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Molecular Vibrations and Force Fields of Alkyl Sulfides. X. Skeletal Bending Vibrations of Several Simple Aliphatic Sulfides

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Synopsis. The skeletal bending vibrations of several normal alkyl sulfides were analysed. It is found that a heterogeneous system as this case can also be explained in the same manner as a homogeneous system.

In recent years, the relations existing between molecular chain lengths and frequencies for the skeletal bending vibrations have been extensively examined on homogeneous oligomer-type molecules, *e.g.*, *n*-paraffines,1) $CH_3(CH_2)_nCONH_2$2) and $CH_3(CH_2)_n$-$COND_2$,2) and $CH_3O(CH_2CH_2O)_nCH_3$.3) On the other hand, Miyazawa *et al.*4) treated the relation between the skeletal bending and the phase-difference on such heterogeneous systems as normal alkyl ethers of the same length. The relationships between the frequency and the phase-difference may show a particular behavior, since alkyl sulfides contain a sulfur atom with a fairly large atomic mass in molecules.

In this experiment, we have tried to analyse the skeletal bending vibration by using the frequency-phase difference relation for such heterogeneous system as alkyl sulfides with different lengths.

Results and Discussion

We have recorded the infrared spectra in the liquid and solid states for methyl propyl (MeSPr), methyl butyl (MeSBu), ethyl propyl (EtSPr), ethyl butyl (EtSBu), and dipropyl (PrSPr) sulfides. The observed frequencies of dimethyl (MeSMe),5) methyl ethyl (MeSEt),6) diethyl (EtSEt)6) sulfides, MeSPr, MeSBu, EtSPr, EtSBu, and PrSPr used are those which may be due to the stable form in the solid state, judging on the basis of the normal coordinate treatment. All of the skeletal bending vibrations are infrared-active. Figure 1 shows the observed $\delta_{nk}=k\pi/(n+1)$ plots. The assignments of the k values are shown on the right-hand side, where $n=1$ corresponds to MeSMe, $n=2$ to MeSEt, $n=3$ to MeSPr or EtSEt, $n=4$ to MeSBu or EtSPr, and $n=5$ to EtSBu or PrSPr. The theoretical studies7) of polyethylene have revealed that the dispersion curve has a ν_{max} of *ca.* 550 cm^{-1} near the phase-difference of $\pi/3$. The plots of the sulfides shifted to a frequency lower region by *ca.* 100 cm^{-1} from that of polyethylene. However, the position of ν_{max} near $\pi/3$ and the shape of the dispersion of the sulfides correspond very well to those of the polyethylene curve. This suggests that the skeltal form in the solid state of the sulfides is the same as that of polyethylene. For the oxygen analogs,4) the bending vibrations observed are explained well by the theoretical curve of polyethylene. It is, therefore, likely that the effects of the sulfur atom and the methylene group on the vibrational spectra are very different from those of the oxygen atom and the methylene group on the vibrational spectra, since sulfur has a fairly large atomic mass.

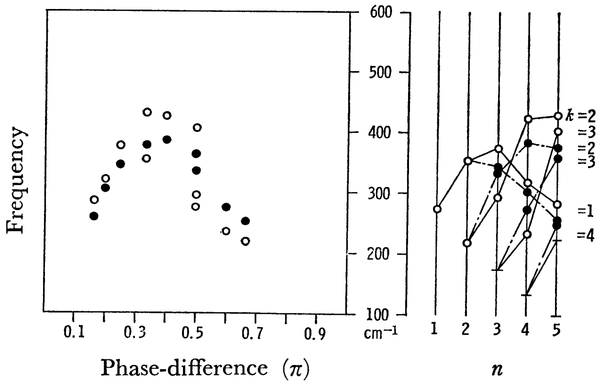

Fig. 1. Frequency-phase difference curve and assignments of k values for the skeletal bending vibrations. ○: MeSMe, MeSEt, MeSPr, MeSBu, EtSBu. ●: EtSEt, EtSPr, PrSPr. —: Calculated.

The skeletal bending vibrations mainly consist of three vibrational modes,—CCC, SCC, and CSC binding, strongly coupled with each other. The bands appearing from the pair of sulfides of the same length are fairly different in frequency, although the regularity is nearly the same in both filled and open circles. These differences arise from the effects of the heavy sulfur atom. Consequently, in the present case it is not simple to explain the relation existing between the chain lengths and the frequencies, but in general it is possible to analyse the band progression in nearly the same manner as in the case of the homogeneous system; rather disperse plots are obtained, though.

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References

1) R. F. Schaufele and T. Shimanouchi, *J. Chem. Phys.*, **47**, 3605 (1967).

2) K. Machida, S. Kojima, and T. Uno, *Spectrochim. Acta*, **28A**, 235 (1972).

3) H. Matsuura, T. Miyazawa, and K. Machida, *ibid.*, **29A**, 771 (1973).

4) K. Kusaki, T. Kitagawa, and T. Miyazawa, Preprints of the 28th Annual Meeting of the Chemical Society of Japan, Vol. **1**, p. 340 (1973).

5) Y. Shiro, M. Ohsaku, M. Hayashi, and H. Murata, This Bulletin, **43**, 609 (1970); M. Ohsaku, Y. Shiro, and H. Murata, *ibid.*, **45**, 113 (1972).

6) M. Ohsaku, Y. Shiro, and H. Murata, *ibid.*, **45**, 954 and 956 (1972); *ibid.*, **46**, 1399 (1973).

7) M. Tasumi and S. Krimm, *J. Chem. Phys.*, **46**, 755 (1967); L. Piseri and G. Zerbi, *ibid.*, **48**, 3561 (1968).