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Molecular Vibrations and Force Fields of Alkyl Sulfides. I. Dimethyl Sulfide and Its Deuterated Compounds

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Dimethyl sulfide and dimethyl sulfide-d_1 were prepared, and their infrared spectra were measured in the gaseous and liquid states. The Raman spectra were measured in the liquid state. The assignments of their spectra were made. On these assigned frequencies, two sets of modified Urey-Bradley force constants and a set of local symmetry force constants were determined by a least-squares technique. The obtained force constants were then transferred to the treatment of the vibrational frequencies of dimethyl sulfide-d_3. The centrifugal distortion constants obtained from the vibrational data were compared with those from the data of the microwave spectra in order to confirm the reasonableness of the obtained force constants.

It would be useful to find a reasonable force field which could reproduce the observed vibrational frequencies and to acertain the assignments of the frequencies of a group of molecules of alkyl sulfides. The present paper, the first of a series of reports on alkyl sulfides, will deal with the molecular vibrations and several force fields of dimethyl sulfide, dimethyl sulfide-d_1, and dimethyl sulfide-d_3.

Although many papers[1-6] on the infrared and Raman spectra of dimethyl sulfide have been reported, the assignments for the methyl group have not consistent with each other. For this reason we have attempted to study the vibrational spectra of dimethyl sulfide in detail. Dimethyl sulfide and dimethyl sulfide-d_1 were prepared, and the observed infrared and Raman bands were newly assigned. Their assigned frequencies were then used to determine the force constants of the modified Urey-Bradley force fields and of the local symmetry force field. When each final set of those force constants was then used in the normal coordinate treatment of dimethyl sulfide-d_3, the calculated frequencies agreed well with the observed frequencies.[4] In order to confirm the reasonableness of the obtained force constants, the centrifugal distortion constants were further calculated from the force constants; their values were found to be consistent with those determined by the microwave study.[7]

Experimental

The dimethyl sulfide was prepared by the reaction of dimethyl sulfate with sodium sulfide.[8] The dimethyl sulfide-d_1 was prepared by the reduction of monochloromethyl methyl sulfide with lithium aluminum deuteride in *n*-buthyl ether, and the monochloro-methyl methyl sulfide was prepared by the reaction of dimethyl sulfide with thionyl chloride.[9]

The infrared spectra of dimethyl sulfide and dimethyl sulfide-d_1 were recorded in the region from 600 to 4000 cm^{-1} in the gaseous and liquid states with Perkin-Elmer Model 112-G and Hitachi Model EPI-S2 Spectrometers. The Raman spectra were measured in the liquid state by the use of a Cary 81 Raman Spectrometer.

Vibrational Assignments

Dimethyl Sulfide. Table 1 shows the observed infrared and Raman data. As the molecule has a C_{2v} symmetry, the fundamental vibrations can be subdivided into these four groups: A_1, A_2, B_1, and B_2. The vibrations belonging to the A_1, B_1, and B_2 species are active in infrared, and all of the A_1, A_2, B_1, and B_2 vibrations are active in Raman. In the gaseous-state absorption spectra, A_1, B_1, and B_2 vibrations have *b*-type, *a*-type, and *c*-type band contours respectively.

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TABLE 1. FUNDAMENTAL FREQUENCIES (cm^{-1}) AND ASSIGNMENT OF THE INFRARED AND RAMAN SPECTRA OF DIMETHYL SULFIDE

Infrared		Raman	Symmetry species	Assignment
Gaseous	Liquid	Liquid		
2990 sh.	2990 sh.	2991 (3) br.	A_1, B_1, B_2	C–H str.
2915 s.	2920 vs.	2916 (10)	A_1	C–H str.
2850 s.	2850 s.	2860 2852 (2) br. 2837	B_1	C–H str.
1456 s.	1456 s.		A_1	CH_3 deg. def.
1440 vs.	1440 vs.	1440 (10)	B_1	CH_3 deg. def.
1420 sh.	1434 sh.		B_2	CH_3 deg. def.
1329 1317 s.[a] 1303	1317 s.		A_1, B_1	CH_3 sym. def.
1036 1017 s.[b]	1028 s.	1030 vw.	A_1	CH_3 rock.
1005 w.	1005 w.		B_2	CH_3 rock.
972 s.[a]	972 s.	965 vw.	B_1	CH_3 rock.
919 vw.	907 w.			impurity ?
703 w.	723 m.	741 (3)	B_1	C–S str.
694 684 m.[b]	693 m.	691 (7)	A_1	C–S str.
		282 (3)	A_1	CSC def.
	182[c]		B_2	torsion

a) The *a*-type or *c*-type band contours, b) the *b*-type band contour, c) from Ref. 6; s. strong, m. medium, w. weak, v. very, sh. shoulder, br. broad. Values in parentheses of Raman data indicate relative intensities.

The CH_3 rocking vibrations of this molecule may be expected in the region from 900 to 1050 cm^{-1}. In Fig. 1-a, the spectrum of the 900—1050 cm^{-1} region observed in dimethyl sulfide is illustrated. The infrared band at 1028 cm^{-1} is obviously a *b*-type band; therefore, it is assigned to the CH_3 rocking vibration belonging to the A_1 species. The infrared band at 972 cm^{-1} is an *a*-type band; this band is assigned to the CH_3 rocking vibration belonging to the B_1 species. As the B_2 rocking band is expected around the region of 1000 cm^{-1} on the basis of the normal coordinate treatment, as will be discussed later, the weak band at 1005 cm^{-1} can perhaps be assigned to the B_2 vibration. Although the band belonging to the A_2 species of the CH_3 rocking vibration should appear in Raman, the corresponding band is not observed in the Raman spectra. The band at 907 cm^{-1} might be an impurity band, since the absorption intensity is much reduced by the fractional distillation. The infrared band at 1317 cm^{-1} is assigned to the symmetrical deformation vibration. In the gaseous state, as is shown in Fig. 1-b, the band at 1317 cm^{-1} splits into three components, at 1329, 1317, and 1303 cm^{-1}, and is considered to be an *a*-type band belonging to the B_1 species overlapped by a *b*-type band belonging to the A_1 species. Therefore, the bands of the A_1 and B_1 species are considered to have nearly the same frequencies. This was also shown by the results of the normal coordinate treatment. Four CH_3 degenerate deformation vibrations may be expected in the region from 1500 to 1400 cm^{-1}. In this region the infrared bands are made up of three components in the liquid state; these are assigned to the vibrational modes as is shown in Table 1 on the basis of the normal coordinate treatment.

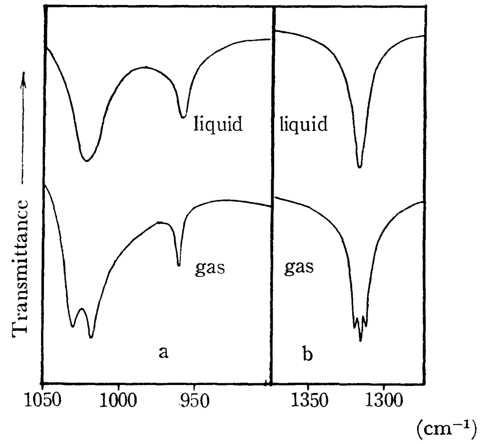


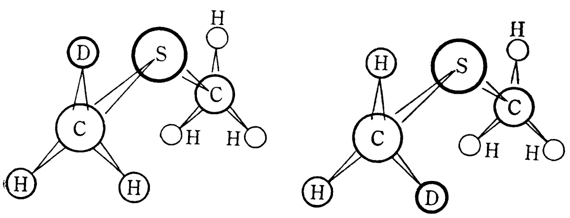
Fig. 1. Infrared spectra of dimethyl sulfide in the gaseous and liquid states in the region of the CH_3 rocking (a) and the CH_3 symmetrical deformation (b) vibrations.

TABLE 2. FUNDAMENTAL FREQUENCIES (cm^{-1}) AND ASSIGNMENT OF THE INFRARED AND RAMAN SPECTRA OF DIMETHYL SULFIDE-d_1

Infrared		Raman	Species	Assignment	
Gaseous	Liquid	Lliquid		Symmetric	Asymmetric
2985 vs.	2985 vs.	2986 (5)	A', A''	C–H str.	C–H str.
2930 vs.	2930 vs.	2919 (10)	A'	C–H str.	C–H str.
		2871 (3)	A'	C–H str.	C–H str.
2202 2189 s. 2179	2185 s.	2189 (10)	A'	C–D str.	C–D str.
1457 1447 sh.	1451 vs. br.	1450 (2)	A'	CH_3 deg. def.	CH_3 deg. def.
1436 s.	1436 vs. br.	1436 (5)	A''	CH_3 deg. def.	CH_3 deg. def.
1424 sh.	1424 sh.	1422 (1)	A'	CH_2 bend.	CH_2 bend.
1340 1327 m. 1315	1327 s.	1329 (3)	A'	CH_3 sym. def.	CH_3 sym. def.
1263 w.	1259 s.	1259 (1)			CH_2 wagg.
1252 s.	1250 sh.	1252 (1)	A'	CH_2 wagg.	
1236 m.	1236 sh.	1236 (1)			CH_2 twist.
1224 1217 w.	1223 vs.	1223 (1)	A''	CH_2 twist.	
1018 1000 vs.	1007 s.		A'	CH_3 rock.	CH_3 rock.
980 sh.	981 s.		A''	CH_3 rock.	CH_3 rock.
961 m.	963 s.		A''	CH_2 rock.	CH_2 rock.
	806 w.	807 (1) br.	A'	SCD def.	
800 m.	789 w.	790 (1) br.			SCD def.
745 w. br.	738 vs.	739 (6)	A'	C–S str.	C–S str.
699 vw.	696 s.	691 (10)			C–S str.
670 659 w.	660 w.	664 (8)	A'	C–S str.	
		274 (2)	A'	CSC def.	CSC def.

Notations are the same to Table 1.

Dimethyl Sulfide-d_1. Table 2 shows the obtained data. The observed infrared spectra of dimethyl sulfide-d_1 are more complicated than those of dimethyl sulfide. For this isotopic species, two rotational isomers, in one of which the deuterium atom is in the plane of the CSC skeleton (sym-dimethyl sulfide-d_1), while in the other it is out of the plane (asym-dimethyl sulfide-d_1), can be expected, as is presented in Fig. 2. Moreover, Pierce and Hayashi[10] have confirmed the existence of the two molecular forms by their analysis of the microwave spectra. The deuterated species has a structure similar to that of monochloro-methyl methyl sulfide, although their atomic masses are different. The CH_2 deformation frequencies of monochloromethyl methyl sulfide have been reported as 1404, 1230, 1149, and 835 cm^{-1}.[11] In the deuterated species, new bands are observed, at 1420, 1260, 1230, and 960 cm^{-1}, which are not observed in the normal species. These frequencies correspond well with those of monochloromethyl methyl sulfide. In view of these aspects of the observed bands, it would be much better to consider the CH_2D group in this isotopic species as two separate groups, one, the CH_2 group and the other, the CD group, much as is the case of monochloromethyl methyl sulfide, rather than to consider the CH_2D group as one group. The experimental result is also confirmed in the L matrix obtained from the normal coordinate treatment. A part of the L matrix of sym-dimethyl sulfide-d_1 is shown in Table 3. Table 3 shows that each normal coordinate has a main contribu-



sym-dimethyl sulfide-d_1 asym-dimethyl sulfide-d_1

Fig. 2. Rotational isomers of dimethyl sulfide-d_1.

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TABLE 3. L-MATRIX OF sym-DIMETHYL SULFIDE-d_1

	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{16}	ν_{17}	ν_{18}	ν_{19}
CH_3 deg. def.	1.468	0.048	−0.006	−0.005	0.280	0.017				
CH_3 deg. def.							1.486	0.008	−0.218	−0.049
CH_3 sym. def.	0.146	0.006	1.141	0.005	−0.039	0.016				
CH_3 rock.	−0.390	0.000	0.057	0.016	0.850	0.148				
CH_3 rock.							0.444	−0.017	1.259	0.310
redundancy[a]	−0.219	−0.001	−0.001	−0.006	−0.006	−0.021				
CH_2 bend.	−0.085	1.509	−0.021	0.005	−0.007	−0.017				
CH_2 wagg.	0.006	−0.014	0.002	1.269	0.042	−0.102				
CH_2 twist.							0.007	1.215	−0.055	−0.156
CH_2 rock.							0.001	0.477	0.231	0.863
SCD def.	0.059	0.003	−0.002	0.232	−0.009	0.553				
redundancy[a]	−0.012	−0.022	−0.011	−0.010	−0.001	0.006				

a) This coordinate is the sum of six coordinates of bond angles in the CH_3 group or the CH_2 group.

tion from each underlined symmetry coordinate; these coordinates are constructed for the CH_3, CH_2, and CD groups, respectively. The new bands at 1420, 1260, 1230, and 960 cm^{-1} are assigned to the CH_2 bending, wagging, twisting, and rocking vibrations respectively, though these CH_2 group vibrations contain other, slight contributions. This is also the case with asym-dimethyl sulfide-d_1.

Two infrared bands are observed close to each other, at 806 and 789 cm^{-1}, in the liquid state. They could not be assigned to the C–S stretching vibrations or to the CH_3 and the CH_2 deformation vibrations by comparing them with those of dimethyl sulfide. From the results of the normal coordinate treatment, the SCD deformation vibrations can be expected to be observed around 800 cm^{-1} and the splitting due to the rotational isomerism can be expected to be 5—10 cm^{-1}. This spacing of the calculated frequencies explains well the observed frequency (17 cm^{-1}). Therefore, the two bands at 789 and 806 cm^{-1} are assigned to the SCD deformation bands of sym-dimethyl sulfide-d_1 and asym-dimethyl sulfide-d_1 respectively. In the region from 750 to 600 cm^{-1}, four bands can be expected, since each rotational isomer has two C–S stretching modes. In the experiment three bands, at 738, 696, and 660 cm^{-1}, are observed in the liquid state. Two modes among the four might be overlapped. From the normal coordinate treatment, the bands at 738 and 660 cm^{-1} are assigned to the C–S stretching vibrations of sym-dimethyl sulfide-d_1, and the bands at 738 and 696 cm^{-1} are assigned to the C–S stretching vibrations of asym-dimethyl sulfide-d_1.

The complicated infrared absorption bands in the region from 1050 to 950 cm^{-1} are assigned to the overlapped CH_3 and CH_2 rocking vibrations. On the basis of the assignments of the CH_3 rocking vibrations for dimethyl sulfide and the normal coordinate treatment, these bands in the liquid state are assigned as follows: the band at 963 cm^{-1} is assigned to the CH_2 rocking vibration, the band at 981 cm^{-1} is assigned to the CH_3 out-of-plane rocking vibration, and the band at 1007 cm^{-1}, to the CH_3 in-plane rocking vibration. These assignments are summarized in the 5th and 6th columns of Table 2.

The CH_2 wagging and twisting vibrations for the CH_2 group could be observed around 1250 cm^{-1}. The frequency differences between sym-dimethyl sulfide-d_1 and asym-dimethyl sulfide-d_1 can be expected from the calculations to be about 10—20 cm^{-1}. Consequently, the bands at 1250 and 1259 cm^{-1} are assigned to the CH_2 wagging vibrations of sym- and asym-dimethyl sulfides respectively, and the bands at 1223 and 1236 cm^{-1} are assigned to the CH_2 twisting vibrations of sym- and asym- sulfides respectively. The band at 1327 cm^{-1} is so close to the band at 1317 cm^{-1} of normal dimethyl sulfide that it can easily be assigned to the CH_3 symmetrical deformation vibration.

The absorption bands in the region from 1500 to 1400 cm^{-1} are much shifted to frequencies lower than those of normal dimethyl sulfide. The CH_2 bending vibrations of the CH_2D group may be expected to appear at slightly lower frequencies than the CH_3 degenerate deformation vibrations. This is also confirmed by the normal coordinate treatment. Since the band at 1424 cm^{-1} is assigned to the CH_2 bending, the bands at 1451 and 1436 cm^{-1} are assigned to the CH_3 degenerate deformation vibrations.

The sum rule and the product rule are used to check the above assignments, assuming that the potential energy is common to dimethyl sulfide, sym-dimethyl sulfide-d_1, and asym-dimethyl sulfide-d_1. The total sums of the squared frequencies are calculated to be 6.470×10^7 for sym-dimethyl sulfide-d_1 and 6.475×10^7 for asym-dimethyl sulfide-d_1. The difference is 0.1%; the assignments of the observed frequencies are thus confirmed to be correct. The ratio of the squares of the product of the observed frequencies to the values of the determinants of the $\boldsymbol{G}$ matrices are found to be 0.8650, 0.8594, and 0.8600 for dimethyl sulfide, sym-dimethyl sulfide-d$_1$, and asym-dimethyl sulfide-d$_1$ respectively; the differences are 0.5%. Therefore, all of our assignments are acceptable.

Normal Coordinate Treatment

The Urey-Bradley force field has been applied to various molecules by many authors, and several modifications have been found to be necessary for complicated molecules. We assumed two following kinds of potential functions of dimethyl sulfide: 1) a modified Urey-Bradley force field, and 2) a local symmetry force field. It has been also supposed that the potential constants of sym- and asym-dimethyl sulfide-d$_1$ are the same as those of normal species. The force constants were determined by a least-squares technique. In the treatment, the observed frequencies of dimethyl sulfide-d$_1$ were used together with those of normal species since the investigation of the CH$_2$D-group vibrations, which have different vibrational modes from those of normal species, as well as of the CH$_3$ group vibrations could lead to reliable findings on the force constants of the methyl group. The obtained force constants were then transferred to dimethyl sulfide-d$_3$. The molecular parameters used in the computation were those reported by Pierce and Hayashi.[10]

1) Modified Urey-Bradley Force Field (MUBFF). At first the normal coordinate treatment was carried out in the simple Urey-Bradley force field. For the CH$_3$ rocking, CH$_3$ degenerate deformation, and C–S stretching vibrations, however, we could not reduce the deviation between the calculated and the observed frequencies to less than 5%. In order to get better agreements of their frequencies, the following modifications of the simple Urey-Bradley force field were attempted: the bond interaction constant of C–H bonds (p), the angle interaction constant between $\angle$HCS and $\angle$HCH (n), the *trans* and *gauche* coupling constants between $\angle$HCS and $\angle$CSC (t and g), and the bond interaction constant of C–S bonds (p'). This is the force field designated as "MUBFF-I" in the present paper.

Table 4. Calculated force constants[a] and their dispersion

	MUBFF-I			MUBFF-II				LSFF		
	Force const.	Dispersion[b]		Force const.	Dispersion[b]			Force const.	Dispersion[b]	
		Calcd 1	Calcd 2		Calcd 1	Calcd 2			Calcd 1	Calcd 2
K(C–H)	4.286	(0.03)	(0.07)	4.267	(0.04)	(0.04)	f(ts)	4.921	(0.06)	(0.06)
K(C–S)	1.691	(0.03)	(0.18)	1.648	(0.03)	(0.19)	f(ds)	4.903	(0.04)	(0.04)
H(HCS)	0.036	(0.00)	(0.04)	0.050	(0.00)	(0.05)	f(cs)	3.659	(0.10)	(0.15)
H(HCH)	0.366	(0.00)	(0.00)	0.348	(0.00)	(0.00)	f(csc)	0.940	(0.00)	(0.02)
H(CSC)	0.244	(0.02)	(0.20)	0.128	(0.05)	(0.24)	f(sd)	0.582	(0.01)	(0.02)
F(HCS)	0.763	(0.01)	(0.13)	0.815	(0.02)	(0.02)	f(dr)	0.668	(0.01)	(0.02)
F(HCH)	0.2[c]			0.2[c]			f(dd)	0.544	(0.00)	(0.01)
F(CSC)	0.21	—	(0.44)	0.21	—	(0.53)	f(to)	0.054[c]		
κ	0.063	(0.01)	(0.01)	−0.010	(0.01)	(0.01)	f(cs, csc)	0.168	—	(0.44)
Y(C–S)	0.054[c]			0.042	(0.03)	(0.03)	f(cs, sd)	−0.673	(0.16)	(0.17)
t	0.070	(0.04)	(0.09)	—			f(cs, cs)	−0.053	(0.02)	(0.12)
g	−0.075	(0.04)	(0.08)	—			f(dr, dd)	−0.056	(0.02)	(0.02)
p(C–H)	−0.130	(0.02)	(0.03)	−0.140	(0.03)	(0.03)	f(ds, dd)	−0.093	(0.00)	(0.00)
p(C–S)	−0.189	(0.00)	(0.03)	−0.186	(0.03)	(0.03)	f(dr, dr)[d]	0.013	(0.01)	(0.01)
n	0.033	(0.00)	(0.03)	—						
q	—			0.009	(0.02)	(0.02)				
q'	—			0.043	(0.01)	(0.01)				

a) K, stretching (mdyn/Å); H, bending (mdyn/Å); F, repulsion (mdyn/Å); $F' = -0.1F$; κ, intramolecular tension (mdyn·Å); Y, internal rotation (mdyn·Å); t, *trans* coupling (mdyn·Å); g, *gauche* coupling (mdyn·Å); p, bond interaction (mdyn/Å); n, angle interaction (mdyn·Å), and q and q', repulsion between two methyl groups (mdyn/Å); cs, C-S stretching; csc, CSC deformation; ts, CH$_3$ symmetrical stretching; ds, CH$_3$ degenerate stretching; dd, CH$_3$ degrenerate deformation; sd, CH$_3$ symmetrical deformation; dr, CH$_3$ rocking; to, torsion.

b) See Ref. 13.

c) Fixed force constants, Calcd 1: F (CSC) or f (cs, csc) is fixed, Calcd 2: F (CSC) or f (cs-csc) is not fixed.

d) Rocking interactions so that diagonal elements with regard to A_1 and B_1 rocking modes are f (dr) $+f$ (dr, dr) and f (dr) $-f$ (dr, dr), respectively.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES OF DIMETHYL SULFIDE (cm^{-1})

		Observed	Calculated					
			MUBFF-I		MUBFF-II		LSFF	
CH_3SCH_3								
A_1	ν_1	2991	3009	0.6	3015	0.8	3015	0.8
	ν_2	2916	2906	0.3	2910	0.2	2907	0.3
	ν_3	1456	1448	0.5	1455	0.0	1447	0.7
	ν_4	1317	1325	0.6	1337	1.5	1323	0.4
	ν_5	1028	1019	0.9	1004	2.3	999	2.8
	ν_6	691	691	0.0	686	0.7	688	0.5
	ν_7	282	277	1.8	277	1.6	280	0.8
A_2	ν_8		3013		3026		3012	
	ν_9		1446		1433		1438	
	ν_{10}		963		977		989	
	ν_{11}		173		207		173	
B_1	ν_{12}	2991	3008	0.6	3011	0.7	3013	0.8
	ν_{13}	2852	2906	1.9	2905	1.9	2907	1.9
	ν_{14}	1440	1450	0.7	1438	0.1	1444	0.3
	ν_{15}	1317	1323	0.5	1337	1.5	1326	0.7
	ν_{16}	972	971	0.1	976	0.4	969	0.3
	ν_{17}	741	742	0.1	742	0.1	743	0.2
B_2	ν_{18}	2991	3013	0.7	3018	1.1	3012	0.7
	ν_{19}	1434	1446	0.9	1423	0.8	1438	0.3
	ν_{20}	1005	979	2.6	992	1.3	1006	0.1
	ν_{21}	182	182	0.0	180	0.9	182	0.0
CH_2DSCH_3 (Symmetric)								
A'	ν_1	2986	3008	0.8	3013	0.9	3014	0.9
	ν_2	2919	2946	0.9	2974	1.2	2946	0.9
	ν_3	2871	2906	1.2	2907	1.3	2907	1.3
	ν_4	2189	2173	0.7	2169	0.9	2176	0.6
	ν_5	1451	1449	0.1	1449	0.1	1445	0.4
	ν_6	1424	1434	0.7	1420	0.3	1430	0.5
	ν_7	1327	1324	0.2	1337	0.8	1324	0.2
	ν_8	1250	1236	1.1	1227	1.8	1233	1.4
	ν_9	1007	996	1.1	989	1.8	984	2.3
	ν_{10}	806	807	0.1	814	1.0	794	1.5
	ν_{11}	739	741	0.3	741	0.3	742	0.4
	ν_{12}	664	673	1.3	675	1.6	674	1.5
	ν_{13}	274	271	1.0	282	2.8	274	0.0
A''	ν_{14}	2986	3013	0.9	3026	1.4	3012	0.9
	ν_{15}	2986	3013	0.9	3018	1.1	3012	0.9
	ν_{16}	1436	1446	0.7	1429	0.5	1438	0.2
	ν_{17}	1223	1234	0.9	1257	2.8	1233	0.6
	ν_{18}	981	975	0.6	987	0.6	1001	2.1
	ν_{19}	963	957	0.7	946	1.7	980	1.7
	ν_{20}		178		205		178	
	ν_{21}		156		165		156	
CH_2DSCH_3 (Asymmetric)								
	ν_1	2986	3013	0.9	3022	1.2	3014	1.0
	ν_2	2986	3010	0.8	3016	1.0	3013	0.9
	ν_3	2986	3008	0.7	3012	0.9	3012	0.9
	ν_4	2919	2944	0.8	2945	0.9	2947	0.9
	ν_5	2871	2906	1.2	2908	1.3	2907	1.2
	ν_6	2189	2176	0.6	2177	0.5	2173	0.7
	ν_7	1451	1449	0.2	1448	0.2	1445	0.4
	ν_8	1436	1446	0.7	1429	0.5	1438	0.2
	ν_9	1424	1430	0.4	1408	1.1	1421	0.2
	ν_{10}	1327	1324	0.2	1337	0.8	1324	0.2
	ν_{11}	1259	1246	1.0	1271	1.0	1249	0.7
	ν_{12}	1236	1242	0.4	1239	0.2	1238	0.2
	ν_{13}	1007	1010	0.3	994	1.3	998	0.9
	ν_{14}	981	972	1.0	985	0.4	991	1.0
	ν_{15}	963	959	0.4	941	2.3	959	0.4
	ν_{16}	789	793	0.5	805	2.1	799	1.3
	ν_{17}	739	724	2.1	732	1.0	731	1.0
	ν_{18}	691	688	0.5	684	1.0	686	0.7
	ν_{19}	274	270	1.4	282	2.8	274	0.0
	ν_{20}		177		200		179	
	ν_{21}		156		170		156	

The force constants obtained by a least-squares technique and the calculated frequencies are shown in Tables 4 and 5. An effect of anharmonicity was seen with the C–H and C–D stretching frequencies. On the SCD deformation vibration, the effect of anharmonicity was not so clear, since the CH_2 deformation coordinate is coupled with it. For the CH_3 rocking vibrations of dimethyl sulfide, the observed frequencies were 1028 (A_1), 972 (B_1), and 1005 cm^{-1} (B_2), and the calculated frequencies in this force field were 1019 (A_1), 971 (B_1), and 979 cm^{-1} (B_2), although the frequencies in the simple Urey-Bradley force field were 962 (A_1) and 949 cm^{-1} (B_1). The calculated frequencies and difference between the A_1 and B_1 vibrations in MUBFF-I satisfactorily agree with the observed values of the A_1 and B_1 frequencies. The B_2 vibration could not be discussed since the observed frequency was ambiguous. The observed spectra could reasonably be explained by MUBFF-I using the five modification terms.

The set of the force constants of MUBFF-I was then transferred to dimethyl sulfide-d_3. The calculated frequencies are shown in Table 6 together with the reported experimental values.[4] These force constants of MUBFF-I are confirm to reproduce the observed frequencies well except for the CD_3 rocking A' vibration on dimethyl sulfide-d_3. Since the band assigned by Perchard *et al.*[4] to the CD_3 rocking mode is so weak, we can not discuss the disagreement between the calculated and observed frequencies at present. In the calculated results the anharmonicity mentioned above is also seen in the case of the C–H and C–D stretching vibrations.

In MUBFF-I we treated the interactions in methyl groups as modification terms, *n*, *t*, and *g*. However, the nearest atomic distance between two hydrogens

Table 6. Observed and calculated frequencies of dimethyl sulfide-d_3 (cm^{-1})

	Assignment	Observed[a]	Calculated					
			MUBFF-I		MUBFF-II		LSFF	
A'	C–H str.	2970.5	3009	1.3	3012	1.4	3014	1.5
	C–H str.	2917	2908	0.8	2904	0.4	2907	0.3
	C–D str.	2231	2227	0.2	2226	0.2	2230	0.0
	C–D str.	2128	2078	2.3	2074	2.5	2076	2.4
	CH_3 deg. def.	1437.5	1444	0.5	1438	0.0	1445	0.5
	CH_3 sym. def.	1332	1325	0.5	1333	0.1	1324	0.6
	CD_3 deg. def.	1050.5	1054	0.3	1032	1.8	1048	0.2
	CH_3 rock.	1013.5	1006	0.7	988	2.5	990	2.3
	CD_3 sym. def.	961	975	1.5	972	1.1	969	0.8
	CD_3 rock.	740	782	5.7	773	4.5	770	4.1
	C–S str.	705	721	2.3	719	2.0	719	2.0
	C–S str.	656	669	2.0	674	2.7	674	2.7
	CSC def.		261		234		263	
A''	C–H str.	2989	3014	0.8	3018	1.0	3012	0.8
	C–D str.	2240	2292	0.5	2230	0.5	2226	0.6
	CH_3 deg. def.	1428.5	1442	0.9	1420	0.6	1438	0.7
	CD_3 deg. def.	1040.5	1054	1.3	1022	1.7	1046	0.5
	CH_3 rock.	983	974	0.9	981	0.2	998	1.5
	CD_3 rock.	725.5	729	0.5	746	2.8	750	3.4
	torsion		176		155		177	
	torsion		129		115		131	

a) From Ref. 4.

situated at the ends of methyl groups is 2.6 Å, and the second nearest is 3.2 Å (see Fig. 3.). Therefore, we could expect the other kind of interaction between methyl groups, namely a direct interaction between two methyl groups. Let us denote the repulsion potentials between the two hydrogen atoms in the case of the nearest and the second nearest atomic distances as q and q' respectively. We then assumed the second modified Urey-Bradley force field (MUBFF-II), in which the modification terms are the bond interaction potential, p, besides the repulsion potentials between two methyl groups, q and q'. The obtained force constants and the calculated frequencies are shown in Tables 4 and 5. This force field reproduces the observed frequencies well. Moreover, the deviation was only about 1%. The determined values of q and q' were 0.009 and 0.043 respectively; these however do not satisfy the relation expected from the van der Waals function ($q \fallingdotseq 2q'$). This suggests that same other weak interactions contribute to the force field of the sulfides.

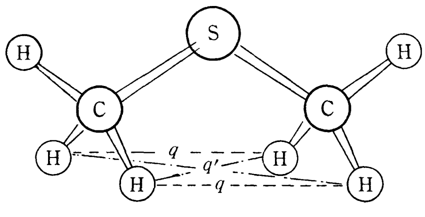

Fig. 3. Repulsion potentials (q and q') between hydrogen atoms.

2) Local Symmetry Force Field (LSFF). In the second place the normal coordinate treatment was carried out using the local symmetry force field reported by Shimanouchi *et al.*[12] All of the diagonal elements and a part of the off-diagonal elements of the $\boldsymbol{F}$ matrix, expressed in terms of local symmetry coordinates, were treated as independent force constants, while the other off-diagonal elements were calculated from the relation of the Urey-Bradley force field. The results thus obtained are shown in Tables 4 and 5. The calculated frequencies agreed well with the observed frequencies. The set of force constants was transferred to the calculation of dimethyl sulfide-d_3. In this force field the calculated frequencies of the CD_3 rocking vibrations agreed fairly well with the observed frequencies. The values of the $\boldsymbol{F}$ matrix elements of LSFF resemble those of MUBFF-I. From these facts it can be said that the off-diagonal elements of the potential energy matrix are, greatly, related to the repulsion force constants.

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[12] T. Shimanouchi, I. Nakagawa, C. Tanaka, I. Suzuki, H. Takahashi, T. Fujiyama, Y. Abe, T. Ueda, M. Mikami, M. Oka, A. Hirakawa and A. Kurokawa, *Molecular Structure Symposium*, October, 1966, Osaka, Japan.

TABLE 7. CENTRIFUGAL DISTORTION CONSTANTS OF DIMETHYL SULFIDE (kHz)

Centri. Destn. Conts.[c)]	Microwave[a)]	Normal vibration		
		MUBFF-I	MUBFF-II	LSFF
T_1	−447.8	−450	−710	−480
T_2	−54.84	−53	−3	−56
T_3	−9.626	−9.4	−5.9	−9.5
T_4'	−26.21	−34.1	12.8	−28.3
T_5'	−2.333	−4.1	−2.4	−2.5
T_6	−5[b)]	−16.8	1.8	−8.6

a) See Ref. 7.

b) Fixed constant which contributes with less than 1.6×10^{-5} MHz to the centrifugal distortion correction.

c) $T_1=\tau_{\mathrm{aaaa}}$, $T_2=\tau_{\mathrm{bbbb}}$, $T_3=\tau_{\mathrm{cccc}}$,

$$T_4=\tau_{\mathrm{abab}}+\frac{1}{2}\left[\tau_{\mathrm{aabb}}-\left(\tau_{\mathrm{cccc}}-\left(\frac{C}{A}\right)^4\tau_{\mathrm{aaaa}}-\left(\frac{C}{B}\right)^4\tau_{\mathrm{bbbb}}\right)\frac{A^2B^2}{2C^4}\right],$$

$$T_5=\tau_{\mathrm{bcbc}}+\frac{1}{2}\left[\tau_{\mathrm{bbcc}}-\left(\tau_{\mathrm{cccc}}-\left(\frac{C}{A}\right)^4\tau_{\mathrm{aaaa}}+\left(\frac{C}{B}\right)^4\tau_{\mathrm{bbbb}}\right)\frac{B^2}{2C^2}\right],$$

$$T_6=\tau_{\mathrm{caca}}+\frac{1}{2}\left[\tau_{\mathrm{ccaa}}-\left(\tau_{\mathrm{cccc}}+\left(\frac{C}{A}\right)^4\tau_{\mathrm{aaaa}}-\left(\frac{C}{B}\right)^4\tau_{\mathrm{bbbb}}\right)\frac{A^2}{2C^2}\right],$$

$T_4'=T_4+0.8426T_6$, $T_5'=T_5+0.1574T_6$, $A=17809.7$, $B=7621.1$ and $C=5717.8$ MHz

Discussion

The normal coordinate treatments presented above lead to the conclusion that the interaction terms of the methyl group with the other group are indispensable in the force fields of dimethyl sulfides. If the interaction terms of the methyl group with the other group, *t*, and *g* in MUBFF-I, *q* and *q*′ in MUBFF-II, and *f*(cs, sd) and *f*(dr, dr) in LSFF, were not introduced, the observed frequencies could not be reproduced satisfactorily by their force fields. In Table 4 the values in brackets beside the force constants represent the dispersion[13)] (Calcd 1) of the force constants around the convergence values. It may be seen that none of the force constants for diagonal and off-diagonal elements relating to the skeletal coordinate are tightly adjusted. At first stage of the calculation by the least-squares technique, some of the force constants for diagonal and off-diagonal elements of the CSC skeletal and C–S stretching vibrational coordinates were reasonablely fixed in several cases. In the final stage, all of the fixed force constants were released from the fixed values. The value of dispersion in this case is shown as Calcd 2 in Table 4. After all, it seems that the force constants relating to the skeleton, especially the off-diagonal elements, can not be exactly determined. Their precise determinations may, however, be accomplished by studies of the isotopic effect of the skeleton or by a completely different approach.

It is well known that the centrifugal distortion constants are closely related to the force constant.[14)] We have attempted to compare the centrifugal distortion constants determined on the basis of the force constants with those determined on the basis of the microwave data.[7)]

The centrifugal distrotion constants of dimethyl sulfide as determined by microwave measurements have been reported by Rudolph *et al.*,[15)] these values were later corrected by Sϕrensen.[7)] He found that none of the six constants could be determined independently when the determinant of the centrifugal distortion matrix (6×6) was almost zero. Therefore, five new linear combinations were selected in such a way that the direct influence of the fixed constant on the observed values was entirely negligible. The determined constants are shown in the 2nd column of Table 7.

The centrifugal distortion constants, $\tau_{\alpha\beta\gamma\delta}$, are defined thus:

$$\tau_{\alpha\beta\delta\gamma}=-\sum_{ij}[\boldsymbol{J}^0_{\alpha\beta}]_i[\boldsymbol{J}^0_{\gamma\delta}]_j[\boldsymbol{F}^{-1}]_{ij}/2\ I^0_{\alpha\alpha}I^0_{\beta\beta}I^0_{\gamma\gamma}I^0_{\delta\delta} \qquad (1)$$

where $I_{\alpha\alpha}$ denotes the moment of inertia and where $\boldsymbol{F}$ is the potential energy matrix expressed in terms of displacement coordinates, and $[\boldsymbol{J}_{\alpha\beta}{}^0]_i$ is defined by:

$$[\boldsymbol{J}^0_{\alpha\beta}]_i=(\partial I_{\alpha\beta}/\partial q_i) \qquad (2)$$

where $I_{\alpha\beta}$ is the inertia tensor and where q_i is the *i*th displacement coordinate. Using Eq. (2) the centrifugal distortion constants were calculated from the above-mentioned three sets of force constants; the six constants were then recalculated in the same form as the constants obtained by Sϕrensen. They are shown in the last three columns of Table 7. The calculated centrifugal distortion constants were in good agreement with the observed values in the cases of MUBFF-I and LSFF, while in the case of MUBFF-II the agreement was not sufficient.

Then we examined the change in the centrifugal distortion constants due to the change in the force constants. From Eq. (1) the following equations were deduced:[16)]

$$(\partial\tau_{\alpha\beta\gamma\delta}/\partial f_{ij})=-\sum_{kl}[\boldsymbol{J}^0_{\alpha\beta}]_k[\boldsymbol{F}^{-1}]_{ik}[\boldsymbol{F}^{-1}]_{jl}[\boldsymbol{J}^0_{\gamma\delta}]_l/$$

$$I^0_{\alpha\alpha}I^0_{\beta\beta}I^0_{\gamma\gamma}I^0_{\delta\delta} \qquad (\text{if } i \neq j)$$

[13)] T. Ogawa and T. Miyazawa, *Spectrochim. Acta*, **20**, 557 (1964).

[14)] D. Kivelson and E. B. Wilson, Jr., *J. Chem. Phys.*, **20**, 1575 (1952).

[15)] M. D. Rudolph, H. Dreizler and W. Maier, *Z. Naturforsh.*, **A 15**, 742 (1960).

[16)] I. M. Mills, *J. Mol. Spectrosc.*, **5**, 334 (1960).

Table 8. Calculated values of derivatives of the centrifugal distortion constants ($\tau_{\alpha\beta\gamma\delta}$) with respect to the elements (f_{ij}) of F matrices[a] of dimethyl sulfide (k·Hz·Å/md)

	CH str.	CH str.	CH_3 deg.	CH_3 sym.	CH_3 rock.	CS str.	CSC def.
τ_{aaaa} (A_1)	−0.1			Symmetric			
	−0.4	−0.7					
	−0.4	−1.5	−0.8				
	−3.6	−11.7	12.9	−51.7			
	2.4	7.9	8.7	70.0	−23.7		
	3.0	9.8	10.8	87.1	−58.9	−36.6	
	−9.4	−30.6	−33.7	−271.0	183.0	228.0	−355.0
τ_{bbbb} (A_1)	0.0			Symmetric			
	0.0	0.0					
	0.1	−0.3	−0.4				
	0.0	0.0	0.0	0.0			
	−0.3	0.7	2.2	−0.1	−3.0		
	0.3	−0.6	−1.7	0.1	4.7	−1.8	
	1.1	−2.6	−7.4	0.5	21.0	−16.1	−35.8
τ_{cccc} (A_1)	0.0			Symmetric			
	0.0	0.0					
	0.0	0.0	0.0				
	−0.2	0.0	−0.1	−0.3			
	−0.2	0.0	−0.1	−0.6	−0.3		
	0.4	−0.2	0.3	1.5	1.5	−1.9	
	0.4	−0.3	0.3	1.6	1.6	−4.0	−2.1
τ_{bbcc} (A_1)	0.0			Symmetric			
	0.0	0.0					
	0.2	0.1	0.0				
	0.0	0.0	0.7	0.0			
	−0.5	0.3	0.7	−2.0	−1.0		
	0.3	−0.6	−1.7	0.1	4.8	−1.8	
	1.8	−1.0	−1.8	0.1	5.1	−16.3	−8.7
τ_{ccaa} (A_1)	0.0			Symmetric			
	0.0	0.0					
	0.0	−0.2	0.0				
	−0.3	−0.9	−1.4	−4.1			
	−0.3	−0.9	0.9	−8.1	2.7		
	1.9	−1.1	1.2	6.8	6.8	−8.3	
	0.7	2.4	−3.6	−21.2	−21.2	−17.6	27.3
τ_{aabb} (A_1)	0.0			Symmetric			
	−0.2	0.2					
	−0.2	0.4	0.6				
	−1.4	3.1	0.0	−0.3			
	0.9	−2.1	−3.1	0.4	8.5		
	2.2	2.2	2.4	19.4	−13.1	−8.2	
	−3.6	8.0	10.7	86.1	−58.3	50.8	113.0
τ_{abab} (B_1)	−0.2			Symmetric			
	0.0	0.0					
	0.2	0.0	0.0				
	−0.8	0.0	0.5	−0.8			
	−0.5	0.0	0.3	−1.1	−0.3		
	2.0	0.1	−1.3	4.4	2.8	−5.8	

TABLE 8. (Continued)

	CH str.	CH_3 deg.	CH_3 rock.	torsion
τ_{caca} (A_2)	0.0		Symmetric	
	0.0	−0.3		
	0.1	1.2	−1.0	
	−1.2	−12.9	23.1	−130.0
τ_{bcbc} (B_2)	0.0		Symmetric	
	0.0	0.0		
	0.0	0.0	0.0	
	−0.3	−0.9	−2.5	−23.9

a) The matrices are expressed with the local symmetry coordinates. The i and j denote the ith and jth coordinates, respectively.

or

$$= -\frac{1}{2}\sum[J^0_{\alpha\beta}]_k[F^{-1}]_{ik}[F^{-1}]_{jl}[J^0_{\gamma\delta}]_l / I^0_{\alpha\alpha}I^0_{\beta\beta}I^0_{\gamma\gamma}I^0_{\delta\delta} \quad (\text{if } i=j)$$

where the i and j denote ith and jth local symmetry coordinates respectively. Therefore, f_{ij} denotes the element of the F matrix represented by the local symmetry coordinates. Normal dimethyl sulfide has a C_{2v} symmetry. Therefore, τ_{aaaa}, τ_{bbbb}, τ_{cccc}, τ_{bbcc}, τ_{ccaa}, and τ_{aabb} are related to the vibrations belonging to the A_1 species; τ_{abab} is related to the B_1 species; τ_{caca}, to the A_2 species, and τ_{bcbc}, to the B_2 species. Table 8 shows the calculated values of $(\delta\tau_{\alpha\beta\gamma\delta}/\delta f_{ij})$ in each symmetry species. The larger values show the more relations between $\tau_{\alpha\beta\gamma\delta}$ and f_{ij}. If $\tau_{\alpha\beta\gamma\delta}$ is completely determined by the microwave analysis, the force constants with a large value of $(\delta\tau_{\alpha\beta\gamma\delta}/\delta f_{ij})$ can be correctly obtained. Such force constants are f(cs), f(cs, csc), f(csc), f(to), and so on. On the other hand, f(ts), f(dd), f(sd), *etc.* can not be correctly determined from the centrifugal distortion constants. In general, the $(\delta\tau_{\alpha\beta\gamma\delta}/\delta f_{ij})$ values related to the vibrational coordinates on hydrogen atoms, *i.e.*, small-mass atoms, are small. Those related to skeletal vibrational coordinates (skeletal stretching, skeletal deformation, and torsional) are large. Therefore, their off-diagonal values are rather larger than the diagonal values. Thus, the force constants related to the hydrogen stretching and deformation vibrations can be determined only with difficulty from the centrifugal distortion constants, whereas those for diagonal and off-diagonal elements related to the skeletal stretching, skeletal deformation, and torsional vibrations can be determined more easily. This fact may be valuable for studies of molecular force fields, since usually it is too hard to determine the force constants related to the skeleton, especially their off-diagonal elements with sufficient accuracy. The determination of the force constants on the basis of the centrifugal distortion constants may be expected to be valuable. In this study, however, we did not calculate the force constants from the centrifugal distortion constants. The comparison of the two sets of centrifugal distortion constants obtained from the vibrational spectra and the microwave spectra reveals that the force field of MUBFF-I and LSFF would be preferable. The application of the force constants we have obtained will be discussed in the near future.

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