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The Assignment of the Vibrational Spectra of Ethyl Mercaptan and the Ethyl Halides, and the Characterization of an SH Deformation Frequency*

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An assignment is given for all the fundamental modes of vibration of the ethyl mercaptan molecule from the observed vibrational spectra. By analogy the observed frequencies in the spectra of ethyl chloride, bromide, and iodide are also assigned to normal modes of vibration of these molecules.

Evidence is presented that one of the deformation modes of the SH linkage in mercaptans has a characteristic frequency lying between the limits of 800 and 900 cm^{-1}. This frequency is usually stronger in the Raman spectrum.

IN the course of an investigation of the infra-red spectra of an extensive series of organic molecules containing sulfur atoms, the infra-red spectrum of ethyl mercaptan has been obtained. This is a fairly small molecule whose vibrational spectra do not appear to have been analyzed, and it was decided to attempt this with a view to the identification of the normal modes of the ethyl group, and the characterization of the SH deformation frequency.

EXPERIMENTAL

The ethyl mercaptan used was a purified commercial sample (b.p. 36°C), contained in a gas cell with rocksalt windows. The infra-red spectrometer was a Hilger D 208 double-beam instrument used under standard conditions as described previously.[1] An absorption curve was obtained in close agreement with that published recently by Trotter and Thompson;[2] it is shown in Fig. 1. Our observed infra-red frequencies, together with the most recent Raman data as given by Wagner[3] and Kohlrausch,[4] are shown in Table I.

Both the infra-red and Raman spectra of ethyl mercaptan and of the ethyl halides are shown

schematically in Figs. 2 and 3. The infra-red data for these halides has been taken from the work of Cross and Daniels,[5] and the Raman data from Wagner's compilation.[6]

THE ASSIGNMENT OF THE ETHYL MERCAPTAN SPECTRA

It is clear that the maximum symmetry that this molecule could have would be a single plane of symmetry (point group C_s). This would occur if one of the CH bonds of the CH_3 group and the SH group were to lie in the plane defined by the carbon and sulfur atoms, or alternatively if both of these groups were in free rotation about the $C-C$ and $C-S$ bonds, respectively. The selection rules for this symmetry group allow all the normal modes of vibration to be active in the infra-red and Raman spectra.
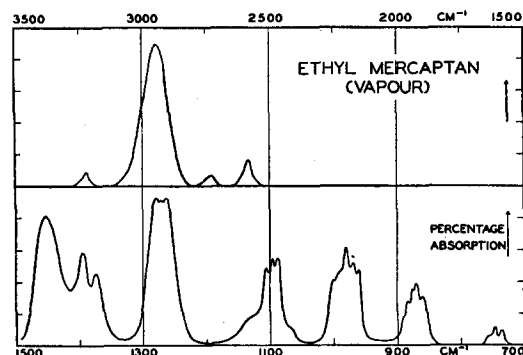
Ethyl mercaptan has nine atoms and hence 21

Fig. 1. The infra-red spectrum of ethyl mercaptan.

[1] N. Sheppard and G. B. B. M. Sutherland, J. Chem. Soc. 1540 (1947).
[2] I. F. Trotter and H. W. Thompson, J. Chem. Soc. 481 (1946).
[3] J. Wagner, Zeits. f. physik. Chemie B40, 439 (1938).
[4] K. W. F. Kohlrausch, "Ramanspektren," *Hand—und Jahrbuch der Chemischen Physik* (Akademische Verlagsgesellschaft, Leipzig, 1943), p. 239.
[5] P. C. Cross and F. Daniels, J. Chem. Phys. 12, 48 (1933).
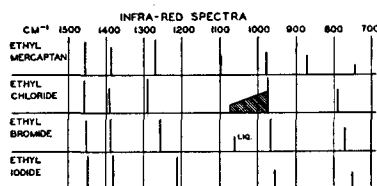[6] J. Wagner, Zeits. f. physik. Chemie B45, 69 (1939).

FIG. 2. The infra-red spectra of ethyl mercaptan and the ethyl halides.

normal modes of vibration. Of these, five will be C—H stretching modes which will occur in the region 2800–3050 cm^{-1}, and can be identified with the unresolved infra-red absorption and the Raman lines that lie in this region. Another will be the SH stretching mode which is well known (see reference 4, pp. 210–211) to correspond to the Raman and infra-red frequency at approximately 2575 cm^{-1}. This leaves fifteen modes to be identified, and as there are no multiple bonds present these will all lie below 1500 cm^{-1}. We can further account for the two asymmetrical CH$_3$ deformation modes and the CH$_2$ bending mode, as these are well known[7] to correspond to frequencies in the region 1400–1470 cm^{-1}. They can almost certainly be identified with the infra-red absorption between 1430 and 1480 cm^{-1}, which centers at 1453 cm^{-1}, and the broad Raman line centered at 1448 cm^{-1}. Thus we are left with twelve modes which should have frequencies below 1400 cm^{-1}. Two of these correspond to restricted rotations or torsional oscillations of the CH$_3$ and SH groups, and the remainder to stretching and deformation vibrations of the molecule. These modes of vibration can be described approximately in terms of group motions as follows: three CH$_2$ deformation modes (wagging, rocking, and twisting),[8] one CH$_3$ symmetrical deformation vibration, two CH$_3$ wagging modes (in and out of the CCS plane), one SH deformation mode, one C—C stretching mode, one C—S stretching mode, and one CCS skeletal bending mode. To correlate with these, we have ten frequencies which are probably fundamentals, viz., 1385, 1269, 1097, 1049, 978, 870, 838, 745, 660, 332 cm^{-1}. Where frequencies have been detected in both the Raman and infra-red spectra, the latter frequencies have usually been chosen,

as they correspond to measurements in the gaseous phase.

The Raman line at 332 cm^{-1} is certainly the skeletal bending mode in view of its low value, and that at 660 cm^{-1} is well known to be the C—S stretching mode (see Kohlrausch's[4] "Ramanspektren," p. 235). In addition, the strong line near 975 cm^{-1} in both the infra-red and Raman spectra is almost certainly the C—C stretching mode. This latter assignment is made on account of the magnitude of this frequency and its strength in the Raman spectrum. We have shown earlier that the CH$_2$ wagging and rocking modes in hydrocarbon molecules occur near 1300 and 750 cm^{-1}, respectively,[8] and on these grounds the

TABLE I. The observed frequencies in the infra-red and Raman spectra of ethyl mercaptan.

Infra-red frequency	Strength	Raman frequency[a]	Strength
		2966	Strong
2800–3050	Strong	2930	Strong
		2872	Strong
2730	V. weak	—	—
2580	Weak	2570	V. strong
1453	Strong	1448	Strong
1385	Strong	1374	Weak
1269	Strong	1265	Medium
1097	Medium	1092	Medium
—	—	1049	Medium
978	Medium	968	Strong
870	Medium	870	Weak
—	—	838	Weak
745	Weak	737	Weak
660[b]	Strong	657	V. strong
Not investigated		440	Weak
		332	Strong

[a] See references 3 and 4.
[b] See reference 2.

frequencies at 1269 and 745 cm^{-1} can very probably be assigned to these modes. The shifts of these frequencies from their normal positions in hydrocarbon molecules are very reasonable in view of the position of the CH$_2$ group next to the sulfur atom. Evidence will be presented below that the S—H deformation mode is to be identified with the Raman line at 838 cm^{-1}, and by analogy with many hydrocarbon molecules the frequency near 1385 cm^{-1} can be attributed to the symmetrical CH$_3$ deformation vibration. We are thus left with three frequencies at 1097, 1049, and 870 cm^{-1} to be assigned to the remaining CH$_2$ twisting and CH$_3$ wagging modes. Of these frequencies, the first and last are strong in the infrared spectrum, and the middle line occurs only in

[7] G. Herzberg, Infra-Red and Raman Spectra (D. Van Nostrand Company, Inc., New York, 1945), p. 195.
[8] N. Sheppard, J. Chem. Phys. 16, 690 (1948).

the Raman spectrum. In view of the fact that methyl wagging modes in other sulfur-containing molecules (e.g., methyl mercaptan[9] and dimethyl sulfide)[10] are strong in the infra-red spectrum, we tentatively assign the frequencies at 1097 and 870 cm^{-1} to the in-plane and out-of-plane CH_3 wagging modes, respectively, and hence the 1049-cm^{-1} line is probably the CH_2 twisting vibration. In support of the above assignment of the methyl wagging modes, is the fact that a similar in-plane wagging mode in the more symmetrical propane molecule has been identified at 1152 cm^{-1} in the infra-red spectrum, on the basis of band contour data.[11] Unfortunately, ethyl mercaptan is a very unsymmetrical molecule, and it is more difficult to predict the band contours in this case. However the 870-cm^{-1} infra-red line has a complex structure (see Fig. 1) which may arise from the multiple Q branches of a perpendicular band in agreement with the above assignment.

There appears to have been no polarization data published on the Raman spectrum of ethyl mercaptan, but such data have been published for the very closely related spectrum of ethyl chloride (see Fig. 3). In this spectrum lines at 335, 656, 968, and 1071 cm^{-1} are appreciably polarized, and it is probably a fair extension to expect that accordingly the corresponding Raman lines at 332, 657, 968, 1092 cm^{-1} in the ethyl mercaptan spectrum have similar qualitative polarizations. The assignment described above for the ethyl mercaptan molecule was originally made without the help of these data, but it can be seen to be in accordance with them, as all these frequencies have been assigned to modes of vibration symmetrical with respect to the CCS plane. The wagging motion of the CH_2 group is also symmetrical with respect to this plane and occurs at 1265 cm^{-1} in the Raman spectrum of ethyl mercaptan and at 1281 and 1248 cm^{-1}, respectively, in the Raman spectra of ethyl chloride and bromide. This line in the ethyl bromide spectrum is also polarized in accordance with the assignment.

The only modes of motion which have so far not been spectroscopically identified in the ethyl

mercaptan spectra are then the CH_3 and SH restricted rotations. However, it appears to be true that such modes are, in general, difficult to detect in these spectra. There is a weak line at 440 cm^{-1} which has not so far been assigned, but in view of its occurrence in the ethyl chloride spectrum also at 439 cm^{-1} it cannot be assigned to the SH torsional mode. It is possible that it may correspond to the methyl restricted rotation, but this appears to be a high value for such a mode. On the other hand, it can, like the other weak unassigned lines, be explained as a difference frequency.

THE IDENTIFICATION OF THE SH DEFORMATION FREQUENCY

The only previous assignment of an SH deformation frequency in mercaptan molecules seems to have been given in the analysis of the vibrational spectra of methyl mercaptan by Thompson and Skerrett.[9] A line at 805 cm^{-1} in the Raman spectrum of this molecule was identified as the SH deformation mode. An obvious first approach to the identification of the corresponding mode in the case of ethyl mercaptan was to look for a line near to the above frequency in the spectrum of this molecule, and which was not present in the very similar spectrum of ethyl chloride. Two lines at 838 and 870 cm^{-1} seemed to fulfil this condition. However, the fact that the latter occurred strongly in the infra-red spectrum also, whereas the former did not, suggested (by analogy with a similar behavior in the methyl mercaptan case) that the line at 838 cm^{-1} might be associated with this mode.

In view of the strong similarity between the Raman spectra of the methyl and ethyl mercaptans and chlorides, a comparison was likewise
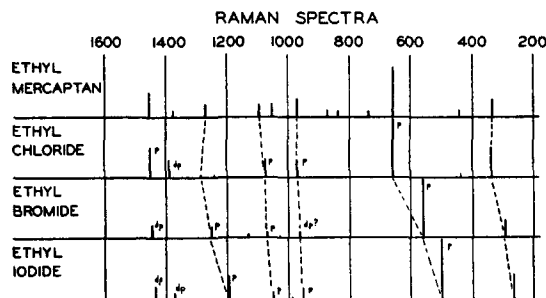
[9] H. W. Thompson and N. P. Skerrett, Trans. Faraday Soc. **36**, 812 (1940).
[10] H. W. Thompson, Trans. Faraday Soc. **37**, 38 (1941).
[11] V. L. Wu and E. F. Barker, J. Chem. Phys. **9**, 487 (1941).

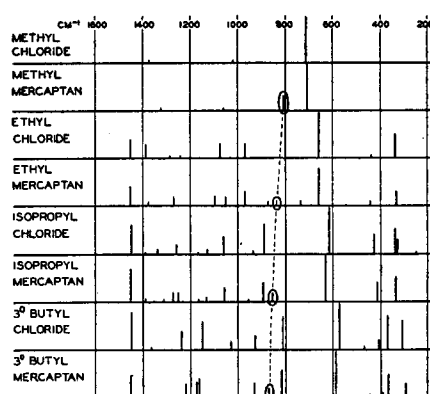FIG. 3. The Raman spectra of ethyl mercaptan and the ethyl halides.

FIG. 4. The Raman spectra of the methyl, ethyl, iso-propyl, and tertiary butyl mercaptans and chlorides. The circled lines are those assigned to the SH deformation frequency.

made between the Raman spectra of isopropyl and tertiary butyl mercaptans and chlorides (see reference 4, p. 240 *et seq.*) with a view to the picking out of extra lines in the mercaptan spectra that might correspond to SH frequencies. In Fig. 4 the Raman spectra of these various compounds are compared, and it can be seen that extra lines occur in the isopropyl and tertiary butyl mercaptan spectra at 856 and 866 cm^{-1}. These, together with the 805- and 838-cm^{-1} lines in the methyl and ethyl mercaptan spectra, are ringed in the figure and form a convincing series for assignment to the SH deformation mode. It is, of course, possible that in comparing the spectra of the chlorides and mercaptans extra lines should appear in the latter which are not caused by the extra SH group. However, it seems unlikely that an extra line should occur in approximately the same region with four structurally very different molecules if it were not due to this cause. We can conclude, therefore, that the deformation SH mode is to be expected to occur between the limits of 800 and 900 cm^{-1} in the Raman spectra of mercaptans. If it can be detected in the infra-red spectra it will probably be weak.

THE ASSIGNMENT OF THE SPECTRA OF THE OTHER ETHYL DERIVATIVES

The similarity between the Raman spectra of ethyl mercaptan and ethyl chloride has already been mentioned, and this extends to some extent also to the infra-red spectra. Thus many of the frequencies in the spectra of the chloride can be identified immediately by a direct comparison of the spectra, and the results of this are shown in Table II. There seems to be little doubt about the assignment of the frequencies in the case of the chloride except for the out-of-plane CH$_3$ wagging and CH$_2$ twisting modes. The former was strong in the infra-red spectrum of the mercaptan, but there is no corresponding absorption in the chloride spectrum and it seems likely that it may have shifted in position and has been lost in the strong absorption between 990 and 960 cm^{-1} caused by the C$-$C stretching mode. Clearly, no precise value can be given for this frequency, although a value near 960 cm^{-1} is suggested by the above reasoning. In the case of the CH$_2$ twisting mode there is no Raman line corresponding to the ethyl mercaptan frequency, but this has been tentatively assigned a value of 1030 cm^{-1} corresponding to an unidentified region of weak absorption stretching from 1000 to 1075 cm^{-1} in the infra-red spectrum of the chloride.

The spectra of ethyl bromide and ethyl iodide are also, on the whole, easily assigned by analogy with the ethyl chloride case. In carrying this out it has been assumed that changes in frequency will probably occur in progression in passing along the sequence chloride→bromide→iodide. As in the case of the chloride molecule, assignments for one of the CH$_3$ wagging and the CH$_2$ twisting vibration are more doubtful in all these molecules and have been made schematically by reference to the completely assigned mercaptan spectrum, but otherwise the spectra seem to be satisfactorily explained. The most recent attempted assignments of these molecules seem to

TABLE II. The assignment of the fundamental frequencies of ethyl mercaptan and the ethyl halides.

	C$_2$H$_5$SH	C$_2$H$_5$Cl	C$_2$H$_5$Br	C$_2$H$_5$I
CH$_3$ stretching	2966 (2) 2870	2966 (2) 2877	2980, 2960 2866	2965 (2) 2859
CH$_2$ stretching	2930 2870	2932 2877	2924 2866	2914 2859
CH$_3$ asymmetrical deformation	1450 (2)	1450 (2)	1440 (2)	1440 (2)
CH$_3$ symmetrical deformation	1385	1385	1385	1372
CH$_3$ wagging (in-plane)	1097	1071	1069	1049
CH$_3$ wagging (out-of-plane)	870	(960)	(960)	(960)
CH$_2$ bending	1450	1450	1440	1440
CH$_2$ wagging	1269	1290	1255	1210
CH$_2$ twisting	1049	1030	1027 (?)	985 (?)
CH$_2$ rocking	745	790	770	740
C$-$C stretching	978	968	960	955
C$-$X stretching	660	656	560	500
C⟍C⟋X bending	332	335	292	262
X$-$H stretching	2575	—	—	—
X$-$H deformation	838	—	—	—

have been made by Wagner,[6] and the present ones are in good agreement with his work, and in all cases extend his conclusions. Attempts have been made to deduce complete schematic assignments for the ethyl chloride molecule by Linnett[12] and Pitzer.[13] Our present results differ somewhat

from the results of these authors in the assignment of non-observed frequencies.

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[12] J. W. Linnett, Trans. Faraday Soc. 36, 527 (1940).
[13] J. Gordon and W. F. Giauque, J. Am. Chem. Soc. 70, 1506 (1948).

Raman Spectra of Polycrystalline Hydrocarbons at Low Temperatures. Rotational Isomerism. II*

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Making use of the low pressure, water-cooled Hg arcs as the source of nearly monochromatic radiation, a simple method was developed for the investigation of the Raman spectra of polycrystalline solids. The method was applied to the study of the first four normal paraffins. The Raman spectra of the solids between 600–1500 cm^{-1} are compared with those in the liquid phase. All these spectra undergo a marked simplification on solidification due to the disappearance of all but one of the rotational isomers. This process is shown to be discontinuous at the melting point.

IN the first paper[1] of this series we have calculated the energy difference of the rotational isomers of *n*-butane by measuring the relative intensity of "line pairs" as a function of temperature in the liquid range. Numerous considerations make it desirable to extend the investigation of the spectra of rotational isomers to the solid phase.

During the war work was done in Japan** on the Raman spectra of some hydrocarbons in the solid phase. These Japanese workers have reported that certain lines in the spectra disappear

in the solid phase. In the light of this work and our observed behavior of line intensity ratios as a function temperature,[1] it would seem to be of importance to investigate whether the intensity ratio of "line pairs" varies continuously or not when one proceeds from the liquid to the solid phase.

It is relatively easy to obtain the Raman spectra of solids if they can be prepared as homogeneous glasses or single crystals. The preparation of solid hydrocarbons in an optically homogeneous state can and has been accomplished by a number of investigators. However, preparation of such solid samples will require practically a special investigation for production of satisfactory solids for each molecule studied.

Crystal powder methods of obtaining Raman spectra have been brought to a state of more or less perfection by Kohlrausch[2] and his coworkers. More recently Cabannes[3] and his col-

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†† Now at U. S. Office of Naval Research, London, England.
[1] G. J. Szasz, N. Sheppard, and D. H. Rank, J. Chem. Phys. 16, 704 (1948).
** T. Shimanouchi and S. Midzushima, J. Chem. Soc. (Japan) 63, 1215 (1942); Chem. Abs. 41, 3332 (1947); Sci. Pap. Inst. Phys. Chem. Research (Tokyo) 40, 467 (1943), Chem. Abs. 41, 6089 (1947); M. Takeda, J. Chem. Soc. Japan 62, 896 (1941); Chem. Abs. 41, 5390 (1947); H. Okazaki, J. Chem. Soc. Japan 63, 1136 (1942); Chem. Abs. 41, 3740 (1947). Unfortunately, the complete papers have been inaccessible to us so far.

[2] K. W. F. Kohlrausch, *Ramanspektren* (Akad. Verlag., Leipzig, 1943), p. 49.
[3] J. Cabannes, R. Lennuier, and M. Harraud, Comptes Rendus 223, 301 (1946).