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The S–H Frequency of the Mercaptans

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The spectra of one aromatic and two aliphatic mercaptans have been studied in the region between 2.75μ and 4.25μ. In addition to the bands near 3.3μ arising from the carbon-hydrogen linkage, absorption maxima were observed at 3.85μ in benzyl mercaptan, at 3.83μ in *n*-propyl mercaptan, and at 3.80μ in *n*-butyl mercaptan. These bands are attributed to a vibration of the S—H group. The data obtained in the present study are compared with the existing Raman data and with the infra-red bands arising from the O—H group.

NUMEROUS studies of the spectra of organic compounds have shown that the vibrational frequencies of certain groups are approximately the same in all compounds. For example, the C—H and O—H groups give rise to bands near 3.3μ and 3.0μ, respectively. It has been of interest to determine the position of the band arising from the S—H groups in the mercaptans. Bell[1] measured the transmission of iso-amyl, *n*-butyl, and *n*-propyl mercaptan in the region between 1μ and 12μ and compared the spectra of these compounds with those of the corresponding sulphides. This author reported that the absorption of the mercaptans in the short wave-length region is similar to that of the amines, which he had investigated previously.[2] However, Ellis[3] was inclined to believe that the S—H group was responsible for a small absorption band near 3.8μ in the transmission curves published by Bell.[1] Ellis studied the spectra of the mercaptans in the region from 0.59μ to 2.8μ in the hope of observing harmonics of the 3.8μ band. A band observed at 1.99μ–2.00μ was identified as the first harmonic of the S—H frequency. The deviation from a simple multiple relationship is obvious. Since the 3.8μ band in Bell's curves is poorly resolved and its presence is indicated by only one or two points, it appeared desirable to make a more intensive study of the mercaptan absorption near 3.8μ. Accordingly, the transmission of benzyl, *n*-propyl, and *n*-butyl mercaptan has been determined in the region 2.75μ to 4.25μ. A rocksalt prism spectrometer with an amplifier was used in obtaining the present data.

The results are shown in Fig. 1. In each curve two bands appear. The bands at shorter wave-

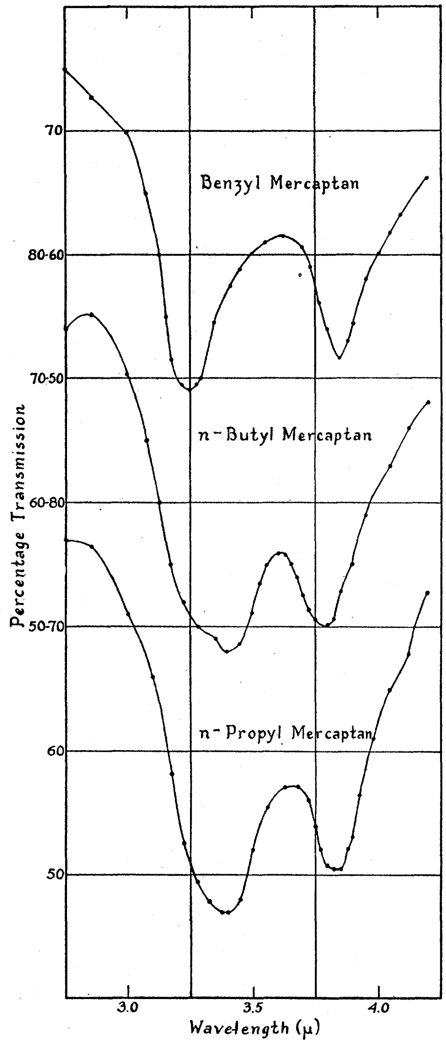

FIG. 1. The transmission of three mercaptans. Region: 2.75μ to 4.25μ. Cell thickness: 0.05 mm.

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[1] F. K. Bell, Berichte **60**, 1749 (1927).
[2] F. K. Bell, J. Am. Chem. Soc. **49**, 1837 (1927).
[3] J. W. Ellis, J. Am. Chem. Soc. **50**, 2113 (1928).

lengths arise from C—H vibrations and have maxima at 3.25μ in the aromatic mercaptan and near 3.4μ in the aliphatic compounds. The bands observed at longer wave-lengths are attributed to the S—H vibration. The positions of the minima are 3.85μ in benzyl mercaptan, 3.80μ in butyl mercaptan, and 3.83μ in *n*-propyl mercaptan. The S—H bands are apparently clearly resolved, but the exact positions of the observed minima are possibly affected slightly by the proximity of the intense C—H bands. The relative intensity of the C—H and S—H bands is different from that observed by Bell.[1] However, the total absorption is in approximate agreement with Bell's results, if differences in cell thickness are taken into consideration.

The differences between the infra-red bands of the mercaptans and those of the alcohols are striking. The O—H bands of the liquid alcohols are broad, while the S—H bands of the liquid mercaptans are sharp, resembling in shape the O—H bands observed in alcohol vapor. Errera[4] has suggested that the broadening and shift of the alcohol bands in the gas-to-liquid transition indicate a strong association between the O—H groups of neighboring molecules. If this interpretation is correct, the sharpness of the S—H band probably indicates the absence of a similar type of association in the mercaptans, a result in accord with chemical data. There is also a marked difference in the absorption coefficient. (See Table I.)

TABLE I. *Comparison of results with Raman data. The relative extinction coefficient in the last column is the ratio of the* SH *extinction coefficient to that of the corresponding* OH *compound.*

COMPOUND	S—H FREQUENCY (CM^{-1}) INFRA-RED	RAMAN*	RELATIVE EXTINCTION COEFFICIENT
Benzyl Mercaptan	2600	—	—
n-Butyl Mercaptan	2630	2574	0.08†
n-Propyl Mercaptan	2610	2575	0.12†

* Raman data: Venkateswaran (reference 5).
† Alcohol data: W. Weniger, Phys. Rev. **31**, 388 (1910).

A comparison of the present infra-red data with the Raman is rather interesting. The S—H vibration is strongly Raman-active[5] but produces a relatively weak infra-red band. The O—H vibration giving rise to intense infra-red absorption is so weakly Raman-active that an O—H line has been observed in only one alcohol (methyl).[6]

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[4] J. Errera and P. Mollett, Comptes rendus **204**, 259 (1937).

[5] S. Venkateswaran, Ind. J. Phys. **5**, 219 (1930).

[6] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (J. Springer, Berlin, 1931), p. 309. (Summary of Raman Work on alcohols.)