Molecular Force Field of Dialkyl Selenides

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The molecular force field in terms of the local symmetry coordinates was determined for unbranched dialkyl selenides. Twenty-six important force constants associated with the selenium part were adjusted by using about two hundred observed vibrational wave numbers for a total of twelve conformational isomers of ethyl methyl selenide, diethyl selenide, methyl propyl selenide, butyl methyl selenide, and ethyl propyl selenide. Remaining force constants of the selenides were assumed to be equivalent to those for unbranched dialkyl sulfides and alkanes. The least-squares calculation gave an overall root-mean-square deviation of 6.7 cm^{-1} between the observed and calculated wave numbers. The force constants and the results of the normal coordinate treatment are given in this paper.

The molecular force field of molecules is fundamentally important for studying various problems in chemistry and physics. To establish the force field, vibrational spectra have been extensively investigated for a number of compounds. The force constants deduced from the experimental data were, however, reliable only, in general, for relatively small molecules. To conquer the difficulty in determining the molecular force field of larger molecules, various attempts have been made.[1–4] One of the approaches is to assume the transferability of the force constants for similar atomic groups in different molecules.[5] This assumption allows ones to reduce the number of force constants to determine. In this model, the symmetry coordinates in each of the atomic groups, namely the local symmetry coordinates, are used to express the molecular force field, as most of organic molecules, which we are interested in, give characteristic group vibrations.

Recent systematic studies[6–15] on the vibrational spectra of unbranched organic compounds made possible to determine the force constants, in terms of the local symmetry force field, for alkanes, dialkyl ethers, dialkyl sulfides, halogenoalkanes, and alkylsilanes.[16,17] In the present study, the molecular force field of unbranched dialkyl selenides was treated by utilizing the experimental data which have been accumulated in our laboratory.[18] The force constants thus obtained are reported in this paper and are discussed in comparison with those for related compounds. A preliminary result of the normal coordinate treatment has been reported previously.[19]

Calculation of Normal Coordinates

The calculation of the normal coordinates for unbranched dialkyl selenides was carried out by a program system MVIB[20] with a HITAC 8700 computing system at Hiroshima University. The force field adopted in the MVIB system is the local symmetry force field which has been successfully applied to a number of unbranched organic compounds.[16,17]

Initial values of the force constants for the selenium part and for the alkyl parts next to the selenium atom were transferred or estimated from the results for the sulfides.[16] The force constants for the unbranched alkyl part, not directly associated with the selenium atom, were the same as those obtained for the alkanes.[16] Some of the important force constants for the selenium and neighboring parts were adjusted by a least-squares procedure by utilizing the observed vibrational wave numbers for the *trans* and *gauche* isomers of ethyl methyl selenide $CH_3SeCH_2CH_3$, the *trans-trans*, *trans-gauche*, and *gauche-gauche* isomers of diethyl selenide $CH_3CH_2SeCH_2CH_3$, and the *trans-trans*, *trans-gauche*, *gauche-trans*, and *gauche-gauche* isomers of methyl propyl selenide $CH_3SeCH_2CH_2CH_3$.[18]

The force field thus obtained was applied to butyl methyl selenide $CH_3SeCH_2CH_2CH_2CH_3$ and ethyl propyl selenide $CH_3CH_2SeCH_2CH_2CH_3$ to study the rotational isomerism. The force field was then refined by using the additional observed data for the *gauche-gauche-trans* isomer of butyl methyl selenide and the *gauche-gauche-trans* and *gauche-gauche-gauche* isomers of ethyl propyl selenide,[18] which have been shown to exist in the solid state.[19] At the final stage of the calculation, twenty-six important force constants

TABLE 1. ATOMIC MASSES AND STRUCTURAL PARAMETERS USED IN THE CALCULATION

Property	Quantity
Atomic masses, u	
Hydrogen (H)	1.007825
Carbon (C)	12.011
Selenium (Se)	78.96
Bond lengths, Å	
r(C–H)	1.100[a]
r(C–C)	1.539[a]
r(C–Se)	1.943[b]
Bond angles, degree	
∠(C–C–C)	112.2[a]
∠(C–C–Se)	113.6[c]
∠(C–Se–C)	96.18[b]
∠(C–C–H)	110.4[a]
∠(Se–C–H)	108.8[d]
Dihedral angles of molecular skeleton, degree	
trans conformation	180
gauche$^+$ conformation	60
gauche$^-$ conformation	−60

a) Ref. 16. b) Taken from dimethyl selenide (Ref. 21). c) Assumed to be equal to ∠(C–C–S) (Ref. 16). d) Assumed to be equal to ∠(S–C–H) (Ref. 16). This value is close to an average value, 108.2°, of two unequivalent ∠(Se–C–H) of dimethyl selenide (Ref. 21).

TABLE 2. DEFINITION AND SYMBOLISM OF ATOMIC GROUPS AND LOCAL SYMMETRY COORDINATES

Atomic group		Local symmetry coordinate		
Description	Symbol	Description	Symbol	Definition[a,b]
CH_3–(X)	1	CH_3 symmetrical stretching	1	$(\Delta r_1+\Delta r_2+\Delta r_3)/\sqrt{3}$
		CH_3 symmetrical deformation	2	$a(\Delta\alpha_{23}+\Delta\alpha_{31}+\Delta\alpha_{12})-b(\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)$
		CH_3 degenerate stretching (in-plane)	3	$(2\Delta r_1-\Delta r_2-\Delta r_3)/\sqrt{6}$
		CH_3 degenerate deformation (in-plane)	4	$(2\Delta\alpha_{23}-\Delta\alpha_{31}-\Delta\alpha_{12})/\sqrt{6}$
		CH_3 rocking (in-plane)	5	$(2\Delta\beta_1-\Delta\beta_2-\Delta\beta_3)/\sqrt{6}$
		CH_3 degenerate stretching (out-of-plane)	6	$(\Delta r_2-\Delta r_3)/\sqrt{2}$
		CH_3 degenerate deformation (out-of-plane)	7	$(\Delta\alpha_{31}-\Delta\alpha_{12})/\sqrt{2}$
		CH_3 rocking (out-of-plane)	8	$(\Delta\beta_2-\Delta\beta_3)/\sqrt{2}$
(X)–CH_2–(Y)	2	CH_2 symmetrical stretching	1	$(\Delta r_1+\Delta r_2)/\sqrt{2}$
		CH_2 scissoring	2	$c\Delta\alpha-d(\Delta\beta_{1X}+\Delta\beta_{2X})-e(\Delta\beta_{1Y}+\Delta\beta_{2Y})$
		CH_2 antisymmetrical stretching[c]	3	$(\Delta r_1-\Delta r_2)/\sqrt{2}$
		CH_2 rocking[c]	4	$(\Delta\beta_{1X}-\Delta\beta_{2X}+\Delta\beta_{1Y}-\Delta\beta_{2Y})/2$
		CH_2 wagging[c]	5	$f(\Delta\beta_{1X}+\Delta\beta_{2X})-g(\Delta\beta_{1Y}+\Delta\beta_{2Y})/2$
		CH_2 twisting	6	$(\Delta\beta_{1X}-\Delta\beta_{2X}-\Delta\beta_{1Y}+\Delta\beta_{2Y})/2$
		X–C–Y deformation	D	$h\Delta\gamma-i\Delta\alpha-j(\Delta\beta_{1X}+\Delta\beta_{2X})-k(\Delta\beta_{1Y}+\Delta\beta_{2Y})$
(X)–Se–(Y)	W	X–Se–Y bending	B	$\Delta\gamma$
Skeleton –(X)–(Y)–	—	Stretching	S	Δr_{XY}
		Torsion[d]	T	Δt_{XY}

a) $a=0.403003$ and $b=0.413427$ for X=Se. $c=0.908651$, $d=0.211232$, $e=0.206297$, $f=0.494055$, $g=0.505875$, $h=0.896458$, $i=0.185032$, $j=0.203690$, and $k=0.198931$ for X=C and Y=Se. b) *Definition of the internal coordinates of the methyl group.* The hydrogen atoms in the CH_3–(X)–(Y) group are numbered in the following way (Refs. 16 and 22). The hydrogen atom located at the *trans* position relative to Y is numbered as 1. The atoms numbered 2 and 3 are defined in the clockwise direction, viewing the atoms along the bond X–C with the atom X nearer to the observer (see Fig. 1 of Ref. 16). $r_1=r(C\text{–}H_1)$, $r_2=r(C\text{–}H_2)$, $r_3=r(C\text{–}H_3)$, $\alpha_{12}=\angle(H_1\text{–}C\text{–}H_2)$, $\alpha_{23}=\angle(H_2\text{–}C\text{–}H_3)$, $\alpha_{31}=\angle(H_3\text{–}C\text{–}H_1)$, $\beta_1=\angle(H_1\text{–}C\text{–}X)$, $\beta_2=\angle(H_2\text{–}C\text{–}X)$, and $\beta_3=\angle(H_3\text{–}C\text{–}X)$. *Definition of the internal coordinates of the methylene group.* The hydrogen atoms in the (X)–CH_2–(Y) group are numbered in the following way (Ref. 16). Viewing the (X)–CH_2–(Y) group from the direction perpendicular to the HCH plane with the atom X nearer to the observer, the hydrogen atoms located at the ten o'clock and two o'clock positions (or, for example, at the four o'clock and eight o'clock positions, respectively) are numbered as 1 and 2, respectively (see Fig. 1 of Ref. 16). $r_1=r(C\text{–}H_1)$, $r_2=r(C\text{–}H_2)$, $\alpha=\angle(H_1\text{–}C\text{–}H_2)$, $\beta_{1X}=\angle(H_1\text{–}C\text{–}X)$, $\beta_{2X}=\angle(H_2\text{–}C\text{–}X)$, $\beta_{1Y}=\angle(H_1\text{–}C\text{–}Y)$, $\beta_{2Y}=\angle(H_2\text{–}C\text{–}Y)$, and $\gamma=\angle(X\text{–}C\text{–}Y)$. c) The signs of the CH_2 antisymmetrical stretching, rocking, and wagging coordinates of the (Y)–CH_2–(X) group (viewing the atomic group from the direction perpendicular to the HCH plane with the atom Y nearer to the observer) are opposite to those of the corresponding coordinates of the (X)–CH_2–(Y) group (viewing the atomic group with the atom X nearer to the observer) (Refs. 16 and 22). The signs of the other coordinates in this table are invariable with the viewing direction. d) For the definition of the torsional coordinate, see Refs. 22 and 23.

associated with the selenium and neighboring parts were determined from a total of 196 observed wave numbers with non-zero weights for the twelve conformers of the five compounds.

In the normal coordinate calculation, the observed wave numbers in the liquid phase were used, so that the origin of the experimental data for any one isomer is consistent with that for any other.

The atomic masses and structural parameters used in the calculation are listed in Table 1. The structural data for the selenium part were taken from a microwave study on dimethyl selenide.[21]

Local Symmetry Coordinates. The local symmetry coordinates defined in Table 2 were used as basis coordinates in the normal coordinate treatment. The deformation coordinates for the methyl or methylene group were constructed in accordance with the bond angles, given in Table 1, around a central carbon atom, so that the redundant coordinate was properly eliminated from the coordinate system. The definition of the local symmetry coordinates adopted in this study for the methyl and methylene groups is in accord with the conventions recommended by IUPAC.[22] The coordinates for the methyl group with a neighboring carbon atom, CH_3–(C), and the methylene group with neighboring carbon atoms, (C)–CH_2–(C), have been defined previously[16] on the basis of ∠(C–C–C) and ∠(C–C–H) values given in Table 1.

According to the coordinate definition mentioned above, the signs of the CH_2 antisymmetrical stretching, rocking, and wagging coordinates for the (X)–CH_2–(Y) group are opposite to those of the corresponding coordinates for the (Y)–CH_2–(X) group. The signs of other coordinates given in Table 2 are invariable with the direction of ordering the atomic groups. One must be careful in defining the coordinates, since the signs of the off-diagonal force constants in terms of these coordinates depend directly upon the signs of the coordinates concerned.

Force Constants. The force constants in the local symmetry force field are expressed on the basis of the local symmetry coordinates.[5] In a series of studies on the local symmetry force field,[16,17] force constants have been denoted by symbols, which are suitable for com-

TABLE 3. FORCE CONSTANTS FOR UNBRANCHED DIALKYL SELENIDES[a)]

Constant[b)]	Value[c)]	Constant[b)]	Value[c)]	Constant[b)]	Value[c)]
01W-1	= 014-1 (4.715)	122W-S	=222W-S	222W-SD	0.013±0.057
01W-2	0.527±0.005	122W-T	=222W-T	222W-2D-t	=2224-2D-t (−0.050)
01W-3	= 014-3 (4.637)	† 122W-5S	=222W-5S	222W-44-t	0.058±0.024
01W-4	0.533±0.002	122W-DS	=222W-DS	† 222W-46-t	=2224-46-t
01W-5	0.566±0.003	† 122W-S5	=222W-S5		=2222-46-t (0.063)
01W-6	= 01W-3	122W-SD	=222W-SD	222W-55-t	−0.053±0.007
01W-7	= 01W-4	122W-2D-t	=222W-2D-t	† 222W-5D-t	=2224-5D-t (−0.034)
01W-8	= 01W-5	122W-44-t	=222W-44-t	† 222W-64-t	=2224-64-t
01W-45	= 014-45 (−0 020)	† 122W-46-t	=222W-46-t		=−2222-46-t (−0.063)
01W-78	= 01W-45	122W-55-t	=222W-55-t	222W-66-t	−0.076±0.008
		† 122W-5D-t	=222W-5D-t	222W-D2-t	=2224-D2-t
12W-1	= 22W-1	† 122W-64-t	=222W-64-t		=2222-2D-t (0.042)
12W-2	= 22W-2	122W-66-t	=222W-66-t	† 222W-D5-t	=2224-D5-t
12W-3	= 22W-3	122W-D2-t	=222W-D2-t		=−2222-5D-t (−0.039)
12W-4	= 22W-4	† 122W-D5-t	=222W-D5-t	222W-DD-t	−0.052±0.057
12W-5	= 22W-5	122W-DD-t	=222W-DD-t	222W-44-g^{+}	0.007±0.025
12W-6	= 22W-6	122W-44-g^{+}	=222W-44-g^{+}	*222W-45-g^{+}	=2224-45-g^{+}
12W-D	0.865±0.036	*122W-45-g^{+}	=222W-45-g^{+}		=2222-45-g^{+} (0.063)
12W-25	= 22W-25	† 122W-46-g^{+}	=222W-46-g^{+}	† 222W-46-g^{+}	=2224-46-g^{+}
12W-2D	= 22W-2D	*† 122W-4D-g^{+}	=222W-4D-g^{+}		=2222-46-g^{+} (−0.029)
† 12W-46	= 22W-46	*122W-54-g^{+}	=222W-54-g^{+}	*† 222W-4D-g^{+}	=2224-4D-g^{+} (−0.026)
† 12W-5D	= 22W-5D	122W-55-g^{+}	=222W-55-g^{+}	*222W-54-g^{+}	=2224-54-g^{+}
12W-SS	= 22W-SS	*† 122W-56-g^{+}	=222W-56-g^{+}		=2222-45-g^{+} (0.063)
		† 122W-5D-g^{+}	=222W-5D-g^{+}	222W-55-g^{+}	0.038±0.009
1W2-B	1.158±0.042	† 122W-64-g^{+}	=222W-64-g^{+}	*† 222W-56-g^{+}	=2224-56-g^{+}
1W2-SS	= 2W2-SS	*† 122W-65-g^{+}	=222W-65-g^{+}		=2222-56-g^{+} (0.026)
		122W-66-g^{+}	=222W-66-g^{+}	† 222W-5D-g^{+}	=2224-5D-g^{+} (−0.036)
22W-1	=224-1 (4.689)	*122W-6D-g^{+}	=222W-6D-g^{+}	† 222W-64-g^{+}	=2224-64-g^{+}
22W-2	0.549±0.003	*† 122W-D4-g^{+}	=222W-D4-g^{+}		=−2222-46-g^{+} (0.029)
22W-3	=224-3 (4.637)	† 122W-D5-g^{+}	=222W-D5-g^{+}	*† 222W-65-g^{+}	=2224-65-g^{+}
22W-4	0.754±0.006	*122W-D6-g^{+}	=222W-D6-g^{+}		=−2222-56-g^{+} (−0.026)
22W-5	0.582±0.003	122W-DD-g^{+}	=222W-DD-g^{+}	222W-66-g^{+}	0.040±0.017
22W-6	0.596±0.004			*222W-6D-g^{+}	=2224-6D-g^{+} (0.162)
22W-D	0.891±0.026	12W1-S	=22W2-S	*† 222W-D4-g^{+}	=2224-D4-g^{+}
22W-25	=224-25 (0.054)	12W1-T	=22W2-T		=−2222-4D-g^{+} (0.074)
22W-2D	=224-2D (0.161)	† 12W1-5S	=22W2-5S	† 222W-D5-g^{+}	=2224-D5-g^{+}
† 22W-46	=224-46 (−0.030)	12W1-DS	=22W2-DS		=−2222-5D-g^{+} (0.017)
† 22W-5D	=224-5D (0.113)	12W1-SB	=22W2-SB	*222W-D6-g^{+}	=2224-D6-g^{+}
22W-SS	=224-SS (0.473)	12W1-2B-t	=22W2-2B-t		=2222-6D-g^{+} (0.079)
		† 12W1-5B-t	=22W2-5B-t	222W-DD-g^{+}	0.021±0.040
2W2-B	1.257±0.054	12W1-DB-t	=22W2-DB-t		
2W2-SS	−0.054±0.036	*† 12W1-4B-g^{+}	=22W2-4B-g^{+}	22W1-S	=22W2-S
		† 12W1-5B-g^{+}	=22W2-5B-g^{+}	22W1-T	=22W2-T
012W-S	=0124-S	*12W1-6B-g^{+}	=22W2-6B-g^{+}	† 22W1-5S	=22W2-5S
	=2224-S (4.424)	12W1-DB-g^{+}	=22W2-DB-g^{+}	22W1-DS	=22W2-DS
012W-T	=0124-T (0.110)			22W1-SB	=22W2-SB
012W-22	=0124-22 (−0.022)	12W2-S	=22W2-S	22W1-2B-t	=22W2-2B-t
† 012W-25	=0124-25 (−0.041)	12W2-T	=22W2-T	† 22W1-5B-t	=22W2-5B-t
012W-2D	=0124-2D (−0.040)	† 12W2-5S	=22W2-5S	22W1-DB-t	=22W2-DB-t
012W-2S	=0124-2S (−0.345)	12W2-DS	=22W2-DS	*† 22W1-4B-g^{+}	=22W2-4B-g^{+}
† 012W-45	=0124-45 (0.025)	12W2-SB	=22W2-SB	† 22W1-5B-g^{+}	=22W2-5B-g^{+}
012W-52	=0124-52 (0.016)	12W2-2B-t	=22W2-2B-t	*22W1-6B-g^{+}	=22W2-6B-g^{+}
† 012W-55	=0124-55 (−0.058)	† 12W2-5B-t	=22W2-5B-t	22W1-DB-g^{+}	=22W2-DB-g^{+}
012W-5D	=0124-5D (0.067)	12W2-DB-t	=22W2-DB-t		
† 012W-84	=0124-84 (−0.064)	*† 12W2-4B-g^{+}	=22W2-4B-g^{+}	22W2-S	2.621±0.037
012W-86	=0124-86 (−0.117)	† 12W2-5B-g^{+}	=22W2-5B-g^{+}	22W2-T	=2242-T (0.045)
† 012W-S5	=0124-S5	*12W2-6B-g^{+}	=22W2-6B-g^{+}	† 22W2-5S	=2242-5S (−0.217)
	=−2222-5S (0.304)	12W2-DB-g^{+}	=22W2-DB-g^{+}	22W2-DS	0.252±0.031
012W-SD	=222W-SD			22W2-SB	−0.134±0.038

TABLE 3. (Continued)

Constant[b)]	Value[c)]	Constant[b)]	Value[c)]	Constant[b)]	Value[c)]
		222W-S	=2224-S (4.424)	22W2-2B-t	=2242-2B-t (−0.169)
01W2-S	=22W2-S	222W-T	=2224-T (0.113)	†22W2-5B-t	=2242-5B-t (−0.091)
01W2-T	=0142-T (0.045)	†222W-5S	=2224-5S	22W2-DB-t	0.001±0.048
01W2-2B	=0142-2B (0.194)		=2222-5S (−0.304)	*†22W2-4B-g$^+$	=2242-4B-g$^+$ (0.415)
01W2-2S	=0142-2S (−0.340)	222W-DS	=2224-DS	†22W2-5B-g$^+$	=2242-5B-g$^+$ (−0.035)
01W2-5B	=0142-5B (0.003)		=2222-DS (0.213)	*22W2-6B-g$^+$	=2242-6B-g$^+$ (0.070)
01W2-SB	=22W2-SB	†222W-S5	=2224-S5	22W2-DB-g$^+$	0.020±0.022
			=−2222-5S (0.304)		

a) Only the force constants with non-zero values are given in this table. Force constants not found in the table have zero values. The atomic-group symbol "4" denotes -Se-. b) Values for the intergroup force constants for the g$^-$ (*gauche*$^-$) conformation are the same as those for the corresponding force constants for the g$^+$ (*gauche*$^+$) conformation, unless they are marked with *. For those marked with *, the absolute values for the g$^+$ and g$^-$ force constants are the same but their signs are opposite to each other. For example, 222W-6D-g$^+$= −222W-6D-g$^-$. For those force constants marked with †, their signs are reversed if they are defined by ordering the atomic groups in an opposite direction. For example, 012W-84= −W210-48. c) Units are mdyn Å^{-1} for the diagonal stretching and off-diagonal sretching-stretching constants, mdyn for the off-diagonal stretching-bending constants, and mdyn Å for the diagonal bending, off-diagonal bending-bending, and diagonal torsional constants.

puter input and output, under a systematic nomenclature rule. Details of the force constant symbols have been described previously.[16)] Only fundamental aspects are quoted here with some examples for dialkyl selenides. The symbols for dialkyl selenides are found to be analogous to those for dialkyl sulfides or ethers.

The symbol for the intragroup force constant on the diagonal has a general form *abc-d* and that on the off-diagonal *abc-de*, where *a*, *b*, and *c* are symbols for the atomic groups, *b* being the group in question and *a* and *c* the two adjacent groups, and *d* and *e* are symbols for the local symmetry coordinates in question. The symbols for the atomic groups and the local symmetry coordinates applicable to dialkyl selenides are given in Table 2. In cases where the atomic group in question is a terminal group (for example, methyl group), a nonexistent adjacent group is denoted by 0.

The symbols for the intergroup force constant on the diagonal has a general form *fghi-j* and that on the off-diagonal *fghi-jk* or *fghi-jk-l*, where *f*, *g*, *h*, and *i* are symbols for the atomic groups, *g* and *h* being the two groups in question and *f* and *i* their adjacent groups, and *j* and *k* are symbols for the local symmetry coordinates in question. The coordinates *j* and *k* belong, respectively, to the atomic groups *g* and *h*. The symbol *l*, if any, denotes the conformation of the molecular skeleton given by the atomic groups *f*, *g*, *h*, and *i*. Possible symbols for *l* are t (for *trans* conformation), g$^+$ (*gauche*$^+$), g$^-$ (*gauche*$^-$), c (*cis*), s$^+$ (*skew*$^+$), and s$^-$ (*skew*$^-$).

Some examples of the symbols for dialkyl selenides are given below.

01W-2: the diagonal force constant for the CH_3 symmetrical deformation in the CH_3 group of the CH_3Se– part.

22W-46: the off-diagonal force constant for the CH_2 rocking and twisting within the C^bH_2 group of the -$C^aH_2C^bH_2Se$– part.

2W2-SS: the off-diagonal force constant for the C^a–Se stretching and the Se–C^b stretching of the -$C^aH_2SeC^bH_2$– part.

01W2-S: the diagonal force constant for the C^a–Se stretching of the $C^aH_3SeC^bH_2$– part.

12W2-5S: the off-diagonal force constant for the C^bH_2 wagging and the C^b–Se stretching of the $C^aH_3C^bH_2SeC^cH_2$– part.

22W2-SB: the off-diagonal force constant for the C^b–Se stretching and the C^bSeC^c bending of the -$C^aH_2C^bH_2SeC^cH_2$– part.

222W-46-g$^+$: the off-diagonal force constant for the C^bH_2 rocking and the C^cH_2 twisting of the -$C^aH_2C^bH_2C^cH_2Se$– part in the *gauche*$^+$ skeletal conformation.

The coordinates *d*, *e*, *j*, and *k* are defined so that their signs are positive when one views the successive atomic groups from *a* to *c* for the intragroup force constant or from *f* to *i* for the intergroup force constant. It should be noticed that the signs of some of the force constants are reversed if the force constants are defined

TABLE 4. OBSERVED AND CALCULATED WAVE NUMBERS, IN cm^{-1}, AND VIBRATIONAL ASSIGNMENTS FOR ETHYL METHYL SELENIDE[a)]

$\tilde{\nu}_{obsd}$[b)]	$\tilde{\nu}_{calcd}$ and assignment			
	trans form (C_s)		*gauche* form (C_1)	
763*	761(a″)	CH_2 rock		
737			741	CH_2 rock
597	594(a′)	CH_3–Se stretch	595	CH_3–Se stretch
577*	572(a′)	Se–CH_2 stretch		
562			560	Se–CH_2 stretch
300	303(a′)	SeCC deform	298	SeCC deform
240	250(a″)	CH_2–CH_3 torsion	251	CH_2–CH_3 torsion
199			203	CSeC bend
174*	191(a′)	CSeC bend		
	156(a″)	CH_3–Se torsion	154	CH_3–Se torsion
	71(a″)	Se–CH_2 torsion	70	Se–CH_2 torsion

a) Only the vibrations below 800 cm^{-1} are given in the table. b) The observed wave numbers in the liquid state are given. The bands whose wave numbers are marked with * disappear on solidification.

TABLE 5. OBSERVED AND CALCULATED WAVE NUMBERS, IN cm^{-1}, AND VIBRATIONAL ASSIGNMENTS FOR DIETHYL SELENIDE[a)]

$\tilde{\nu}_{\mathrm{obsd}}$[b)]	$\tilde{\nu}_{\mathrm{calcd}}$ and assignment		
	trans-trans form (C_{2v})	*trans-gauche* form (C_1)	*gauche-gauche* form (C_2)
772[c)]	762(b_2) CH_2 rock 758(a_2) CH_2 rock		
761*		761 CH_2 rock	
755*			760(b) CH_2 rock
741*		740 CH_2 rock	
720*			722(a) CH_2 rock
581	582(a_1) Se–CH_2 stretch		
577	567(b_1) Se–CH_2 stretch	574 Se–CH_2 stretch	
568*			575(b) Se–CH_2 stretch
559*		564 Se–CH_2 stretch	552(a) Se–CH_2 stretch
314	306(b_1) SeCC deform	315 SeCC deform	
304*			306(a) SeCC deform
277	292(a_1) SeCC deform	278 SeCC deform	285(b) SeCC deform
247	251(b_2) CH_3–CH_2 torsion 249(a_2) CH_3–CH_2 torsion	251 CH_3–CH_2 torsion 249 CH_3–CH_2 torsion	249(b) CH_3–CH_2 torsion 246(a) CH_3–CH_2 torsion
181*			175(a) CSeC bend
160*		164 CSeC bend	
139[c)]	140(a_1) CSeC bend		
	84(a_2) Se–CH_2 torsion		80(b) Se–CH_2 torsion
		69 Se–CH_2 torsion	
		59 Se–CH_2 torsion	
	49(b_2) Se–CH_2 torsion		46(a) Se–CH_2 torsion

a), b) See footnotes a) and b), respectively, to Table 4. c) Observed in the solid state.

TABLE 6. OBSERVED AND CALCULATED WAVE NUMBERS, IN cm^{-1}, AND VIBRATIONAL ASSIGNMENTS FOR METHYL PROPYL SELENIDE[a)]

$\tilde{\nu}_{\mathrm{obsd}}$[b)]	$\tilde{\nu}_{\mathrm{calcd}}$ and assignment			
	trans-trans form (C_s)	*trans-gauche* form (C_1)[c)]	*gauche-trans* form (C_1)[d)]	*gauche-gauche* form (C_1)
773*		773 CH_2 rock		
766*				766 CH_2 rock
731*	728(a″) CH_2 rock			
716			719 CH_2 rock	
660*	653(a′) Se–CH_2 stretch			
646			649 Se–CH_2 stretch	
591	593(a′) CH_3–Se stretch	594 CH_3–Se stretch	590 CH_3–Se stretch	595 CH_3–Se stretch
576*		578 Se–CH_2 stretch		
559*				564 Se–CH_2 stretch
403*		405 CCC deform		402 CCC deform
312	316(a′) CCC deform		309 CCC deform	
288*				291 SeCC deform
263	268(a′) SeCC deform	271 CH_2–CH_3 torsion	256 SeCC deform	
221	228(a″) CH_2–CH_3 torsion		230 CH_2–CH_3 torsion	
208*		215 CSeC bend		210 CH_2–CH_3 torsion
195			191 CSeC bend	
		172 SeCC deform		171 CSeC bend
	159(a″) CH_3–Se torsion	156 CH_3–Se torsion	151 CH_3–Se torsion	154 CH_3–Se torsion
	154(a′) CSeC bend			
	106(a″) CH_2–CH_2 torsion	99 CH_2–CH_2 torsion	96 CH_2–CH_2 torsion	103 CH_2–CH_2 torsion
	66(a″) Se–CH_2 torsion		65 Se–CH_2 torsion	
		48 Se–CH_2 torsion		46 Se–CH_2 torsion

a), b) See footnotes a) and b), respectively, to Table 4. c) *trans* and *gauche* conformations about the axes CSe–C–CC, respectively. d) *gauche* and *trans* conformations about the axes CSe–C–CC, respectively.

by ordering the atomic groups in a different direction. These force constants are indicated in Table 2.

Results of the Normal Coordinate Treatment

The force constants for unbranched dialkyl selenides are given in Table 3. In this table only the force constants with non-zero values are given and force constants not found in the table have zero values. Most of the force constants have been assumed to be equivalent to those for unbranched dialkyl sulfides and alkanes, and only twenty-six important force constants have been determined by a least-squares procedure. Results of the normal coordinate calculation for ethyl methyl selenide, diethyl selenide, and methyl propyl selenide are given in Tables 4—6. In these tables, only the vibrations below 800 cm^{-1}, which are more important in examining the rotational isomerism than those with higher wave numbers, are listed in comparison with the observed ones. Assignments of the vibrations are given on the basis of the calculated potential-energy distributions.

The calculation gave an overall root-mean-square deviation of 6.69 cm^{-1} between the observed wave numbers $\tilde{\nu}_{obsd}$ and the calculated wave numbers $\tilde{\nu}_{calcd}$ for 196 experimental data. Distribution of the wave number differences $\tilde{\nu}_{obsd}-\tilde{\nu}_{calcd}$ is shown in Fig. 1. The result indicates that 134 calculated wave numbers (68% of the total number 196) are within ± 5 cm^{-1} of the observed values and 173 (88%) are within ± 10 cm^{-1}.

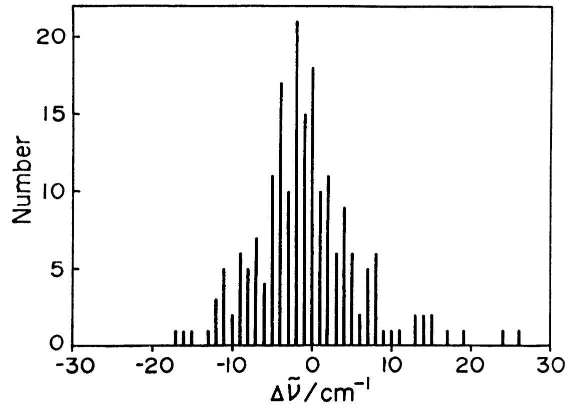

Fig. 1. Distribution of the wave number differences $\Delta\tilde{\nu}=\tilde{\nu}_{obsd}-\tilde{\nu}_{calcd}$ for the unbranched dialkyl selenides.

Discussion

In this study, the local symmetry force field for unbranched dialkyl selenides has been deduced from experimental data for the fundamental selenide molecules. The force constants listed in Table 3 fully cover any dialkyl selenide compound consisting of the following molecular fragments: CH_3CH_2Se–, CH_3SeCH_2–, –CH_2CH_2Se–, and –CH_2SeCH_2–. The present experience in studying the molecular force field indicates that most of the off-diagonal force constants for the dialkyl selenides and the dialkyl sulfides have similar values to each other. Common values have been, in fact, assumed for many constants for these compounds (Table 3). According to the previous[16] and present results, the difference of the force field is more significant between the sulfides and the ethers than between the sulfides and the selenides. This must be related to a closer resemblance of the chemical nature between sulfur and selenium atoms than between sulfur and oxygen atoms.

The diagonal force constants, which have been determined by the least-squares method, show a systematic variation of the values going from the ethers to the sulfides and the selenides. Their values have been compared and discussed in a previous letter.[19]

A comparison is made between the force constants for the dialkyl selenides and the bromoalkanes[24] and between those for the dialkyl sulfides and the chloroalkanes.[24] The methylene deformation diagonal constants (in units of mdyn Å) for the (C)–CH_2–(X) groups are as follows. CH_2 scissoring: 0.549, 0.535, 0.551, and 0.537 for X=Se, Br, S, and Cl, respectively; CH_2 rocking: 0.754, 0.700, 0.804, and 0.756; CH_2 wagging: 0.582, 0.621, 0.607, and 0.662; CH_2 twisting: 0.596, 0.613, 0.626, and 0.649; CCX deformation: 0.891, 0.977, 0.846, and 0.984. These data show that the values for the Group VI and Group VII compounds are not necessarily similar to each other, though the structural parameters and atomic masses are close. It is interesting to note that for the scissoring and rocking constants, the values for Se or S are larger than those for Br or Cl, while for the wagging, twisting, and CCX deformation constants, the values for Br or Cl are larger than those for Se or S. On the other hand, the diagonal C–X stretching force constants are 2.621, 2.609, 2.959, and 2.983 mdyn $Å^{-1}$ for X=Se, Br, S, and Cl, respectively, indicating that the values for Se and Br coincide and those for S and Cl coincide within errors in the values.

The present set of the force constants reproduced about two hundred observed wave numbers for the dialkyl selenides with a root-mean-square deviation of 6.7 cm^{-1}. This accuracy of the normal coordinate calculation is good enough to analyze the observed spectra and to study the rotational isomerism. The distribution of wave number differences $\tilde{\nu}_{obsd}-\tilde{\nu}_{calcd}$ (Fig. 1) is close to the normal distribution. This means that the least-squares calculation has been made on the basis of the proper vibrational assignments of the observed spectra and that the force field obtained has high validity in the normal vibration study.

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