyl and the higher mercaptans show a number of very diffuse lines which are ascribable to the oscillations of the carbon chain. This character is presumably due to the influence of the sulphur atom on these oscillations.

A remarkable feature of the SH oscillation is that unlike the CH, NH and OH oscillations the value of this frequency does not change appreciably in any of its compounds. In like manner there is no large difference in the magnitude of the oscillation frequencies of C-S and C=S.

The data are compared with direct *infra-red* measurements made by Coblenz and Bell.

### 1. Introduction.

It is well known that from a study of the Raman spectra it is possible to identify certain oscillation frequencies with the presence of definite chemical linkages or groups. Several successful attempts have already been made in this direction. So far, however, no compounds containing SH groups have received any attention. In the present paper a study of the Raman spectra of some mercaptans has been made for the first time and the results of the investigation are reported.

### 2. Experimental.

With the exception of methyl mercaptan the liquids were all supplied by Messrs. Kahlbaum and were in all cases further purified by distillation in vacuum. Methyl mercaptan was prepared in the Palit Chemical laboratory by Mr. Adhikari and the liquid was purified by repeated distillation. The usual experimental arrangements were followed. The liquids were kept in Wood's tubes which were sealed off in vacuum. A two glass-prism spectrograph supplied by Adam Hilger giving a dispersion of about 20 A.U. per mm. at  $\lambda 4000$  was used for the experiments. The following tables show the analysis of the Raman lines. Under the columns I,  $\nu$ ,  $\Delta\nu$ , are given respectively, the intensities and the frequencies of the Raman lines and the differences in wave

numbers between the exciting lines and the Raman lines. The incident lines  $\lambda 3650.1$ ,  $3654.8$ ,  $3663.3$ ,  $4046.6$ ,  $4077.8$ ,  $4339.2$ ,  $4347.5$  and  $4358.3$  are represented by the letters  $a, b, c, d, e, f, g$  and  $h$  respectively.

TABLE I.  
Methyl mercaptan.  $\text{CH}_3\text{SH}$ .

I	$\nu$	$\Delta\nu$	I	$\nu$	$\Delta\nu$
5d	24814	a-2575	0	22291	g-704
2d	24779	b-2575	10	22235	h-708
3	24457	a-2932	10d	22133	d-2573
2	24122	b-2932	...	...	h-805
0d	24381	b-2973	1d	21944	e-2572
1	24359	c-2931	1b	21880	h-1058
8	24001	d-704	1b	21833	d-2872
1d	23900	d-805	10b	21772	d-2933
1	23810	e-706	2d	21728	d-2977
0d	23713	e-803	0d	21646	e-2870
0	23646	d-1059	1d	21585	e-2931
0	23457	e-1059	0d	21513	h-1425

$\Delta\nu$  : -704 (10), 805 (1d), 1059 (0), 1425 (0), 2573 (10), 2871 (0d), 2933 (10b) 2975 (2d).

TABLE II.  
Ethyl mercaptan  $C_2H_5SH$ .

$l$	$\nu$	$\Delta\nu$	$l$	$\nu$	$\Delta\nu$
$5d$	24816	$a-2573$	10	22279	$h-659$
$2d$	24732	$b-2572$	0	22198	$h-740$
5	24456	$a-2933$	$10 d$	22132	$d-2573$
5	24422	$a-2967$	0	22065	$h-873$
		$b-2932$	1	21971	$h-967$
1	24388	$b-2966$	1	21943	$e-2573$
2	24357	$c-2933$	$0 b$	21885	$h-1053$
$10 dr$	24046	$d-659$	$5 b$	21830	$d-2972$
$0 d$	23967	$d-738$	$10b$	21772	$d-2933$
1	23858	$e-658$	6	21737	$d-2968$
			$1b$	21677	$h-1261$
1	23831	$d-874$	0	21641	$e-2875$
1	23741	$d-964$	$1 b$	21586	$e-2930$
$1 b$	23651	$d-1054$	$2 b$	21487	$h-1451$
0	23550	$c-966$	2	20064	$h-2874$
$2 b$	23440	$d-1265$	3	20008	$h-2930$
$3 b$	23258	$d-1447$			
2	22605	$h-333$			

$\Delta\nu$  :—333 (2), 659 (10), 739 (0d), 874 (0), 965 (0), 1054 (1b), 1263 (1b), 1449 (3b), 2573 (10), 2872 (5b), 2933 (10b), 2968 (7b).

TABLE III.

Propyl mercaptan  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$ .

I	$\nu$	$\Delta\nu$	I	$\nu$	$\Delta\nu$
4 b	24814	a-2575	8	22571	h-367
1	24778	b-2576	4	22286	h-652
4 b	24455	a-2934	1d	22234	h-694
5 b	24423	a-2969	1d	22208	h-730
		b-2929	8b	22130	d-2575
		c-2865	0	22064	h-884
2	24384	b-2970	0	21974	h-964
2	24359	c-2931	2b	21904	d-1034
3 b	24052	d-653	4 b*	21831	d-2874
0 d	24008	d-697	8b*	21779	d-2936
0 d	23976	d-729	5b	21739	d-2966
0	23864	e-652	0	21694	g-1301
0	23823	d-882	1	21638	h-1300
0	23741	d-964	1	21582	e-2934
1 b	23673	d-1032	0	21552	g-1443
0 b	23482	e-1034	2d	21494	h-1444
0 b	23407	d-1298	2b	20066	h-2872
1	23266	d-1439	3b	20011	h-2927
			2	19972	h-2966

$\Delta\nu$ :—367 (3), 652 (4), 695 (1d), 730 (1d), 883 (0), 964 (0), 1033 (2b), 1299 (1b), 1441 (2b), 2575 (8d), 2874 (4b), 2930 (8b), 2966 (5b).

\* Each of these lines appears to be accompanied by a component, but owing to want of proper resolution exact measurements could not be made.

TABLE IV.

Butyl mercaptan  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$ 

I	$\nu$	$\Delta\nu$	I	$\nu$	$\Delta\nu$
4d	24816	a-2573	0	22501	h-437
1	24780	b-2574	0	22340	g-655
1	24480	b-2874	6	22282	h-656
3	24456	a-2993	0b	22231	h-707
3	24422	a-2967	10d	22131	d-2574
0	24395	b-2959	0	22096	h-842
0	24354	c-2936	0b	22049	h-889
0	24269	d-436	1	21983	h-955
5	24048	d-657	1	21941	e-2575
0b	23997	d-708	1b	21890	h-1048
1b	23860	{ e-656	8b	21836	d-2869
		{ d-845	7b	21779	d-2906
1b	23820	d-889	10b	21771	d-2934
0	23758	d-947	6b	21741	d-2964
1b	23655	d-1050	2b	21644	h-1294
0	23599	d-1106	1b	21576	{ e-2940
2b	23408	d-1297			{ h-1362
0b	23346	d-1359	0b	21555	e-2961
8b	23271	h-1434	3b	21495	h-1443
1	22640	d-298	2	20069	h-2869
2	22605	h-383	2	20033	h-2905
			2	20004	h-2934

$\Delta\nu$  :—298 (1), 333 (2), 437 (0), 656 (6), 707 (0b), 843 (0), 889 (0b), 951 (1), 1049 (1b), 1106 (0), 1296 (2b), 1361 (0b), 1438 (3b), 2574 (10d), 2869 (8b), 2905 (7b), 2934 (10b), 2964 (0b).

TABLE V.  
Isobutyl mercaptan,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\text{SH}$ .

I	$\nu$	$\Delta\nu$	I	$\nu$	$\Delta\nu$
5d	24814	a-2575	2	22510	h-428
2d	24780	b-2574	0	22416	h-523
3b	24473	a-2916	3	22267	h-671
6b	24423	{ a-2961 b-2926	5dr	22231	h-707
			1d	22169	h-769
3b	24395	b-2959	10d	22127	d-2878
3b	24369	{ c-2921 d-336	0b	22098	h-840
			1b	22010	h-898
2	24277	d-428	3d	21962	h-956
0	24089	e-429	1	21942	e-2874
1	24036	d-669	0	21868	h-1070
3dr	23997	d-708	10b*	21833	d-2872
1d	23934	d-771	8b*	21780	d-2925
0d	23877	d-828	10b	21733	d-2972
1d	23787	d-918	0	21689	h-1249
2d	23750	d-955	2b	21629	{ h-1309 e-2887
0b	23488	d-1317	.....	.....	
0b	23452	d-1253	2b	21545	e-2971
2b	23378	d-1327	3b	21511	h-1427
2b	23284	d-1421	3b	21480	h-1458
3b	23243	d-1462	3	20071	h-2862
0	22705	h-233	2	20013	h-2920
3	22599	h-339	3	19962	h-2966
0	22534	h-404	...	.....	.....

$\Delta\nu$ : -233 (0), 338(3), 404(0), 428(2), 522(0), 670(3), 707(5dr), 770(1d), 834(0b), 923(1b), 956(3d), 1070(0), 1217(0b), 1251(0b), 1327(2b), 1424(3b), 1460(3b), 2575(10d), 2870(10b), 2925(8b), 2966(10b).

\* These lines appear to have components but owing to want of proper resolution exact measurements could not be made.

TABLE VI.  
Isoamyl mercaptan,  $(\text{CH}_3)_2\text{CHCH}_2\text{SH}$ .

I	$\nu$	$\Delta\nu$	I	$\nu$	$\Delta\nu$
5d	24815	a-2574	3	22514	h-424
2	24777	b-2577	5	22276	h-662
2	24456	a-2933	2d	22223	h-715
8	24426	a-2963	2dr	22197	h-741
...	.....	b-2928	10d	22127	d-2578
...	.....	d-279	...	.....	h-811
2	24392	b-2962	0	22081	h-857
1	24354	c-2935	0	22009	h-929
1	24286	d-419	2	21983	h-955
4	24049	d-656	2	21942	e-2574
0b	23983	d-722	0b	21899	h-1039
1dr	23964	d-741	10b*	21836	d-2869
1b	23887	d-818	7b*	21773	d-2932
1b	23852	d-853	10b*	21743	d-2962
...	.....	e-664	0b	21698	g-1297
0b	23668	d-1037	5b	21641	{ h-1297
0b	23591	d-1114	...	.....	{ e-2875
0dr	23520	d-1185	5b	21592	{ h-1346
1	23418	d-1287	...	.....	{ e-2924
1	23405	d-1300	4b	21555	e-2961
1dr	23377	d-1328	6do	21467	h-1471
4do	23237	d-1468	5	20067	{ h-2871
0	23220	h+282	...	.....	{ g-2928
5	22659	h-279	3	20014	h-2924
0	22556	g-429	5	19976	h-2962

$\Delta\nu$  :-279(5), 422(3b), 659(5), 719(2d), 741(2dr), 818(1b), 855(0), 929(0), 955(1), 1038(0b), 1114(0b), 1185(0b), 1287(1), 1300(1), 1337(2dr), 1470(6do), 2574(10d), 2870(10b), 2929(7b), 2962(10b).

\* All these lines appear to have a structure but as they are not properly resolved exact measurements could not be made.



TABLE VII.  
Phenyl mercaptan,  $C_6H_5SH$ .

I	$\nu$	$\Delta\nu$	I	$\nu$	$\Delta\nu$
0	24425	d-280	5d	22744	h-194
2b	24324	a-3065	2d	22656	h-282
...	.....	e-192	3	22523	h-415
2	24290	d-415	0	22419	f-620
...	.....	b-3064	0	22375	g-620
2	24235	c-3055	0	22339	h-599
...	.....	e-281	3	22319	h-619
0	24118	d-592	3	22243	h-695
2	24090	d-615	0b	22216	h-722
2	24010	d-695	7d	22136	d-2569
0b	23967	d-738	4d	22020	h-918
0	23820	e-696	0	21991	g-1004
2d	23786	d-919	...	.....	.....
...	.....	.....	10	21938	{h-1000
10a	23705	d-1000	...	.....	{e-2578
4a	23680	d-1025	4	21915	h-1023
0	23637	d-1068	0	21865	h-1073
3	23613	d-1092	3	21845	h-1093
3	23587	d-1118	3	21819	h-1119
2	23551	d-1154	2	21779	h-1159
...	.....	.....	1b	21760	d-2945
2	23516	e-1000	8d	21646	d-3054
0	23429	e-1087	7d	21567	h-1371
0	23402	e-1114	0d	21506	h-1430
0b	23347	d-1351	2	21462	e-3054
0b	23271	d-1434	0b	21415	g-1580
0b	23203	d-1502	...	.....	h-1523
7	23123	d-1582	5	21352	h-1586

$\Delta\nu$ : -194(5d), 282(2d), 415(3), 596(0), 618(3), 695(3), 730(0b), 918(4d), 1000(10), 1024(4), 1071(0), 1092(3), 1118(3), 1157(2), 1361(1d), 1432(0d), 1502(0b), 1584(5), 2573(7d), 2945(1b), 3059(8d).

3. *Discussion of Results.*

In the following table are given the Raman frequencies which are common to all the aliphatic mercaptans investigated in this paper. The figures in the brackets indicate their intensities.

TABLE VIII.

Substance.	$\Delta\nu$ .			
Methyl mercaptan ...	704 (10)	805 (1)	1059 (0)	2573 (10)
Ethyl ...	659 (10)	739 (0)	1054 (1)	2573 (10)
Propyl .. ...	652 (4)	730 (1)	1033 (2)	2575 (8)
Butyl .. ...	656 (6)	707 (0)	1049 (1)	2574 (10)
Isobutyl, .. ...	670 (3)	770 (1)	1070 (0)	2575 (10)
Isosmyl .. ...	659 (5)	741 (2)	1038 (0)	2574 (10)

It will be seen that there are four frequencies 704, 805, 1059 and 2573 which persist throughout the group. Evidently they

all arise from a common configuration  $S \begin{matrix} \diagup C \\ \diagdown H \end{matrix}$  present in them.<sup>1</sup>

On the view that  $\Delta\nu$  600 and 800 represent only one oscillation, (this point will be dealt with more fully in a later section), the total number of vibrational frequencies, namely, three, suggests clearly that the three atoms are arranged in the form of a bent model. In this connection we may mention that

$S \begin{matrix} \diagup H \\ \diagdown H \end{matrix}$  molecule is known to be highly polar<sup>2</sup> which indicates that

<sup>1</sup> Similar discussions have been given by Venkateswaran and Bhagavantam in a previous paper on alcohols in the same volume.

<sup>2</sup> See P. Debye "Polar Molecules," p. 40 (1929).

this molecule has a triangular arrangement. Since the mercaptans may be considered as derivatives of  $S \begin{matrix} \text{H} \\ \text{H} \end{matrix}$  this offers a further support to the above view regarding the arrangement of the configuration  $S \begin{matrix} \text{C} \\ \text{H} \end{matrix}$ . However, as we do not know the nature of the forces or the inclination of the bonds a precise theoretical treatment is not possible.

A consideration of methyl mercaptan, which is the simplest of the compounds investigated, throws however, some light on the nature of these oscillations. The spectrum of this compound is comparatively simple and shows Raman lines corresponding to  $\Delta\nu$  704, 805, 1059, 1425, 2573, 2871, 2932 and 2975 (See Table I). Of these, the lines at 1425, 2871, 2932 and 2975 may be definitely attributed to the presence of the CH group. Of the remaining frequencies  $\Delta\nu$ 2573 is the most important as it appears prominently in all the mercaptans and is not found in any other class of compounds investigated so far. Liquid hydrogen sulphide which has recently been investigated in this laboratory by Bhagavantam also shows this line prominently in the same position. One may therefore conclude that this frequency (2573) is characteristic of the SH group present in these compounds.

It is of interest to compare here the SH oscillation frequency with those characteristic of the CH, OH and NH groups. In conformity with the fact that hydrogen which is involved in these oscillations is the lightest atom all these frequencies are high. All of them give rise to broad bands. The case of CH group is particularly interesting as the band consists of various components ranging from 2800 to 3320. All these oscillation frequencies differ, however, entirely from that due to the SH group in one important aspect. While considerable variations are observed in the magnitude of the CH, OH, and NH oscillations as we pass from the simplest to

the more complex compounds containing these groups, there is no change at all in the value of the SH frequency in hydrogen sulphide and in the various aliphatic and aromatic mercaptans. Such a remarkable constancy (See Table VII) in the SH frequency is of fundamental significance. This difference in the nature of the SH oscillation as contrasted with the other oscillation frequencies mentioned above implies an essential difference in the manner of combination of the sulphur atom on the one hand and the group of carbon, oxygen and nitrogen atoms on the other. In addition to this it is also to be remembered that the sulphur atom is comparatively heavy and hence less liable to be influenced by the neighbouring groups.

In this connection it is interesting to compare the behaviour of the OH and SH oscillations in the early members. In water the presence of the OH group gives rise to a broad band at 3400 which is less intense and sharper in methyl alcohol and does not appear in the higher alcohols. Quite unlike this, the Raman frequency characteristic of the SH group which is prominent and sharp in hydrogen sulphide continues to appear with more or less the same intensity in methyl mercaptan and the higher members of the series, but is distinctly more diffuse.

The value of the frequency characteristic of the SH group may be calculated from the masses of these atoms and the strength of binding on the basis of the formula  $\nu = k \sqrt{\frac{A}{\mu}}$ .

Taking the thermochemical dissociation constant between sulphur and hydrogen as 75 K cal. per Mol. we get the value 2486 as compared with the observed value 2573.

Next in importance are the ones at  $\Delta\nu 704$  and 805. These frequencies appear although slightly shifted in position in all the mercaptans and evidently owe their origin to the presence of the SC group. Of the two  $\Delta\nu 704$  is very intense

and fairly sharp while  $\Delta\nu$  805 is comparatively less intense and much more diffuse. The values of these frequencies fall down to 659 and 739 in ethyl and 652 and 730 in propyl mercaptans, thus assuming more or less steady values in the higher members. Such a shift of these oscillations towards the longer wave length is very significant in that it indicates the influence of the heavier groups on them.

The appearance of such an additional and less prominent frequency characteristic of the CS oscillation is not easily understood. In this connection we may refer to the case of carbon disulphide. Here also we get two frequencies at 655 and 800, the first one being much sharper and more intense than the other. In view of the nonpolar nature of this liquid and the now accepted linear model for this molecule it is difficult to reconcile the appearance of these two frequencies so close together in the spectrum of CS<sub>2</sub>. Carbon dioxide which is also nonpolar and has a linear model presents similar difficulties. In a recent paper Bhagavantam<sup>1</sup> has discussed this question and has shown from polarisation measurements that all these Raman lines represent in reality only variants of one symmetrical or inactive oscillation. Similar conclusions have also been recently arrived at by Snow<sup>2</sup> for CO<sub>2</sub> and CS<sub>2</sub>. It is therefore not surprising that in the mercaptans we have a similar phenomenon and that the characteristic oscillation of the SC group consists of two frequencies, one of them being the principal one and the other subsidiary.

Another important feature of the oscillations due to the SC group may be noted here. In the mercaptans the sulphur and carbon atoms are attached with a single bond, whereas in carbon-disulphide they are obviously attached with a double bond. One should therefore expect that the characteristic oscillations due to these two different kinds of bindings would be widely different. In fact, changes

<sup>1</sup> S. Bhagavantam, *Ind. J. Phys.*, Vol. V, p. 59, 1930.

<sup>2</sup> C. P. Snow, *Proc. Roy. Soc.*, Vol. 128, p. 294, 1930.

in the nature of the linkage between a carbon atom and a carbon or other atom such as C—C, C=C, or C—C, and C—O or C=O etc. are known to produce large variations in the magnitude of the characteristic frequencies according as the bond between them is single, double or triple. Surprisingly, however, in the case of the oscillations of the SC group the nature of the linkage between the two atoms does not appear to influence to any great extent the magnitude of these frequencies. In other words, the chemical difference between the S—C and S=C groups is not accompanied by any appreciable difference in the oscillation frequencies of the two groups. We may here refer to the results obtained by Pal and Sen Gupta<sup>1</sup> who find that the frequency 756 which is presumably due to C=S bond in phenyl mustard oil does not differ appreciably from that of C—S bond in thiocyanates, namely, 741.

Coming to the other aliphatic mercaptans we find that in addition to the lines present in methyl mercaptan several new lines appear in the spectra of the higher members. In addition to the lines which may be attributed to the characteristic oscillation frequencies of the SH, CH and SC groups the spectra show a number of broad bands many of them being 5 to 8 A. U. wide. All these oscillations are ascribable to the carbon chain. The unusual width and diffuseness of these lines in the mercaptans as contrasted with similar C—C oscillations in the corresponding alcohols and hydrocarbons may presumably be referable to the influence of sulphur atom on these oscillations.

Of the oscillations common to the mercaptans it should be remarked that unlike the CS frequencies the change in the magnitude of  $\Delta\nu$  1059 is very small from methyl to ethyl mercaptans.

Of the many smaller frequencies which occur in the

<sup>1</sup> N. N. Pal and Sen Gupta, Ind. J. Phy., Vol. V, p. 13, 1930.

higher mercaptans the one at 332 is of interest. This is absent in methyl mercaptan but appears with large intensity in the other compounds. It shows some variations in its magnitude in the compounds investigated.

A remark regarding the difference in behaviour of the C—S and the analogous C—O oscillations may be made here. While the latter oscillation with a frequency of 1050 wave numbers appears strongly in methyl alcohol, but only very weakly in the higher alcohols the C—S oscillation continues to appear prominently in all the mercaptans.

The character of the CH band<sup>1</sup> in the various hydrocarbons has already been discussed in a previous paper. One observation regarding the relative intensities of the components of this band may be noted. The central component of this band is the most intense in methyl, ethyl and propyl, but is the weakest in isobutyl and isoamyl mercaptans. This feature appears to be of a general nature as a comparison of the CH band in other organic compounds also shows that the central component is usually the most intense in the normal compounds, but is the weakest in the isomers.

It may be mentioned that some of the components of the CH band with the liquids recorded in this paper were rather broad and apparently capable of further resolution. Under suitable conditions a doublet structure in some of them could be seen although exact measurements were not possible. Especially is this the case with propyl and the higher mercaptans.

Phenyl mercaptan is the only aromatic compound investigated in this paper and a few remarks may be made regarding its spectrum. The liquid shows strong absorption in the ultra-violet region beyond  $\lambda 4046$ . The most prominent frequency is the one at 1000, the CH and SH frequencies

<sup>1</sup> S. Venkateswaran and S. Bhagavantam, *Ind. J. Phys.*, Vol. V, p. 129, 1930.

coming next in order of intensity. The two frequencies at 2945 and 3059 of which the latter is more intense are both attributable to the CH group. A striking feature of the spectrum of this liquid is the presence in it of a number of doublets. Practically every benzene line is accompanied by a more or less bright line on the longer wave length side. The significance of such a splitting in benzene derivatives and its relation to a similar phenomenon in the electronic band spectra of these molecules have been pointed out in a recent paper by Venkateswaran and Bhagavantam.<sup>1</sup> In conformity with the observations made in this paper we find in phenyl mercaptan the appearance of a prominent new frequency at 1024 and the shifting of the 992 benzene frequency to 1000.

The spectrum of phenyl mercaptan shows several fairly intense small frequency shifts at 194, 282, and 415, of which the one at 194 is strikingly prominent. The appearance of such small frequency shifts may be understood when we remember that the benzene ring is subjected to a great strain owing to the loading of one end with a heavy sulphur atom.

<sup>1</sup> S. Venkateswaran and S. Bhagavantam, Proc. Roy Soc., Vol. 128, p. 252, 1930.



TABLE IX.

Ethyl mercaptan		Propyl mercaptan		Butyl mercaptan		Isosmyl mercaptan.	
$\lambda$ Ra	$\lambda$ i.r.	$\lambda$ Ra	$\lambda$ i.r.	$\lambda$ Ra	$\lambda$ i.r.	$\lambda$ Ra	$\lambda$ i.r.
30.0(2)		27.2(8)		33.6(4)		35.8(5)	
				30.0(0)			
				22.9(0)		23.7(8)	
15.17(10)		15.34(4)		15.24(6)		15.17(5)	
		14.39(1)		14.14(0)		13.91(2)	
13.53(0)		13.70(1)				13.50(4)	
	12.65(m)					12.22(1)	
			11.8(w)	11.86(0)	11.9(w)		11.9(w)
11.44(0)	11.6(s)	11.33(0)	11.4(w)	11.25(0)	11.4(w)	11.66(0)	11.5(w)
			10.8(w)			10.76(1)	10.8(m)
10.36(0)	10.34(s)	10.37(0)		10.52(1)	10.4(m)	10.47(1)	10.1(w)
9.49(1)		9.68(2)	9.8(w)	9.53(1)	9.7(w)	9.63(0)	9.8(w)
	9.25(s)				9.4(w)		9.4(s)
			8.9(s)	9.04(0)	9.0(s)	8.98(1)	9.0(m)
						8.44(1)	8.6(w)
7.92(1)	8.05(s)	7.70(1)	7.9(s)		8.0(s)	7.77(1)	8.0(s)
			7.6(s)	7.72(2)	7.7(s)	7.69(1)	7.7(s)
			7.2(m)	7.35(0)	7.3(m)	7.48(2)	7.2(s)
	7.2(s)						
6.90(3)	7.1(s)	6.94(2)	6.8(s)	6.95(3)	6.8(s)	6.80(5)	6.8(s)
	5.8(m)						6.4(s)
							6.0(s)
			4.9(w)		4.8(w)		5.0(s)
			4.6(w)		4.4(w)		4.1(w)
3.687(4)	4.0(s)	3.883(8)	3.8(s)	3.885(10)	3.8(s)	3.885(10)	3.8(s)
3.482(5)		3.479(4)		3.486(8)		3.484(10)	
3.409(10)	3.45(s)	3.418(8)		3.413(7)		3.414(7)	
				3.408(10)			
3.369(7)		3.372(5)	3.3(s)	3.374(6)	3.3(s)	3.372(10)	3.3(s)

The infra-red absorption spectra of ethyl, n-propyl and isoamyl mercaptans in the region 1 to 12  $\mu$  have been investigated, the first by Coblenz<sup>1</sup> and the other two by Bell.<sup>2</sup> The values obtained by them are tabulated for comparison with those shown by the Raman spectra (see Table VIII). The intensities of the infra-red absorption bands are represented by the letters *s*, *m*, and *w* indicating strong, medium and weak respectively. It will be seen that there is a fair agreement between the two sets of values. The value of the SH band obtained by Bell from infra-red absorption varies from 3.85  $\mu$  to 3.90  $\mu$  which is in good agreement with the value 3.88  $\mu$  shown by the Raman spectra. The value obtained by Coblenz for this band in ethyl mercaptan is somewhat large. It may be mentioned, however, that according to Coblenz the value obtained by Julius with this liquid is 3.88  $\mu$  which agrees surprisingly well with 3.883  $\mu$  shown by the Raman spectrum. The absorption spectra of some mercaptans in the near infra-red region have been investigated by Ellis<sup>3</sup> who finds a band at 1.99  $\mu$  to 2.0  $\mu$  characteristic of this class of compounds. He suggests that the 3.9  $\mu$  and 2.0  $\mu$  bands are probably the fundamental and the first overtone bands associated with the SH linkage.

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<sup>1</sup> W. W. Coblenz, "Investigations of Infra-red Spectra," Vol. I, Carnegie Institution, 1905.

<sup>2</sup> F. K. Bell, *Berichte*, 60 B, p. 1749, 1927.

Bell's values (unpublished) quoted by J. W. Ellis (*J. Amer. Chem. Soc.* Vol. I, p. 2116, 1929).

<sup>3</sup> J. W. Ellis, *loc. cit.*