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Molecular Vibrations and Force Fields of Alkyl Sulfides. VI. Methyl Ethyl Sulfide and Its Deuterated Compounds, and Diethyl Sulfide

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Deuterated methyl ethyl sulfides, $CD_3SCH_2CH_3$ and $CH_3SCD_2CD_3$, were prepared, and their infrared spectra were recorded in the gaseous, liquid, and solid states. The normal coordinates of methyl ethyl sulfide, its deuterated analogues, and diethyl sulfide have been treated by the use of a modified Urey-Bradley potential field. The conformational analyses of these sulfides were made by the aid of the calculations. In the gaseous and liquid states, two forms (T and G) have been confirmed to exist for $CH_3SCH_2CH_3$, and three forms (TT, TG, and GG), for $CH_3CH_2SCH_2CH_3$. In the solid state, $CH_3SCH_2CH_3$ or $CH_3CH_2SCH_2CH_3$ exists in one form: T or TT. The observed infrared frequencies were compared with the calculated frequencies and were fully assigned.

In our previous papers, we reported the infrared spectra of methyl ethyl sulfide[1] and diethyl sulfide;[2] we postulated two and three conformations for methyl ethyl and diethyl sulfides respectively. However, we could not assign all of the infrared bands observed in the CH_3 rocking, CH_2 deformation, and C–S stretching regions. The purpose of this paper is to make the full assignments of the infrared bands of these sulfides, and to determine the skeletal conformations of methyl ethyl and diethyl sulfides. In order to confirm the vibrational assignments, the normal coordinates have been treated for these molecules. The vibrational analysis has also been extended to deuterated methyl ethyl sulfides: $CD_3SCH_2CH_3$ and $CH_3SCD_2CD_3$.

Vibrational Assignment

Deuterated methyl ethyl sulfides were prepared from CD_3I and CH_3CH_2SH, and from CD_3CD_2Br and CH_3SNa. The method of infrared recording and the instrument used have been described previously.[1] Both samples are contaminated with a very small amount of the normal species. The obtained infrared data are summarized in Tables 1 and 2. The spectra of $CD_3SCH_2CH_3$ are more complicated than those of the normal species. The spectra of $CH_3SCD_2CD_3$ are the most complicated of the three. The observed bands of annealed films are well resolved in both deuterated species. The assignments of the observed bands were made on the basis of the band intensities, band envelopes, and normal coordinates.

Methyl Ethyl Sulfide-d_3. The bands of the methyl group which is bonded to the sulfur atom are shifted directly upon deuteration. The two CD_3 degenerate deformation bands are expected around 1050 cm^{-1}. In this frequency region, we observed fairly complex band peaks. The bands at 1045 and 1040 cm^{-1} in the liquid state are assigned to the CH_3 rocking and the CD_3 degenerate deformation vibrations with reference to the band intensities. The CD_3 symmetrical deformation band is expected around 950 cm^{-1}, while the two CD_3 rocking vibrations are expected around 750 cm^{-1}. We observed some bands in the expected regions and assigned these bands as is shown in Table 1, although the assignments are not straightforward. Below 1400 cm^{-1}, in particular below 800 cm^{-1}, over half of the bands disappear in the solid state. Most of the disappearing bands may be related to the rotational isomerism.

Methyl Ethyl Sulfide-d_5. The ethyl-group vibrations are shifted to a lower frequency region upon deuteration. The other bands except for the C–C stretching band are not so much affected upon deuteration. For this species, the bands observed below 1100 cm^{-1} are very complex. According to the result of the normal-coordinate calculation, each of the normal coordinates can be said to be fairly well coupled with one another—in particular in the CD_3 and CD_2 deforma-

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[1] M. Ohsaku, Y. Shiro, and H. Murata, This Bulletin, **45**, 954 (1972).

[2] M. Ohsaku, Y. Shiro, and H. Murata, *ibid.*, **45**, 956 (1972).

TABLE 1. INFRARED FREQUENCIES (cm^{-1}) AND ASSIGNMENTS OF $CD_3SCH_2CH_3$[a)]

Gaseous Room temp.	Liquid Room temp.	Solid Annealed	Assignment[b)]
2994 2985 vvs 2975	2972 vs	2972 s	ν_{C-H}
2967 sh, s	2965 sh, s	2959 s	ν_{C-H}
		2951 sh, m	—
2947 2942 vvs 2934	2929 vs	2930 m	ν_{C-H}
2925 sh, s 2916 sh, m	2916 sh, s	2918 m	ν_{C-H}
2895 s		2904 w	—
2883 s		2885 vvw	—
2880 s	2875 s	2873 m	ν_{C-H}
2855 m	2855 m	2843 w	—
2844 m	2833 m	2823 vvw	—
2259 2253 s 2240	2235 s	2235 m	ν_{C-D}
	2155 sh, vw	—	—
2147 2140 s 2133	2131 vs	2129 m	ν_{C-D}
2092 w	2090 w	2089 vvw	—
2083 sh, w	2070 w	2074 vvw	—
2020 vw		—	—
2010 vw	2004 w	2004 vvw	—
1464 s	1460 sh, s	1462 s 1455 s	$\delta^{d}_{CH_3}$
1452 s	1452 vs	1447 m	$\delta^{d}_{CH_3}$
1443 sh, m	1440 sh, s	—	$\delta^{d}_{CH_3}$, G
1427 w	1426 s	1432 s	$\delta^{b}_{CH_2}$
1420 sh, w	1420 sh, m	—	$\delta^{b}_{CH_2}$, G
1390 1383 w 1377	1377 s	1377 s	$\delta^{s}_{CH_3}$
	1365 sh, w	—	$\delta^{s}_{CH_3}$, G
1325 vvw	1320 vvw	—	—
1279 1271 vs 1265	1278 sh, s	1283 s	$\delta^{w}_{CH_2}$
	1266 vs 1248 sh, m	1269 s 1255 s	$\delta^{t}_{CH_2}$, $\delta^{r}_{CH_3}$
1064 m	1063 sh, m	—	$\delta^{r}_{CH_3}$, G
1056 1053 m 1049	1056 sh, m	1056 w	$\delta^{r}_{CH_3}$
1045 m	1049 s	1049 vs	$\delta^{d}_{CD_3}$
1040 sh, w	1045 sh, m	1045 w	$\delta^{r}_{CH_3}$, $\delta^{t}_{CH_2}$
1030 sh, w	1040 s	1035 vs	$\delta^{d}_{CD_3}$
1008 vw	1013 m	1013 w	ν_{C-C}
990 w 985 w	983 m	—	ν_{C-C}, G
977 970 w 965	971 s	966 vs	$\delta^{s}_{CD_3}$
795 788 w 784	789 s	797 s	$\delta^{r}_{CH_2}$, $\delta^{r}_{CH_3}$
777 w 765 sh, w	761 w	—	$\delta^{r}_{CD_3}$
	750 sh, vw	—	$\delta^{r}_{CD_3}$, G
726 vvw	724 w	731 m	ν_{C-S}, δ^{r}_{CD3}
718 vvw	720 sh, vw	721 w	$\delta^{r}_{CD_3}$
705 vvw	698 vw	—	ν_{C-S}, G
685 vvvw	689 sh, vw	—	—
653 w 646 w	645 sh, w	—	ν_{C-S}, G
641 635 w 632	640 m	640 s 634 w	ν_{C-S}
523 vvw	520 vw	—	—
	360 vvw	—	δ_{skel}, G
	345 vw	348 w	δ_{skel}
	264 vvw	—	δ_{skel}, G
	244 vvw		δ_{skel}

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

a) Above 3000, 2800—2300, and 2000—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 (including torsions).

TABLE 2. INFRARED FREQUENCIES (cm^{-1}) AND ASSIGNMENTS OF $CH_3SCD_2CD_3$[a)]

Gaseous Room temp.	Liquid Room temp.	Solid Annealed	Assignment
3005 s 2998 s	2985 s	2987 w	ν_{C-H}
2988 2980 s 2976	2973 s	2972 m	ν_{C-H}
		2959 sh, vw	—
2936 vs 2924 vs	2917 vs	2917 s	ν_{C-H}
2880 w		2873 vw	—
2872 w 2860 w	2862 m	2864 w	—
2845 w	2838 s	2840 m	—
2240 2233 vs 2226	2228 vs	2232 s	ν_{C-D}
		2222 m	ν_{C-D}
2205 vw	2205 sh, m	2209 vw	—
2195 w		2192 vw	—
2164 w	2174 m	2174 vw	—
2155 w 2145 w	2145 m	2148 w	ν_{C-D}
2130 w	2118 s	2122 w	ν_{C-D}
2089 w		2095 vvw	—
2079 w	2071 s	2071 m	ν_{C-D}
2050 sh, w	2038 w	2038 vvw	—
		2033 vvw	—
1454 s 1448 s	1437 vs	1439 vs	$\delta^{d}_{CH_3}$
1440 s 1436 s	1427 vs	1428 vs	$\delta^{d}_{CH_3}$
1425 sh, m	1420 sh, s	—	$\delta^{d}_{CH_3}$, G
1333 1325 w 1317	1320 m	1327 vw 1320 m	δ^{s}_{CH3}
	1305 vw	—	—
1220 vvw	1220 vw	—	—

Gaseous Room temp.	Liquid Room temp.	Solid Annealed	Assignment
1151 1141 m 1135	1143 sh, m 1136 m	1141 m 1136 s	ν_{C-C}, $\delta^{d}{}_{CD_3}$
1070 s	1071 m	1068 vs	$\delta^{d}{}_{CD_3}$
1063 s	1062 s	1055 vs	$\delta^{d}{}_{CD_3}$
1057 s	1050 vs	1044 m	$\delta^{b}{}_{CD_2}$, $\delta^{s}{}_{CD_3}$
1052 s	1046 sh, s	—	$\delta^{b}{}_{CD_2}$, $\delta^{s}{}_{CD_3}$, G
1038 1031 s 1024	1025 vs	1025 vs	$\delta^{w}{}_{CD_2}$, $\delta^{s}{}_{CD_3}$
	1013 vvw	1011 vvw	—
988 m 982 s 972 s	978 vs	982 vs	$\delta^{r}{}_{CH_3}$
	970 sh, w	975 w	$\delta^{r}{}_{CH_3}$
965 sh, m 957 m 950 sh, w	958 s	962 vs	$\delta^{s}{}_{CD_3}$, $\delta^{t}{}_{CD_2}$
893 887 w 883	887 w	893 w	$\delta^{r}{}_{CD_3}$, ν_{C-C}
	885 vw	—	$\delta^{r}{}_{CD_3}$, ν_{C-C}, G
		795 vvw	—
785 sh, vw	786 w	786 w	$\delta^{r}{}_{CD_3}$, $\delta^{t}{}_{CD_2}$, $\delta^{w}{}_{CD_2}$
777 w 772 w	770 m	767 m	$\delta^{t}{}_{CD_2}$, $\delta^{r}{}_{CD_3}$
765 sh, vw 755 sh, vw	756 w	—	$\delta^{r}{}_{CD_3}$, $\delta^{r}{}_{CD_2}$, G
725 vw	725 w	—	ν_{C-S}, G
718 vw 712 vw	716 w	717 s	ν_{C-S}
610 vw	610 w	612 m	ν_{C-S}
577 w 566 w	576 w	—	$\delta^{r}{}_{CD_2}$, $\delta^{r}{}_{CD_3}$, G
558 w 555 w	565 m	569 s	$\delta^{r}{}_{CD_2}$, $\delta^{r}{}_{CD_3}$
		534 vvw	—
	525 vvw	527 vvw	—
	512 vvw	512 vvw	—
	332 sh, vvw	—	δ_{skel}, G
	321 vw	320 w	δ_{skel}
	235 vvw	—	δ_{skel}, G
	218 vvw		δ_{skel}

a) Above 3010, 2800—2300, and 2000—1500 cm^{-1} regions are omitted.

The other descriptionl are the same to Table 1.

tion regions. However, the bands arising from CH_3 and CD_2CD_3 groups are fairly well separated.

Normal Coordinate Treatment

We made the normal coordinate treatment for four species: $CH_3SCH_2CH_3$, $CD_3SCH_2CH_3$, $CH_3SCD_2CD_3$, and $CH_3CH_2SCH_2CH_3$. The molecular parameters used in the computations were: r(C–H) or r(C–D) = 1.09 Å, r(C–S) = 1.81 Å, r(C–C) = 1.54 Å, and ϕ(CSC) = 99°; the other bond angles were assumed to be tetrahedral. The force field used was the Urey-Bradley type potential modified by some interactions. The correction terms were: p, p', p'', n, n', t, g, t', g', t'', g'', and l. The corrections of p, p', n, t, and g have been explained in the first paper of this series.[3] The additional corrections were the bond-interaction constant, p'', between the C–S and C–C bonds; the angle interaction constant, n', between the CCH (or CCD) and HCH (or DCD) angles in the methyl group bonded to the carbon atom; the *trans* and *gauche* coupling constants, t' and g', between the CCH (or CCD) and SCC angles in the methyl group bonded to the carbon atom; the *trans* and *gauche* coupling constants, t'' and g'', between the methylene HCC (or DCC) and methyl CCH (or CCD) angles in the ethyl group, and the angle-interaction constant, l, between the SCH and HCC (or DCC) angles or the CCH (or

Table 3. Modified Urey-Bradley force constants[a] of methyl ethyl and diethyl sulfides

K(C–H)	4.250[b]	CH_3 and CH_2 groups
K(C–S)	1.750[b]	CH_3–S and S–CH_2 bonds
K(C–C)	2.100[c]	CH_2–CH_3 bond
H(HCS)	0.030[b,d]	CH_3 group
H(HCH)	0.370[b,d]	CH_3 group
H(CSC)	0.244[b,d]	CH_3–S–CH_2 and CH_2–S–CH_2 angles
H(SCC)	0.070[c]	S–CH_2–CH_3 angle
H(CCH)	0.210[c]	CH_2 group
H(SCH)	0.170[d]	CH_2 group
H(HCH)	0.350[d]	CH_2 group
H(CCH)	0.186[c]	CH_3 group
F(HCS)	0.763[b,d]	
F(HCH)	0.200[b,d]	
F(CSC)	0.210[b,d]	
F(SCC)	0.700[c]	
F(CCH)	0.470[c]	
F(SCH)	0.390[d]	
F(HCH)	0.200[d]	
F(CCH)	0.540[c]	
κ	0.060[b,d]	CH_3 group
	0.005[d]	CH_2 group
Y	0.054[b,d]	CH_3–S and S–CH_2 bonds
	0.100[c]	CH_2–CH_3 bond
p	−0.115[b,d]	CH_3 and CH_2 groups
p'	−0.100	CH_3–S and S–CH_2 bonds
p''	−0.100	S–CH_2 and CH_2–CH_3 bonds
n	0.033[b,d]	CH_3 group (∠HCS and ∠HCH)
n'	0.040	CH_3 group (∠CCH and ∠HCH)
t	0.070[b,d]	CH_3 group (∠HCS and ∠CSC, *trans*)
g	−0.050[b,d]	CH_3 group (∠HCS and ∠CSC, *gauche*)
t'	0.070	CH_3 group (∠CCH and ∠SCC, *trans*)
g'	−0.050	CH_3 group (∠CCH and ∠SCC, *gauche*)
t''	0.070	CH_3CH_2 group (∠HCC and ∠CCH, *trans*)
g''	−0.050	CH_3CH_2 group (∠HCC and ∠CCH, *gauche*)
l	0.000	S–CH_2–C

a) Unit of K, H, F, p, p', and p'' is in mdyn/Å; κ, Y, n, n', t, g, t', g', t'', g'', and l is in mdyn·Å; $F' = -0.1\,F$.

b) From Ref. 3. c) From Ref. 4. d) From Ref. 5.

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}), AND APPROXIMATE POTENTIAL ENERGY DISTRIBUTION, PED, (%) OF $CH_3SCH_2CH_3$

Obsd[a]	Calcd		PED
	T	G	
2985_s	2988	2988	$\nu_{C-H}(100)$
2965_s	2987	2987	$\nu_{C-H}(100)$
2957_s	2977	2977	$\nu_{C-H}(100)$
2950_s	2969	2969	$\nu_{C-H}(100)$
2926_s	2963	2963	$\nu_{C-H}(100)$
2915_s	2913	2913	$\nu_{C-H}(100)$
2874_s	2899	2899	$\nu_{C-H}(100)$
2866_s	2878	2878	$\nu_{C-H}(100)$
2855_s			—
2834_s			—
1465_l	1449	1449	$\delta^d_{CH_3}(100)$
1457_l	1448	1448	$\delta^d_{CH_3}(100)$
1448_l	1447	1474	$\delta^d_{CH_3}(100)$
1436_l	1446	1446	$\delta^d_{CH_3}(100)$
1427_l	1427		$\delta^b_{CH_2}(90)$
(1420_l)		1427	$\delta^b_{CH_2}(90)$
1405_s			—
1374_l	1373	1373	$\delta^s_{CH_3}(100)$
1319_l	1320	1320	$\delta^s_{CH_3}(100)$
1305_l			—
(1278_l)		1274	$\delta^w_{CH_2}(95)$
1264_l	1276		$\delta^w_{CH_2}(95)$
1249_l	1260		$\delta^t_{CH_2}(65)$, $\delta^r_{CH_3}(25)$
(1246_l)		1260	$\delta^t_{CH_2}(60)$, $\delta^r_{CH_3}(25)$
(1140_g)			—
1115_l			—
1062_l	1075	1072	T : $\delta^r_{CH_3}(80)$, G: $\delta^r_{CH_3}(85)$
(1045_l)	1046	1050	$\delta^r_{CH_3}(50)$, $\delta^t_{CH_2}(55)$
1008_l			—
995_l	1001		$\nu_{C-C}(60)$, $\delta^r_{CH_3}(35)$
(982_l)		996	$\delta^r_{CH_3}(50)$, $\nu_{C-C}(45)$
968_l	979		$\delta^r_{CH_3}(70)$, $\nu_{C-C}(35)$
(960_l)		977	$\nu_{C-C}(55)$, $\delta^r_{CH_3}(50)$
(955_l)		967	$\delta^r_{CH_3}(100)$
948_l	967		$\delta^r_{CH_3}(100)$
813_s			—
(783_l)		771	$\delta^r_{CH_2}(65)$, $\delta^r_{CH_3}(30)$, $\nu_{C-S}(20)$
758_l	762		$\delta^r_{CH_2}(80)$, $\delta^r_{CH_3}(35)$
726_l	742	731	$\nu_{C-S}(100)$
(676_l)		643	$\nu_{C-S}(100)$
654_l	644		$\nu_{C-S}(100)$
(528_l)			—
(505_l)			—
(363_l)		367	$\delta^b_{SCC}(55)$, $\delta^b_{CSC}(30)$
354_l	348		$\delta^b_{SCC}(60)$, $\delta^b_{CSC}(25)$
(272_l)		272	$\delta^b_{CSC}(35)$, $\tau_{C-C}(35)$, $\delta^b_{SCC}(20)$
238_l	242		$\tau_{C-C}(95)$
220_l	236		$\delta^b_{CSC}(70)$, $\delta^b_{SCC}(25)$
(215_l)		216	$\tau_{C-C}(60)$, $\delta^b_{CSC}(30)$
	175	172	$\tau_{C-S}(95)$
	80	79	$\tau_{C-S}(95)$

[a] Figures in parentheses show the bands which disappear in the solid state.
s, solid-, l, liquid-, and g, gaseous-state bands.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}), AND APPROXIMATE POTENTIAL ENERGY DISTRIBUTION, PED, (%) OF $CD_3SCH_2CH_3$

Obsd[a]	Calcd		PED
	T	G	
2972_s	2977	2977	$\nu_{C-H}(100)$
2959_s	2969	2969	$\nu_{C-H}(100)$
2930_s	2963	2963	$\nu_{C-H}(100)$
2918_s	2913	2913	$\nu_{C-H}(100)$
2873_s	2878	2878	$\nu_{C-H}(100)$
2235_s	2211	2211	$\nu_{C-D}(100)$
2235_s	2209	2209	$\nu_{C-D}(100)$
2129_s	2071	2071	$\nu_{C-D}(100)$
1460_l	1449	1449	$\delta^d_{CH_3}(100)$
1452_l	1446		$\delta^d_{CH_3}(100)$
(1440_l)		1446	$\delta^d_{CH_3}(100)$
1426_l	1427		$\delta^b_{CH_2}(90)$
(1420_l)		1427	$\delta^b_{CH_2}(90)$
1377_l	1373		$\delta^s_{CH_3}(100)$
(1365_l)		1373	$\delta^s_{CH_3}(100)$
1278_l	1276	1274	$\delta^w_{CH_2}(95)$
$\left(\begin{matrix}1266_l\\1248_l\end{matrix}\right.$	1259	1260	T: $\delta^t_{CH_2}(65)$, $\delta^r_{CH_3}(25)$, G: $\delta^t_{CH_2}(60)$, $\delta^r_{CH_3}(25)$
(1063_l)		1073	$\delta^r_{CH_3}(85)$
1056_l	1075		$\delta^r_{CH_3}(80)$
1049_l	1057	1058	$\delta^d_{CD_3}(100)$
1045_l	1046	1049	T: $\delta^r_{CH_3}(50)$, $\delta^t_{CH_2}(55)$, G: $\delta^r_{CH_3}(45)$, $\delta^t_{CH_2}(50)$
1040_l	1055	1055	$\delta^d_{CD_3}(100)$
1013_l	995		$\nu_{C-C}(90)$
(983_l)		987	$\nu_{C-C}(100)$
971_l	975	975	$\delta^s_{CD_3}(100)$
789_l	764	776	T: $\delta^r_{CH_2}(75)$, $\delta^r_{CH_3}(30)$, G: $\delta^r_{CH_2}(50)$, $\delta^r_{CD_3}(25)$, $\delta^r_{CH_3}(25)$
(761_l)	762		$\delta^r_{CD_3}(90)$
(750_l)		754	$\delta^r_{CD_3}(70)$, $\delta^r_{CH_2}(20)$
724_l	727	726	T: $\nu_{C-S}(100)$, G: $\delta^r_{CD_3}(100)$
720_l	724		$\delta^r_{CD_3}(100)$
(698_l)		716	$\nu_{C-S}(100)$
(645_l)		633	$\nu_{C-S}(95)$
640_l	631		$\nu_{C-S}(90)$
(360_l)		358	$\delta^b_{SCC}(60)$, $\delta^b_{CSC}(25)$
345_l	342		$\delta^b_{SCC}(65)$, $\delta^b_{CSC}(20)$
(264_l)		265	$\tau_{C-C}(50)$, $\delta^b_{CSC}(30)$
244_l	241		$\tau_{C-C}(95)$
	218		$\delta^b_{CSC}(75)$, $\delta^b_{SCC}(20)$
		208	$\delta^b_{CSC}(40)$, $\tau_{C-C}(45)$
	128	125	T: $\tau_{C-S}(100)$, G: $\tau_{C-S}(95)$
	77	75	$\tau_{C-S}(95)$

[a] See a) of Table 4.

CCD) angles in the methylene group. Most of the force constants used were transferred from or referred to those of related molecules previously reported.[3–5]

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[3] Y. Shiro, M. Ohsaku, M. Hayashi, and H. Murata, This Bulletin **43**, 609 (1970).

[4] M. Hayashi, Y. Shiro, and H. Murata, *ibid.*, **39**, 112 (1966).

[5] M. Ohsaku, Y. Shiro, and H. Murata, *ibid.*, **45**, 3035 (1972).

TABLE 6. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}), AND APPROXIMATE POTENTIAL ENERGY DISTRIBUTION, PED, (%) OF $CH_3SCD_2CD_3$

Obsd[a)]	Calcd		PED
	T	G	
2987_s	2988	2988	$\nu_{C-H}(100)$
2972_s	2987	2987	$\nu_{C-H}(100)$
2917_s	2899	2899	$\nu_{C-H}(100)$
2232_s	2205	2205	$\nu_{C-D}(100)$
2222_s	2201	2201	$\nu_{C-D}(100)$
2148_s	2195	2196	$\nu_{C-D}(100)$
2122_s	2110	2110	$\nu_{C-D}(100)$
2071_s	2058	2058	$\nu_{C-D}(100)$
1437_l	1448	1448	$\delta^d_{CH_3}(100)$
1427_l	1447		$\delta^d_{CH_3}(100)$
(1420_l)		1447	$\delta^d_{CH_3}(100)$
1320_l	1320	1320	$\delta^s_{CH_3}(100)$
1143_l 1136_l	1104	1096	T: $\nu_{C-C}(70)$, $\delta^d_{CD_3}(40)$, $\delta^w_{CD_2}(25)$ G: $\nu_{C-C}(70)$, $\delta^d_{CD_3}(50)$, $\delta^w_{CD_2}(20)$
1071_l	1070	1070	$\delta^d_{CD_3}(85)$
1062_l	1069	1069	$\delta^d_{CD_3}(95)$
1050_l	1059		$\delta^b_{CD_2}(55)$, $\delta^s_{CD_3}(45)$
(1046_l)		1057	$\delta^b_{CD_2}(65)$, $\delta^s_{CD_3}(35)$
1025_l	1031	1030	$\delta^w_{CD_2}(40)$, $\delta^s_{CD_3}(50)$
978_l	987	988	$\delta^r_{CH_3}(100)$
970_l	968	967	$\delta^r_{CH_3}(100)$
958_l	945	945	$\delta^s_{CD_3}(60)$, $\delta^t_{CD_2}(40)$
887_l	873		$\delta^r_{CD_3}(45)$, $\nu_{C-C}(25)$
(885_l)		872	$\delta^r_{CD_3}(45)$, $\nu_{C-C}(30)$
786_l	793	797	T: $\delta^r_{CD_3}(45)$, $\delta^w_{CD_2}(30)$ G: $\delta^t_{CD_2}(45)$, $\delta^r_{CD_3}(25)$, $\nu_{C-S}(20)$
770_l	778		$\delta^t_{CD_2}(80)$, $\delta^r_{CD_3}(25)$
(756_l)		787	$\delta^r_{CD_3}(35)$, $\delta^r_{CD_2}(55)$
(725_l)		726	$\nu_{C-S}(100)$
716_l	739		$\nu_{C-S}(100)$
610_l	599	598	$\nu_{C-S}(90)$
(576_l)		569	$\delta^r_{CD_2}(70)$, $\delta^r_{CD_3}(45)$
565_l	566		$\delta^r_{CD_2}(70)$, $\delta^r_{CD_3}(25)$
(332_l)		335	$\delta^b_{SCC}(50)$, $\delta^b_{CSC}(35)$
321_l	318		$\delta^b_{SCC}(50)$, $\delta^b_{CSC}(35)$
(235_l)		240	$\delta^b_{CSC}(50)$, $\delta^b_{SCC}(30)$
218_l	223		$\delta^b_{CSC}(60)$, $\delta^b_{SCC}(35)$
	184		$\tau_{C-C}(50)$, $\tau_{C-S}(50)$
		171	$\tau_{C-S}(90)$
	166	164	T: $\tau_{C-S}(50)$, $\tau_{C-C}(45)$ G: $\tau_{C-C}(80)$
	72	71	T: $\tau_{C-S}(100)$ G: $\tau_{C-S}(95)$

a) See a) of Table 4.

TABLE 7. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}), AND APPROXIMATE POTENTIAL ENERGY DISTRIBUTION, PED, (%) OF $CH_3CH_2SCH_2CH_3$

Obsd[a)]	Calcd			PED
	TT[b)]	TG	GG	
2978_s	2977	2977	2977	$\nu_{C-H}(100)$
2978_s	(2976)	2977	2977	$\nu_{C-H}(100)$
2967_s	2969	2969	2969	$\nu_{C-H}(100)$
2967_s	2969	2969	2969	$\nu_{C-H}(100)$
2943_s	(2963)	2963	2963	$\nu_{C-H}(100)$
2936_s	2963	2963	2963	$\nu_{C-H}(100)$
2924_s	2913	2914	2913	$\nu_{C-H}(100)$
2904_s	2913	2913	2913	$\nu_{C-H}(100)$
2873_s	2878	2878	2878	$\nu_{C-H}(100)$
2862_s				—
2853_s	2878	2878	2878	$\nu_{C-H}(100)$
2823_s				—
1478_l	1449	1449	1449	$\delta^d_{CH_3}(100)$
1459_l	1449	1449	1449	$\delta^d_{CH_3}(100)$
1453_l	1446	1446	1446	$\delta^d_{CH_3}(100)$
1449_l	(1446)	1446	1446	$\delta^d_{CH_3}(100)$
1438_l	1428	1427	1427	$\delta^b_{CH_2}(90)$
(1425_l)	1426	1426	1426	$\delta^b_{CH_2}(90)$
1381_l	1373	1373	1373	$\delta^s_{CH_3}(100)$
1373_l	1373	1373	1373	$\delta^s_{CH_3}(100)$
(1294_c)				—
1282_l	1279	1276	1274	TT: $\delta^w_{CH_2}(90)$, TG: $\delta^w_{CH_2}(95)$, GG: $\delta^w_{CH_2}(95)$,
(1272_l)		1274	1273	$\delta^w_{CH_2}(95)$
1258_l	1273			$\delta^w_{CH_2}(90)$
1248_l*	(1258)	1261	1262	TT: $\delta^t_{CH_2}(65)$, $\delta^r_{CH_3}(30)$, TG: $\delta^t_{CH_2}(65)$, $\delta^r_{CH_3}(25)$, GG: $\delta^r_{CH_2}(60)$, $\delta^r_{CH_3}(30)$
1236_l	1261	1260	1259	$\delta^t_{CH_2}(65)$, $\delta^r_{CH_3}(30)$

Table 7. Continued.

Obsd[a)]	Calcd			PED
	TT[b)]	TG	GG	
1074_l	1079	1076	1074	TT: $\delta^r_{CH_3}(80)$, TG: $\delta^r_{CH_3}(80)$, GG: $\delta^r_{CH_3}(85)$
(1066_c)	1069	1072	1071	$\delta^r_{CH_3}(85)$
1047_l	1049	1051	1051	$\delta^r_{CH_3}(50)$, $\delta^t_{CH_2}(55)$
(1035_c)			1047	$\delta^r_{CH_3}(50)$, $\delta^t_{CH_2}(55)$
1028_l*	(1042)	1045		$\delta^r_{CH_3}(50)$, $\delta^t_{CH_2}(55)$
1005_l				—
992_l	1004	995		TT: $\nu_{C-C}(90)$, TG: $\nu_{C-C}(95)$
983_l	984		987	$\nu_{C-C}(100)$
(981_l)			986	$\nu_{C-C}(100)$
(971_l)		985		$\nu_{C-C}(100)$
(967_l)				—
(958_c)				—
797_c	768			$\delta^r_{CH_2}(80)$, $\delta^r_{CH_3}(35)$
(792_l)			776	$\delta^r_{CH_2}(75)$, $\delta^r_{CH_3}(35)$
(789_l)			765	$\delta^r_{CH_2}(80)$, $\delta^r_{CH_3}(35)$
(782_l)		769		$\delta^r_{CH_2}(80)$, $\delta^r_{CH_3}(35)$
(762_l)	(757)	765		TT: $\delta^r_{CH_2}(85)$, $\delta^r_{CH_3}(30)$, TG: $\delta^r_{CH_2}(80)$, $\delta^r_{CH_3}(35)$
(738_l)				—
(696_l)		667		$\nu_{C-S}(100)$
688_l	669			$\nu_{C-S}(100)$
(656_l)	648		664	$\nu_{C-S}(100)$
(638_l)		638	630	$\nu_{C-S}(100)$
(515_l)				—
(500_l)				—
(475_l)				—
(450_l)				—
(425_l)				—
(390_l)			391	$\delta^b_{CCS}(50)$, $\delta^b_{CSC}(35)$
(384_l)		381		$\delta^b_{CCS}(60)$, $\delta^b_{CSC}(25)$
(376_l)				—
345_l	360			$\delta^b_{CCS}(90)$
337_l	321		335	TT: $\delta^b_{CCS}(40)$, $\delta^b_{CSC}(30)$, GG: $\delta^b_{CCS}(80)$
(306_l)		312		$\delta^b_{CCS}(80)$
(294_l)				—
(260_l)		261		$\tau_{C-C}(70)$
(255_l)			255	$\tau_{C-C}(55)$, $\delta^b_{CCS}(25)$
245_l	239	241	241	$\tau_{C-C}(95)$
	(243)			$\tau_{C-C}(95)$
		190	193	TG: $\delta^b_{CSC}(50)$, $\tau_{C-C}(25)$, GG: $\delta^b_{CSC}(40)$, $\tau_{C-C}(35)$
	175			$\delta^b_{CSC}(60)$, $\delta^b_{CCS}(35)$
			101	$\tau_{C-S}(95)$
	91	95		$\tau_{C-S}(95)$
		75		$\tau_{C-S}(90)$
	(60)		59	TT: $\tau_{C-S}(95)$, GG: $\tau_{C-S}(90)$

* See text. a) c, solution-bands. b) A_2 species in parentheses.
The other notations are the same to Table 4.

The constants of p', p'', n', t', g', t'', g'', and l were assumed to be reasonable in value. It has been supposed that the potential constants are common for all species. The obtained set of the force constants is listed in Table 3. The calculated frequencies of methyl ethyl and diethyl sulfides are summarized in Tables 4—7, together with the observed frequencies.

Molecular Forms. We may suppose two forms, T (C_s) and G (C_1), on methyl ethyl sulfide and three forms, TT (C_{2v}), TG (C_1), and GG (C_2), on diethyl sulfide. Since the GG′ form of diethyl sulfide may have a higher energy than the other forms, we excluded this form from the conformational analysis of diethyl sulfide. The analysis of the molecular forms is made mainly on the bands observed in the CH_2 (or CD_2) rocking, C–S stretching, and skeletal deformation regions. Considering the numbers of the bands which remain in the crystalline films, we may conclude that methyl ethyl and diethyl sulfides exist in one form in the solid state. For methyl ethyl sulfide and the deuterated analogues, the frequencies calculated for the T form correspond well to their solid bands. For diethyl sulfide, the frequencies calculated for the TT form agreed well with their solid bands. We may, therefore, conclude that the stable forms in the solid state for methyl ethyl and diethyl sulfides are the T and TT forms respectively. The results are in accord with the previous results.[6–9]

In the liquid-state or gaseous-state spectra, we observed more bands than would be expected for one conformation. The bands which disappear in the solid state of methyl ethyl sulfide and its deuterated species correspond well with the frequencies calculated for the G form. For diethyl sulfide, the bands at 1425, 1272, 1066, 971, 782, 762, 696, 638, 384, 306, and at 260 cm^{-1}, which disappear in the solid state, agreed well with the frequencies calculated for the TG form. We still have several bands remaining unassigned in the liquid or gaseous spectra of diethyl sulfide: one band in the CH_3 rocking region, one to three bands in the C–C stretching region, two bands in the CH_2 rocking region, and two to four bands in the skeletal deformation regions. It is unlikely that all of these bands are due to overtones or sum-combinations. Most of these bands correspond well with the frequencies calculated for the GG form. We, therefore, assigned most of these bands to the vibrations of the GG form.

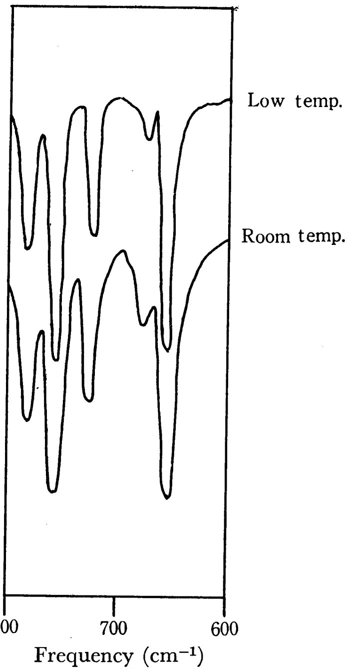

Fig. 1. Infrared spectra of methyl ethyl sulfide in the 800—600 cm^{-1} region observed in the liquid state.

Discussion

Perchard[10] made the vibrational analyses of eight isotopic species of methyl ethyl ether. He concluded that two forms, T and G, exist at room temperature, the former being more stable, and the T form in the solid state, and that the energy difference between the two forms in the liquid state is *ca.* 1.35 kcal/mol. For methyl ethyl sulfide, the intensities of the bands at 783 and 676 cm^{-1} decrease upon cooling, as is shown in Fig. 1. The low-temperature spectrum was recorded at a temperature slightly above its melting point. These bands correspond well to the frequencies calculated for the G form. Thus, the G form is the less stable conformation in the liquid state. The conformations of sulfides correspond well with those of ethers. For methyl isopropyl sulfide,[11] we previously obtained the energy difference of *ca.* 1—1.5 kcal/mol. We suppose that the energy difference for methyl ethyl sulfide is *ca.* 1 kcal/mol.

Recently, Scott and El-Sabban[12] made the normal coordinate treatment for diethyl sulfide, and concluded that the GG form has too much energy to exist as the stable form. Moreover, Snyder and Zerbi[13] and Wieser *et al.*[14] have treated the vibrational spectra and normal coordinates for diethyl ether, and have denied that diethyl ether exists in the GG form with stability. Wieser *et al.* assumed that diethyl ether exists in the TT and TG conformations at room temperature; the TT form is more stable than the TG form by *ca.* 1.1 kcal/mol. They also suggested that the C–H···O intramolecular hydrogen bond stabilizes the TT form. On the other hand, Snyder[15] reported a few of the bands due to the GG conformation for *n*-pentane. He also suggested that the TG form is more stable than the GG form, although there is not so much energy difference between the TG and GG, and TT and TG conformations; the stability is in the order of TT>TG>GG. With reference to the cases of diethyl ether and *n*-pentane, one of the less stable forms of diethyl sulfide may be the TG conformations. As we discussed in the last section, we observed very weak bands which fit the frequencies calculated for the GG form well. Therefore, the existence of the GG form has also been confirmed. The result for *n*-pentane also supports this result. We may now conclude for diethyl sulfide that three conformations of the TT, TG, and GG coexist in the liquid and gaseous states, while only one, namely, the TT form, exists in the solid state.

Figure 2 shows the relations in the observed and calculated frequencies and the frequency shift upon deuteration for the three isotopic methyl ethyl sulfides. The calculated frequencies in general correspond well

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6) 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).

7) M. Hayashi, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **26**, 608 (1957).

8) 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).

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10) J. P. Perchard, *Spectrochim. Acta*, **A 26**, 707 (1970).

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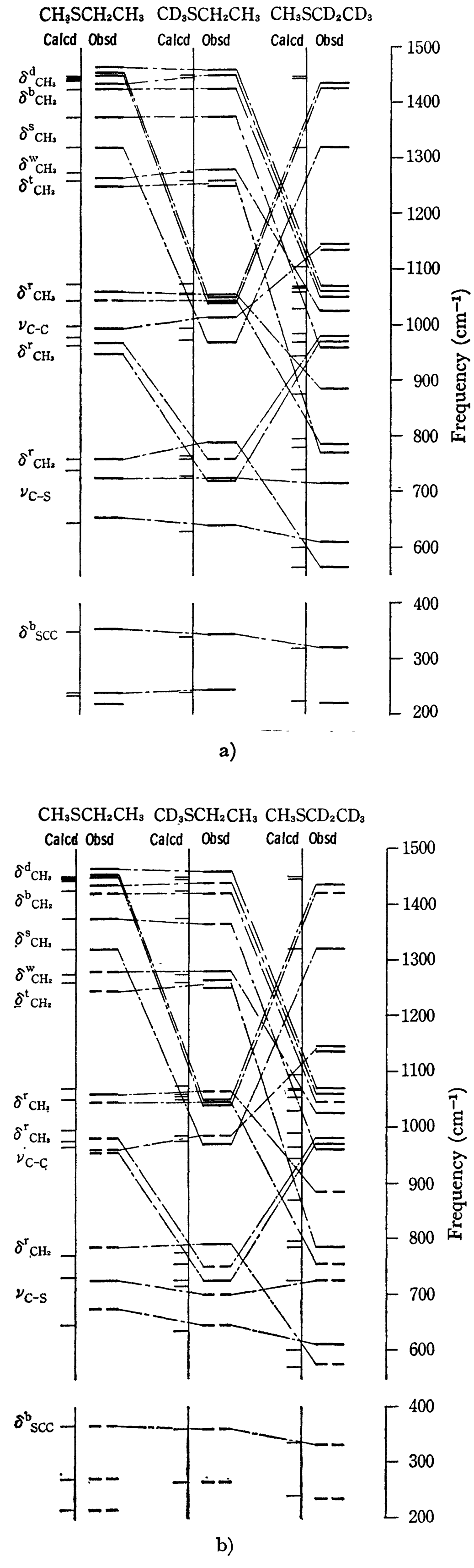
13) R. G. Snyder and G. Zerbi, *Spectrochim. Acta*, **A 23**, 391 (1967).

14) H. Wieser, W. G. Laidlaw, P. L. Krueger, and H. Fuhrer, *ibid.*, **24A**, 1055 (1968).

15) R. G. Snyder, *J. Chem. Phys.*, **47**, 1316 (1967).



a)

b)

Fig. 2. Comparison of the observed and calculated frequencies (cm^{-1}) among the three isotopic species. Obsd; solid line: the bands appearing in the solid state, broken line: the bands disappearing in the solid state.
a) T form. b) G form.

TABLE 8. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) OF THE C–C STRETCHING, C–S STRETCHING, AND THE SCC BENDING BANDS IN THE T FORM

	$CH_3SCH_2CH_3$		$CD_3SCH_2CH_3$		$CH_3SCD_2CD_3$	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
ν_{C-C}	995	1001	1013	995	1141$^{a)}$	1104
ν_{C-S}	726	742	724	727	716	739
ν_{C-S}	654	644	640	631	610	599
δ_{SCC}	354	348	345	342	321	318

a) Gaseous-state band.

with the observed ones. The frequency shifts upon deuteration can also be well explained by the calculations. In Table 8 the observed and calculated frequencies for the C–C stretching, C–S stretching, and SCC bending bands for the T form are listed. The observed C–C stretching bands are shifted to a higher frequency region through the $CH_3SCH_2CH_3$, CD_3SCH_2-CH_3, and $CH_3SCD_2CD_3$ species. The calculated frequencies also show this tendency. On the other hand, the C–S stretching and SCC bending bands are shifted to a lower-frequency region through the above-mentioned species. The calculated frequencies fairly well support the observed tendency. For the G form, the observed frequency shifts upon deuteration are also explained by the normal coordinate treatment. The higher-frequency shift of the C–C stretching band can be understood if we consider that the band is pushed up to a higher frequency region by the CD_3 and CD_2 deformation vibrations.

A_2 Modes of Diethyl Sulfide. For the TT form of diethyl sulfide, the two C–H stretching bands and one each of the CH_3 degenerate deformation, CH_2 twisting, CH_3 rocking, CH_2 rocking, C–C torsion, and the C–S torsional bands belong to the A_2 species. We previously made the assignments of the A_2 modes of dimethyl sulfide[16] by examining the annealed spectra. In the diethyl sulfide, we can expect the distortion of the molecular structure upon crystallization. If the site symmetry of C_{2v} for diethyl sulfides does not remain in the solid state, the former seven bands may appear in the region we recorded.

One of the doublet bands around 2940 cm^{-1} can be assigned to the A_2 mode. The analyses of the annealed bands at 1449, 1442, and 1436 cm^{-1} are very difficult. We may, however, assign one of these bands to the A_2 species. The liquid bands at 1248 and 1028 cm^{-1} persist in the solid state with intensities much weaker than in the liquid state. We can assign these bands to the A_2 twisting and rocking vibrational modes. The frequencies of the observed bands fit the calculated A_2 frequencies well. Among the A_2 modes, the CH_2 rocking, and C–C torsional bands were not observed in the annealed spectra. We now consider that the CH_2 rocking and C–C torsional bands are essentially too weak to appear in the spectrum. Thus, we were able to identify most of the bands belonging to the A_2 species of diethyl sulfide.

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

TABLE 9. CHARACTERISTIC FREQUENCIES (cm^{-1}) OF THE CH_3 AND CH_2 DEFORMATION REGIONS IN THE [T] FORM

	CH_3-SCH_3[a)]	CH_3-SCH_2-CH_3	CD_3-SCH_2-CH_3	CH_3-SCD_2-CD_3	$(CH_3$-$CH_2)_2S$
CH_3 deg def	1448	1465	1460	1437	1478
	1432	1457	1452	1427	1459
	1428	1448			1453
	1421	1436			1449
CH_3 sym def	1331	1374	1377	1320	1381
	1303	1319			1373
CH_3 rock	1039	1062	1056	978	1074
	985	1045	1045	970	1066
	952	968			1047
	910	948			1028
CH_2 bend		1427	1426		1438
					1425
CH_2 wag		1264	1278		1282
					1258
CH_2 twist		1249	1266 1248		1248
					1236
CH_2 rock		758	789		797
					762

a) Solid-state bands.

Snyder and Zerbi[13)] assigned the bands at 1148 (vw) and 811 cm^{-1} (vw) of diethyl ether to the A_2 species. Also, the bands which may be due to the A_2 modes appear in the C–H stretching and CH_3 degenerate deformation regions in the solid-state spectra. On the other hand, for the species of dimethyl ether, Snyder and Zerbi[13)] observed bands which may be due to the A_2 species in the annealed spectra —at 2907 (w) or 2877 (m), 1445 (w), and 1152 cm^{-1} (w)—, although they did not identify them as the A_2 modes. Therefore, it is likely that dimethyl and diethyl ether do not maintain the C_{2v} site symmetry in the solid state either.

CH_3 and CH_2 Deformation Regions. The CH_3 and CH_2 deformation bands of the sulfides in the [T] form are summarized in Table 9. The observed data of dimethyl sulfides are taken from Reference 16. The CH_3 degenerate deformation vibrations appear in the 1480—1420 cm^{-1} region. There are two sorts of symmetrical deformation vibrations, namely, the vibrations of the methyl groups bonded to the sulfur atom (I) and those bonded to the carbon atom (II). The CH_3 symmetrical deformation bands of Case I appear around 1320 cm^{-1}, and the corresponding bands of Case II, around 1380 cm^{-1}. The CH_3 rocking vibrations in the ethyl group are strongly coupled together with the C–C stretching and/or the CH_2 deformation vibrations. In a previous note on methyl ethyl sulfide,[1)] we assigned the five bands in the 990—940 cm^{-1} region to the CH_3 rocking vibrations, but we noticed that the bands in the higher-frequency region were not assigned to the sole vibrational mode. It is more reasonable to consider now that the bands at 968 and 962 cm^{-1} in the annealed state of methyl ethyl sulfide are the results of crystal-field splitting. The band at 960 cm^{-1} in the liquid spectrum is assigned to the vibration of the G form. The CH_2 bending vibrations appear in the 1440—1420 cm^{-1} region. The bands assignable to the CH_2 wagging and twisting vibrations appear very close together.

C–S Stretching Region. The C–S stretching bands are shifted to a lower frequency region from dimethyl to diethyl sulfides. This is easily recognized by considering the masses of the groups bonded to the sulfur atom. In a previous note on diethyl sulfide,[2)] the band at 738 cm^{-1} in the liquid state was identified as the C–S stretching fundamental. However, this band is too high to assign to the C–S stretching fundamental and too low to assign to the CH_2 rocking fundamental in view of the results on the normal coordinates. At the present time, we cannot reasonably explain this liquid band.