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Molecular Vibrations, Conformational Analyses, and Force Fields of Normal and Monodeuterated (Methylthio)methanethiol

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(Methylthio)methanethiol, CH_3SCH_2SH, and (methylthio)methanethiol-d_1, CH_3SCH_2SD, were prepared, and their infrared spectra were obtained in the gaseous, liquid, and solid states. The obtained spectra have been assigned. The frequency shifts by D-substitution, gaseous-liquid transition, and liquid-solid transition have also been discussed. The normal coordinates of these thiols have been treated by a modified Urey-Bradley force field. The force constants used in the computation have been transferred from those previously reported, but we adjusted them to produce the experimental wave numbers. The calculated wave numbers correspond well with those observed. The stable molecular conformations of the normal and deuterated species have been determined by the aid of the normal coordinate treatment. In the gaseous and liquid states, at least three to four forms from among TT, TG, GT, GG, and GG′ have been confirmed to exist. In the solid state, though, CH_3SCH_2SH or CH_3SCH_2SD exists in only one form: GG.

Recently, the molecular vibrations and conformations of alkanethiols have been extensively studied.[1-6] At present, however, we can find no report on the vibrational and structural analysis of (methylthio)methanethiol. In this paper we will discuss the vibrational assignments; we prepared CH_3SCH_2SH and CH_3SCH_2SD and recorded their infrared spectra. From the vibrational data thus obtained, we will first treat the molecular vibrations of these molecular species in detail. (Methylthio)methanethiol, CH_3SCH_2SH has a molecular unit in common with CH_3SCH_2–D and CH_3SCH_2–SCH_3. We previously reported the existence of rotational isomers on the CH_3SCH_2D species.[7] As for the $CH_3SCH_2SCH_3$ species, we also postulated the existence of rotational isomers around the C–S bond.[8] Therefore, we will now try to establish the existence of rotational isomers on the CH_3SCH_2SH and CH_3SCH_2SD species. In order to determine the molecular conformation and confirm the vibrational assignment, the normal coordinate treatment has also been carried out for normal and monodeuterated (methylthio)methanethiol. For the organo-sulfur compounds without the SCS skeleton, Scott and El-Sabban carried out[5] the normal coordinate treatment by the use of the valence force field; they thus obtained a set of valence force constants. In the present study, the molecular vibrations were treated with a modified Urey-Bradley-type potential function, and the force constants were determined on a part of the SCS skeleton. The obtained force constants were then compared with Scott and El-Sabban's force constants.

Experimental

(Methylthio)methanethiol, CH_3SCH_2SH, was prepared by the method of Fehér and Vogelbruch.[9]

Bp 61°C/47 mmHg, (reported[9] bp 60°C/47 mmHg). The purity of the sample was above 98%, as estimated by gas chromatography. The deuterated species, CH_3SCH_2SD, was prepared from normal (methylthio)methanethiol by the direct exchange of thiol-hydrogen with D_2O in the presence of a small amount of catalytic potassium carbonate. The gaseous spectra (4000—550 cm^{-1}) were recorded by means of a 10-cm gas cell equipped with KBr windows under an appropriate vapour pressure. The liquid spectra (4000—200 cm^{-1}) were recorded by means of a liquid cell equipped with CsI windows. The solution spectra (4000—550 cm^{-1}) were recorded in carbon disulfide. The solid spectra (4000—200 cm^{-1}) were recorded near the temperature of liquid nitrogen with a low-temperature cell. The instrument used for the infrared measurement was a Perkin-Elmer Model 621 Spectrophotometer.

Vibrational Assignment

Tables 1 and 2 show the vibrational data obtained for CH_3SCH_2SH and CH_3SCH_2SD respectively. In the obtained spectra of the 3000—1000 cm^{-1} region,

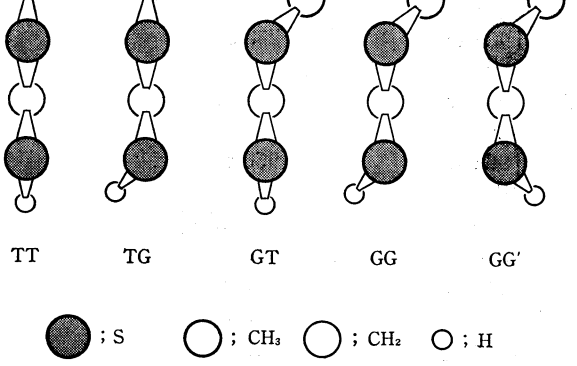

Fig. 1. Structures and conformations of (methylthio)-methanethiol.
T = *trans*, G = *gauche*.

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

Gaseous	Liquid	CS_2 soln	Solid[b)]	Assignment[c)]
3010 sh, vw 3003 w 2996 sh, vw		2985 sh, s	2985 sh, w	ν_{C-H}
2987 w 2980 w	2975 s	2974 s	2971 m	ν_{C-H}
2951 w 2941 w				
2937 2932 vs 2927	2915 vs	2913 vs	2914 s	ν_{C-H}
2918 sh, w 2913 sh, w				
2905 sh, vw 2902 sh, vw				
~2850 w	2854 w	2852 w	2853 vw	over or combi
~2835 sh, vw	2829 w	2827 w	2825 vw	over or combi
	2605 sh, vw, br	2610 sh, vw, br	—	
	2545 s, vvbr	2550 m, vbr	2515 s, vbr	ν_{S-H}
	2500 sh, w	2500 sh, w	—	
	2430 sh, vw		—	
1461 w	1437 sh, vw		1438 sh, w	
1451 m 1447 m 1445 m 1441 m 1435 m	1435 vs		1433 s	$\delta^d_{CH_3}$
1428 1426 m 1423	1422 vs		1418 s	$\delta^d_{CH_3}$
1415 w 1405 w	1415 sh, vw		—	over or combi
1395 vw	1393 m	1393 m	1383 w	$\delta^b_{CH_2}$
1323 vvw	1318 w	1317 w	1313 vw	$\delta^s_{CH_3}$
	1220 sh, m	1220 sh, m	—	$\delta^w_{CH_2}$
1224 1219 s 1211	1214 vs	1212 vs	1217 vs	$\delta^w_{CH_2}$
	1200 sh, m	1201 sh, m	—	$\delta^w_{CH_2}$
	1164 w	1162 w	1169 w	$\delta^t_{CH_2}$
	1137 sh, w	1135 sh, w	—	over or combi
1000 sh, vw	994 sh, vw	992 sh, vw	—	$\delta^r_{CH_3}$
995 989 w 983	988 s	985 s	992 vs	$\delta^r_{CH_3}$
980 w	977 sh, vw	975 sh, vw	—	$\delta^r_{CH_3}$
970 962 w 955	960 s	959 s	961 m	$\delta^r_{CH_3}$
935 vw	934 sh, vw	933 sh, vw	—	δ^b_{CSH}
928 vw	927 m	926 m	925 w	δ^b_{CSH}
917 vw	917 sh, vw	916 sh, vw	—	δ^b_{CSH}
	805 vw	805 vvw	807 vw	$\delta^r_{CH_2}$
765 m 758 m	755 sh, s	756 s	—	ν_{C-S}
753 sh, m 751 sh, m 747 sh, m	745 vs	746 vs	745 vs	ν_{C-S}
740 sh, m	740 sh, w	740 sh, w	—	ν_{C-S}

Table 1. Continued

Gaseous	Liquid	CS_2 soln	Solid[b]	Assignment[c]
712 w 705 w	705 sh, m	705 sh, s	—	$\nu_{\mathrm{C-S}}$
698 w 694 w 687 sh, w	697 vs	700 vs	697 vs	$\nu_{\mathrm{C-S}}$
	693 sh, vw	696 sh, vw	—	$\nu_{\mathrm{C-S}}$
670 vvw	669 sh, vw	669 vw	—	$\nu_{\mathrm{C-S}}$
639 vw	639 w	638 w	643 w	$\nu_{\mathrm{C-S}}$
	345 sh, vvw		—	δ_{skel}
	335 vw		338 vw	
	~295 sh, vvw		—	
	~285 vvw		—	
	272 sh, vvw		—	
	~260 vw		—	
	237 vw		235 vvw	
	220 sh, vvw		—	

s, -strong; m, -medium; w, -weak; v, -very; sh, -shoulder; br, -broad; and ~, poorly estimated bands.

a) Above 3100 cm^{-1}, 2800—2650 cm^{-1}, and 2400—1500 cm^{-1} regions are omitted.

b) —, bands disappeared in the solid state.

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

there appeared nearly the same number of bands as we expected for one conformation. In the 1000—200 cm^{-1} region, however, a fairly larger number of bands appeared than that expected for one form. Therefore the question of the existence of rotational isomers comes to mind.

Now we can see five possible molecular conformations of (methylthio)methanethiol: TT (C_s), TG (C_1), GT (C_1), GG (C_1), and GG' (C_1), all of which are shown in Fig. 1. All of the fundamental vibrations of each conformation are infrared-active.

Liquid-state Spectra. The liquid-state spectra of CH_3SCH_2SH and CH_3SCH_2SD are shown in Figs. 2 and 3 respectively. The obtained spectra of normal (methylthio)methanethiol are similar to those of bis(methylthio)methane.[8)]

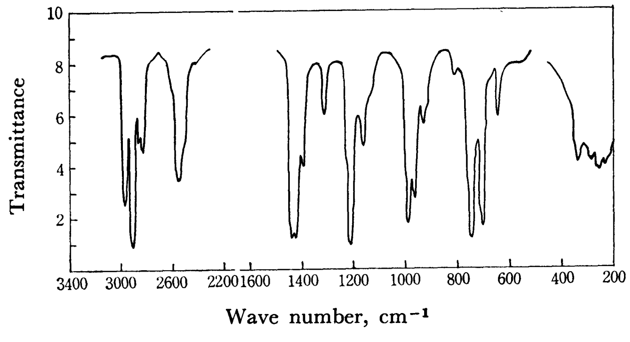

Fig. 2. Infrared spectra of (methylthio)methanethiol in the liquid state.

Five C–H stretching vibrations are expected for one conformation. In this region, we observed five bands. The bands at 2854 and 2829 cm^{-1} (2828 cm^{-1} in D-species), however, may not be due to the fundamentals. The characteristic bands of normal thiols (or deuterated thiols) are expected in the 2600—2500 cm^{-1} (or 1900—1800 cm^{-1}) region. The very broad bands around 2540 and 1860 cm^{-1} are assigned to the S–H and S–D stretching vibrations respectively. From the assignments of dimethylsulfide and $CH_3S(CH_2S)_nCH_3$ (n=1—3),[8)] the bands appearing around 1430 cm^{-1} are assigned to the CH_3 degenerate deformation, and a band around 1390 cm^{-1} is assigned to the CH_2 bending vibrations, although, these vibrations are not independent of each other. For the CH_3 symmetrical deformation, the band at 1318 cm^{-1} of the normal species and the band at 1317 cm^{-1} of the deuterated species are assigned. The band maxima at 1214 and 1164 cm^{-1} of the normal species, and at 1210 and 1158 cm^{-1} of the deuterated species, are assigned to the CH_2 wagging and twisting vibrations respectively. The CH_2 wagging and twisting bands are shifted in *ca.* 5 cm^{-1} to the lower-frequency region by D-substitution. The two shoulder bands around 1210 cm^{-1} of both the normal and deuterated species may be due to the rotational isomerism. The strong bands accompanied by weak shoulder bands at 988 and 960 cm^{-1} of the normal species and at 974 and 961 cm^{-1} of the deuterated species are assigned to the CH_3 rocking vibrations. The CSH bending vibration is expected around 900—800 cm^{-1}. Nothing appears in this region. Although the medium bands with weak

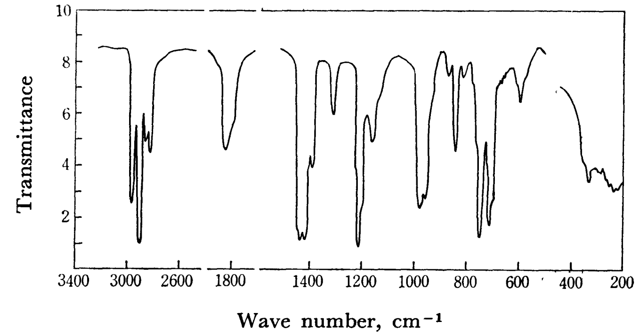

Fig. 3. Infrared spectra of (methylthio)methanethiol-d_1 in the liquid state.

TABLE 2. INFRARED FREQUENCIES (cm^{-1}) AND ASSIGNMENTS OF (METHYLTHIO)METHANETHIOL-d_1[a)]

Gaseous	Liquid	CS_2 soln	Solid[b)]	Assignment[c)]
3010 sh, vw 3005 w 2996 sh, vw		2985 sh, s	2985 sh, w	ν_{C-H}
2990 2980 w 2965	2975 s	2974 s	2971 m	ν_{C-H}
2946 sh, w 2942 sh, w				
2937 2932 vs 2927	2915 vs	2914 vs	2913 s	ν_{C-H}
2915 sh, w 2905 sh, w				
2894 sh, w 2880 sh, w				
2864 sh, vw 2853 w 2844 sh, vw	2854 w	2852 w	2853 vw	over or combi
2835 sh, vw	2828 w	2827 w	2824 vw	over or combi
	1900 vw, vvbr	1900 vw, vvbr	—	
	1850 s, vvbr	1850 s, vvbr	1830 s, vvbr	ν_{S-D}
	1810 sh, w	1810 sh, w	—	
1460 w	1437 sh, w		1438 sh, w	
1451 m 1447 m 1443 m 1440 m 1437 m	1435 vs		1433 s	$\delta^d_{CH_3}$
1428 m 1426 m 1425 m 1423 m	1421 vs		1418 s	$\delta^d_{CH_3}$
1415 w 1405 w	1418 sh, w		—	over or combi
1395 vw	1393 m	1393 m	1383 w	$\delta^b_{CH_2}$
1322 vvw	1317 w	1317 w	1314 vw	$\delta^s_{CH_3}$
	1217 sh, m	1214 sh, m	—	$\delta^w_{CH_2}$
1219 1213 s 1207	1210 vs	1207 vs	1210 vs	$\delta^w_{CH_2}$
	1200 sh, m	1200 sh, m	—	$\delta^w_{CH_2}$
	1158 w	1156 w	1162 w	$\delta^t_{CH_2}$
	1137 sh, vw	1135 sh, vvw	—	over or combi
988 981 w 978	974 s	973 s	977 vs	$\delta^r_{CH_3}$
970 w	970 sh, vw	969 sh, vw	—	$\delta^r_{CH_3}$
967 sh, w 962 w 954 w	961 s	959 s	961 s	$\delta^r_{CH_3}$
	870 vw		—	over or combi ?
	840 m		842 m	$\delta^r_{CH_2}$
	808 vw	807 vw	—	$\delta^r_{CH_2}$
774 w	774 sh, vw	774 sh, vw	—	ν_{C-S}
765 m 759 m	758 sh, m	757 m	—	ν_{C-S}
754 m 749 sh, m 746 sh, m	746 vs	747 vs	747 vs	ν_{C-S}

Table 2. Continued

Gaseous	Liquid	CS_2 soln	Solid[b)]	Assignment[c)]
724 sh, vw 720 vw	725 sh, vw	728 sh, w	—	ν_{C-S}
711 705 w 700	707 vs	708 vs	707 vs	ν_{C-S}
695 w	695 s	695 s	—	ν_{C-S}
670 vvw	670 vw	670 vw	—	ν_{C-S}
~660 vvw	661 vw	661 vw	663 w	ν_{C-S}
	658 sh, vw		—	ν_{C-S}
600 vvw	600 sh, vw	600 sh, vw	—	$\delta^b{}_{CSD}$
594 vvw	594 w	593 w	597 w	$\delta^b{}_{CSD}$
587 vvw	587 sh, vw	587 sh, vw	—	$\delta^b{}_{CSD}$
	338 sh, vvw		—	δ_{skel}
	330 vw		330 vw	
	~295 vvw		—	
	~285 vvw		—	
	272 sh, vvw		—	
	~260 vw		—	
	235 vw		225 vvw	
	219 vvw		—	

s, -strong; m, -medium; w, -weak; v, -very; sh, -shoulder; br, -broad; and ~, poorly estimated bands.
a) Above 3100 cm^{-1}, 2800—1950 cm^{-1}, and 1800—1500 cm^{-1} regions are omitted.
b), c) See b), c) of Table 1.

shoulders around 930 cm^{-1} are fairly higher than those expected, these bands may be assigned to the CSH bending vibrations. In the deuterated species, a band accompanied by two shoulders around 600 cm^{-1} is assigned to its also. The bands appearing in this region are many more than those expected for one conformation. The obtained band at 805 cm^{-1} of the normal species, and the 840 and 808 cm^{-1} bands of the deuterated species may be assigned to the CH_2 rocking vibrations. The C–S stretching vibrations may appear in the 800—600 cm^{-1} region. Three bands are expected for each conformation. In the infrared measurements, eight bands were observed—at 755, 745, 740, 705, 697, 693, 669, and 639 cm^{-1}—for the normal species, and nine bands—at 774, 758, 746, 725, 707, 695, 670, 661, and 658 cm^{-1}—for the deuterated species. The numbers of observed bands show the possibility of rotational isomerism. In this region, the bands of the normal species are shifted to a higher-frequency region by D-substitution. In the 400—200 cm^{-1} region, we observed eight bands, including very weak shoulder bands, for both the normal and deuterated species. In this region, the bands obtained are also many more than those expected for one form.

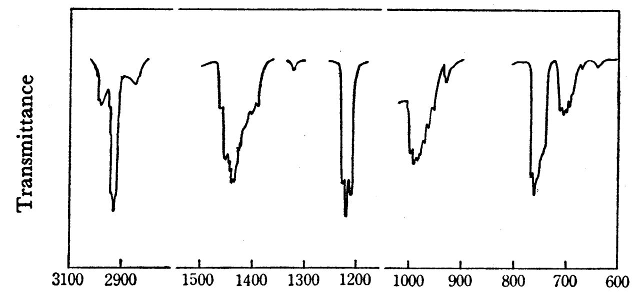

Fig. 4. Infrared spectra of (methylthio)methanethiol in the gaseous state.

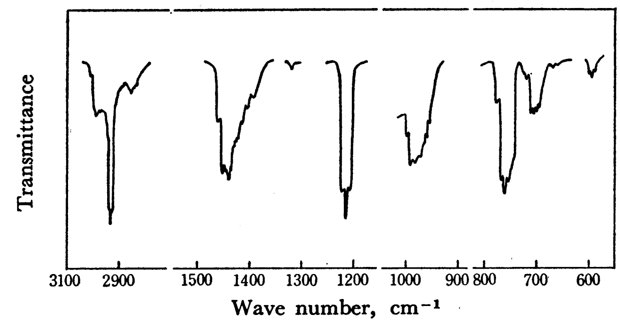

Fig. 5. Infrared spectra of (methylthio)methanethiol-d_1 in the gaseous state.

Gaseous-state Spectra. The gaseous-state spectra of CH_3SCH_2SH and CH_3SCH_2SD are shown in Figs. 4 and 5 respectively. We could not observe the S–H stretching, S–D stretching, CH_2 twisting, or CH_2 rocking vibrations. In the C–H stretching region, the resolution was fairly good. In both species, very strong and sharp PQR bands were obtained around 2930 cm^{-1}. Those bands are shifted by *ca.* 20 cm^{-1} to a higher frequency region than that in the liquid state. In the CH_3 degenerate deformation and the CH_2 bending region, rotational bands of the water vapor in the atmosphere are overlapped. Therefore, the band assignments are very difficult. In the CH_2 wagging region around 1200 cm^{-1}, very strong RQP peaks appeared at 1224, 1219, and 1211 cm^{-1} for the normal species, and at 1219, 1213, and 1207 cm^{-1} for the deuterated species. The Q-branch of the D-species shifts lower 6 cm^{-1} than that of the normal species. In the CH_3 rocking region, a lower-frequency shift upon D-substitution is also observed. In the C–S stretching region, fairly complex spectra were obtained. The bands in this region may be mutually overlapped. In this region, a higher-frequency shift upon D-substitution was observed. In order to confirm the existence of the rotational isomers on CH_3SCH_2SH species, we attempted to investigate the temperature dependence of the intensity of the gaseous bands in the 850—600 cm^{-1} region (33—124°C). However, we could not obtain intensity changes sufficient to decide the energy differences because of the rotational isomerism in this temperature region.

Solid-state Spectra. Near the temperature of liquid nitrogen, we obtained the solid-state spectra of CH_3SCH_2SH and CH_3SCH_2SD shown in Figs. 6 and 7 respectively. Although we repeated annealing above and below their melting points, the samples were not completely crystallized. In the C–H stretching region, the difference between the liquid and solid spectra was not observed. In the S–H or S–D stretching region, a large lower-frequency shift due to the liquid-solid transition was observed. The reason for this lower frequency shift is not clear. In the solid state, however, it is supposed that the intermolecular hydrogen bonding is formed more strongly than the liquid, and that the S–H (S–D) stretching band is shifted lower on a weakening of the S–H or S–D bond. In the CH_3 degenerate deformation, CH_3 symmetrical deformation, CH_2 wagging, CH_2 twisting, CH_3 rocking, CSH or CSD bending, CH_2 rocking, and the skeletal deformation regions, the liquid-solid transition shifts stay within *ca.* 10 cm^{-1}. In the C–S stretching region, the frequency shift due to the liquid-solid transition was not so clear.

From the infrared spectra we have obtained, the following questions arise. The first concerns the extraordinary breadth of the S–H and S–D stretching bands. The second concerns the very large lower-frequency shift (*ca.* 330 cm^{-1}) of the CSH bending vibration upon D-substitution. The third concerns the large higher-frequency shift (*ca.* 35 cm^{-1}) of the CH_2 rocking vibration upon D-substitution. The first can be explained as the result of the rotational isomerism; it may also be due to the hydrogen bond just as in the alcohols. As for the second and third problems, these large frequency shifts will be explained in the following section.

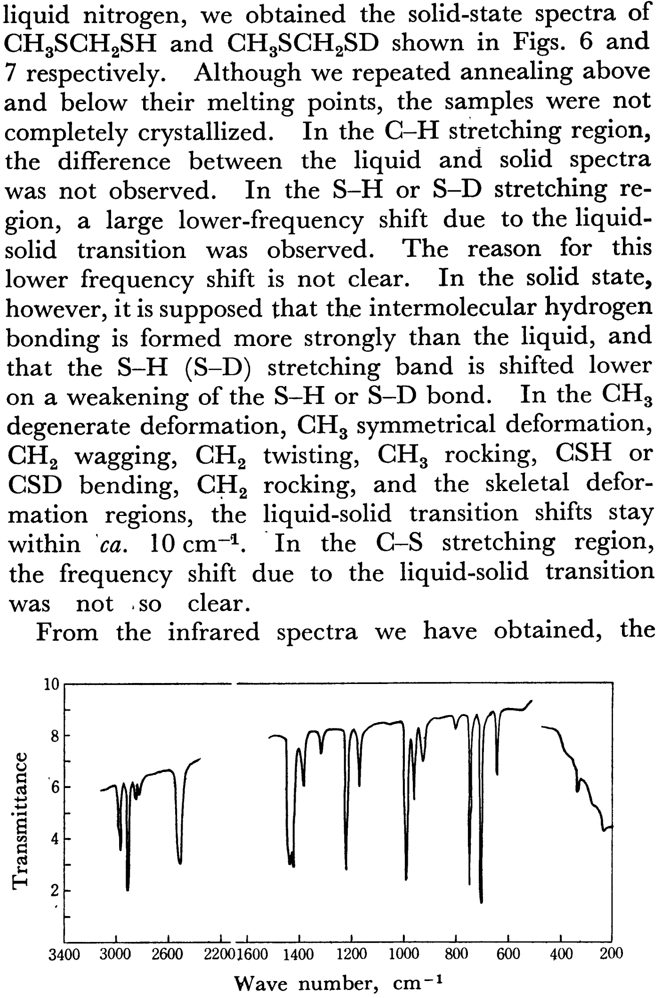

Fig. 6. Infrared spectra of (methylthio)methanethiol in the solid state.

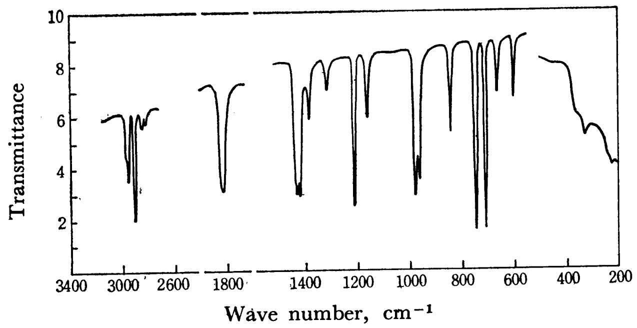

Fig. 7. Infrared spectra of (methylthio)methanethiol-d_1 in the solid state.

Normal Coordinate Treatment

We made the normal coordinate treatment for the five most probable forms: TT, TG, GT, GG, and GG′. The molecular parameters used in the computations were as follows:

$$r(\text{C-H})=1.09\text{Å}, \quad \phi(\text{CSC})=99°,$$
$$r(\text{C-S})=1.81\text{Å}, \quad \phi(\text{CSH})=96.5°,$$
$$r(\text{S-H})=1.335\text{Å}.$$

Table 3. Modified Urey-Bradley force constants[a] of (methylthio)methanethiol

K(C-H)	4.286	CH_3 and CH_2 groups
K(C-S)	1.691	CH_3-S, S-CH_2, and CH_2-SH bonds or CH_2-SD bond
K(S-H)	3.500	S-H bond
K(S-D)	3.591	S-D bond
H(HCS)	0.030	CH_3 group
H(HCH)	0.366	CH_3 group
H(CSC)	0.244	CH_3-S-CH_2 angle
H(SCS)	0.150	S-CH_2-S angle
H(SCH)	0.170	CH_2 group
H(HCH)	0.335	CH_2 group
H(CSH)	0.060	CH_2-S-H or CH_2-S-D angle
F(HCS)	0.763	
F(HCH)	0.200	
F(CSC)	0.210	
F(SCS)	0.500	
F(SCH)	0.390	
F(HCH)	0.200	
F(CSH)	0.580	
κ	0.060	CH_3 group
	−0.005	CH_2 group
Y	0.054	CH_3-S and S-CH_2 bonds
	0.035	CH_2-SH or CH_2-SD bond
p	−0.115	CH_3 and CH_2 groups
p′	−0.189	CH_3-S, S-CH_2, and CH_2-SH bonds or CH_2-SD bond
n	0.033	CH_3 group (∠HCS and ∠HCH)
t	0.070	CH_3 group (∠HCS and ∠CSC, *trans*)
g	−0.050	CH_3 group (∠HCS and ∠CSC, *gauche*)
l	0.005	S-CH_2-S

[a] *K*, stretching (mdyn/Å); *H*, bending (mdyn/Å); *F*, repulsion (mdyn/Å); $F'=-0.1\,F$; κ, intramolecular tension (mdyn·Å); *Y*, internal rotation (mdyn·Å); *p* and *p*′, stretching interaction (mdyn/Å); *n*, angle interaction (mdyn·Å); *t* and *g*, *trans*- and *gauche* couplings (mdyn·Å); and *l*, angle interaction (mdyn·Å).

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

Obsd$^{a)}$	Calcd TT	PED$^{b)}$	Calcd TG	PED$^{b)}$	Calcd GT	PED$^{b)}$	Calcd GG	PED$^{b)}$	Calcd GG′	PED$^{b)}$
2985	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(110)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)
2985	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)
2975	2963	ν_{C-H}(100)	2964	ν_{C-H}(100)	2964	ν_{C-H}(100)	2964	ν_{C-H}(100)	2964	ν_{C-H}(100)
2915	2910	ν_{C-H}(100)	2910	ν_{C-H}(100)	2910	ν_{C-H}(100)	2910	ν_{C-H}(100)	2910	ν_{C-H}(100)
2915	2901	ν_{C-H}(100)	2901	ν_{C-H}(100)	2901	ν_{C-H}(100)	2901	ν_{C-H}(100)	2901	ν_{C-H}(100)
2545	2542	ν_{S-H}(100)	2542	ν_{S-H}(100)	2542	ν_{S-H}(100)	2542	ν_{S-H}(100)	2542	ν_{S-H}(100)
1435	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)
1422	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)
1393	1396	$\delta^{b}_{CH_2}$(100)	1397	$\delta^{b}_{CH_2}$(100)	1396	$\delta^{b}_{CH_2}$(100)	1397	$\delta^{b}_{CH_2}$(100)	1397	$\delta^{b}_{CH_2}$(100)
1318	1317	$\delta^{s}_{CH_3}$(100)	1317	$\delta^{s}_{CH_3}$(100)	1317	$\delta^{s}_{CH_3}$(100)	1317	$\delta^{s}_{CH_3}$(100)	1317	$\delta^{s}_{CH_3}$(100)
1220$^{c)}$	1224	$\delta^{w}_{CH_2}$(100)			1221	$\delta^{w}_{CH_2}$(100)				
1214							1211	$\delta^{w}_{CH_2}$(100)		
1200$^{c)}$			1214	$\delta^{w}_{CH_2}$(100)					1211	$\delta^{w}_{CH_2}$(100)
1164	1158	$\delta^{t}_{CH_2}$(100)	1158	$\delta^{t}_{CH_2}$(100)	1158	$\delta^{t}_{CH_2}$(100)	1158	$\delta^{t}_{CH_2}$(100)	1158	$\delta^{t}_{CH_2}$(100)
994$^{c)}$									991	$\delta^{r}_{CH_3}$(100)
988	989	$\delta^{r}_{CH_3}$(100)	990	$\delta^{r}_{CH_3}$(100)	990	$\delta^{r}_{CH_3}$(100)	990	$\delta^{r}_{CH_3}$(100)		
977$^{c)}$	968	$\delta^{r}_{CH_3}$(100)								
960			968	$\delta^{r}_{CH_3}$(100)	967	$\delta^{r}_{CH_3}$(100)	967	$\delta^{r}_{CH_3}$(100)	967	$\delta^{r}_{CH_3}$(100)
934$^{c)}$			932	δ^{b}_{CSH}(75) $\delta^{r}_{CH_2}$(10)					933	δ^{b}_{CSH}(74) $\delta^{r}_{CH_2}$(11)
927							931	δ^{b}_{CSH}(78) $\delta^{r}_{CH_2}$(11)		
917$^{c)}$	928	δ^{b}_{CSH}(73) ν_{C-S}(13)			926	δ^{b}_{CSH}(74) ν_{C-S}(11)				
805	805	$\delta^{r}_{CH_2}$(96)	791	$\delta^{r}_{CH_2}$(86)	814	$\delta^{r}_{CH_2}$(90)	801	$\delta^{r}_{CH_2}$(78) ν_{C-S}(11)	797	$\delta^{r}_{CH_2}$(76) ν_{C-S}(14)
755$^{c)}$			746	ν_{C-S}(100)						
745							745	ν_{C-S}(100)		
740$^{c)}$	740	ν_{C-S}(100)			733	ν_{C-S}(100)			742	ν_{C-S}(100)
705$^{c)}$			714	ν_{C-S}(100) δ^{b}_{CSH}(12)					702	ν_{C-S}(100) δ^{b}_{CSH}(12)
697							698	ν_{C-S}(100) δ^{b}_{CSH}(13)		
693$^{c)}$	698	ν_{C-S}(100) δ^{b}_{CSH}(30)								
669$^{c)}$					687	ν_{C-S}(100) δ^{b}_{CSH}(30)				
639	633	ν_{C-S}(90) δ^{b}_{SCS}(20)	630	ν_{C-S}(86) δ^{b}_{SCS}(21) δ^{b}_{CSH}(13) δ^{b}_{CSC}(10)	620	ν_{C-S}(98) δ^{b}_{SCS}(19)	616	ν_{C-S}(95) δ^{b}_{SCS}(20) δ^{b}_{CSH}(14)	615	ν_{C-S}(96) δ^{b}_{SCS}(20) δ^{b}_{CSH}(14)
345$^{c)}$					335	δ^{b}_{CSC}(50) δ^{b}_{SCS}(29) ν_{C-S}(11)				
335							336	δ^{b}_{CSC}(50) δ^{b}_{SCS}(28) ν_{C-S}(10)	332	δ^{b}_{CSC}(50) δ^{b}_{SCS}(30) ν_{C-S}(10)
295$^{c)}$	289	δ^{b}_{SCS}(40) δ^{b}_{CSC}(22) ν_{C-S}(21)								
285$^{c)}$			289	δ^{b}_{SCS}(40) δ^{b}_{CSC}(21) ν_{C-S}(20)						
272$^{c)}$									245	δ^{b}_{SCS}(31) δ^{b}_{CSC}(35) τ_{C-S}(25)

TABLE 4. Continued

Obsd[a)]	Calcd TT	PED[b)]	Calcd TG	PED[b)]	Calcd GT	PED[b)]	Calcd GG	PED[b)]	Calcd GG'	PED[b)]
260[c)]					239	$\delta^b_{SCS}(34)$ $\delta^b_{CSC}(37)$ $\tau_{C-S}(19)$				
237							235	$\delta^b_{SCS}(37)$ $\delta^b_{CSC}(38)$ $\tau_{C-S}(15)$		
220[c)]	220	$\delta^b_{CSC}(67)$ $\delta^b_{SCS}(31)$	223	$\delta^b_{CSC}(66)$ $\delta^b_{SCS}(28)$						
	192	$\tau_{C-S}(99)$	193	$\tau_{C-S}(93)$			187	$\tau_{C-S}(91)$		
					183	$\tau_{C-S}(90)$			181	$\tau_{C-S}(88)$
	174	$\tau_{C-S}(99)$	174	$\tau_{C-S}(99)$	169	$\tau_{C-S}(92)$	169	$\tau_{C-S}(93)$	168	$\tau_{C-S}(88)$
	73	$\tau_{C-S}(98)$	71	$\tau_{C-S}(97)$	70	$\tau_{C-S}(94)$	69	$\tau_{C-S}(95)$	69	$\tau_{C-S}(94)$

a) From Table 1.
b) ν, -stretching; δ^d, -degenerate deformation; δ^b, -bending; δ^s, -symmetrical deformation; δ^w, -wagging; δ^t, -twisting; δ^r, -rocking; and τ, -torsion.
c) Bands disappeared in the solid state.

The other bond angles were tetrahedral. The force field used was one in which we added some correction terms to the simple Urey-Bradley force field. The correction terms are: the bond-interaction constant of C–H bonds (p), the bond-interaction constant of C–S bonds (p'), the angle-interaction constant between ∠HCS and ∠HCH in the CH_3 group (n), the *trans* and *gauche* coupling constants between ∠HCS and ∠CSC in the CH_3 group (t and g), and the angle-interaction constant between SCH angles in the CH_2 group (l). Most of the force constants relating to the CH_3 group were transferred from those of dimethyl sulfide.[7)] Some of the force constants relating to the CH_3 group were used by being changed within their dispersion.[10)] The other force constants were referred to those of 1,2-ethanedithiol,[11)] *n*-propanethiol,[12)] polymethylene disulfide,[13)] and bis(methylthio)-methane.[14)] It has been supposed that the potential constants of CH_3SCH_2SH and CH_3SCH_2SD are common except for the S–H or S–D stretching constant.

The force constants of (methylthio)methanethiol obtained in the present study are listed in Table 3. The calculated wavenumbers are listed in Tables 4 and 5, together with the observed wavenumbers. Figs. 8 and 9 show the observed and calculated frequencies (1250—200 cm^{-1}), together with the observed band intensities. The calculated frequencies, in general, reproduced the observed frequencies well. The problems described in the previous section, that is, the very large lower-frequency shift of the CSH (CSD) bending and the large higher-frequency shift of the CH_2 rocking upon D-substitution, can also be well explained in the calculated wavenumbers.

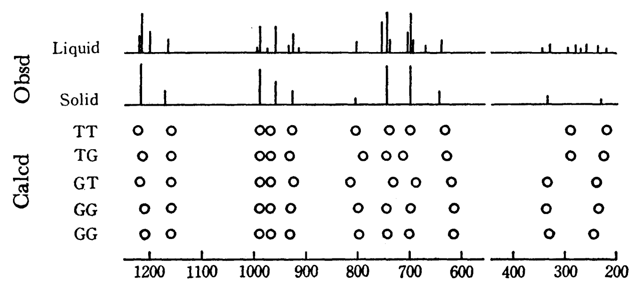

Fig. 8. Observed frequencies and relative intensities, and calculated frequencies of (methylthio)methanethiol (1250—200 cm^{-1}).

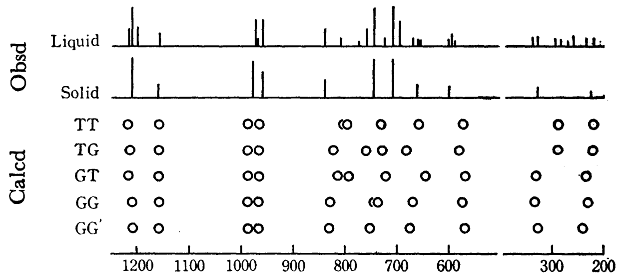

Fig. 9. Observed frequencies and relative intensities, and calculated frequencies of (methylthio)methanethiol-d_1 (1250—200 cm^{-1}).
The sets of the calculated wave numbers with close together are shown by the complete open circle which attached to the incomplete open circle.

C–H Stretching Region. The calculated C–H stretching frequencies did not reproduce the observed frequencies so well. The reason may be that we assumed the values of all the C–H stretching constants to be equal. This poor agreement might be overcome by distinguishing between two K(C–H) force constants in relation to the CH_3 and CH_2 groups.

S–H and S–D Stretching Regions. The S–H or S–D stretching vibration mainly depended on the S–H or S–D stretching constant, K(S–H) or K(S–D), and the CSH or CSD repulsion constant, on F(CSH) or F(CSD). We at first used the common value

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11) M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, This Bulletin, **38**, 1734 (1965).
12) M. Hayashi, Y. Shiro, and H. Mruata, *ibid.*, **39**, 112 (1966).
13) M. Hayashi, Y. Shiro, and H. Murata, *ibid.*, **39**, 1857 (1966).
14) M. Ohsaku, unpublished work.

Table 5. Observed and calculated frequencies (cm^{-1}), and potential energy distribution, PED, (%) of (methylthio)methanethiol-d_1

Obsd[a]	Calcd TT	PED[b]	Calcd TG	PED[b]	Calcd GT	PED[b]	Calcd GG	PED[b]	Calcd GG′	PED[b]
2985	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)
2985	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)	2999	ν_{C-H}(100)
2975	2963	ν_{C-H}(100)	2964	ν_{C-H}(100)	2964	ν_{C-H}(100)	2964	ν_{C-H}(100)	2964	ν_{C-H}(100)
2915	2910	ν_{C-H}(100)	2910	ν_{C-H}(100)	2910	ν_{C-H}(100)	2910	ν_{C-H}(100)	2910	ν_{C-H}(100)
2915	2901	ν_{C-H}(100)	2901	ν_{C-H}(100)	2901	ν_{C-H}(100)	2901	ν_{C-H}(100)	2901	ν_{C-H}(100)
1850	1845	ν_{S-D}(100)	1845	ν_{S-D}(100)	1845	ν_{S-D}(100)	1845	ν_{S-D}(100)	1845	ν_{S-D}(100)
1435	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)
1421	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)	1441	$\delta^{d}_{CH_3}$(100)
1393	1396	$\delta^{b}_{CH_2}$(100)	1396	$\delta^{b}_{CH_2}$(100)	1396	$\delta^{b}_{CH_2}$(100)	1396	$\delta^{b}_{CH_2}$(100)	1396	$\delta^{b}_{CH_2}$(100)
1317	1317	$\delta^{s}_{CH_3}$(100)	1317	$\delta^{s}_{CH_3}$(100)	1317	$\delta^{s}_{CH_3}$(100)	1317	$\delta^{s}_{CH_3}$(100)	1317	$\delta^{s}_{CH_3}$(100)
1217[c]	1220	$\delta^{w}_{CH_2}$(100)			1217	$\delta^{w}_{CH_2}$(100)				
1210							1211	$\delta^{w}_{CH_2}$(100)		
1200[c]			1214	$\delta^{w}_{CH_2}$(100)					1211	$\delta^{w}_{CH_2}$(100)
1158	1158	$\delta^{t}_{CH_2}$(100)	1158	$\delta^{t}_{CH_2}$(100)	1158	$\delta^{t}_{CH_2}$(100)	1158	$\delta^{t}_{CH_2}$(100)	1158	$\delta^{t}_{CH_2}$(100)
974					990	$\delta^{r}_{CH_3}$(100)	990	$\delta^{r}_{CH_3}$(100)	990	$\delta^{r}_{CH_3}$(100)
970[c]	989	$\delta^{r}_{CH_3}$(100)	989	$\delta^{r}_{CH_3}$(100)						
961	968	$\delta^{r}_{CH_3}$(100)	968	$\delta^{r}_{CH_3}$(100)	967	$\delta^{r}_{CH_3}$(100)	967	$\delta^{r}_{CH_3}$(100)	967	$\delta^{r}_{CH_3}$(100)
840			823	$\delta^{r}_{CH_2}$(78) δ^{b}_{CSD}(11)			828	$\delta^{r}_{CH_2}$(80)	832	$\delta^{r}_{CH_2}$(75) δ^{b}_{CSD}(11)
808[c]	804	$\delta^{r}_{CH_2}$(96)			815	$\delta^{r}_{CH_2}$(85) ν_{C-S}(10)				
774[c]	797	ν_{C-S}(72) δ^{b}_{CSD}(16)			793	ν_{C-S}(68) δ^{b}_{CSD}(17)				
758[c]			760	ν_{C-S}(90) $\delta^{r}_{CH_2}$(10)					753	ν_{C-S}(100)
746							746	ν_{C-S}(100)		
725[c]	733	ν_{C-S}(100)	730	ν_{C-S}(100)	722	ν_{C-S}(100)			722	ν_{C-S}(82) $\delta^{r}_{CH_2}$(16)
707							738	ν_{C-S}(83) δ^{b}_{CSD}(12)		
695[c]			683	ν_{C-S}(75) δ^{b}_{CSD}(27) δ^{b}_{SCS}(11)						
670[c]	660	ν_{C-S}(81) δ^{b}_{CSD}(30) δ^{b}_{SCS}(20)							676	ν_{C-S}(82) δ^{b}_{CSD}(30)
661							670	ν_{C-S}(84) δ^{b}_{CSD}(25)		
658[c]					644	ν_{C-S}(88) δ^{b}_{CSD}(35) δ^{b}_{SCS}(19)				
600[c]			581	δ^{b}_{CSD}(71) ν_{C-S}(50)						
594							574	δ^{b}_{CSD}(66) ν_{C-S}(60)		
587[c]	572	δ^{b}_{CSD}(62) ν_{C-S}(52)			569	δ^{b}_{CSD}(55) ν_{C-S}(56)			571	δ^{b}_{CSD}(66) ν_{C-S}(63)
338[c]					333	δ^{b}_{CSC}(50) δ^{b}_{SCS}(28) ν_{C-S}(11)				
330							335	δ^{b}_{CSC}(51) δ^{b}_{SCS}(28) ν_{C-S}(10)	328	δ^{b}_{CSC}(50) δ^{b}_{SCS}(30)
295[c]	289	δ^{b}_{SCS}(39) δ^{b}_{CSC}(23) ν_{C-S}(21)								

TABLE 5. Continued

Obsd[a]	Calcd TT	PED[b]	Calcd TG	PED[b]	Calcd GT	PED[b]	Calcd GG	PEG[b]	Calcd GG′	PED[b]
285[c]			287	δ^b_{SCS}(40) δ^b_{CSC}(23) ν_{C-S}(19)						
272[c]									241	δ^b_{SCS}(34) δ^b_{CSC}(39) τ_{C-S}(17)
260[c]					237	δ^b_{SCS}(36) δ^b_{CSC}(39) τ_{C-S}(14)				
235							231	δ^b_{SCS}(38) δ^b_{CSC}(39) τ_{C-S}(12)		
219[c]	218	δ^b_{CSC}(66) δ^b_{SCS}(31)	222	δ^b_{CSC}(66) δ^b_{SCS}(31)						
	178	τ_{C-S}(100)	178	τ_{C-S}(100)	169	τ_{C-S}(92)	169	τ_{C-S}(91)	169	τ_{C-S}(94)
	138	τ_{C-S}(98)	140	τ_{C-S}(97)	134	τ_{C-S}(95)	139	τ_{C-S}(96)	133	τ_{C-S}(89)
	73	τ_{C-S}(98)	69	τ_{C-S}(98)	70	τ_{C-S}(94)	67	τ_{C-S}(95)	67	τ_{C-S}(95)

a) From Table 2. b), c) See b), c) of Table 4.

for the S–H and S–D stretching constants, which gave higher S–H and lower S–D stretching frequencies than the observed ones. This phenomenon is known[15] to be common when the stretching constants of K(X–H) and K(X–D) are used. Therefore, we assumed that the K(S–D) to be 1.026 times[16,17] the K(S–H) constant, that is, K(S–H)=3.500 and K(S–D)=3.591 mdyn/Å; we thus obtained adequate calculated results.

1500—550 cm^{-1} Region. Two calculated CH_3 degenerate deformation frequencies were fairly higher (5—20 cm^{-1}) than the observed values; also the spacing of the calculated wavenumbers did not explain the observed spacing. The CH_3 degenerate deformation vibrations depend mainly on the potential constants, H(HCS), F(HCH), and $\kappa(CH_3)$, and on the angle interaction constant, n. Each of these four constants relates almost equally to both frequencies. The observed CH_2 wagging vibration in the liquid spectra is shifted 4 cm^{-1} by the D-substitution. In the calculated frequency, this tendency is also seen. The calculated CH_3 rocking vibrations are mainly due to the potential constants, H(HCS), H(HCH), and $\kappa(CH_2)$. They depend on the two rocking bands nearly equally. The CH_3 rocking vibration of normal and monodeuterated band maxima were obtained in the liquid spectra at 988 and 960 cm^{-1}, and at 974 and 961 cm^{-1}, respectively. The spacings of the observed spectra are 28 and 13 cm^{-1} for the normal and deuterated species. In the calculated wavenumbers, however, these spacings were not reasonably explained. The potential field of the CH_3 group of the molecule may not have a C_3 symmetry. The similar spacing of dimethyl sulfide was explained[7] in terms of the non-bonded interaction between two CH_3 groups. In this treatment, however, such interactions were not taken into consideration, since the constants could not be directly transferred. The calculated wavenumbers of the CH_2 rocking and the C–S stretching changed fairly much according to their molecular conformations.

Skeletal Deformation Region. The skeletal bending vibrations are mainly affected by the force constants, H(CSC), H(SCS), F(CSC), and F(SCS). The calculated frequencies fairly well reproduced the observed ones.

Molecular Forms

From the results of the calculated frequencies, we have seen that the CH_2 wagging, CH_3 rocking, CSH (CSD) bending, CH_2 rocking, C–S stretching, and skeletal deformation vibrations are fairly much affected by the internal rotation angles. In the observed spectra, there appeared three bands for the CH_2 wagging, four bands for the CH_3 rocking, three bands for the CSH bending, eight bands for the C–S stretching, and eight bands for the skeletal deformation regions on the normal species. On the deuterated species, we have seen three bands for the CH_2 wagging, three bands for the CH_3 rocking, two bands for the CH_2 rocking, nine bands for the C–S stretching, three bands for the CSD bending, and eight bands for the skeletal deformation regions. One CH_2 wagging, two CH_3 rocking, one CSH or CSD bending, three C–S stretching, and two to three bands for the skeletal deformation can be expected for each conformation. Therefore, if all of the observed bands are fundamentals, we can expect at least three or four conformations to coexist in the liquid and gaseous states.

The numbers of the bands appearing in the solid state suggest that only one form stays in the solid state. It was seen from the calculated results for the various molecular conformations that, in the region below

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[15] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J. (1950), pp. 519, 537, and 561.

[16] T. Shimanouchi and I. Suzuki, *J. Chem. Phys.*, **42**, 296 (1965).

[17] T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishii, *J. Mol. Spectrosc.*, **19**, 78 (1966).

TABLE 6. OBSERVED AND CALCULATED FREQUENCY SHIFTS, Δ (cm^{-1}),[a] OF (METHYLTHIO)METHANETHIOL BY D-SUBSTITUTION

Mode	Obsd[b]			Calcd				
	H[c]	D[d]	Δ	TT, Δ	TG, Δ	GT, Δ	GG, Δ	GG′, Δ
$\delta^{w}_{CH_2}$	1217	1210	7	4	0	4	0	0
$\delta^{t}_{CH_2}$	1169	1162	7	0	0	0	0	0
$\delta^{r}_{CH_3}$	992	977	15	0	1	0	0	1
δ^{b}_{CSH}	925	597	328	356	351	357	357	362
$\delta^{r}_{CH_2}$	807	842	−35	1	−32	−1	−27	−35
ν_{C-S}	745	747	−2	−57	−14	−60	−1	−11
ν_{C-S}	697	707	−10	−35	−16	−35	−40	−20
ν_{C-S}	643	663	−20	−27	−53	−24	−54	−61
δ_{skel}	338	330	8	0	2	2	1	4
δ_{skel}	235	225	10	2	1	2	4	4

a) $\Delta=\nu_H-\nu_D$. b) Solid bands. c) H, CH_3SCH_2SH. d) D, CH_3SCH_2SD.

1500 cm^{-1}, their rotational angles affect the wave numbers. The calculated wave numbers themselves, however, are not definite enough for us to decide the molecular conformation, since the force constant has an arbitrary value. The isotopic frequency shifts, however, give us more information about the molecular conformations if we compare the calculated results with the observed results, because the isotopic shifts of the calculated frequencies are, in general, little affected by the ambiguity of the force field.

In the obtained spectra, we observed frequency shifts in the S–H (S–D) stretching, CH_2 wagging, CH_2 twisting, CH_3 rocking, CSH (CSD) bending, CH_2 rocking, C–S stretching, and skeletal deformation regions. The calculated results have also shown shifts. Table 6 shows the observed results in the solid spectra and the calculated frequency shifts upon deuteration. In Table 6, the plus signs of Δ show the lower frequency shifts, while the minus signs show the higher ones, upon D-substitution. In the wagging region, the observed frequency shift is 7 cm^{-1}; the calculated frequency shifts are: TT (4 cm^{-1}), TG (0 cm^{-1}), GT (4 cm^{-1}), GG (0 cm^{-1}), GG′ (0 cm^{-1}). The observed frequency shift of the CH_2 twisting vibration is 7 cm^{-1}. On the other hand, the shift is not seen in the calculated frequencies. In the CH_3 rocking region, one of the observed shifts is 15 cm^{-1}; we can see the calculated frequency shift in the TG and GG′ conformations—1 cm^{-1}. In the CSH (CSD) bending region, we observed a frequency shift of 328 cm^{-1} upon deuteration. The calculated shifts of the TT, TG, GT, GG, and GG′ conformations are 356, 351, 357, 357, and 362 cm^{-1} respectively. In the CH_2 rocking region, the observed frequency shift is −35 cm^{-1}; the calculated frequency shifts are: TG (−32 cm^{-1}), GT (−1 cm^{-1}), GG (−27 cm^{-1}), and GG′ (−35 cm^{-1}). The shift of the TT form is in the reverse direction—1 cm^{-1}. The higher frequency shifts of the observed results in the C–S stretching bands become wide, —−2, −10, and −20 cm^{-1}, from short to long wavelengths. The conformations of TG, GG, and GG′ show the above-mentioned tendency. In the skeletal deformation region, the shifts of the five forms of the calculated results show nearly the same behavior. Above all, the calculated frequency shifts of the TG, GG, and GG′ conformations explain well the observed frequency shifts due to D-substitution. On the other hand, in the skeletal deformation region, the calculated wave numbers of the GT, GG, and GG′ conformations correspond well to the observed wave numbers in the solid state. The calculated wave numbers of the TG form do not explain the observed wave numbers of the skeletal vibrations. In the case of the GT form, the isotopic shifts are not reasonably explained either. Therefore, we excluded the TG and GT forms from the stable form in the solid state. There, the possibility of the GG and GG′ forms remains. In the cases of the GG and GG′ forms, the repulsion forces between the S–H (S–D) and CH_3 groups may be stronger in the GG′ form than in the GG form, so long as a strong hydrogen bond is not formed between S–H (S–D) and CH_3 groups. We, therefore, postulated the stable conformation in the solid state to be the GG form.

The molecular conformations existing in the liquid and gaseous states were also taken into consideration among the five conformation. Since the distance between S–H (S–D) and CH_3 groups is not so close in the GG′ conformation, we did not neglect the GG′ form, unlike the case of bis(methylthio)methane.[8] The molecular form in the solid state, GG, also exists in the gaseous and liquid states. Therefore, we will discuss mainly the liquid and gaseous band which disappear in the solid state. In the CH_2 wagging region of the liquid and gaseous spectra, we observed three bands of the normal species and also of the deuterated species. Among these three bands, two shoulder bands disappeared in the solid state. According to the calculated results of the normal species, the band at 1220 cm^{-1} corresponds to the TT and/or GT conformation, and the band at 1200 cm^{-1} corresponds to the TG and/or GG′ conformation. In the deuterated species, the band at 1217 cm^{-1} corresponds to the TT and/or GT form, and the band at 1200 cm^{-1} corresponds to the TG and/or GG′ conformation. In the CH_3 rocking region, two very weak shoulders and one very weak shoulder band are observed in the normal and deuterated species respectively. These shoulder bands correspond to the TT, TG, and/or GG′ conformations.

TABLE 7. $\mathscr{F}$-MATRICES OF THE MODIFIED UREY-BRADLEY AND VALENCE FORCE FIELDS[a]

A[b]

	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
R_1	4.879 4.663								
R_2	0.509 0.	3.633 3.213							
R_3	0.025 0.026	0.509 0.	4.879 4.663						
R_4	0.025 0.026	0.509 0.	0.025 0.026	4.879 4.663					
R_5	0. 0.	−0.059 0.	0. 0.	0. 0.	2.744 3.213				
R_6	0. 0.	0. 0.	0. 0.	0. 0.	0.161 0.	3.011 3.213			
R_7	0. 0.	0. 0.	0. 0.	0. 0.	0.260 0.	0.260 0.	4.760 4.663		
R_8	0. 0.	0. 0.	0. 0.	0. 0.	0.260 0.	0.260 0.	0.025 0.026	4.760 4.663	
R_9	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0.337 0.	0. 0.	0. 0.	3.712 3.800

B[b]

	R_{10}	R_{11}	R_{12}	R_{13}	R_{14}	R_{15}	R_{16}
R_{10}	0.675 0.615						
R_{11}	0.042 −0.015	0.675 0.615					
R_{12}	0.075 0.	0.075 0.	0.594 0.536				
R_{13}	0.042 −0.015	0.042 −0.015	0. 0.	0.675 0.615			
R_{14}	0.075 0.	0. 0.	0.042 0.	0.075 0.	0.594 0.536		
R_{15}	0. 0.	0.075 0.	0.042 0.	0.075 0.	0.042 0.	0.594 0.536	
R_{16}	0.070 0.150	−0.050 −0.150	0. 0.	−0.050 −0.150	0. 0.	0. 0.	1.129 1.422

C[b]

	R_{16}	R_{17}	R_{18}	R_{19}	R_{20}	R_{21}	R_{22}	R_{23}
R_{17}	0. —	1.141 —						
R_{18}	0. 0.	−0.004 —	0.613 0.615					
R_{19}	0. −0.150	−0.004 —	0.002 0.	0.613 0.615				
R_{20}	0. 0.	−0.004 —	−0.009 −0.015	0. 0.	0.613 0.615			
R_{21}	0. −0.150	−0.004 —	0. 0.	−0.009 −0.015	0.002 0.	0.613 0.615		
R_{22}	0. 0.	0. —	−0.004 0.	−0.004 0.	−0.004 0.	−0.004 0.	0.479 0.536	
R_{23}	0. 0.	0. —	0. 0.184	0. 0.	0. 0.184	0. 0.	0. 0.	0.817 0.814

D[b]

	R_{24}	R_{25}	R_{26}
R_{24}	0.054 0.054		
R_{25}	0. 0.	0.054 0.054	
R_{26}	0. 0.	0. 0.	0.035 0.035

Table 7. Continued

E[b)]

	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
R_{10}	0.327 0.	0.509 0.349						
R_{11}	0. 0.	0.509 0.349	0.327 0.					
R_{12}	0.093 0.	0. 0.	0.093 0.	0. 0.				
R_{13}	0. 0.	0.509 0.349	0. 0.	0.327 0.	0. 0.			
R_{14}	0.093 0.	0. 0.	0. 0.	0.093 0.	0. 0.	0. 0.		
R_{15}	0. 0.	0. 0.	0.093 0.	0.093 0.	0. 0.	0. 0.	0. 0.	
R_{16}	0. 0.	0.169 0.251	0. 0.	0. 0.	0.169 0.251	0. 0.	0. 0.	0. 0.

F[b)]

	R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}
R_{17}	0.384 —	0.384 —						
R_{18}	0. 0.	0.260 0.349	0.167 0.					
R_{19}	0.260 0.349	0. 0.	0.167 0.	0. 0.				
R_{20}	0. 0.	0.260 0.349	0. 0.	0.167 0.	0. 0.			
R_{21}	0.260 0.349	0. 0.	0. 0.	0.167 0.	0. 0.	0. 0.		
R_{22}	0. 0.	0. 0.	0.093 0.	0.093 0.	0. 0.	0. 0.	0. 0.	
R_{23}	0. 0.	0.459 0.322	0. 0.	0. 0.	0.317 0.	0. 0.	0. 0.	0. 0.

a) Figures are listed in order: Urey-Bradley, valence; matrices are symmetrical; and the non-listed parts are all zero; valence constants from Ref. 5.

b) See an appended map.

In the CSH or CSD bending region, two shoulders of three bands disappeared in the solid state. On the normal species, the weak shoulder band at 934 cm^{-1} may be due to the TG and/or GG′ form, and the band at 917 cm^{-1}, to the TT and/or GT form. The bands at 600 and 587 cm^{-1} of the deuterated species correspond to the TG, and to the TT, GT, and/or GG′ form, respectively. In the CH_2 rocking region, we can expect more than one band in view of the calculated frequencies. We obtained one band for the normal species and two for the deuterated species. The band at 808 cm^{-1} of the deuterated species corresponds well to the TT and/or GT conformation. In the C–S stretching region, we observed that five (or six) bands of the normal (or deuterated) disappeared in the solid state. The calculated frequencies of the TT, TG, GT, and GG′ forms correspond well to the bands which disappeared in the solid state. In the skeletal deformation region, eight bands were observed in both the normal and deuterated species. If all of these eight bands are due to the fundamentals, more than four conformations coexist in the gaseous and liquid states. Since the most stable GG form in the solid state has two bands in both the normal and deuterated species, the remaining six bands may due to the other conformations: TT, TG, GT, and GG′.

We have discussed the conformations coexisting in the liquid and gaseous states. In the liquid and gaseous spectra, the isotopic frequency shift cannot be used for the conformational analysis, since the selection of the corresponding pairs from among many bands is difficult. We can postulate that at least three to four conformations, including the GG form, coexist in the liquid and gaseous states. However, we cannot decide, from the results we have obtained, how many conformations, and which conformations among the TT, TG, GT, and GG′ forms, persist, except for the GG form, which exists in all three states. The existence of the GG′ form cannot now be denied.

Force Constants

In order to confirm the reasonableness of our obtained Urey-Bradley force constants, we attempted to compare these Urey-Bradley constants and Scott and El-Sabban's force constants.[5)] Scott and El-Sabban reported valence force constants for various organosulfur compounds which did not have the SCS skeleton. Table 7 shows the non-zero parts of both types of ***F***-matrix elements. The coordinate numbering is shown

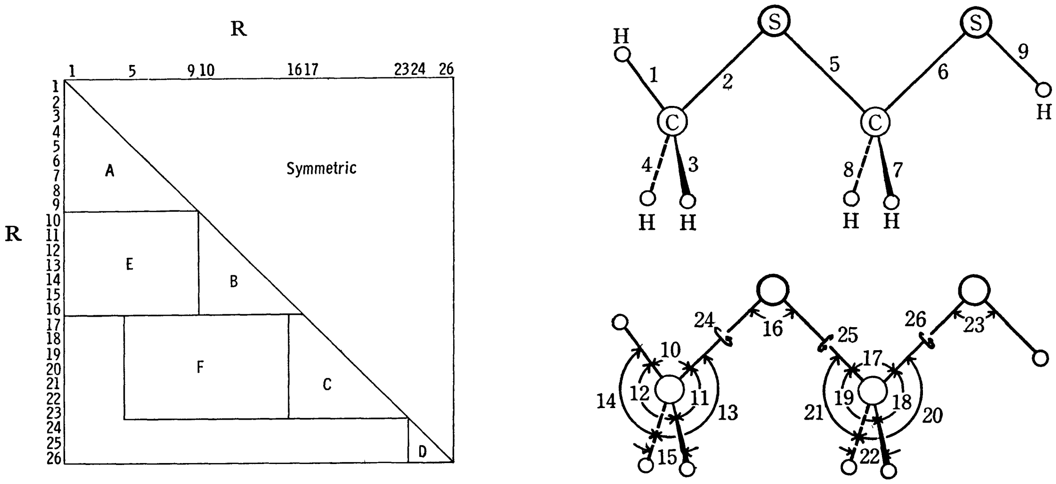

Fig. 10. Coordinates numbering for (methylthio)methanethiol.

in Fig. 10. The figures are listed in this order: Urey-Bradley, and valence force constants. No angle constant of ϕ(SCS) in the valence force field was obtained. In the diagonal elements, f_{ii} (i=1—26), our values agree well with Scott and El-Sabban's. Even for the off-diagonal parts, f_{ij} ($i \neq j$), the modified Urey-Bradley force elements and valence elements are in fairly good agreement. This shows that there is a good transferability of the obtained force constants for a wide range of organo-sulfur compounds. The newly-determined values for the SCS angle may be used on the valence force-type potential, *e.g.*, $f_{\mathrm{SCS,SCS}}=1.141$ and $f_{\mathrm{CS,SCS}}=0.384$ mdyn/Å.

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