BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 954—956(1972)

Molecular Vibrations and Force Fields of Alkyl Sulfides. III. Infrared Spectra of Methyl Ethyl Sulfide

Masaru OHSAKU, Yuji SHIRO,* and Hiromu MURATA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

**Shinonome Branch School, Faculty of Education, Hiroshima University, Shinonome-3-chome, Hiroshima*

(Received August 26, 1971)

The vibrational spectra of methyl ethyl sulfide have been extensively examined by several authors.[1-6] The rotational isomerism, C_s (T) and C_1 (G), has also been discussed.[2-5] Lately, Scott *et al.*[6] carried out a normal coordinate treatment using the valence force field. In the previous papers, however, the assignments of the observed bands were not consistent with each other, and in the C–H stretching, CH_3 degenerate deformation, CH_2 bending, and CH_3 rocking regions, the spectra were not well-resolved. In order to obtain the complete infrared data, we have newly recorded the infrared spectra of methyl ethyl sulfide in the gaseous, liquid, and solid states; on the basis of our results, we have then revised a few of the previous assignments. The vibrational data thus obtained will be used in a normal coordinate treatment of methyl ethyl sulfide.

Results and Discussion

The infrared data obtained and the consequent assignments of methyl ethyl sulfide are summarized in Table 1. The C–H stretching, CH_3 degenerate deformation, CH_2 bending, and CH_3 rocking regions are well-resolved in the unannealed or the annealed spectra. In the C–H stretching region, 3000—2800 cm^{-1}, we observed six and ten bands in the liquid and solid states respectively. Among these bands, the overtone bands of the CH_3 degenerate deformation vibrations may be confused. They are hardly distinguishable from each other. In the region around 1300 cm^{-1} two weak bands remain in the annealed spectra (1319 and 1305 cm^{-1}). The band at 1319 cm^{-1} may be assigned to the fundamental with reference to the data of dimethyl sulfide.[7] Scott *et al.*[2] assigned the band at 1305 cm^{-1} to the CH_2 wagging band. We consider this band to be too high to identify as the CH_2 wagging fundamental. The band at 1305 cm^{-1} may be due to the overtone or to the sum-combination. In the CH_2 wagging and twisting regions, some bands disappeared in the solid state. These bands may be

1) D. H. Rank, E. R. Shull, and D. W. E. Axford, *J. Chem. Phys.*, **18**, 392 (1950).
2) D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, G. Waddington, and H. M. Huffman, *J. Amer. Chem. Soc.*, **73**, 261 (1951).
3) M. Hayashi, *Nippon Kagaku Zasshi*, **77**, 1692 (1956).
4) M. Hayashi, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **26**, 608 (1957).
5) M. Hayashi, *Nippon Kagaku Zasshi*, **78**, 627 (1957).
6) D. W. Scott and M. Z. El-Sabban, *J. Mol. Spectrosc.*, **30**, 317 (1969).
7) M. Ohsaku, Y. Shiro, and H. Murata, This Bulletin, **45**, 113 (1972).

TABLE 1. INFRARED FREQUENCIES (cm^{-1}) AND ASSIGNMENTS OF METHYL ETHYL SULFIDE[a)]

Gaseous Room temp.	Liquid Room temp.	CS_2 soln	Liquid Low temp.	Solid Annealed	Assignment[b)]
2987 sh, vs 2983 vvs 2977 sh, vs				2985 sh, w	ν_{C-H}
2965 sh, vs			2964 vs	2965 vs	ν_{C-H}
2946 sh, vs				2957 s	ν_{C-H}
2940 vs				2950 sh, s	ν_{C-H}
2925 vs			2926 sh, s	2926 s	ν_{C-H}
2910 sh, s			2915 vs	2915 vs	ν_{C-H}
2896 2888 s 2880				2874 sh, m	ν_{C-H}
2860 s			2868 s	2866 s	
2845 m			2855 sh, s	2855 sh, w	
2830 m			2833 m	2834 m	
1465 m			1465 sh, w	1463 s	$\delta^d_{CH_3}$
1454 s			1457 sh, m	1456 s	$\delta^d_{CH_3}$
1448 s			1448 vs	1444 s	$\delta^d_{CH_3}$
1436 s			1436 vs	1430 s	$\delta^d_{CH_3}$
1427 sh, m			1427 vs	1422 m	$\delta^b_{CH_3}$
1420 sh, w			1420 sh, s	—	
1405 vvw				1405 vw	
1392 1381 w 1374		1375 s	1374 s	1375 s	$\delta^s_{CH_3}$
1335 1327 vw 1320		1319 m	1319 w	1319 w	$\delta^s_{CH_3}$
		1305 w	1305 vw	1305 w	
		1278 sh, w	1278 sh, m	—	
1279 1270 vs 1261		1263 vs	1264 vs	1270 s	$\delta^w_{CH_3}$
1249 sh, w		1249 sh, m	1249 sh, m	1255 s	$\delta^t_{CH_3}$
1246 vw		1246 sh, m	1246 sh, m	—	
~1140 vw				—	
~1130 vw		1116 vvw	1115 vvw	1116 vw	
1072 1066 m 1058		1061 s	1062 s	1061 m	
1046 sh, w		1045 sh, vw	1045 sh, vw	—	
		1010 vw	1008 vw	1009 vw	
993 sh, w 990 w		995 sh, vw	995 sh, vw	996 vvw	
982 sh, w 978 m		982 m	982 m	—	$\delta^r_{CH_3}$
970 sh, m 967 m		970 s	968 s	968 vs	$\delta^r_{CH_3}$
960 s		961 sh, w	960 sh, w	962 vs	$\delta^r_{CH_3}$
953 m 950 m		954 s	955 s	—	$\delta^r_{CH_3}$
947 w 941 w		947 sh, s	948 sh, s	947 m	$\delta^r_{CH_3}$
				813 vw	
792 vw 786 w 778 sh, w		783 w	783 w	—	$\delta^r_{CH_3}$
767 758 w 750		758 m	758 m	764 s	$\delta^r_{CH_3}$
730 725 vw 720		727 w	726 m	724 m	ν_{C-S}

TABLE 1. (Continued)

Gaseous Room temp.	Liquid Room temp.	CS_2 soln.	Liquid Low temp.	Solid Annealed	Assignment[b]
671 666 w 660		677 vw	676 vw	—	ν_{C-S}
650 w 647 w 643 sh, vw		654 m	654 m	655 m	ν_{C-S}
	528 vvw, br			—	
	~505 vvw			—	
	363 sh, vw			—	
	354 vw			354 w	δ_{skel}
	272 vvw, br			—	
	238 vvw			235 vvw	δ_{skel}
	~220 vvw			220 vvvw	δ_{skel}
	~215 vvw			—	

s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

a) Above 3000 cm^{-1} and 2800—1500 cm^{-1} regions are omitted.

b) ν, stretching; δ^d, degenerate deformation; δ^b, bending; δ^s, symmetrical deformation; δ^w, wagging; δ^t, twisting; δ^r, rocking; δ_{skel}, skeletal deformation.

due to the less stable conformation. Methyl ethyl sulfide has four CH_3 rocking vibrational freedoms for each conformation. In the 990—940 cm^{-1} region, we observed five and three bands in the liquid and solid states respectively. These bands may be due to the CH_3 rocking fundamentals. Scott *et al.*[2] and Hayashi *et al.*[4] identified one band of this region as the C–C stretching vibration. For the CH_2 rocking vibrations, two bands were obtained in the liquid state and one band remained in the solid state. The C–S stretching vibration has two vibrational freedoms for each conformation. In the liquid state, three bands are observed. Among them, two bands remain in the annealed spectra. If two conformations may coexist in the liquid state, one band may overlap with the other one. In the skeletal deformation region, 400—200 cm^{-1}, three bands for each conformation may be expected. In the liquid state, we observed five bands. Two bands remain in the solid state.

Experimental

The methyl ethyl sulfide was commercially obtained (Tokyo Kasei Co., Tokyo) and distilled; bp 66.5—67°C/760 mmHg. The gaseous spectra (4000—600 cm^{-1}) were recorded at room temperature. The liquid spectra were recorded at room temperature in the 600—200 cm^{-1} region and at low temperatures, slightly above its mp in the 4000—600 cm^{-1} region. The solution spectra (1400—600 cm^{-1}) were obtained in CS_2. The solid state spectra (4000—200 cm^{-1}) were recorded near the temperature of liquid nitrogen. The instrument used for recording was a Perkin-Elmer Model 621 Spectrophotometer.