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Molecular Vibrations and Force Fields of Alkyl Sulfides. IV. Infrared Spectra of Diethyl Sulfide

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Many papers on the vibrations of diethyl sulfide have appeared.[1-5] Scott *et al.*[2] postulated three conformations: C_{2v} (TT), C_1 (TG), and C_2 (GG). Hayashi[3] carried out a normal coordinate analysis for skeletal vibrations using a Urey-Bradley type potential and assigned the obtained spectra assuming C_{2v}, C_1, and C_2 conformations. Lately, Scott *et al.*[5] carried out a normal coordinate treatment using a valence force-type potential; they suggested that the C_{2v} and C_1 conformations are stable and that the C_2 conformation must have a high energy. In the previous papers, however, the assignments of the observed bands were not con-

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[1] N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950).

[2] D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, G. D. Oliver, M. E. Gross, C. Katz, K. D. Williamson, G. Waddington, and H. M. Huffman, *J. Amer. Chem. Soc.*, **74**, 4656 (1952).

[3] M. Hayashi, *Nippon Kagaku Zasshi*, **77**, 1804 (1956).

[4] H. J. Boonstra and L. C. Rinzema, *Rec. Trav. Chim. Pays-Bas*, **79**, 962 (1960).

[5] D. W. Scott and M. Z. El-Sabban, *J. Mol. Spectrosc.*, **30**, 317 (1969).

Table 1. Infrared frequencies (cm^{-1}) and assignments of diethyl sulfide[a)]

Gaseous Room temp.	Liquid Room temp.	CS_2 soln.	Liquid Low temp.	Solid Annealed	Assignment[b)]
2990 sh, vs 2980 vvs 2975 vs				2978 sh, w	ν_{C-H}
2967 sh, vs			2963 vs	2967 vvs	ν_{C-H}
2946 sh, vs				2943 sh, m	ν_{C-H}
2937 vs				2936 sh, m	ν_{C-H}
2929 sh, vs 2926 sh, vs 2923 sh, s			2923 vs	2924 s, br	ν_{C-H}
~2910 sh, s				2904 sh, m	ν_{C-H}
2895 2888 s 2880			2867 s	2873 s	ν_{C-H}
2860 s				2862 sh, vw	ν_{C-H}
2855 s			2855 sh, m	2853 s	ν_{C-H}
~2835 m			2826 sh, w	2823 sh, vvw	
1480 sh, m 1475 s 1471 s			1478 sh, w	1479 m	$\delta^{d}_{CH_3}$
1462 s			1459 sh, s	1463 vs	$\delta^{d}_{CH_3}$
1455 s 1452 sh, s			1453 sh, w	1453 s	$\delta^{d}_{CH_3}$
1449 sh, s			1449 vs	1449 vs	$\delta^{d}_{CH_3}$
1440 m				1442 vs	
1435 m			1438 sh, s	1436 sh, s	
1420 sh, w			1425 m	—	
1393 sh, w 1389 w 1381 w 1375 sh, w		1381 sh, vw	1381 sh, vw	1379 s	$\delta^{s}_{CH_3}$
1373 sh, w 1369 sh, vw 1366 sh, vw		1374 s	1373 s	1375 m	$\delta^{s}_{CH_3}$
1295 sh, vw 1290 sh, w		1294 sh, vw		—	
1285 sh, w 1282 sh, w 1280 sh, w		1282 sh, w	1282 sh, w	1283 vs	$\delta^{w}_{CH_2}$
1271 sh, s		1272 sh, m	1272 sh, m	—	
1265 1261 vs 1255		1257 vs	1258 vs	1254 vs	
1246 sh, m 1243 sh, w		1246 sh, s	1248 sh, s	1242 vw	
~1235 sh, w		1238 sh, m	1236 sh, w	1236 sh, vvw	
1085 w 1081 w		1073 m	1074 m	1081 vw	
1070 w 1067 w		1066 sh, w		—	
1047 vw 1040 vw		1047 w	1047 vw	1042 vw	
1035 vvw		1035 vw		—	
		1028 vvw	1028 sh, vw	1025 vvw	
1005 vvw		1005 vvw	1005 vvw	—	
992 sh, w		992 sh, vw	992 sh, vw	992 s	
984 sh, w		982 sh, w	983 sh, vw	983 m	
980 w		979 sh, m	981 m	—	
972 w		971 s	971 s	—	
969 w 966 w		967 sh, w	967 sh, vw	—	
960 sh, w		958 sh, vw		—	
798 sh, vw		797 sh, w		798 vvs	$\delta^{r}_{CH_2}$
793 sh, vw		792 sh, w	792 sh, vw	—	

Table 1. (Continued)

Gaseous Room temp.	Liquid Room temp.	CS_2 soln.	Liquid Low temp.	Solid Annealed	Assignment[b)]
787 w		788 sh, m	789 sh, w	—	
783 w 774 w		782 s	782 m	—	$\delta^r_{CH_2}$
765 w		763 m	762 m	—	$\delta^r_{CH_2}$
743 736 vw 730		737 w	738 w	—	ν_{C-S}
705 700 vw 694		695 w	696 w	—	ν_{C-S}
686 vw 680 vw		688 sh, w	688 sh, w	692 w	ν_{C-S}
665 655 vw 647		655 w	656 w	—	ν_{C-S}
635 vw		638 m	638 w	—	ν_{C-S}
	515 vvw			—	
	500 vvw			—	
	475 vvw			—	
	450 vvw			—	
	425 vvw			—	
	390 sh, vw			—	
	384 vw			—	
	376 sh, vw			—	
	345 vw			337 vw	δ_{skel}
	337 sh, vw			330 sh, vw	δ_{skel}
	306 vw			—	
	294 sh, vvw			—	
	~260 vvw			—	
	~255 vvvw			—	
	~245 vvvw			~250 vvw	δ_{skel}

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 deformaion; δ^w, wagging; δ^t, twisting; δ^r, rocking; δ_{skel}, skeletal deformation.

sistent with each other; moreover, the conformational analyses of this compound have not agreed with each other. In this paper, in order to complete the infrared data, we report anew on the infrared spectra of diethyl sulfide recorded in the gaseous, liquid, and solid states. We will treat the normal coordinates of this molecule and will report its full assignments in the succeeding paper.

Results and Discussion

The infrared data of diethyl sulfide obtained are summarized in Table 1. The existence of the rotational isomers may be confirmed by the spectra in the CH_2 rocking, C–S stretching, and skeletal deformation regions. For the CH_2 rocking region, 800—760 cm^{-1}, we observed five bands in the liquid state and only one band in the annealed film. Diethyl sulfide has two vibrational freedoms of the CH_2 rocking vibrations for each conformation. However, one band of the CH_2 rocking belonging to the A_2 species of the C_{2v} (TT) conformation is infrared-inactive. Therefore, five bands in the liquid spectra would arise from three conformations (TT, TG, and GG); we can not deny the existence of the C_2 conformation at present. The spectra of this region suggest that the stable form in the solid state is the C_{2v} conformation. In the 750—600 cm^{-1} region, C–S stretching vibrations are to be expected. Diethyl sulfide has two vibrational freedoms of the C–S stretching for each conformation. If the three conformations of C_{2v}, C_1, and C_2 coexisted in the liquid state, six bands would arise. In this region we observed five bands in the liquid state and one band in the solid state. Therefore, the stable conformation (TT) represents only one C–S stretching band in the solid state. The other four bands must arise from the other two conformations. Scott *et al.*[2)] assigned the band at 688 cm^{-1} (liquid) to the accidentally-degenerate C–S stretching vibration of the C_{2v} conformation. Since this means, however, that the interaction between the two C–S bonds is zero, the assignment is not acceptable. The band at 692 cm^{-1} in the solid state is not overlapped. It is a weak band. Therefore, the dipole change due to the vibration may be small. Another C–S stretching band would be too weak to be observed, since, in the case of dimethyl sulfide,[6)] one C–S stretching band is very weak in comparison with the other band. In

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[6)] M. Ohsaku, Y. Shiro, and H. Murata, This Bulletin, **45**, 113 (1972).

the skeletal deformation region, 450—200 cm^{-1}, fifteen bands are to be expected for three conformations, and five bands, including two C–C torsions, for one conformation. Twelve bands are observed in the liquid spectra. Although all of the observed bands are not always considered to be fundamentals, the three bands remaining in the annealed spectra may be due to the skeletal deformation vibrations of the C_{2v} conformation. Therefore, there remain nine bands in this region. Most of these nine bands may correspond to the other two conformations. From the spectra of this region, therefore, we can not deny the existence of the C_2 conformation.

Experimental

The diethyl sulfide was commercially obtained (Tokyo Kasei Co., Tokyo) and distilled; bp 92°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 solidstate 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.