Vibration Spectra and Rotational Isomerism of Chain Molecules. III.[1] Ethyl Methyl Sulfide and Deuterium Compounds

Masaaki SAKAKIBARA, Hiroatsu MATSUURA, Issei HARADA, and Takehiko SHIMANOUCHI
Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received July 26, 1976)

The Raman spectra of ethyl methyl sulfide and its three deuterated compounds $CD_3SC_2H_5$, $CH_3SCH_2CD_3$, and $CH_3SC_2D_5$ were measured for the liquid and crystalline states. The Raman spectra of the undeuterated species in the gaseous state were measured at different temperatures. The normal vibration frequencies were calculated by using a consistent set of force constants for aliphatic sulfides. The combination of the spectral observations of the deuterated compounds and the normal vibration calculations showed that only the *gauche* form exists in the crystalline state and the *trans* and *gauche* forms coexist in the liquid and gaseous states. The enthalpy difference between the *gauche* and *trans* forms in the gaseous state, ΔH_{G-T}, was obtained as -30 ± 50 cal/mol.

Ethyl methyl sulfide is the simplest sulfide with one internal rotation axis associated with the rotational isomerism. It has long been accepted that this molecule takes the *trans* form in the crystalline state and the *trans* and *gauche* forms in the liquid and gaseous states, although some ambiguities have been left out.[2]

Recently, Nogami *et al.*[3] compared the spectra of ethyl methyl sulfide with those of related molecules and reached the conclusion that the crystalline ethyl methyl sulfide takes the *gauche* form but not the *trans* form as had been thought.

In the series of studies to establish the intramolecular force field as well as to clarify the existing rotational isomers of chain molecules,[1,4—6] we have investigated the Raman spectra of ethyl methyl sulfide and its deuterium compounds of $CD_3SC_2H_5$, $CH_3SCH_2CD_3$, and $CH_3SC_2D_5$ and determined the rotational isomerism and vibrational assignments for these molecules. The temperature dependence of the Raman spectra of the undeuterated species in the gaseous state has also been examined. The results are reported in the present paper.

Experimental and Calculation

The deuterium compounds were prepared from sodium salts of appropriate thiols and deuterium compounds of methyl iodide or ethyl bromide and the undeuterated compound was purchased from Tokyo Kasei Kogyo Co., Ltd. All of the samples were purified by fractional distillations. The Raman spectra were recorded on a JEOL JRS-400D spectrometer. The Raman spectra in the gaseous state were measured at five different temperatures between 21 and 112 °C. Temperature measurements of the vapor in the laser beam were made by using nitrogen gas as a thermometer.[7]

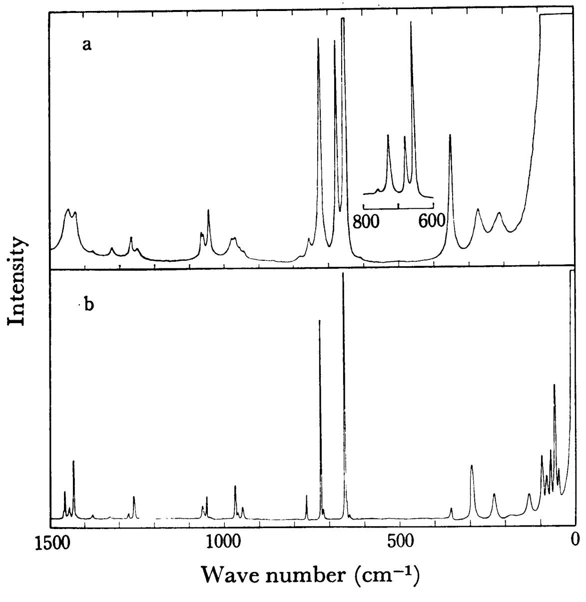

Fig. 1. Raman spectra of $CH_3SC_2H_5$.
a: Liquid, b: crystal.

The Raman spectra in the liquid and crystalline states in the region below 1500 cm^{-1} are shown in Figs. 1—4. The Raman spectra and the calculated frequencies in the 400—150 cm^{-1} region are compared in Fig. 5.* The gaseous-state Raman spectrum of the undeuterated species is shown in Fig. 6. The

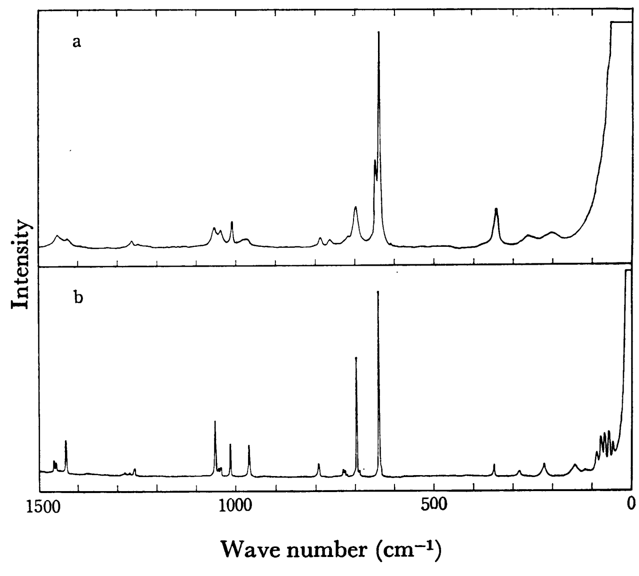

Fig. 2. Raman spectra of $CD_3SC_2H_5$.
a: Liquid, b: crystal.

---

* The relative intensities of the low-frequency bands (below 400 cm^{-1}) in the crystalline-state spectra are often found to vary depending on the condition of solidification (compare Figs. 1—4 and 5). It is certain that only one isomer exists in the crystalline state as is evident from the complete disapperance of some of the bands in the CS stretching vibration region. One possible explanation of the above observations is that the sample is composed of partially oriented crystallites and gives different intensity patterns due to the different orientation with respect to the polarization direction of the incident light.

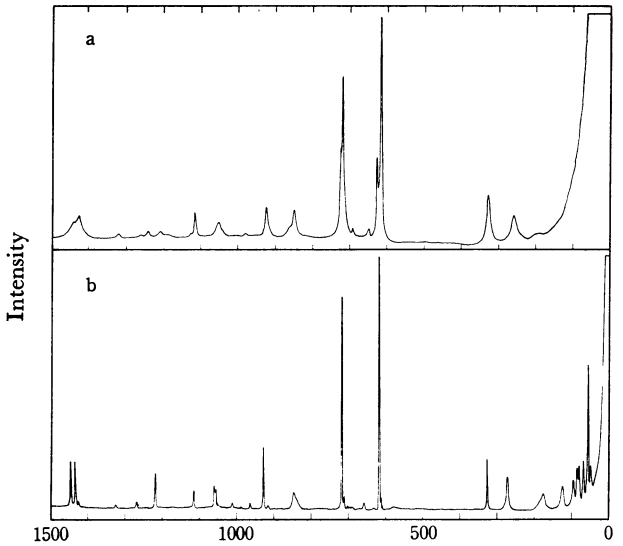

Fig. 3. Raman spectra of $CH_3SCH_2CD_3$.
a: Liquid, b: crystal.

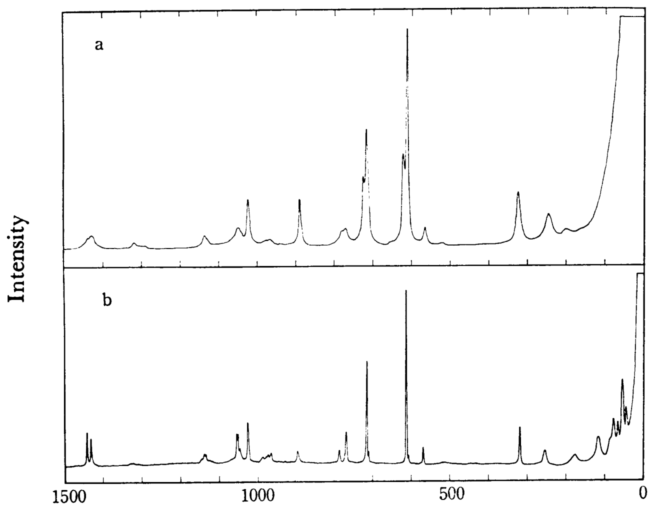

Fig. 4. Raman spectra of $CH_3SC_2D_5$.
a: Liquid, b: crystal.

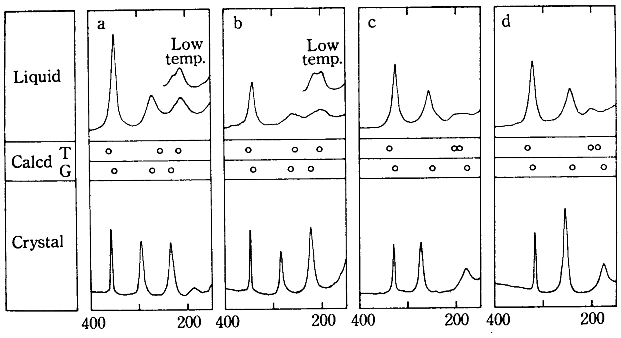

Fig. 5. Raman spectra and calculated frequencies in the 400—150 cm⁻¹ region.
a: $CH_3SC_2H_5$, b: $CD_3SC_2H_5$, c: $CH_3SCH_2CD_3$, d: $CH_3SC_2D_5$.

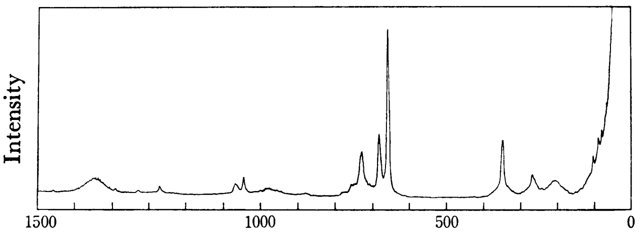

Fig. 6. Raman spectrum of $CH_3SC_2H_5$ in the gaseous state (120 Torr).

Table 1. Observed Raman frequencies and vibrational assignments of $CH_3SC_2H_5$

Observed Raman frequency (cm⁻¹)[a]		Assignment[b]
Liquid	Crystal	
	1461 VW, sh	CH_3 ip-d-deform
1455 VW, sh	1457 VW	CH_3 op-d-deform
1444 VW	1444 VW	CH_3 ip-d-deform
1427 VW	1431 VW	CH_3 op-d-deform, CH_2 scis
1377 VW	1376 VW	CH_3 s-deform
1320 VW	1326 VW	CH_3 s-deform
1267 VW	1272 VW	CH_2 wag
1251 VW	1257 VW	CH_2 twist
1065 VW		CH_3 ip-rock (T)
1060 VW, sh	1060 VW	CH_3 ip-rock (G)
1044 VW	1049 VW	CH_3 op-rock (G, T)
982 VW		CC stretch (T)
973 VW	968 VW	CC stretch (G)
960 VW, sh	962 VW	CH_3 ip-rock (G, T)
955 VW, sh		CH_3 op-rock (T)
948 VW, sh	948 VW	CH_3 op-rock (G)
785 VW		CH_2 rock (T)
758 VW	764 VW	CH_2 rock (G)
725 M	723 S 717 VW	CH_3-S stretch (G, T)
678 M		S-CH_2 stretch (T)
653 VS	656 VS 651 VW	S-CH_2 stretch (G)
353 W	355 VW	SCC deform, CSC bend (G, T)
273 VW	294 W	CSC bend, CC torsion (G), CC torsion (T)
232 VW, sh	232 VW	CC torsion, CSC bend (G)
211 VW		CSC bend, SCC deform (T)
	184 VW	Torsions (G) and lattice vibrations
	133 VW	
	95 W	
	83 VW	
	71 W	
	59 M	
	47 VW	

a) VS: very strong, S: strong, M: medium, W: weak, VW: very weak, sh: shoulder. b) For the notation and definition of the local symmetry coordinates, see Ref. 8.

TABLE 2. OBSERVED RAMAN FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF $CD_3SC_2H_5$

Observed Raman frequency (cm^{-1})a)		Assignmentb)
Liquid	Crystal	
	1462 VW	CH_3 ip-d-deform
1454 VW	1457 VW	CH_3 op-d-deform
1426 VW	1431 VW	CH_2 scis
1378 VW	1376 VW	CH_3 s-deform
1278 VW	1282 VW	CH_2 wag
1266 VW	1268 VW	CH_2 twist
1063 VW, sh		CH_3 ip-rock (T)
1056 VW	1056 VW, sh	CH_3 ip-rock (G)
1049 VW, sh	1052 W	CD_3 ip-d-deform (G, T)
1040 VW	1042 VW	CD_3 op-d-deform (G, T)
	1038 VW	CD_3 s-deform (G), CH_3 op-rock (T)
1013 VW	1014 VW	CH_3 op-rock (G), CD_3 s-deform (T)
983 VW		CC stretch (T)
971 VW	968 VW	CC stretch (G)
789 VW	793 VW	CH_2 rock (G, T)
761 VW		CD_3 ip-rock (T)
728 VW, sh	731 VW	CD_3 ip-rock (G)
720 VW	726 VW	CD_3 op-rock (G, T)
698 W	698 M	CD_3–S stretch (G, T)
648 M		S–CH_2 stretch (T)
639 VS	641 VS	S–CH_2 stretch (G)
345 VW	349 VW	SCC deform, CSC bend (G, T)
263 VW	285 VW	CC torsion, CSC bend (G), CC torsion (T)
215 VW, sh	221 VW	CSC bend, CC torsion (G)
200 VW		CSC bend, SCC deform (T)
	142 VW 116 VW 88 VW 77 VW 68 VW 57 VW 46 VW	Torsions (G) and lattice vibrations

a), b) See a and b, respectively, of Table 1.

TABLE 3. OBSERVED RAMAN FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF $CH_3SCH_2CD_3$

Observed Raman frequency (cm^{-1})a)		Assignmentb)
Liquid	Crystal	
1444 VW	1446 VW	CH_3 ip-d-deform
1432 VW	1431 VW	CH_3 op-d-deform
1425 VW	1425 VW	CH_2 scis
1321 VW	1326 VW	CH_3 s-deform
1263 VW	1269 VW	CH_2 wag (G)
1244 VW		CH_2 wag (T)
1210 VW	1219 VW	CH_2 twist (G, T)
1127 VW		CD_3 s-deform (T)
1115 VW	1115 VW	CD_3 s-deform (G)
	1060 VW	CD_3 ip-d-deform (G)
1052 VW	1054 VW	CD_3 op-d-deform (G, T), CD_3 ip-d-deform (T)
985 VW	988 VW	CH_3 ip-rock (G)
955 VW	963 VW	CH_3 op-rock (G, T), CH_3 ip-rock (T), CH_2 rock (T)
932 VW, sh		CC stretch (T)
924 VW	928 W	CH_2 rock (G)
917 VW, sh	915 VW	CC stretch (G)
863 VW, sh		CD_3 ip-rock (T)
851 VW	848 VW	CD_3 ip-rock (G)
724 M, sh		CH_3–S stretch (T)
719 S	719 S 712 VW	CH_3–S stretch (G)
692 VW		Origin unknown
651 VW	657 VW	CD_3 op-rock (G, T)
628 M		S–CH_2 stretch (T)
617 VS	618 VS	S–CH_2 stretch (G)
329 W	327 W	CSC bend, SCC deform (G, T)
258 VW	272 VW	CSC bend, SCC deform (G)
200 VW		CSC bend, SCC deform (T), CC torsion (T)
	176 VW	CC torsion (G)
	125 VW 95 VW 85 VW 80 VW 67 VW 56 M 48 VW	Torsions (G) and lattice vibrations

a), b) See a and b, respectively, of Table 1.

observed frequencies and assignments on the basis of the calculated potential-energy distributions are listed in Tables 1—4.

The normal vibration frequencies were calculated by using a consistent set of force constants for aliphatic sulfides.5) Detailed results of the calculations and the force constants are reported in a separate paper.6)

Results and Discussion

Spectra below 400 cm^{-1} and Rotational Isomerism. In the frequency region below 400 cm^{-1}, five normal vibrations are expected for each isotopic species, two skeletal deformation (bending) and three torsional vibrations. As seen from Fig. 5, the frequencies calculated for the *trans* and *gauche* forms of $CH_3SC_2H_5$ or $CD_3SC_2H_5$ are not much different from each other. On the other hand, $CH_3SCH_2CD_3$ and $CH_3SC_2D_5$ give the frequencies which are distinctly different between the two forms. The comparison between the observed and calculated frequencies of these isotopic species shows clearly that the crystalline-state spectra are explained only by the *gauche* form and the liquid-state spectra by the *trans* and *gauche* forms. Thus, the Raman spectra of the deuterium compounds are found to be important in studying the rotational isomerism of ethyl methyl sulfide.

As shown in Tables 1—4, the SCC deformation and CSC bending modes are highly coupled in all of the isotopic species. Such vibrational couplings are known to yield conformation-sensitive frequencies. However, the frequencies of the *trans* and *gauche* forms of $CH_3SC_2H_5$ or $CD_3SC_2H_5$ resemble each other (Fig. 5). This is explained by a further coupling of the CSC bending

Table 4. Observed Raman frequencies and vibrational assignments of $CH_3SC_2D_5$

Observed Raman frequency (cm^{-1})[a]		Assignment[b]
Liquid	Crystal	
1442 VW, sh	1442 VW	CH_3 ip-d-deform
1430 VW	1431 VW	CH_3 op-d-deform
1320 VW	1325 VW	CH_3 s-deform
1140 VW, sh		CC stretch (T)
1138 VW	1135 VW	CC stretch (G)
1067 VW, sh	1067 VW, sh	CD_2 scis (G, T)
1050 VW	1055 VW 1052 VW	CD_3 op-d-deform (G, T)
1044 VW	1046 VW	CD_3 ip-d-deform (G, T)
1025 VW	1025 VW	CD_3 s-deform (G, T)
978 VW	982 VW	CH_3 ip-rock (G)
968 VW	975 VW 970 VW	CH_3 op-rock (G), CH_3 ip-rock (T)
960 VW, sh	962 VW	CD_3 op-rock (G, T), CH_3 op-rock (T)
887 W	894 VW	CD_3 ip-rock (G, T)
786 VW, sh	786 VW	CD_2 twist (G, T)
770 VW	767 VW	CD_2 wag (G, T)
723 W		CH_3–S stretch (T)
716 M	714 S 711 VW	CH_3–S stretch (G)
622 M		S–CD_2 stretch (T)
612 VS	613 VS 607 VW	S–CD_2 stretch (G)
564 VW	569 VW	CD_2 rock (G)
322 W	319 W	CSC bend, SCC deform (G, T)
244 VW	254 VW	CSC bend, SCC deform(G)
200 VW		CSC bend, SCC deform (T), CC torsion (T)
	178 VW	CC torsion (G)
	117 VW	
	85 VW, sh	Torsions (G) and lattice vibrations
	78 W	
	66 VW	
	55 M	
	45 VW	

a), b) See a and b, respectively, of Table 1.

mode with the CH_2–CH_3 torsional mode in the *gauche* form of these isotopic species. This coupling is removed, however, in $CH_3SCH_2CD_3$ or $CH_3SC_2D_5$ owing to the downward frequency shift of the CH_2–CD_3 or CD_2–CD_3 torsional vibration.

The calculated frequencies of the CH_3–S torsion (160—150 cm^{-1}), the CD_3–S torsion (120—110 cm^{-1}) and the S–CH_2 or S–CD_2 torsion (lower than 100 cm^{-1}) do not differ between the *trans* and *gauche* forms.

It is noted for all of the isotopic species that the Raman band at 270—250 cm^{-1} shifts appreciably to higher frequency in going from the liquid to the crystalline state. The magnitude of the shift is larger for the vibration with a larger contribution from the C–C torsional mode. This large difference between the frequencies of the two states have led previously to misinterpretation of the spectra.[2b] The shifting of this band is confirmed in the present study by observing the Raman spectra of the liquid state at several low temperatures; namely the observed frequency is higher at lower temperature and approaches the crystalline-state value. It is also noted that the *gauche* bands of $CH_3SC_2H_5$ at 232 cm^{-1} and of $CD_3SC_2H_5$ at 215 cm^{-1} are clearly resolved in the low-temperature spectra (Fig. 5).

Sectra in Higher-Frequency Regions. In the 800—600 cm^{-1} region, the bands due to the C–S stretching, CH_2 rocking and CD_3 rocking vibrations are expected. The C–S stretching vibration is known to give rise to much stronger Raman bands than the rocking vibrations.

In the crystalline state, all of the isotopic species exhibit two strong Raman bands separated by 70—100 cm^{-1} (Figs. 1—4). The results of the normal coordinate treatment indicate that the higher-frequency band is assigned to the CH_3–S (CD_3–S) stretching vibration and the lower-frequency band to the S–CH_2 (S–CD_2) stretching vibration, respectively, of the *gauche* isomer.

The 678 cm^{-1} Raman band of liquid $CH_3SC_2H_5$ which disappears on crystallization is assigned to the S–CH_2 stretching vibration of the *trans* isomer. On the other hand, the CH_3–S stretching vibration of the *trans* form has been considered to overlap with the *gauche* band at 725 cm^{-1}.[3] This assignment is confirmed by the present experimental observation that the corresponding bands for $CH_3SCH_2CD_3$ and $CH_3SC_2D_5$ are split into two components in the liquid state. It is seen from the observed spectra of the various isotopic species that the C–S stretching frequencies of the *trans* form are slightly higher than those of the *gauche* form.

The vibrational assignments in other frequency regions have also been established in this study on the basis of the systematic treatment of normal coordinates (see Tables 1—4). The observed Raman frequencies of the deuterated species were found to be important in determining the force field of aliphatic sulfides.[5]

Enthalpy Difference in the Gaseous State. The enthalpy difference between the *gauche* and *trans* forms in the gaseous state, ΔH_{G-T}, has been determined to be -30 ± 50 cal/mol through the analysis of the temperature dependence of the intensities of the band pairs at 682 (*trans*) and 657 cm^{-1} (*gauche*) of the undeuterated species. It is of interest to compare the ΔH_{G-T} values of butane, ethyl methyl ether, and ethyl methyl sulfide. They are 966 ± 54,[7] 1500 ± 200,[9] and -30 ± 50 cal/mol, respectively. The differences in the bond nature of CC–XC (X=C, O, S) groups, as is evident from the above values of enthalpy difference together with those of XC–CY (Y=C, O, S) groups, yield a variety of the structures and properties of longer chain molecules.

References

1) Part II: I. Harada, H. Takeuchi, M. Sakakibara, H. Matsuura, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 102 (1977).

2) a) D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, G. Waddington, and H. M. Huffman, *J. Am. Chem. Soc.*, **73**, 261 (1951); b) M. Hayashi, *Nippon Kagaku Zasshi*, **77**, 1692 (1956); **78**, 627 (1957); M. Hayashi, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **26**, 608 (1957); c) D. W. Scott and M. Z. El-Sabban, *J. Mol. Spectrosc.*, **30**, 317 (1969); d) M. Ohsaku, Y. Shiro, and

H. Murata, *Bull. Chem. Soc. Jpn.*, **45**, 954 (1972); **46**, 1399 (1973).

3) N. Nogami, H. Sugeta, and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **48**, 3573 (1975).

4) T. Shimanouchi, Y. Ogawa, M. Ohta, H. Matsuura, and I. Harada, *Bull. Chem. Soc. Jpn.*, **49**, 2999 (1976).

5) M. Ohta, Y. Ogawa, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, in press.

6) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, *J. Phys. Chem. Ref. Data*, to be published.

7) A. L. Verma, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **60**, 1540 (1974).

8) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies," Consolidated Vol. 1, U. S. Govt. Printing Office, No. C13.48: 39 (1972).

9) T. Kitagawa and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **41**, 1976 (1968).