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Molecular Vibrations and Force Fields of Alkyl Sulfides. XI. C-S Stretching Vibrations of Some Simple Aliphatic Sulfides

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Synopsis. Infrared spectra of alkyl sulfides were measured. Some correlations of the C–S stretching frequencies to the molecular conformations were proposed.

For alkyl chlorides[1] and alkyl disulfides,[2] the correlations between the C–Cl or C–S stretching frequencies and the molecular conformations have been extensively discussed. In the case of alkyl sulfides, such a relation can also be expected. In the present note, therefore, the observed C–S stretching frequencies of the sulfides will be studied in relation to their molecular conformations.

The infrared spectra of the sulfides were measured in the liquid and solid states by means of a Perkin-Elmer Model 621 spectrophotometer. Table 1 shows the frequencies of the infrared bands, which may be due to the stable form in the solid state. The notations in this table, P_H, P_C, and S_{HH}, are the same as those used in the previous papers.[1,2] From this table we can find the frequency dependence upon the molecular conformations, similar to the C–Cl stretching frequencies of alkyl chlorides[1] and to the C–S stretching frequencies of alkyl disulfides.[2]

A characteristic CH_3–S stretching vibration is observed in the 690—750 cm^{-1} region. The C–S stretching vibrations due to the P_H and P_C conformations appear in the regions of 640—700 cm^{-1} and 710—750 cm^{-1} respectively. In the case of the secondary sulfides, the C–S stretching vibration due to the S_{HH} conformation lies in the 630—660 cm^{-1} region. Our observed frequencies on the alkyl sulfides, therefore, in general correspond very well to the C–Cl stretching frequencies of alkyl chlorides[1] and the C–S stretching frequencies of alkyl disulfides,[2] although we cannot make a straightforward comparison of them with each other, since we could not take into consideration the bands due to the rotational isomers. The CH_3–S stretching frequencies of the fulfides fit the CH_3–Cl stretching frequency of methyl chloride better than the CH_3–S stretching frequencies of alkyl disulfides. Detailed vibrational treatments including the rotational isomers of these sulfides are now in progress; the results will be reported elsewhwere in the near future.

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Table 1. Characteristic C–S stretching frequencies (cm^{-1}) of alkyl sulfides

Molecule	ν(CH_3-S)	ν(-CH_2-S)		ν(>CH-S)	Ref.
		P_H	P_C	S_{HH}	
C-S-C	744, 693				3
C-S-C_2	724	655			4
C-S-C_3	745		717		5
C-S-C_4	728		718		5
C_2-S-C_2		692, 656[a)]			6
C_2-S-C_3		646	739		5
C_2-S-C_4		657[a)]	731[b)]		5
C_3-S-C_3			721, 711		5
C_3-S-C_4			744, 734		5
C_4-S-C_4			742, 733		5
C-S-C_3^i	727			638	7
C_2-S-C_3^i		678[a)]		632[a)]	8
C_3-S-C_3^i			740[a)]	635[a)]	8
C_4-S-C_3^i			731	652	8
C_3^i-S-C_3^i				658,[a)] 655	8
	690—750	640—700	710—750	630—660	
Alkyl chlorides	732	645—690	720—730	605—640	1
Alkyl disulfides	680—700	630—670	700—750	590—640	2

a) Liquid-state bands. b) Average of the doublet-band.

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