



# Vibrational Spectra and Structure of Dimethyl Diselenide and Dimethyl Diselenided 6

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there would appear to be no obvious need to include any nonadditivity correction terms in the crystal-state N-body calculations. The limitations of these calculations are quite obvious. We have included nonadditivity only in the long-range attractive potential, that is in the static lattice sum. Despite the apparent brutality of these calculations the nonadditivity term is set firmly to zero in a remarkably self-consistent manner. The suggestion of corresponding-states type of behavior is also well established for second virial and viscosity data.

From the consideration of the Kihara core potentials, identical  $\beta$  values were found for a given m:n potential for both argon and xenon. From the simple bireciprocal Lennard-Jones potential calculations the resulting "best" values of the two reduction parameters for argon, xenon, and krypton are seen to be remarkably adept in satisfying the corresponding-states requirements of simple two-body experimental data. The ratios of these "best" parameters are in good agreement with the ratios of the temperatures and molar volume of these gases at the Boyle point  $T_B[B(T_B)=0]$  and at the critical point  $T_c$ . These ratios are given in Ref. 9. Perhaps of greater significance is the agreement of the ratios of  $\epsilon$  and  $\sigma$  for argon and xenon with those ratios determined by Levelt.<sup>10</sup> The values found by Levelt pertain to an examination of the corresponding-states behavior of argon and xenon over a wide pressure and temperature range. These are, then, values pertaining to a "bulk" property and the agreement with the values found in the present study is worthy of note.

Against the above seemingly well-established rejection of "nonadditivity" it is certainly true that the seemingly appropriate pair potential, the 12:6 Kihara core potential with  $\beta = 0.009$  is quite inconsistent with the *prediction* of the second virial behavior of any of the three gases. As would appear to be any potential function whose attractive well depth is as small as those found in the present calculations. It is also well known that these potentials cannot satisfy the required stability of the fcc lattice structure favored by these inert-gas solids. Leadbetter,9 in a discussion of the corresponding-states behavior of the inert gases, has suggested that any deviation from this pattern of behavior in the condensed state due to many-body forces is less than would be obtained of a few percent in the parameters of the pair potential. This conclusion certainly contrasts with recent calculations of the perturbation "nonadditivity" term.<sup>5</sup> It is perhaps safer to say that in the condensed state the true "many-body" potential retains a reasonable "corresponding" relationship, particularly since in the solid phase the actual "geometric" term (i.e., the crystal structure) is the same for each solid.

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## Vibrational Spectra and Structure of Dimethyl Diselenide and Dimethyl Diselenide-d.\*

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The vibrational behavior of the dimethyl disclenide and dimethyl disclenide- $d_6$  molecules has been studied in the infrared region (4000-70 cm<sup>-1</sup>) and by Raman shifts (4000-50 cm<sup>-1</sup>). The molecule has been found to belong to point group  $C_2$ . The fundamental vibrations, with the exception of the methyl torsions, have been assigned and supported by a normal-coordinate analysis.

#### INTRODUCTION

In the past it has been noted that molecules which contain two substituted Group VI atoms bonded together  $[(RM)_2$  where R=H,  $CH_3$ ,  $\phi$ , etc., and M=O, S, Se, etc.,] possess neither cis  $(C_{2v})$  nor trans  $(C_{2h})$  symmetry, but are skewed  $(C_2)$  between the cis and trans extremes at dihedral angles ranging from 80°-120°. The first member of the series, hydrogen peroxide,<sup>1</sup> was found to possess  $C_2$  symmetry and a dihedral angle near 111°. Hydrogen persulfide similarly was found to have a dihedral angle of about 91°.2 When the protons were replaced by methyl groups to form dimethyl disulfide, microwave work showed a dihedral angle near 85°.3

In order to study these systems further, and since the

<sup>&</sup>lt;sup>9</sup> A. J. Leadbetter, Trans. Faraday Soc. 61, 10 (1965).

<sup>&</sup>lt;sup>10</sup> J. M. M. Levelt, Physica 26, 361 (1960).

<sup>\*</sup> Presented at the Seventh National Meeting of the Society for Applied Spectroscopy at the Sheraton-Chicago Hotel, Chicago, Ill., 13-17 May 1968, Paper No. 46. † NAS-NRC Postdoctoral Research Fellow.

<sup>&</sup>lt;sup>1</sup> R. Hunt, R. Leacock, C. Peters, and K. Hecht, J. Chem. Phys. 42, 1931 (1965). <sup>3</sup> G. Winnewisser, M. Winnewisser, and W. Gordy, Symp. Mol.

Struct. Spectry., Ohio State University, Columbus, Ohio, 1966,

Paper AA-7. \* D. Sutler, H. Dreizler, and H. D. Rudolph, Z. Naturforsch. 20a, 1676 (1965).

C <sub>24</sub>		ir	R	C2v	· ·	ir	R	C2	ir	R	<i>C</i> 1	ir	R
8	$A_q$		<b>√</b> (p)	8	$A_1$	$\checkmark$	<b>√</b> (p)	13 A	$\checkmark$	<b>√</b> (p)	24 A	$\checkmark$	<b>√</b> (p)
5	Bq		( <b>d</b> p)	5	<i>A</i> 2		$\sqrt{(dp)}$	11 B	$\checkmark$	$\sqrt{(dp)}$			
7	$A_{*}$	$\checkmark$		4	$B_1$	$\checkmark$	$\checkmark$		24	24			
4	Bu	$\checkmark$		7	B2	$\checkmark$	$\checkmark$		•				
		11	13			19	24						
Among the Raman inactive modes are the nonsymmetric skeletal bending and the skeletal torsion.		A2: C- C	C-H st -H roc H₃ tors	retch, C-I k, skeletal ion (ir ina	H def., torsion, active).	All bands active 11 dep lines.	s are mutu —13 polar olarized F	ally rized and Raman	All ban active	ds are m e and po	utually larized.		

TABLE I. Possible symmetries for the dimethyl diselenide molecule.

spectral assignments and molecular structure of dimethyl diselenide have not been previously reported, the molecule and its perdeutero derivative have been prepared and investigated by infrared and Raman techniques. Twenty-two of the 24 fundamental modes have been assigned and analyzed by a force-constant calculation.

## EXPERIMENTAL

Dimethyl diselenide was prepared from the reaction of sodium diselenide with methyl iodide in liquid ammonia by a method similar to that of Brandsma and Wijers,<sup>4</sup>

$$2Na+2Se \xrightarrow[NH_3]{liq} Na_2Se_2, \qquad (I)$$

Na<sub>2</sub>Se<sub>2</sub>+2CH<sub>3</sub>I
$$\xrightarrow{\text{liq}}$$
 (CH<sub>8</sub>Se)<sub>2</sub>+2NaI. (II)

The purified compound was obtained via vacuum distillation. Dimethyl diselenide- $d_6$  was prepared as above with methyl iodide- $d_8$  as the methyl source. Dimethyl diselenide is a deeply colored, reddish-orange liquid which boils at 153°C (760 mm) and has an extremely evil, persistent odor. Compound purity was checked by NMR and mass spectroscopy.

The mid-infrared spectra were obtained with a Beckman IR-12 infrared spectrophotometer; the liquids were studied as films held between CsI plates; the vapors were studied at 1 mm sample pressure and 8.2-m path. The far-infrared spectrum of liquid dimethyl diselenide was measured on a Beckman IR-11 far-infrared spectrophotometer; the neat sample was contained in a high-density polyethylene cell of 1 mm thickness. The infrared data obtained are listed in Table II and the spectra are reproduced in Figs. 1-3.

Raman spectra of the liquid samples were recorded

on a Cary Model 81 Raman spectrophotometer which was equipped with a He–Ne laser (6328 Å) source. (It should be mentioned that the red color of dimethyl diselenide necessitated a long-wavelength exciting source.) Because of the limitations of coaxial viewing of the scattered Raman radiation, the depolarization values obtained were only qualitative. The Raman data are listed in Table II, and the spectra are reproduced in Fig. 1. The various computations were performed by a CDC-3800 computer.

## **RESULTS AND DISCUSSION**

Selection rules for the most probable symmetries of the dimethyl diselenide molecule are summarized in Table I. The *trans* ( $C_{2h}$ ) structure, which possesses a center of symmetry, would be expected to obey the rule of mutual exclusion. Strong evidence against  $C_{2h}$ symmetry is found in the infrared activity of the Se-Se stretching (286-cm<sup>-1</sup>) and the in-phase skeletal bending (177-cm<sup>-1</sup>) modes (see Fig. 3). Both of these modes would be infrared inactive were the molecular symmetry  $C_{2h}$ . Similarly, the out-of-phase skeletal-bending (192 cm<sup>-1</sup>) mode should be Raman inactive for  $C_{2h}$ symmetry, yet it is definitely present as a shoulder on the 177-cm<sup>-1</sup> line (see Fig. 1).

For the cis  $(C_{2v})$  structure, five modes  $(A_2)$  are infrared inactive, whereas all 24 modes are mutually active for the  $C_2$  or  $C_1$  structures. The assignment of the skeletal torsional motion at about 100 cm<sup>-1</sup> in both infrared and Raman eliminates the cis and the trans configurations since this vibration is Raman inactive for the  $C_{2h}$  point group and *infrared* inactive for  $C_{2v}$ symmetry.

The above considerations immediately suggest a point group somewhere between the  $C_{2h}$  and  $C_{2v}$  configurations, i.e.,  $C_2$  or  $C_1$ . The presence of both polarized and depolarized Raman lines is evidence for the former, so that the molecule is apparently skewed with  $C_2$  symmetry as was found to be the case for the sulfur

<sup>&</sup>lt;sup>4</sup> L. Brandsma and H. Wijers, Rev. Trav. Chim. 82, 69 (1963).



FIG. 1. (a) Infrared spectrum (ordinate in percent transmission) of liquid dimethyl diselenide recorded neat. (b) Raman spectrum (ordinate in arbitrary intensity units) of liquid dimethyl diselenide. Slits, single 2 cm<sup>-1</sup>×5 cm; sensitivity,  $1.2 \times 20$  (25–1500 cm<sup>-1</sup>)  $1.5 \times 200$  (800–1500 cm<sup>-1</sup>),  $2.3 \times 200$  (2700–3200 cm<sup>-1</sup>); period, 0.3 sec; scan. 1.0 cm<sup>-1</sup>/sec. (c) Infrared spectrum (ordinate in percent transmission) of liquid dimethyl diselenide- $d_6$  recorded neat. (d) Raman spectrum (ordinate in arbitrary intensity units) of liquid dimethyl diselenide- $d_6$  solits, single 4 cm<sup>-1</sup>×cm; sensitivity,  $1.7 \times 50$  (bottom),  $1.0 \times 500$  (top); period, 0.5 sec; scan, 0.5 cm<sup>-1</sup>/sec.

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	Infr	ared		Raman					
Frequency <sup>a</sup> vapor (cm <sup>1</sup> )	Relative intensity	Frequency liquid (cm <sup>-1</sup> )	Relative intensity	Frequency liquid (cm <sup>-1</sup> )	Relative intensity	Depolarization value	Assignment		
			A. Di	methyl diselenide	e		<u> </u>		
3920 3838 2778	vvw vvw	3900	vvw				$2\nu_6 + \nu_4 = 3961$ $\nu_2 + \nu_3 + \nu_{10} = 3886$		
3/18	vvw	3740 3430 <sup>ь</sup> (b)	vvw w				3v6=3810		
3192 3120(sh) 3021 P	vw w						$\nu_1 + \nu_{11} = 3204$ $\nu_1 + \nu_{12} = 3127$		
3027Q 3017 <i>P</i> , <i>R</i>	S	3008	m	3009(sh)	w	$^{\mathrm{dp}}$	$\nu_1, \nu_{14}$		
3011Q 3006P 2944 R	S	2996	m	2997	w	dp	<i>ν</i> <sub>2</sub> , <i>ν</i> <sub>15</sub>		
2940Q 2935P	vs	2920	S	2919	S	р	<i>ν</i> <sub>8</sub> , <i>ν</i> <sub>16</sub>		
2880 2833 <i>R</i> 28280	vvs	2804	w	2803	vw	D	$2\nu_{12} 2\nu_{5}$		
2824 <i>P</i> 2710	vvw	2004	W	2000	•••	P	$2\nu_{17}, 2\nu_{18}$ $\nu_{6} + \nu_{7} + \nu_{9} = 2758$		
2530	W	2510	vw				$2\nu_{\theta} = 2540$		
2310	vw	2305	vw				$\nu_5 + \nu_9 = 2315$		
2177	w	2160	vw				$\nu_6 + \nu_7 = 2164$		
1848 1786 1522	w vw						$\nu_6 + \nu_9 = 1854$ $2\nu_7 = 1788$ $\nu_1 + \nu_2 = 1530$		
1332 1470(sh) 1435 <i>R</i>	w vw	1460(sh)	vvw				$\nu_{17} + \nu_{19} = 1478$		
1430Q 1425 <i>P</i> , <i>R</i>	s	1420(sh)	m	1416(b)	m	dp	<i>v</i> <sub>4</sub> , <i>v</i> <sub>17</sub>		
1421Q 1416 <i>P</i> 1275 <i>R</i>	S	1412(sh)	ms				ν <sub>5</sub> , ν <sub>18</sub>		
1270Q 1265P	S	1259	S	1265	ms	р	<i>v</i> <sub>6</sub> , <i>v</i> <sub>19</sub>		
~1100 965(sh)	vvw vw						$(\nu_7 + \nu_{13})$ ?		
894Q 890P	S	<b>893</b> (b)	s	894	w	р	$\nu_{20}, \nu_{21}$		
5847 577?)	S	576	m	577	vs	p	<i>v</i> <sub>9</sub> , <i>v</i> <sub>22</sub>		
		530 390	vw vvw				$2\nu_{10}t$ $\nu_{10}+\nu_{12}=395$		
291Q? 285?	vv₩	286	vw	286	vvs	р	<i>v</i> 10		
		192	vw	192(sh)	vw	$^{\mathrm{dp}}$	V23		
		177(sh)	vvw	177	w	р	<b>11</b>		
		<b>99</b> (vb)	vw	<b>100</b> (b)	vw	$^{\mathrm{dp}}$	<b>7</b> 12		
		86?	vvw				v18, v24?		

TABLE II. Infrared and Raman data of dimethyl diselenide and dimethyl diselenide-d<sub>8</sub>.

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	Infra	ured		Raman					
Frequency <sup>a</sup> vapor (cm <sup>-1</sup> )	Relative intensity	Frequency liquid (cm <sup>-1</sup> )	Relative intensity	Frequency liquid (cm <sup>-1</sup> )	Relative intensity	Depolarization value	Assignment		
			B. Dim	ethyl disele <b>n</b> ide-a	l <sub>6</sub> .	······································	· · · · · · · · · · · · · · · · · · ·		
		<b>3430</b> <sup>b</sup> (b)	w						
3310	vw	3285	vw				$\nu_1 + \nu_4 = 3320$		
3245	vvw	3228	vvw				$\nu_1 + \nu_6 = 3249$		
3120	vvw						$\nu_4 + \nu_5 + \nu_{17} = 3131$		
3020°	vvw								
<b>2940</b> °	w	2920	vw						
2273Q	m	2262	w	2260(sh)	w	dp	<i>v</i> 1, <i>v</i> 14		
2264P, R						-			
2258Q	m	2248(sh)	w	2249	w	dp	$\nu_2, \nu_{15}$		
2254P						-			
2141 <i>R</i>									
2137Q	vs	2123	s	2121	S	р	<i>v</i> <sub>3</sub> , <i>v</i> <sub>16</sub>		
2132P									
		2065(sh)	vw	2067(sh)	vw	?	$2\nu_4 = 2094$		
		2058	w	2053(sh)	vw	?	$2\nu_5 = 2074$		
1725	vw	1715	vvw				$\nu_5 + \nu_7 = 1740$		
1654	w	1640(sh)	vvw				$\nu_8 + \nu_7 = 1656$		
1 500		1630	W				$(\nu_{19}+\nu_{20})?$		
1509	w	1500	w				$\nu_6 + \nu_9 = 1520$		
14210	vw								
1360	vvw						$2\nu_7 = 1366$		
1270	w	1205	vw						
1220	w	1400/12 / 12					$\nu_7 + \nu_9 = 1230$		
1052 7	W	1100(b) (sn)	W				$\nu_9 + 2\nu_{10} = 1097$		
1033K		1040							
10472 P	VS	1040	5	1029(1)		da	<i>v</i> <sub>4</sub> , <i>v</i> <sub>17</sub>		
10421 , K	q	1031 (sh)	e	1038(0)	w	ар			
977 P	5	1001 (311)	3				<i>v</i> <sub>5</sub> , <i>v</i> <sub>18</sub>		
9730	s	963	e .	966	m	'n			
968P	•	200	5	200	111	Р	<i>P</i> 6, <i>P</i> 19		
898 <i>R</i>									
893Q.	vw	895	vvw						
887P									
825	vvw						$v_9 + v_{10} = 822$		
							[ WT. W20		
683Q?	s	682	S	680	vw	p ·	{		
678						•	v8, v21		
553R									
547Q	S	537	m	538	s	р	V9, V22		
544 <i>P</i> ?						-			
	-			275	VS	p	P10		
			·	172(sh)	W	dp	<i>v</i> <sub>23</sub>		
	•		1. A. A. A. A.	160	m	P	<i>v</i> <sub>11</sub>		
				~94	VW	dp?	<b>v</b> <sub>12</sub>		

TABLE II. (Continued)

 $^{\rm a}$  Abbreviations used are: cm $^{-1}$ , wavenumbers; w, weak; m, medium; s, strong; v, very; b, broad; sh, shoulder; p, polarized; dp, depolarized; R, Q, P, rotational structures of vapor bands.

Ξ

<sup>b</sup> Background absorption.

<sup>6</sup> Bands resulting from partially deuterated molecules.

Antisym C-H str.	$S_{1,14}^{b} = (12)^{-1/2} \left[ (2\Delta r_{4} - \Delta r_{5} - \Delta r_{6}) \pm (2\Delta r_{8} - \Delta r_{9} - \Delta r_{10}) \right]$
Antisym C-H str.	$S_{2,15} = (2)^{-1} [(\Delta r_5 - \Delta r_6) \pm (\Delta r_{10} - \Delta r_9)]$
Sym C–H str.	$S_{3,16} = (6)^{-1/2} \left[ (\Delta r_4 + \Delta r_5 + \Delta r_6) \pm (\Delta r_8 + \Delta r_9 + \Delta r_{10}) \right]$
Antisym CH <sub>3</sub> def.	$S_{4,17} = (12)^{-1/2} \left[ (2\Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6) \pm (2\Delta\alpha_8 - \Delta\alpha_9 - \Delta\alpha_{10}) \right]$
Antisym CH <sub>3</sub> def.	$S_{5,18} = (2)^{-1} \left[ (\Delta \alpha_5 - \Delta \alpha_6) \pm (\Delta \alpha_{10} - \Delta \alpha_9) \right]$
Sym CH₃ def.	$S_{6,19}^{\circ} = (N)^{-1/2} \{ [A (\Delta \alpha_4 + \Delta \alpha_5 + \Delta \alpha_6) - B (\Delta \beta_4 + \Delta \beta_5 + \Delta \beta_6)] \\ \pm [A (\Delta \alpha_8 + \Delta \alpha_9 + \Delta \alpha_{10}) - B (\Delta \beta_8 + \Delta \beta_9 + \Delta \beta_{10})] \}$
Antisym CH2 rock	$S_{7,20} = (2)^{-1} \left[ \left( \Delta \beta_5 - \Delta \beta_6 \right) \pm \left( \Delta \beta_{10} - \Delta \beta_9 \right) \right]$
Sym CH <sub>3</sub> rock	$S_{8,21} = (12)^{-1/2} \left[ (2\Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6) \pm (2\Delta\beta_8 - \Delta\beta_9 - \Delta\beta_{10}) \right]$
C-Se str.	$S_{9,22} = (2)^{-1/2} [(\Delta R_1) \pm (\Delta R_7)]$
Se-Se str.	$S_{10} = \Delta D$
Se-Se-C bend.	$S_{11,23} = (2)^{-1/2} \left[ (\Delta \gamma_2) \pm (\Delta \gamma_3) \right]$
Skeletal torsion	$S_{12} = \tau$
Redundancy	$S_{0,0'} = (N)^{-1/2} \{ [B(\Delta \alpha_4 + \Delta \alpha_5 + \Delta \alpha_6) + A(\Delta \beta_4 + \Delta \beta_5 + \Delta \beta_6)] \\ \pm [B(\Delta \alpha_8 + \Delta \alpha_9 + \Delta \alpha_{10}) + A(\Delta \beta_8 + \Delta \beta_9 + \Delta \beta_{10})] \}$
	=0

TABLE III. Symmetry coordinates for dimethyl diselenide.\*

\* Methyl torsions are excluded.

<sup>b</sup> First subscript denotes the symmetry coordinate (species A) obtained when sign option is positive; second denotes those obtained when negative option is used (species B).

analog<sup>3,5</sup> and similar species. It should also be mentioned that there is a very good correspondence of the data obtained here (see Table II) with those reported for  $(CH_3S)_2$  by Scott *et al.*<sup>5</sup>

It is interesting to note that corresponding pairs of in-phase and out-of-phase fundamentals of the two Se-CH<sub>3</sub> groups are very nearly degenerate. The only obvious splittings of in-phase and out-of-phase modes arise from the symmetric and antisymmetric Se-Se-C bending and symmetrical methyl deformation vibrations. Certain vibrations within the same symmetry species, such as the antisymmetric C-H stretching, the antisymmetric CH<sub>3</sub> deformation, and the symmetric and antisymmetric methyl rocking modes, exhibit near-accidental degeneracy.

## ASSIGNMENT OF FUNDAMENTALS

If one assumes  $C_2$  molecular symmetry, the 24 predicted fundamental modes of dimethyl diselenide may be subclassed into 13 species A and 11 species B vibrations. The vibrations in species A should give rise to polarized Raman lines, while those in species B will be depolarized. As mentioned in the previous section,

<sup>5</sup> D. W. Scott, H. L. Finke, M. E. Gross, G. B. Gutherie, and H. M. Huffman, J. Am. Chem. Soc. 72, 2424 (1950); G. A. Crowder and D. W. Scott, J. Mol. Spectry, 16, 122 (1965). corresponding in-phase (A species) and out-of-phase (B species) modes are essentially degenerate, so that the molecule may be treated as having 11 pairs of pseudodegenerate fundamental vibrations along with the Se-Se stretching and skeletal torsion modes. The 11 pairs of nearly degenerate A and B species modes may be described in the following manner: antisymmetric C-H stretching (2), symmetric C-H stretching (1), antisymmetric CH<sub>3</sub> deformation (2), symmetric CH<sub>3</sub> deformation (1), antisymmetric CH<sub>3</sub> rocking (1), symmetric CH<sub>3</sub> rocking (1), Se-Se-C bending (1), and CH<sub>3</sub> torsion (1).

The antisymmetric C-H stretching modes,  $\nu_{1,14}$  and  $\nu_{2,15}$ , are assigned to bands at 3027 and 3011 cm<sup>-1</sup> in the infrared spectrum of vaporous dimethyl diselenide. Deuteration results in shifts to 2273 and 2258 cm<sup>-1</sup>. The symmetric C-H stretching vibration,  $\nu_{3,16}$ , is located at 2940 and 2137 in the vapor spectra of the light and heavy molecules, respectively. A good correspondence is found with the analogous vibrations of CH<sub>3</sub>SeH and CD<sub>3</sub>SeH.<sup>6</sup> Similarly, the two antisymmetrical,  $\nu_{4,17}$  and  $\nu_{5,18}$ , and one symmetrical,  $\nu_{6,19}$ , CH<sub>3</sub> deformations are assigned to bands at 1430, 1421, and 1270 cm<sup>-1</sup> which shift to 1047, 1037, and 973 cm<sup>-1</sup>, respectively, in the spectrum of dimethyl diselenide- $d_6$ .

<sup>6</sup> A. B. Harvey and M. K. Wilson, J. Chem. Phys. 45, 678 (1966).

 $<sup>^{\</sup>circ}A = 0.5529; B = 0.5714; N = 6(A^2 + B^2).$ 



FIG. 3. Far-infrared spectrum of liquid dimethyl diselenide.

The  $\nu_{6,19}$  symmetrical deformation (1270 cm<sup>-1</sup>) occurs at a significantly lower frequency than the antisymmetrical deformations as a result of coupling with the C-Se stretching mode. Analogous behavior has been observed for other compounds that contain a methyl-group-toheavy-atom bond<sup>5,6</sup> and seems to be amplified by increasing the mass of the heavy atom. [For (CH<sub>3</sub>S)<sub>2</sub> the symmetrical methyl deformation occurs at 1307 cm<sup>-1</sup>.]<sup>5</sup> The importance of this coupling is also reflected in the normal-coordinate analysis reported below. It should be mentioned that the symmetrical methyl deformation appears at a slightly higher  $(6-cm^{-1})$ wavenumber in the infrared than in the Raman spectrum (see Table II). The difference is beyond experimental error. Because of the proximity to  $C_{2h}$  symmetry, it appears that in-phase and out-of-phase vibrations are quite weak in the infrared and Raman spectra, respectively. It is therefore believed that the infrared band (1259 cm<sup>-1</sup>) represents the out-of-phase motion,

whereas the Raman line  $(1270 \text{ cm}^{-1})$  results from the in-phase vibration (there is a very weak shoulder near  $1270 \text{ cm}^{-1}$  on the  $1259\text{-cm}^{-1}$  band). Except for the skeletal bending motions (which will be discussed below) the remaining in-phase and out-of-phase vibrations are nearly degenerate. Thus, it is difficult to distinguish individual modes, but it can be said that, for the most part, Raman intensities arise from in-phase modes whereas the corresponding infrared intensities result from out-of-phase motions which are accidentally degenerate with the in-phase counterparts.

The antisymmetric and symmetric CH<sub>3</sub> rocking fundamentals,  $\nu_{7,20}$  and  $\nu_{8,21}$ , are assigned to the somewhat broad Raman line at 894 cm<sup>-1</sup> and exhibit a shift to 680 cm<sup>-1</sup> with deuterium substitution. The nearly degenerate pair of C-Se stretching vibrations,  $\nu_{9,22}$ , gives rise to a strong Raman line at 577 cm<sup>-1</sup> that shifts to 538 cm<sup>-1</sup> with deuteration; the 577-cm<sup>-1</sup> line compares favorably with lines at 582 and 589 cm<sup>-1</sup>



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TABLE IV. Assignments of the fundamental vibrations.						TABLE V. Potential-energy distribution.							
	_	(CH <sub>3</sub>	Se)₂	(CD <sub>3</sub>	Se)2	Vib <sup>a</sup> No.	F11 <sup>b</sup>	F <sub>22</sub>	F <sub>38</sub>	F44	F 55	F 55	F 77
V	Approx. description	Obs	Calc	Obs	Calc	ν1	100° 99	1					
		A Species				V2	100 99	1					
1	Antisym CH str.	3027	3039	2273	2265	$\nu_3$	100						
2	Antisym CH str.	3011	3038	2258	2264		99			1			
3	Sym CH str.	2940	2914	2137	2091	¥4		95	5				
4	Antisym CH₃ def.	1430	1428	1047	1031		1	97	2				
5	Antisym CH₂ def.	1421	1428	1037	1030	$\nu_5$	1	95 97	5 2				
6	Sym CH₃ def.	1270	1281	973	970	Ve	•	50	- 58	3			
7	Antisym CH <sub>3</sub> rock	894	894	680ª	671	× 6	1	51	59	11			
8	Sym CH <sub>3</sub> rock	894	892	680ª	666	ν7		4	95			1	
9	C-Se str.	584	590	547	551		1	2	95			2	
10	Se-Se str.	286ª	283	275ª	279	νs		5	95 07				1
11	Se-Se-C bend	177 <b>ª</b>	177	160ª	162			2	97	107			L
12	Skeletal torsion	~100*	102	~94*	91	$\nu_{9}$		1	2	107 99			
13	CH <sub>2</sub> torsion		•••	•••	•••	<b>V</b> 10					82	18	
10									1		86	13	
		B Species				<b>v</b> 11					18	80	2
14	Antisym CH str.	3027	3039	2273	2265				1	,	14	82	3
15	Antisym CH str.	3011	3038	2258	2263	V13			1			2	98 07
16	Sym CH str.	2940	2914	2137	2091				1			4	91
17	Antisym CH3 def.	1430	1428	1047	1031	V18	100-	•••	•••	•••	•••	•••	•••
18	Antisym CH₃ def.	1421	1428	1037	1030	<i>V</i> 14	100° 99	1					
19	Sym CH3 def.	1270	1281	973	970	<b>P</b> 16	100						
20	Antisym CH <sub>2</sub> rock	894	894	680ª	670	. 10	99	1					
21	Sym CH <sub>8</sub> rock	894	891	680ª	664	P16	100						
22	C-Se str.	584	590	547	551		99			1			
23	Se–Se–C bend	192ª	205	172ª	187	P17	1	95 07	5				
24	CH <sub>2</sub> torsion	•••	•••	•••	•••		T	97	2				
						P18	1	95 97	2				
A The	ese frequencies are take	n from the	e Raman a taken fro:	spectra of th m infrared s	ie liquid pectra of	<b>V1</b> 0	-	50	58	3			
he var	pors.	-					1	51	59	11			

assigned to the C-Se stretching modes of CH<sub>3</sub>SeH<sup>6</sup> and CH3SeCH3,7 respectively. The most intense Raman line (and one of the weakest infrared bands) at 286 cm<sup>-1</sup> is assigned to the Se-Se stretching mode,  $v_{10}$ ; a minor shift to 275 cm<sup>-1</sup> is noted with isotopic substitution. As pointed out earlier, the in-phase, v11, and out-ofphase, v22, Se-Se-C bending modes are assigned to lines at 177 and 192 cm<sup>-1</sup> in the Raman spectrum of the light molecule, respectively; these lines are shifted to 160 and 172 cm<sup>-1</sup> in the spectrum of the heavy molecule.

<sup>7</sup> J. R. Allkins and P. J. Hendra, Spectrochim. Acta 22, 2075 (1966).

TABLE V. Potential-energy distribution.

F34

-11 -22

-10 1

. . .

B Con T	able IV							
V24	····	•••	•••	•••	•••	•••	•••	•••
		1	2			97		
V23			1			99		
				98				2
$\nu_{22}$		1	2	107				-10
	1	2	97					
$\nu_{21}$		5	95					
	1	2	95			2		
$\nu_{20}$		4	95			1		
	1	51	59	11				-22
<b>v</b> 19		50	58	3				-11
	1	91	4					

<sup>b</sup> See Table VI.

<sup>o</sup>Listed in the order: (CH<sub>2</sub>Se)<sub>1</sub>, (CD<sub>2</sub>Se)<sub>2</sub>.

The high-frequency out-of-phase component appears as a weak shoulder on the corresponding in-phase Raman line; in the far-infrared spectrum (see Fig. 3) the two components of this doublet reverse in relative intensity. Such behavior supports  $C_2$  symmetry for dimethyl diselenide but reflects the proximity to the  $C_{2h}$  point group.

The skeletal torsion (about the Se-Se bond),  $\nu_{12}$ , is assigned to a broad, weak band centered near  $100 \text{ cm}^{-1}$ in both the Raman and far-infrared spectra of dimethyl diselenide. Support for this assignment is once again found with the value  $(115 \text{ cm}^{-1})$  reported for the dimethyl disulfide molecule.<sup>5</sup> The two methyl torsional oscillations,  $\nu_{13,24}$ , have not yet been assigned, but would be expected to be nearly degenerate.

The vibrational assignment precludes both  $C_{24}$  and  $C_{2*}$  structures for the molecule.  $C_{2h}$  is ruled out because of the Raman activity of  $\nu_{12}$  and  $\nu_{22}$ , and  $C_{2\nu}$  because of the activity of  $v_{12}$  in the infrared spectrum. The  $C_2$ structure is preferred over  $C_1$  since several of the Raman lines appear to be depolarized and also because it is consistent with the structures found for similar molecules.

### NORMAL-COORDINATE ANALYSIS

To test the vibrational assignments with particular regard to the skeletal modes and to make a comparison with the sulfur analog, a normal-coordinate calculation was undertaken. Because no structural data for the dimethyl diselenide molecule were available, it was necessary to employ an assumed structure in the computations. Although bond lengths may be transferred from similar molecules with little error, skeletal bond angles estimated in such a manner are much less certain; consequently, the Se-Se-C and dihedral angles were chosen by varying each until a best fit of the observed and calculated vapor-phase band contours was obtained (the P and R rotational wing spacing of a particular band type depends on the rotational constants, which in turn depend on the angles in question). Although the values obtained are highly tentative, they provide a reasonable structure when the known geometry of the sulfur analog is considered.<sup>3</sup> The molecular geometry thus assumed is depicted in Fig. 4.

The normal-coordinate calculation was carried out by the Wilson FG-matrix method<sup>8</sup> with computer programs written by Schachtschneider.<sup>9</sup> The symmetrized G-matrix elements of the two isotopic species were computed from the assumed structure. The orthonormal symmetry coordinates employed in the calculation are listed in Table III.

TABLE VI. Potential constants for dimethyl diselenide.

 Motion	Constant <sup>a</sup>
(1) C-H stretching	$F_{11} = 4.906$
(2) H-C-H bending	$F_{22} = 0.513$
(3) H–C–Se bending	$F_{83} = 0.553$
(4) C-Se stretching	$F_{44} = 2.625$
(5) Se-Se stretching	$F_{55} = 1.674$
(6) Se-Se-C bending	$F_{66} = 1.025$
(7) Skeletal torsion	$F_{77} = 0.160$
(8) Interaction (3-4)	$F_{34} = 0.290$

<sup>a</sup> Stretching potential constants are in millidynes per Ångstrom units; bending constants are in millidynes. Ångstrom units.

The vibrational frequencies-observed and calculated-are listed in Table IV. The average error is 1.3% or 10 cm<sup>-1</sup>. Table V contains the potential-energy distribution, and Table VI lists the values of the (MVFF) potential constants for dimethyl diselenide. The important off-diagonal  $F_{34}$  constant has been found to be significant in other compounds which contain methyl groups bonded to relatively heavy atoms.6 A further refinement of the normal-coordinate treatment must await a more accurate structural determination.

#### SUMMARY

The dimethyl diselenide molecule has been found to possess  $C_2$  symmetry with an estimated dihedral angle of 82°. The fundamental vibrations, save the methyl torsions, have been assigned and reasonably well reproduced by a normal-coordinate calculation which fitted 44 observed frequencies with seven diagonal and one off-diagonal force constants. The significant offdiagonal term arises from the interaction of the symmetric methyl deformation and the C-Se stretching modes.

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<sup>&</sup>lt;sup>8</sup> E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., New York, 1958). <sup>9</sup> J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules. V and VI," Tech. Rept. Nos. 231-264 and 57-65, proceedings of Schull Dependence of Emperative Collife respectively, Shell Development Co., Emeryville, Calif.