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The Group Coordinate Force Field of Oxymethylene and Thiomethylene Chain Molecules

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Force field was systematically determined in terms of the group symmetry coordinates for series of $CH_3(OCH_2)_mOCH_3$ (m=1—3), the polymer $(\text{–}OCH_2\text{–})_n$, and their deuterated derivatives, and of $CH_3(SCH_2)_mSCH_3$, $(\text{–}SCH_2\text{–})_n$, and their deuterated derivatives. Twenty-five force constants for the oxymethylene molecules and twenty-two force constants for the thiomethylene molecules were adjusted by using 178 and 126 observed wavenumbers, respectively. The force constants obtained were compared with those for related molecules. The results of the normal coordinate treatment on the polymers were discussed in comparison with the results in previous works.

The intramolecular force field is one of the essential factors that characterize the properties of a molecule. The data concerning the force field are, therefore, of great importance in various fields of chemistry and physics, and the accumulation of such data is highly desired. In fact, systematic researches to establish the molecular force constants have been initiated by Shimanouchi *et al.* and the results so far obtained have been compiled as standard reference data.[1–3] The force constants thus published include those for unbranched chain molecules of alkanes, dialkyl ethers, dialkyl sulfides,[1] fluoroalkanes, chloroalkanes, bromoalkanes, and iodoalkanes.[2]

The force constants in these studies have been expressed in terms of the symmetry coordinates of the atomic groups constituting the molecule. This type of force field, called the group coordinate force field (GCFF)[3] or the local symmetry force field, has been proved to be suitable for describing the intramolecular potential of such classes of molecules as those mentioned above.

Having established the force field for dialkyl ethers ROR′, where R and R′ are alkyl groups,[1] and studied closely a conformational stability of dimethoxymethane $CH_3OCH_2OCH_3$,[4] it seems timely to work thoroughly on the GCFF for a series of $CH_3(OCH_2)_mOCH_3$ and the polymer $(\text{–}OCH_2\text{–})_n$. In the present work, therefore, the force constants in the GCFF were derived for the oxymethylene chain molecules and the sulfur analogues, namely the thiomethylene chain molecules. The force constants determined and the results of the normal coordinate calculations are reported in the present paper.

Normal Coordinate Treatment

The force constants in the GCFF were calculated for the oxymethylene and thiomethylene chain molecules by means of the normal coordinate treatment.[5] The calculations were carried out by using a computer program MVIB[3] which has been developed for treating vibrations of chain molecules.

Molecules Treated. The calculations were performed on the following molecules; the oxymethylene series: $CH_3OCH_2OCH_3$ *gauche-gauche* form (to be abbreviated as G_2), $CH_3OCD_2OCH_3$ G_2, $CD_3OCH_2OCD_3$ G_2, $CD_3OCD_2OCD_3$ G_2, $CH_3(OCH_2)_2OCH_3$ G_4, $CH_3(OCH_2)_3OCH_3$ G_6, $(\text{–}OCH_2\text{–})_n$ G_∞, and $(\text{–}OCD_2\text{–})_n$ G_∞, and the thiomethylene series: $CH_3SCH_2SCH_3$ G_2, $CH_3SCD_2SCH_3$ G_2, $CH_3(SCH_2)_2SCH_3$ G_4, $CH_3(SCH_2)_3SCH_3$ G_6, $(\text{–}SCH_2\text{–})_n$ G_∞, and $(\text{–}SCD_2\text{–})_n$ G_∞. The observed infrared and Raman wavenumbers were taken from the literature: $CH_3OCH_2OCH_3$,[4,6] $CH_3OCD_2OCH_3$,[6] $CD_3OCH_2OCD_3$,[6] $CD_3OCD_2OCD_3$,[6] $CH_3(OCH_2)_2OCH_3$,[7] $CH_3(OCH_2)_3OCH_3$,[7] $(\text{–}OCH_2\text{–})_n$,[8–10] $(\text{–}OCD_2\text{–})_n$,[8–10] $CH_3SCH_2SCH_3$,[11] $CH_3SCD_2SCH_3$,[12] $CH_3(SCH_2)_2SCH_3$,[11] $CH_3(SCH_2)_3SCH_3$,[11] $(\text{–}SCH_2\text{–})_n$,[13] and $(\text{–}SCD_2\text{–})_n$.[14]

TABLE 1. ATOMIC MASSES FOR THE OXYMETHYLENE AND THIOMETHYLENE MOLECULES

Atom	Atomic mass[a]/u
Hydrogen, protium	1.007825
Hydrogen, deuterium	2.014102
Carbon	12.011[b]
Oxygen	15.9994[b]
Sulfur	32.06[b]

a) Atomic mass in units of unified atomic mass unit. $1\ u \approx 1.660531 \times 10^{-27}$ kg. b) Isotope-abundance weighted atomic mass.

Atomic Masses and Structural Parameters. The values of the atomic masses and the structural parameters used in the normal coordinate treatment are listed in Tables 1 and 2. Isotope-abundance weighted atomic masses were used for carbon, oxygen, and sulfur, since the experimental vibrational wavenumbers were not resolved into components of individual isotopic species except for hydrogen under the spectral resolution utilized.

The structural parameters for the polymers are based on the results of the X-ray diffraction analyses,[15,16] and are in conformity with the 9/5 helix for poly(oxymethylene) and the 17/9 helix for poly(thiomethylene). Some of the structural parameters were recalculated by making use of equations for helix parameters.[17] The geometries of the oligomer molecules, $CH_3(OCH_2)_mOCH_3$ and $CH_3(SCH_2)_mSCH_3$ (m=1–3), were deduced from those of related molecules.[18]

Group Symmetry Coordinates. The symmetry coordinates in the methyl group, CH_3(O) or CH_3(S), and the methylene group, (O)CH_2(O) or (S)CH_2(S),

TABLE 2. STRUCTURAL PARAMETERS FOR THE OXYMETHYLENE AND THIOMETHYLENE MOLECULES

Structural parameter	Values			
	$CH_3(OCH_2)_mOCH_3$ (m=1—3)	$(\text{-}OCH_2\text{-})_n$	$CH_3(SCH_2)_mSCH_3$ (m=1—3)	$(\text{-}SCH_2\text{-})_n$
Bond lengths				
r(C-H)/Å[a)]	1.100	1.100	1.100	1.100
r(C-O)/Å	1.410	1.4219	—	—
r(C-S)/Å	—	—	1.816	1.816
Valence angles				
∠(C-O-C)/°	111.8	112.40	—	—
∠(O-C-O)/°	110.8	110.82	—	—
∠(O-C-H)/°	109.8	109.8	—	—
∠(C-S-C)/°	—	—	98.6	97.1
∠(S-C-S)/°	—	—	117.4	117.40
∠(S-C-H)/°	—	—	108.8	108.8
Dihedral angles				
τ(O-C-O-C)/°	60.0	78.005	—	—
τ(S-C-S-C)/°	—	—	60.0	66.866

a) 1 Å = 1×10^{-10} m.

TABLE 3. FORCE CONSTANTS IN THE GCFF FOR THE OXYMETHYLENE AND RELATED MOLECULES

Intragroup force constants		Values[a),b)]		
Symbol[c)]	Description	X=Y=O	X=CH_2, Y=O[d)]	X=Y=CH_2[d)]
$f_{(X)CH_2(Y)\text{-}2}$	CH_2 scissor.	0.596(6)	0.590(4)	0.589(2)
$f_{(X)CH_2(Y)\text{-}4}$	CH_2 rock.	1.088(45)	0.820(31)	0.766(5)
$f_{(X)CH_2(Y)\text{-}5}$	CH_2 wag.	0.812(17)	0.764(11)	0.622(3)
$f_{(X)CH_2(Y)\text{-}6}$	CH_2 twist.	0.756(9)	0.699(16)	0.639(4)
$f_{(X)CH_2(Y)\text{-}D}$	XCY deform.	1.356(16)	1.153(26)	0.941(8)
$f_{(X)CH_2(Y)\text{-}2D}$	CH_2 scissor./XCY deform.	−0.049(20)	0.076(21)	0.047(12)

Intergroup force constants		Values[b),e)]	
Symbol[c)]	Description	X=O	X=CH_2[d)]
$f_{(X)CH_2O(CH_2)\text{-}S}$	CH_2-O stretch.	4.673(24)	5.037(22)
$f_{(X)CH_2O(CH_2)\text{-}2S}$	CH_2 scissor./CH_2-O stretch.	−0.223(16)	−0.176(24)
$f_{(X)CH_2O(CH_2)\text{-}5S}$	CH_2 wag./CH_2-O stretch.	−0.551(27)	−0.588(22)
$f_{(X)CH_2O(CH_2)\text{-}DS}$	XCO deform./CH_2-O stretch.	0.214[f)]	0.386(18)
$f_{(X)CH_2O(CH_2)\text{-}SB}$	CH_2-O stretch./COC bend.	0.177(31)	0.363(16)
$f_{(X)CH_2(O)\text{-}SS}$	X-CH_2 stretch./CH_2-O stretch.	0.663(20)	0.314(28)

a) Force constant values in units of aJ = mdyn Å. b) Errors in the force constants, given in parentheses, apply to the last significant figure(s). c) Ref. 3. d) Ref. 1. e) Force constant values in units of aJ $Å^{-2}$ = mdyn $Å^{-1}$ for $f_{(X)CH_2O(CH_2)\text{-}S}$ and $f_{(X)CH_2(O)\text{-}SS}$, and of aJ $Å^{-1}$ = mdyn for the others. f) Constrained in the final least-squares calculation.

were constructed in accordance with the group symmetry of C_{3v} and C_{2v}, respectively. General expressions to give the group symmetry coordinates with arbitrary valence angles have been formulated.[3)] The coordinates and their signs were thus defined on the basis of these formulations, with the structural parameters given in Table 2. The group coordinates for the molecules treated in this work are similar to those for ROR′ and RSR′ molecules[1)] with different coefficients only for the CH_2 scissoring, CH_2 wagging, and OCO or SCS deformation coordinates. Full details of the coordinate definition are found in Table 1 of Ref. 3.

Force Constants. The force constants in the GCFF are given in terms of the group symmetry coordinates given above and are classified into intragroup force constants and intergroup force constants.[1—3)] The intragroup force constants for the terminal methyl group and the intergroup force constants between the methyl group and the adjoining oxygen or sulfur atom were constrained to those determined previously for CH_3OR or CH_3SR[1)] and were not adjusted further in the present work. Other force constants were refined by the least-squares method in order that the calculated wavenumbers of normal vibrations agreed more closely with the observed ones. In the course of the refinement calculations, some of the force constants were found to be ill-determined with large errors. Such force constants were eventually assumed to be equiv-

TABLE 4. FORCE CONSTANTS IN THE GCFF FOR THE THIOMETHYLENE AND RELATED MOLECULES

Intragroup force constants		Values[a,b)]		
Symbol[c)]	Description	X=Y=S	X=CH_2, Y=S[d)]	X=Y=CH_2[d)]
$f_{\rm (X)CH_2(Y)\text{-}2}$	CH_2 scissor.	0.534(5)	0.551(5)	0.589(2)
$f_{\rm (X)CH_2(Y)\text{-}4}$	CH_2 rock.	0.921(48)	0.804(15)	0.766(5)
$f_{\rm (X)CH_2(Y)\text{-}5}$	CH_2 wag.	0.571(27)	0.607(11)	0.622(3)
$f_{\rm (X)CH_2(Y)\text{-}6}$	CH_2 twist.	0.571(3)	0.626(4)	0.639(4)
$f_{\rm (X)CH_2(Y)\text{-}D}$	XCY deform.	1.115(18)	0.846(41)	0.941(8)
$f_{\rm (X)CH_2(Y)\text{-}2D}$	CH_2 scissor./XCY deform.	0.031(30)	0.161(35)	0.047(12)

Intergroup force constants		Values[b,e)]	
Symbol[c)]	Description	X=S	X=CH_2[d)]
$f_{\rm (X)CH_2S(CH_2)\text{-}S}$	CH_2-S stretch.	2.955(51)	2.959(57)
$f_{\rm (X)CH_2S(CH_2)\text{-}2S}$	CH_2 scissor./CH_2-S stretch.	0.0[f)]	0.0[f)]
$f_{\rm (X)CH_2S(CH_2)\text{-}5S}$	CH_2 wag./CH_2-S stretch.	−0.271(84)	−0.217(44)
$f_{\rm (X)CH_2S(CH_2)\text{-}DS}$	XCS deform./CH_2-S stretch.	0.226[f)]	0.226(30)
$f_{\rm (X)CH_2S(CH_2)\text{-}SB}$	CH_2-S stretch./CSC bend.	−0.239(54)	0.058(27)
$f_{\rm (X)CH_2(S)\text{-}SS}$	X-CH_2 stretch./CH_2-S stretch.	0.629(50)	0.473(26)

a), b), c), d) See footnotes a), b), c), d), respectively, to Table 3. e) Force constant values in units of aJ Å^{-2} =mdyn Å^{-1} for $f_{\rm (X)CH_2S(CH_2)\text{-}S}$ and $f_{\rm (X)CH_2(S)\text{-}SS}$, and of aJ Å^{-1}=mdyn for the others. f) Assumed.

TABLE 5. OBSERVED AND CALCULATED WAVENUMBERS FOR $(\text{-}OCH_2\text{-})_n$

Symmetry species	$\tilde{\nu}_{\rm obsd}$/cm^{-1}	$\tilde{\nu}_{\rm calcd}$/cm^{-1} and P.E.D.[a)]				
		This work		Sugeta[b)]	Piseri and Zerbi[c)]	Tadokoro *et al.*[d)]
a_1		2869	1(99)	2897	2920	2924
	1491	1484	2(100)	1501	1491	1508
	1339	1334	6(96)	1342	1324	1330
	920	932	S(85)	928	962	916
	539	528	D(57), B(57)	536	499	587
a_2	2978	2961	3(99)	2978	2971	2977
	1381	1378	5(94)	1385	1419	1425
	1097	1093	4(84)	1109	1110	1118
	903	923	S(110), 5(25)	905	928	922
	235	227	T(96)	234	223	237
e_1	2980	2969	3(99)	2984	2979	2982
	2924	2868	1(99)	2896	2919	2926
	1471	1465	2(100)	1481	1486	1506
	1434	1440	5(88)	1446	1418	1407
	1286	1291	6(92)	1289	1303	1318
	1235	1240	4(63), 5(24)	1240	1224	1169
	1091	1093	S(78)	1098	1077	1072
	932	938	S(111)	938	916	930
	630	633	D(74)	633	649	634
	455	472	B(80)	453	466	483
		20	T(92)	21	26	22

a) Potential-energy distributions (P.E.D.) calculated in this work are given in parentheses following the symmetry coordinates; 1: CH_2 symmetrical stretching, 2: CH_2 scissoring, 3: CH_2 antisymmetrical stretching, 4: CH_2 rocking, 5: CH_2 wagging, 6: CH_2 twisting, D: OCO deformation, B: COC bending, S: C-O stretching, and T: C-O torsion. b) Ref. 7. c) Ref. 19. d) Ref. 8.

alent to those for similar atomic groups so that the remaining constants converged properly. The calculations also revealed that the interaction force constants between the coordinates belonging to the second-neighboring atomic groups were required for satisfactory fitting of the observed and calculated wavenumbers. These constants include the interactions between the CH_2 rocking and CH_2 rocking coordinates, CH_2 wagging and CH_2 wagging, *etc.* of the neighboring methylene groups with an oxygen or sulfur atom in between, and the interaction between the COC (or CSC) bending and COC (or CSC) bending coordinates of the neighboring COC (or CSC) groups. The constants associated with the CH_2 symmetrical and antisymmetrical stretching coordinates were not refined in the present study.

TABLE 6. OBSERVED AND CALCULATED WAVENUMBERS FOR $(\text{-OCD}_2\text{-})_n$

Symmetry species	$\tilde{\nu}_{\mathrm{obsd}}$ cm^{-1}	$\tilde{\nu}_{\mathrm{calcd}}$/cm^{-1} and P.E.D.[a)] This work		Sugeta[b)]	Piseri and Zerbi[c)]	Tadokoro *et al.*[d)]
a_1		2107	1(97)	2123	2140	2121
	1120	1102	2(88)	1112	1126	1126
	1015	1018	6(66), S(23)	1017	1031	1013
	850	836	S(51), 6(30)	838	838	828
	508	501	D(56), B(54)	511	470	557
a_2	2235	2209	3(98)	2225	2220	2193
	1050	1050	5(57), S(11)	1046	1106	1154
	970	973	S(89), 5(70)	973	974	1026
	835	822	4(73), S(29)	819	813	769
	212	207	T(97)	213	205	212
e_1	2235	2232	3(95)	2243	2241	2207
	2106	2106	1(97)	2122	2138	2121
	1156	1146	4(40), B(19)	1144	1142	1178
	1128	1118	S(61), 2(25)	1121	1131	1145
	1078	1072	5(90), S(73)	1071	1078	1047
	1064	1057	2(69)	1058	1045	1044
	909	900	6(79)	906	896	916
	838	838	S(55), 4(22)	836	806	810
	618	616	D(70)	615	632	618
	363	373	B(72), 4(20)	365	369	372
		19	T(93)	20	25	21

a), b), c), d) See footnotes a), b), c), d), respectively, to Table 5.

A full list of the force constants finally determined for the oxymethylene and thiomethylene chain molecules, together with the calculated results for all the molecules treated, has been deposited with the Chemical Society of Japan (Document No. 8247). In Tables 3 and 4, some important force constants are compared with those for related molecules. The calculated wavenumbers and assignments are given in this article only for the polymers.

Results and Discussion

In the present study, twenty-five force constants in the GCFF were determined for the oxymethylene chain molecules from 178 observed wavenumbers and twenty-two force constants for the thiomethylene chain molecules from 126 observed wavenumbers. The calculations with these force constants gave overall root-mean-square deviations of 9.6 and 8.2 cm^{-1}, respectively, for the oxymethylene and thiomethylene molecules, between the observed and calculated wavenumbers.

Table 3 shows that the values of the diagonal force constants for the $(\mathrm{X})\mathrm{CH_2}(\mathrm{Y})$ group increase systematically in going from $(\mathrm{CH_2})\mathrm{CH_2}(\mathrm{CH_2})$ to $(\mathrm{CH_2})\mathrm{CH_2}(\mathrm{O})$ and $(\mathrm{O})\mathrm{CH_2}(\mathrm{O})$. For the sulfides in Table 4, on the other hand, the values of the $\mathrm{CH_2}$ scissoring, $\mathrm{CH_2}$ wagging, and $\mathrm{CH_2}$ twisting force constants decrease in going from $(\mathrm{CH_2})\mathrm{CH_2}(\mathrm{CH_2})$ to $(\mathrm{CH_2})\mathrm{CH_2}(\mathrm{S})$ and $(\mathrm{S})\mathrm{CH_2}(\mathrm{S})$, but the value of only the $\mathrm{CH_2}$ rocking constant increases. The $\mathrm{CH_2}$–O stretching constant for the $(\mathrm{O})\mathrm{CH_2}$–$\mathrm{O}(\mathrm{CH_2})$ group (4.67 mdyn Å^{-1}) is found to be considerably smaller than that for the $(\mathrm{CH_2})\mathrm{CH_2}$–$\mathrm{O}(\mathrm{CH_2})$ group (5.04 mdyn Å^{-1}). This contrasts with the essentially same value (2.96 mdyn Å^{-1}) of the $\mathrm{CH_2}$–S stretching constant for the $(\mathrm{S})\mathrm{CH_2}$–$\mathrm{S}(\mathrm{CH_2})$ and $(\mathrm{CH_2})\mathrm{CH_2}$–$\mathrm{S}(\mathrm{CH_2})$ groups.

The calculated results for poly(oxymethylene) and poly(oxymethylene-d_2) are given in Tables 5 and 6 in comparison with those reported previously.[7,8,19)] The agreement between the observed and calculated wavenumbers is less satisfactory in the earlier studies. The nature of the normal modes is represented by the potential-energy distributions (P.E.D.).† The P.E.D.'s for the undeuterated species is almost the same among the studies, but some of the P.E.D.'s for the deuterated species differ considerably from one another. For example, the vibration at 1156 cm^{-1} (e_1) is assigned in this work to the $\mathrm{CD_2}$ rocking, but was assigned to the $\mathrm{CD_2}$ wagging and $\mathrm{CD_2}$ scissoring,[7)] to the C–O stretching and $\mathrm{CD_2}$ scissoring,[19)] or to the C–O stretching and $\mathrm{CD_2}$ wagging,[8)] and the vibration at 1078 cm^{-1} (e_1) is assigned in this work to the $\mathrm{CD_2}$ wagging and C–O stretching, but was assigned to the $\mathrm{CD_2}$ rocking,[7)] to the $\mathrm{CD_2}$ rocking and C–O stretching,[19)] or to the $\mathrm{CD_2}$ scissoring and C–O stretching.[8)] We believe that the present assignment based on the systematic treatment is more likely than the previous ones.

The assignment of the observed bands of poly(thiomethylene) and poly(thiomethylene-d_2) is now estab-

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† The potential-energy distribution, as defined by $(\mathrm{P.E.D.})_{ji}=100\times L_{ji}^2 f_{jj}/\lambda_i$,[3)] may exceed 100 because of neglecting the contribution of off-diagonal force constants. This effect is particularly enhanced for polymers.

TABLE 7. OBSERVED AND CALCULATED WAVENUMBERS FOR $(\text{-SCH}_2\text{-})_n$ AND $(\text{-SCD}_2\text{-})_n$

Symmetry species	$(\text{-SCH}_2\text{-})_n$			$(\text{-SCD}_2\text{-})_n$		
	$\tilde{\nu}_{\text{obsd}}/\text{cm}^{-1}$	$\tilde{\nu}_{\text{calcd}}/\text{cm}^{-1}$	P.E.D.[a]	$\tilde{\nu}_{\text{obsd}}/\text{cm}^{-1}$	$\tilde{\nu}_{\text{calcd}}/\text{cm}^{-1}$	P.E.D.[a]
a_1	2905	2905	1(100)		2128	1(98)
	1373	1386	2(99)		1025	2(92)
	1180	1179	6(99)		844	6(96)
	648	658	S(90)		618	S(83)
	355	340	D(99), B(47)		330	D(101), B(46)
a_2		2940	3(100)		2183	3(99)
	1225	1231	5(109)	962	954	5(108), S(25)
	882	886	4(95)	752	732	4(51), S(40)
	729	738	S(104)		670	4(47), S(45)
		117	T(98)		103	T(99)
e_1	2965	2938	3(100)		2178	3(99)
	2910	2905	1(100)		2128	1(98)
	1361	1372	2(99)	1012	1014	2(92)
	1173	1180	5(108)	908	902	5(113), S(30)
	1120	1117	6(99)		797	6(97)
	743	743	S(87)	697	700	S(95)
	711	712	4(95), S(35)	648	653	S(66), D(22)
	674	688	S(66), D(23)		529	4(136)
	299	300	D(75)		298	D(76)
	299	291	B(176), 4(57)		264	B(171), 4(40)
		3	T(95)		3	T(95)

a) Potential-energy distributions (P.E.D.) are given in parentheses following the symmetry coordinates; 1: CH_2 symmetrical stretching, 2: CH_2 scissoring, 3: CH_2 antisymmetrical stretching, 4: CH_2 rocking, 5: CH_2 wagging, 6: CH_2 twisting, D: SCS deformation, B: CSC bending, S: C–S stretching, and T: C–S torsion.

lished, as given in Table 7, in the light of the force field determined in the present work. The vibrational assignment of this polymer was first made by Hendra *et al.*,[13] who acknowledged, however, that their assignment based on empirical basis was very tentative. The normal coordinate treatment of poly(thiomethylene) and the deuterated derivative has been reported by Ohsaku.[14] His calculation is unfortunately erroneous as evidenced by the unlikely number of normal vibrations belonging to each symmetry species.

The group coordinate force field derived in this work for the $\text{-OCH}_2\text{O-}$ and $\text{-SCH}_2\text{S-}$ groups may be applied to other molecules consisting of similar atomic groups. The accumulation of the force constants for various types of atomic groups will eventually make possible the calculation of normal vibrational wavenumbers and modes of a large number of molecules.

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References

1) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, *J. Phys. Chem. Ref. Data*, **7**, 1323 (1978).

2) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, *J. Phys. Chem. Ref. Data*, **9**, 1149 (1980).

3) H. Matsuura and M. Tasumi, "Force Fields for Large Molecules," in "Vibrational Spectra and Structure," ed by J. R. Durig, Elsevier, Amsterdam (1982), Vol. 12, Chap. 2' in press.

4) M. Sakakibara, Y. Yonemura, H. Matsuura, and H. Murata, *J. Mol. Struct.*, **66**, 333 (1980).

5) T. Shimanouchi, "The Molecular Force Field," in "Physical Chemistry, An Advanced Treatise," ed by H. Eyring, D. Henderson, and W. Jost, Academic Press, New York (1970), Vol. IV, Chap. 6, p. 233.

6) K. Nukada, *Spectrochim. Acta*, **18**, 745 (1962).

7) H. Sugeta, Ph. D. Thesis, Osaka University (1969).

8) H. Tadokoro, M. Kobayashi, Y. Kawaguchi, A. Kobayashi, and S. Murahashi, *J. Chem. Phys.*, **38**, 703 (1963).

9) G. Zerbi and P. J. Hendra, *J. Mol. Spectrosc.*, **27**, 17 (1968).

10) H. Sugeta, T. Miyazawa, and T. Kajiura, *J. Polym. Sci., Pt. B*, **7**, 251 (1969).

11) M. Ohsaku, Y. Shiro, and H. Murata, *Bull. Chem. Soc. Jpn.*, **45**, 113 (1972).

12) M. Sakakibara, unpublished work.

13) P. J. Hendra, D. S. Watson, and M. Mammi, *Spectrochim. Acta, Part A*, **28**, 351 (1972).

14) M. Ohsaku, *Bull. Chem. Soc. Jpn.*, **47**, 965 (1974).

15) T. Uchida and H. Tadokoro, *J. Polym. Sci., A-2*, **5**, 63 (1967).

16) G. Carazzolo and G. Valle, *Makromol. Chem.*, **90**, 66 (1966).

17) T. Miyazawa, *J. Polym. Sci.*, **55**, 215 (1961).

18) Structure Data of Free Polyatomic Molecules, "Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology," New Series, Group II: Atomic and Molecular Physics, Springer-Verlag, Berlin (1976), Vol. 7.

19) L. Piseri and G. Zerbi, *J. Chem. Phys.*, **48**, 3561 (1968).