BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 619—622 (1970)

Molecular Vibrations and Force Fields of Dimethyl Selenide and Dimethyl Selenide-d_6

Yuji SHIRO,*1 Masaru OHSAKU, Michiro HAYASHI and Hiromu MURATA

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

(Received May 6, 1969)

A set of the modified Urey-Bradley force constants and of the local symmetry force constants of dimethyl selenide have been calculated by a least-squares technique, using the vibrational frequencies of the two isotopic species, $(CH_3)_2Se$ and $(CD_3)_2Se$. The calculated frequencies thus obtained are in good agreement with the observed values. Comparison has been made for the force constants among dimethyl ether, dimethyl sulfide, and dimethyl selenide. This has shown the reasonable relation to be expected among the force constant, the bond length, the bond angle, and the atomic number of the central atom. The centrifugal distortion constants, which were calculated from the two sets of force constants, were then compared with those obtained from the microwave spectra; their values are found to be consistent with those obtained from a microwave study in a three-body approximation.

The force fields of dimethyl ether[1-3] and dimethyl sulfide[4] have been extensively investigated. For dimethyl selenide, the vibrational data have been reported by Allkins and Hendra,[5,6] who made a treatment of the simple valence force field for the skeleton. Although Fritz and Keller[7] made a simple computation of the vibrational frequencies of dimethyl ether, dimethyl sulfide, dimethyl selenide, and dimethyl telluride, no study has been made of the Urey-Bradley and the local symmetry force fields. In our paper[4] on the most probable force fields of dimethyl sulfide, we determined two sets of force constants. One of them was a set of modified Urey-Bradley force constants which contained such modification constants as C–H bond interaction, p(C–H); C–S bond interaction, p(C–S); *trans* coupling, t; *gauche* coupling, g, between ∠HCS and ∠CSC, and angle interaction, n, between ∠HCS and ∠HCH. The other set was the local symmetry potential constants. For dimethyl selenide, we have attempted to estimate, by a least-squares technique, a set of the force constants of the modified Urey-Bradley force field (MUBFF) and of the local symmetry force field (LSFF) from the reported vibrational frequencies of the normal[5] and fully-deuterated[6] species. To make sure of the propriety of the two sets of the force constants thus obtained, the centrifugal distortion constants were calculated and compared with those reported by Beecher[8] on the basis of his microwave study.

Calulated Vibrational Frequencies

Assuming that dimethyl selenide and dimethyl selenide-d_6 belong to the same symmetry class as a C_{2v} symmetry, 21 fundamental modes of vibrations can be subdivided by symmetry properties into four species, $7A_1$, $4A_2$, $6B_1$, and $4B_2$. Two types of potential function were treated as in the case of dimethyl sulfide. One is the modified Urey-Bradley force field. This contains the C–H bond interaction term, p(C–H); the C–Se bond interaction term, p(C–Se); the *trans* and *gauche* coupling terms, t, and g, between ∠HCSe and ∠CSeC, and the angle interaction term, n, between ∠HCSe and ∠HCH. The other is the local symmetry force field. Normal coordinate treatments were carried out by a least-squares technique on the basis of the observed frequencies of the normal[5] and fully deuterated[6] species by Allkins and Hendra. Computation has been carried out assuming that the

*1 Present address: Shinonome Branch School, Faculty of Education, Hiroshima University, Shinonome-3-chome, Hiroshima.

1) 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.

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

3) P. Labarbe, M. T. Forel and G. Bessis, *ibid.*, **24A**, 2165 (1968).

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

5) J. R. Allkins and P. J. Hendra, *Spectrochim. Acta*, **22**, 2075 (1966).

6) J. R. Allkins and P. J. Hendra, *ibid.*, **23A**, 1671 (1967).

7) H. P. Fritz and H. Keller, *Chem. Ber.*, **94**, 1524 (1961).

8) J. F. Beecher, *J. Mol. Spectroscopy*, **21**, 414 (1966).

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

			CH_3SeCH_3					CD_3SeCD_3				
			Obsd[a]	Calcd				Obsd[b]	Calcd			
				MUBFF		LSFF			MUBFF		LSFF	
A_1	ν_1	CH_3,CD_3 deg. str.	2992	3018	0.9	3009	0.6	2256	2239	−0.8	2246	−0.4
	ν_2	CH_3,CD_3 sym. str.	2920	2953	1.1	2942	0.7	2134	2108	−1.2	2118	−0.8
	ν_3	CH_3,CD_3 deg. def.	1423	1426	0.2	1442	1.3	1038	1036	−0.2	1034	−0.4
	ν_4	CH_3,CD_3 sym. def.	1284	1295	0.9	1278	−0.5	983	965	−1.9	971	−1.2
	ν_5[d]	CH_3,CD_3 rock.	954	955	0.1	960	0.6	744	743	−0.1	726	−2.4
	ν_6	C–Se str.	589	581	−1.3	591	0.3	548	555	1.4	547	−0.2
	ν_7	CSeC def.	233[c]	234	0.6	230	−1.3	201[c]	200	−0.5	204	1.3
A_2	ν_8	CH_3,CD_3 deg. str.	2996[f]	3020		3007			2235		2242	
	ν_9	CH_3,CD_3 deg. def.	1424[f]	1425		1428			1033		1026	
	ν_{10}[e]	CH_3,CD_3 rock.	890	886	−0.4	922	3.6	680	660	−2.9	688	1.2
	ν_{11}	torsion		160		160			114		115	
B_1	ν_{12}	CH_3,CD_3 deg. str.	2992	3016	0.8	3008	0.5	2256	2233	−1.0	2243	−0.6
	ν_{13}	CH_3,CD_3 sym. str.	2920	2953	1.1	2942	0.7	2134	2108	−1.2	2118	−0.8
	ν_{14}	CH_3,CD_3 deg. def.	1423	1450	0.5	1431	0.6	1038	1035	−0.3	1029	−0.9
	ν_{15}	CH_3,CD_3 sym. def.	1263	1290	2.1	1278	1.2	968	958	−1.1	971	0.3
	ν_{16}[d]	CH_3,CD_3 rock.	857	888	3.6	862	0.6	658	666	1.2	646	−1.9
	ν_{17}	CSe str.	604	597	−1.2	606	0.3	564	571	1.2	562	−0.4
B_2	ν_{18}	CH_3,CD_3 deg. str.	2992	3020	0.9	3007	0.5	2256	2235	−0.9	2242	−0.6
	ν_{19}	CH_3,CD_3 deg. def.	1423	1425	0.1	1428	0.4	1038	1033	−0.5	1026	−1.1
	ν_{20}[e]	CH_3,CD_3 rock.	908	981	−1.8	927	2.1	696	667	−4.1	695	−0.1
	ν_{21}	torsion		163		164			118		119	
		MUBFF m.d. 1.1% r.m.s.d. 1.4%										
		LSFF m.d. 0.9% r.m.s.d. 1.1%										

a) See Ref. 5. b) See Ref. 6. c) Raman. d) In plane vibration.
e) Out of plane vibration. f) Not used in calculation.

potentials of dimethyl selenide and dimethyl selenide-d_6 are common. The molecular parameters used on the computation were those reported by Beecher.[8] Table 1 shows the observed frequencies and two cases of the calculated frequencies with the deviation between the observed and calculated frequencies.

For normal dimethyl selenide in the modified Urey-Bradley force field, the calculated frequencies of the CH_3 rocking region, $\nu_{16}(B_1)$ and $\nu_{20}(B_2)$, and of CH_3 symmetric deformation, $\nu_{15}(B_1)$, are fairly different from each observed frequency. However, the other vibrations are in good agreement within a deviation of about 1%. In the local symmetry force field the CH_3 rocking vibrations, $\nu_{10}(A_2)$ and $\nu_{20}(B_2)$, also have fairly large deviations.

For dimethyl selenide-d_6 in the modified Urey-Bradley force field, the vibrations of the CD_3 rocking region, $\nu_{10}(A_2)$ and $\nu_{20}(B_2)$, and those in the local symmetry force field, $\nu_5(A_1)$ and $\nu_{16}(B_1)$, of the CD_3 rocking vibrations have also fairly large deviations. That is, CH_3 or the CD_3 rocking vibrations were not reproduced in good agreement either in the modified Urey-Bradley or in the local symmetry force fields. This tendency was also shown in our work on dimethyl sulfides.[4] The calculated mean deviation (m.d.) and the root mean squared deviation (r.m.s.d.) are as follows: MUBFF; m.d. 1.1%, r.m.s.d. 1.4%, LSFF; m.d. 0.9%, r.m.s.d. 1.1%. Thus the modified Urey-Bradley force field and the local symmetry force field are appropriate as the force fields of dimethyl selenide.

Force Constants

Table 2 shows the two final sets of the force constants and their dispersion, together with the sets obtained from dimethyl ether[1] and dimethyl sulfide.[4] Although some modification constants taken into consideration differ from each other, the force constants among the listed molecules will be made compared in order to establish a definite tendency.

The C–X bond length in these compounds with the formula $(CH_3)_2X$ increases and, on the other hand, the CXC angle decreases towards 90°, with an increase in the atomic number of the atom X (X: O, S, and Se). The data provided by the microwave studies are as follows:

TABLE 2. CALCULATED FORCE CONSTANTS WITH THEIR DISPERSION

	Modified Urey-Bradley force constants[a]				Local symmetry force constants[b]				
	$(CH_3)_2O$[c]	$(CH_3)_2S$[d]	$(CH_3)_2Se$			$(CH_3)_2O$[c]	$(CH_3)_2S$[d]	$(CH_3)_2Se$	
K(C–H)	4.112	4.286	4.467	0.04	f(ts)	4.613	4.921	4.937	0.13
K(C–X)	3.366	1.691	1.288	0.10	f(ds)	4.851	4.903	4.778	0.09
H(HCX)	0.282	0.036	0.03[e]		f(cx)	5.123	3.659	2.716	0.01
H(HCH)	0.361	0.366	0.355	0.55	f(cxc)	1.169	0.940	0.849	0.02
H(CXC)	0.445	0.244	0.259	0.04	f(sd)	0.670	0.582	0.547	0.04
F(HCX)	0.756	0.763	0.617	0.07	f(dr)	0.942	0.668	0.590	0.03
F(HCH)	0.200	0.2	0.19[e]		f(dd)	0.547	0.544	0.524	0.03
F(CXC)	0.3	0.21	0.2[e]		f(to)	—	0.054	0.047[e]	
κ	0.059	0.063	0.029	0.09	f(cx, cxc)	0.059	0.168	0.12[e]	
Y(CX)	0.074	0.054	0.047[e]		f(cx, sd)	−0.523	−0.673	−0.322	0.04
t	—	0.070	0.09[e]		f(cx, cx)	−0.275	−0.053	−0.008	0.01
g	—	−0.075	−0.211	0.05	f(dr, dd)	−0.043	−0.056	0.006	0.05
p(C–H)	−0.219	−0.130	−0.073	0.03	f(ds, dd)	−0.093	−0.093	0.124	0.14
p(C–X)	−0.302	−0.189	−0.118	0.04	f(dr, dr)	0.067	0.013	0.063	0.01
n	—	0.033	0.003	0.05					

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, *gaushe* coupling (mdyn·Å); p, bond interaction (mdyn/Å); n, angle interaction (mdyn·Å), and q and q', repulsion between two methyl groups (mdyn/Å).
b) cx, C–X stretching: cxc, CXC deformation; ts, CH_3 symmetrical stretching; ds, CH_3 degenerate stretching; dd, CH_3 degenerate deformation; sd, CH_3 symmetrical deformation; dr, CH_3 rocking; to, torsion.
c) See Ref. 1. d) See Ref. 4. e) Fixed force constants.

∠COC 111°43′, r(C–O) 1.410 Å Ref. 9;
∠CSC 98°52′, r(C–S) 1.802 Å Ref. 10;
∠CSeC 96°11′, r(C–Se) 1.943 Å Ref. 8.

K; Stretching Force Constants. The stretching force constant of K(C–H) does not show any clear tendency. The results due to the simple computation of Fritz and Keller[7] show that the C–X stretching force constants with the general formula of $(CH_3)_2X$ decrease with an increase in the atomic number (X; O, S, Se, and Te). Such a phenomenon is also shown in this work. The force constants of K(C–O) and K(C–S) were found to be 3.366 and 1.691 respectively, and the force constant of K(C–Se) was found to be 1.288, both decreasing with an increase in the atomic number.

H: Bending Force Constants. As the C–X bond length increases and the CXC angle decreases, the bending force constant, H(HCX), decreases, but H(CXC) shows no definite tendency.

F: Repulsion Force Constants. This kind of force constant decreases with an increase in the atomic number of central atom. This shows that the repulsive force in each case decreases with an increase in the C–X bond length.

κ: Internal Tension. These constants also decrease in the order O<S<Se.

Y: Torsional Force Constants. These constants can be calculated from the barrier height (V_3) of each molecule; the barrier heights of the normal species with the formula $(CH_3)_2X$ (X; O, S, and Se) were found to be 2720, 2132, and 1500 cal/mol.[8,10,11] Therefore, the constants also decrease in the order O<S<Se.

Modification Constants. Generally, the modification constants are in the same order, as have been mentioned above. However, most of the modification constants have a fairly large dispersion. This suggests that these potentials bear at the same time the effect of other interactions which are not taken into consideration, and also that these constants are not tightly adjusted. Therefore, the modification constants are fairly arbitrary and a regular comparison could not be made.

In the case of the local symmetry force constants, our results were nearly the same as the modified Urey-Bradley force constants. That is, the constants decrease in the order O<S<Se. However, the physical meanings of the local symmetry force constants are not obvious enough for us to discuss the local symmetry force constants.

Centrifugal Distortion Constants

In order to confirm the reasonableness of the

9) U. Blukis, P. H. Kasai and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963).
10) L. Pierce and M. Hayashi, *ibid.*, **35**, 479 (1961).
11) P. H. Kasai and R. J. Myers, *ibid.*, **30**, 1096 (1959).

obtained force constants, we calculated the centrifugal distortion constants. Table 3 shows the centrifugal distortion constants calculated from the two final sets of the force constants and those from the microwave study by Beecher,[8] who determined the centrifugal distortion constants in the three-body approximation. The two cases of the modified Urey-Bradley force field and the local symmetry force field are in good agreement with those from the microwave study. In comparing Beecher's results and the present results we noticed the following two results; (1) the four observed values of constants, τ_{aaaa}, τ_{bbbb}, τ_{aabb}, and τ_{abab} agreed well with the calculated values, and (2) three constants, τ_{cccc}, τ_{bbcc}, and τ_{ccaa}, which are ignored by Beecher are found in this work to have small values.

Therefore, it is confirmed that the obtained force constants are reasonable in the light of the first finding, while, on the other hand, Beecher's assumption is reasonable as the first approximation in the light of the second finding.

TABLE 3. CENTRIFUGAL DISTORTION CONSTANTS OF DIMETHYL SELENIDE (Mc/sec)

	Microwave[a]	Normal vibration	
		MUBFF	LSFF
τ_{aaaa}	−0.2422	−0.219	−0.223
τ_{bbbb}	−0.0604	−0.046	−0.055
τ_{cccc}	—	−0.005	−0.005
τ_{bbcc}	—	−0.009	−0.011
τ_{ccaa}	—	−0.005	−0.002
τ_{aabb}	0.0721	0.069	0.079
τ_{abab}	−0.0092	−0.014	−0.015

a) See Ref. 8, the values determined on $(CH_3)_2{}^{80}Se$ species.