Out-of-Plane Hydrogen Vibrations of ortho-, meta- and para-Deuterated Mono-substituted Benzenes

By Yuzo Kakiuti and Jiro Ogura

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The authors have recently reported a theoretical explanation of the out-of-plane CH vibrations of benzene derivatives for both the fundamentals and their combination tones which appear in the regions of 650 to 1000 cm^{-1} and of 1650 to 2000 cm^{-1}, respectively[1,2]. The results of the calculations were in good agreement with those observed[1-3]. This enabled us to calculate frequencies and absorption intensities of the out-of-plane hydrogen vibration bands for some deuterium homologs of benzene derivatives.

In the present paper, normal coordinate treatments have been made on the out-of-plane hydrogen vibrations for *ortho*-, *meta*- and *para*-deuterated compounds of mono-substituted benzenes. This treatment seems to be applicable for the identification of each molecule as well as for the purpose of confirming the validity of our earlier theories[1,2].

Calculated Frequencies

The normal coordinate treatment was carried out according to the method using $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices, as introduced by Wilson[4]. The procedures of the calculations were the same as those given in the preceding papers[1,2], except for some minor modifications in the form of the $\boldsymbol{G}$ matrix.

Fig. 1 shows the molecular model used, where X is a substituent atom or group and

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[1] T. Shimanouchi, Y. Kakiuti and I. Gamo, *J. Chem. Phys.*, **25**, 1245 (1956); Y. Kakiuti, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **77**, 1572, 1591 (1956).

[2] Y. Kakiuti, *J. Chem. Phys.*, **25**, 777 (1956); *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **77**, 1839 (1956).

[3] Y. Kakiuchi, ibid., **80**, 28 (1959).

[4] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

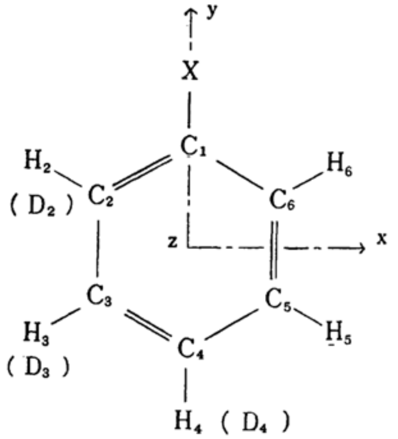

Fig. 1. *o*-, *m*- and *p*-Deuterated monosubstituted benzene.

$$\begin{array}{c|cccccccc|}
 & r_2\gamma_2 & r_3\gamma_3 & r_4\gamma_4 & r_5\gamma_5 & r_6\gamma_6 & \sigma_2 & \sigma_3 & \sigma_4 \\
\hline
r_2\gamma_2 & H & J & K & 0 & K & u & -v & w \\
r_3\gamma_3 & & H & J & K & 0 & -u & v & w \\
r_4\gamma_4 & & & H & J & K & u & 0 & -2w \\
r_5\gamma_5 & & & & H & J & -u & -v & w \\
r_6\gamma_6 & & \text{(Symmetric)} & & & H & u & v & w \\
\sigma_2 & & & & & & P & 0 & 0 \\
\sigma_3 & & & & & & & Q & 0 \\
\sigma_4 & & & & & & & & Q \\
\hline
\end{array}$$

Fig. 2. ***G*** or ***F*** matrix.

H(D) denotes H or D atom; that is, *ortho*-, *meta*- and *para*-deuterated molecules are designated as 1-X-benzene-2-*d* -3-*d* and -4-*d*, respectively. The ***G*** and ***F*** matrices are expressed as shown in Fig. 2, where the meanings of the notations are as given in the preceding papers1); that is, r_0 is the equilibrium length of C–H or D bond, γ_i and σ_i are the internal coordinates referring to bending of the C_i–H_i or D_i bond and twisting of the C–C bond, respectively.

The approximation according to Crawford, Edsall and Wilson4,5) has been applied, and the first row and column corresponding to the low-frequency coordinate of the substituent (X), $r_1\gamma_1$ are omitted. As shown in Table I, the values of the elements of the ***G*** matrix are nearly the same as those presented in our earlier papers1), and those of the ***F*** matrix are exactly the same, because the same force constants obtained by the analysis of out-of-plane vibrations of benzene and its deuterium homologs6) were also applied in this case.

TABLE I. ELEMENTS OF ***G*** AND ***F*** MATRICES SHOWN IN FIG. 2 (FORCE CONSTANT IN mdyn./Å, LENGTH IN Å, AND MASS IN amu)

in ***G***	in ***F***
$H=1.635888$ $(1.140309)^{a)}$	0.402
$J=-0.330622$	−0.073
$K=0.050292$	0
$P=3.998719$	0.205
$Q=1.332906$	0.193
$u=0.967934$	−0.106961
$v=0.554978$	−0.113449
$w=0.320417$	−0.0655

a) When a hydrogen atom is replaced by deuterium, the *H*-value in parenthesis must be used (See text).

Exchanging the H atom for the D affects only the value of the corresponding diagonal term, ***H***, in the ***G*** matrix. When the hydrogen atom of the *i*-th C_i–H_i bond shown in Fig. 1 is replaced by deuterium, the *H*-value in parenthesis shown in Table I must be used for the diagonal term corresponding to the coordinate $r_i\gamma_i$ in the ***G*** matrix.

The secular equation to be solved is expressed as

$$|\boldsymbol{GF}-\boldsymbol{E}\lambda|=0 \qquad (1)$$

where ***E*** is the unit matrix, λ is $4\pi^2\boldsymbol{c}^2\nu^2$, ***c*** is the light velocity, and ν is the wave number. In the case of the *para*-deuterated molecule, the secular Eq. 1 is further split due to the symmetry of the molecule by using suitable symmetry coordinates which are shown in Table II, where the s_1, s_2 and σ_3 belong to the species A_2 and the s_3, s_4, s_5, σ_2 and σ_4 to the species B_2. The roots of the secular equation of each molecule are shown in Table III and illustrated in Fig. 3. The Latin and Greek notations denote the fundamentals and binary combinations, respectively.

TABLE II. SYMMETRY COORDINATES USED FOR *p*-DEUTERATED MONO-SUBSTITUTED BENZENE

	$r_2\gamma_2$	$r_3\gamma_3$	$r_4\gamma_4$	$r_5\gamma_5$	$r_6\gamma_6$
$s_1^{a)}$	1/2	−1/2	0	1/2	−1/2
s_2	1/2	1/2	0	−1/2	−1/2
s_3	1/2	1/2	0	1/2	1/2
s_4	1/2	−1/2	0	−1/2	1/2
s_5	0	0	1	0	0

a) For example, $s_1=(r_2\gamma_2-r_3\gamma_3+r_5\gamma_5-r_6\gamma_6)/2$.

Normal Coordinates

When the relation between the normal coordinates and the intensity in infrared absorption is discussed, it is necessary to express normal coordinates, *Q*, in terms of Cartesian displacement coordinates, *Z*, as discussed

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5) B. L. Crawford, Jr. and J. T. Edsall, ibid., 7, 223 (1939).

6) Y. Kakiuti and T. Shimanouchi, ibid., 25, 1252 (1956); Y. Kakiuti, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 80, 21 (1959).

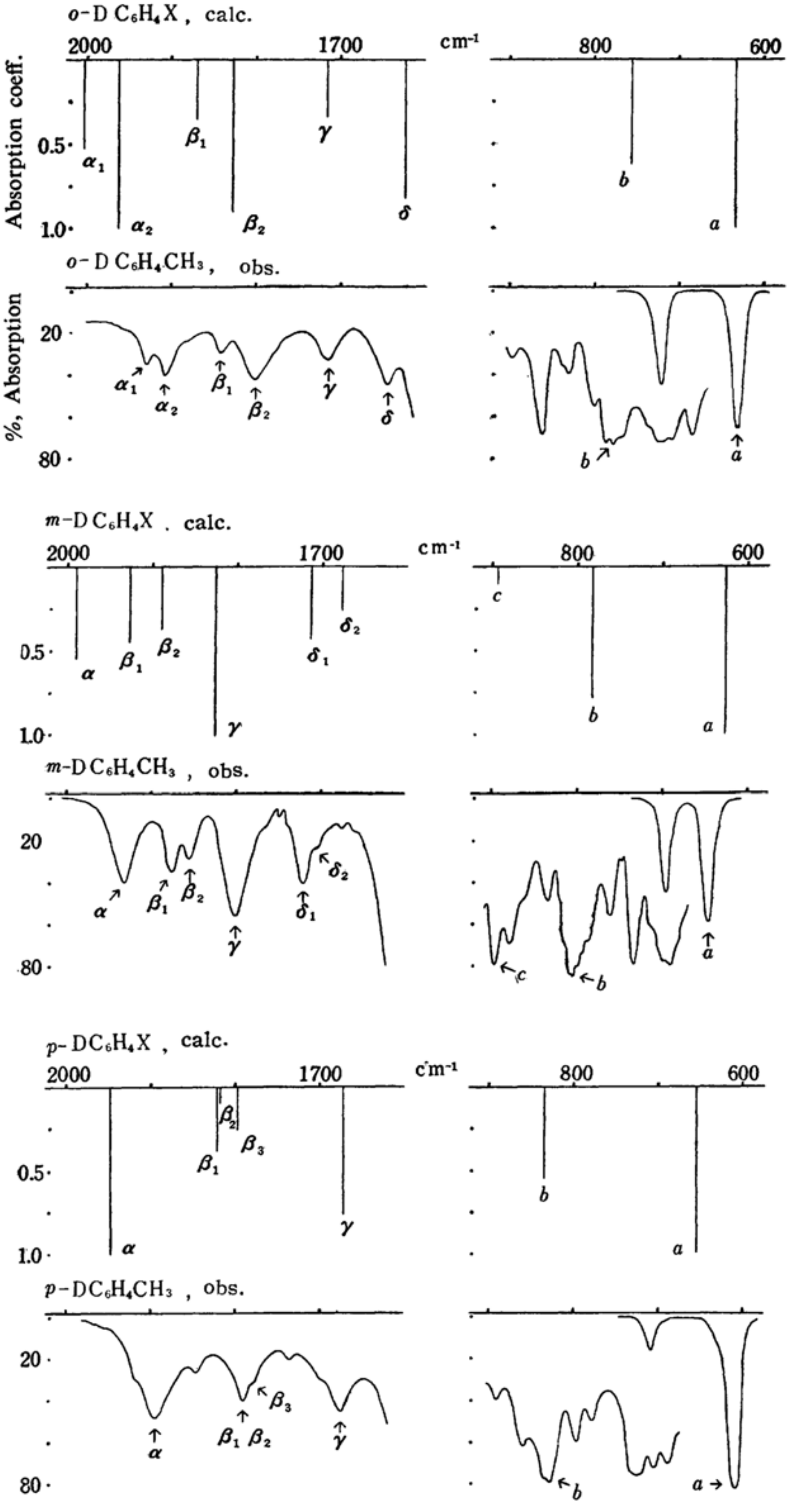

Fig. 3. Illustration of calculated frequencies, absorption intensities, and observed absorption spectra[9,10] (See Table III.).

TABLE III-A. FUNDAMENTALS OUT-OF-PLANE HYDROGEN VIBRATIONS

Freq. calc., cm^{-1}			κ_i[a] calcd.	For $DC_6H_4CH_3$ Freq. anal. cm^{-1}	For $DC_6H_4CH_3$[9,10] freq. obs. cm^{-1}	For $DC_6H_4CH_3$[9,10] %, absorption obs.
o-$DC_6H_4X(C_s)$						
A''(IR,R)	a	634	1.000	631	631	very strong
	b	756	0.621	779	775	75, broad
	c	868	0.000	867		
	d	960	0.036	937		
	e	1002	0.000	968		
m-$DC_6H_4X(C_s)$						
A''(IR,R)	a	626	1.000	645	645	very strong
	b	782	0.776	813	806	90, broad
	c	894	0.101	891	894	80
	d	931	0.055	909		
	e	995	0.000	965		
p-$DC_6H_4X(C_{2v})$						
B_2(IR,R)	a	630	1.000	607	607	very strong
	b	835	0.551	838	838	80, broad
	c	963	0.007	942		
A_2(R)	d	837	0	837		
	e	984	0	952		

a) Relative values for each molecule.

TABLE III-B. BINARY COMBINATIONS OF OUT-OF-PLANE HYDROGEN VIBRATIONS

Freq. calc., cm^{-1}			κ_{ij} calcd.[a]	For $DC_6H_4CH_3$ freq. anal. cm^{-1}	For $DC_6H_4CH_3$[9,10] freq. obs. cm^{-1}	For $DC_6H_4CH_3$[9,10] %, absorption obs.
o-DC_6H_4X (C_s)						
α_1	2e	2004	0.534	1936	1930	35
α_2	d+e	1962	1.000	1905	1908	40
β_1	c+e	1870	0.359	1835	1842	30
β_2	c+d	1828	0.904	1804	1800	40
γ	b+d	1716	0.346	1716	1718	30
δ	b+c	1624	0.821	1646	1645	45
	2b	1512	0.234	1558		
	a+c	1502	0.464	1498		
	a+b	1390	0.295	1410		
	2a	1268	0.274	1262		
m-DC_6H_4X (C_s)						
α	2e	1990	0.550	1930	1931	40
β_1	d+e	1926	0.462	1874	1875	35
β_2	c+e	1889	0.376	1856	1855	30
γ	c+d	1825	1.000	1800	1800	55
δ_1	b+d	1713	0.443	1722	1721	40
δ_2	b+c	1676	0.270	1704	1705	20
	2b	1564	0.190	1626		
	a+c	1520	0.341	1536		
	a+b	1408	0.155	1458		
	2a	1252	0.286	1290		
p-DC_6H_4X (C_{2v})						
α	c+e	1947	1.000	1894	1894	50
β_1	d+e	1821	0.391	1789	1789	40
β_2	b+e	1819	0.104	1790		
β_3	b+c	1798	0.261	1780	~1780	~30
γ	b+d	1672	0.773	1675	1675	45
	a+d	1467	0.418	1444		
	a+b	1465	0.107	1445		
	2a	1260	0.192	1214		

a) Relative values for each molecule. The combinations whose κ_{ij}-values are very small, are omitted in this Table.

TABLE IV. ELEMENTS OF ***L***-MATRICES[a] (FOR THE UNITS USED, SEE TABLE I)

o-DC_6H_4X (C_s)

Freq. calcd.[b]	A''(IR, R)							
cm^{-1}	388	459	634†	756†	802	868†	960†	1002†
$Z(C_1)$	0.0170	−0.1409	−0.0213	0.0974	−0.1281	0.0109	0.0070	0.0003
$Z(C_2)$	−0.1064	0.0300	−0.1094	−0.0011	0.1512	−0.0388	−0.0389	−0.0059
$Z(C_3)$	0.1297	0.1409	−0.0394	0.0237	−0.0585	0.0816	0.0828	0.0497
$Z(C_4)$	0.0015	−0.1637	0.0074	−0.0917	0.0307	0.0543	−0.0423	−0.0824
$Z(C_5)$	−0.1341	0.0927	−0.0406	−0.0083	−0.1057	−0.0236	−0.0577	0.0783
$Z(C_6)$	0.1193	0.0538	0.0364	−0.1031	0.0684	−0.0891	0.0658	−0.0401
$Z(D_2)$	−0.2555	0.0686	0.5262	−0.2107	−0.0929	0.0975	0.0960	0.0202
$Z(H_3)$	0.2113	0.1834	0.2906	0.2944	−0.1451	−0.4863	−0.5369	−0.3386
$Z(H_4)$	0.0216	−0.2873	0.2727	0.3458	0.2892	−0.4030	0.2517	0.5625
$Z(H_5)$	−0.2421	0.1567	0.1252	0.5482	0.1828	0.2061	0.3963	−0.5324
$Z(H_6)$	0.1981	0.0862	0.2481	0.2231	0.3577	0.5449	−0.5011	0.2713

m-DC_6H_4X (C_s)

Freq. calcd.[b]	A''(IR, R)							
cm^{-1}	385	453	626†	782†	801	894†	931†	995†
$Z(C_1)$	0.0096	−0.1299	0.0645	−0.1010	0.1132	0.0001	0.0103	0.0004
$Z(C_2)$	0.1285	0.0561	−0.0374	0.0809	−0.0654	−0.0952	−0.0799	0.0173
$Z(C_3)$	−0.1125	0.0615	−0.1256	−0.0033	0.1194	0.0228	0.0624	0.0094
$Z(C_4)$	0.0288	−0.1682	−0.0276	0.0085	−0.0687	0.0610	−0.0771	−0.0669
$Z(C_5)$	0.1087	0.1201	0.0080	−0.1112	0.0035	0.0271	0.0057	0.0942
$Z(C_6)$	−0.1330	0.0254	−0.0398	0.0331	−0.1274	−0.0494	0.0641	−0.0588
$Z(H_2)$	0.2091	0.1071	0.2444	0.1774	−0.2117	0.6817	0.4862	−0.1124
$Z(D_3)$	−0.2699	0.1669	0.4916	−0.1643	−0.1329	−0.0590	−0.1757	−0.0303
$Z(H_4)$	0.0306	−0.2789	0.3069	0.3654	0.0646	−0.3919	0.4873	0.4571
$Z(H_5)$	0.1826	0.2134	0.2508	0.3649	0.4811	−0.1544	0.0112	−0.6337
$Z(H_6)$	−0.2423	0.0404	0.0966	0.5273	0.2343	0.3822	−0.4611	0.4026

p-DC_6H_4X (C_{2v})

Freq. calcd.[b]	B_2(I, RR)					A_2(R)		
cm^{-1}	436	630†	784	835†	963†	398	837†	984†
$Z(C_1)$	−0.1372	−0.0257	0.1572	0.0468	0.0008	0	0	0
$Z(C_2)$	0.0361	0.0167	−0.1320	0.0170	−0.0546	0.1284	0.0661	0.0659
$Z(C_3)$	0.1077	−0.0174	0.0590	0.0566	0.0755	−0.1284	0.0661	−0.0659
$Z(C_4)$	−0.1221	−0.1417	−0.0382	−0.1106	−0.0417	0	0	0
$Z(C_5)$	0.1077	−0.0174	0.0590	0.0566	0.0755	0.1284	−0.0661	0.0659
$Z(C_6)$	0.0361	0.0167	−0.1320	0.0170	−0.0546	−0.1284	−0.0661	−0.0659
$Z(H_2)$	0.0332	0.2321	0.0051	−0.5317	0.3553	0.2273	−0.4427	−0.4431
$Z(H_3)$	0.1435	0.3088	0.2764	−0.1891	−0.4893	−0.2273	−0.4427	0.4431
$Z(D_4)$	−0.3459	0.4652	−0.1211	0.2237	0.1291	0	0	0
$Z(H_5)$	0.1435	0.3088	0.2764	−0.1891	−0.4893	0.2273	0.4427	−0.4431
$Z(H_6)$	0.0332	0.2321	0.0051	−0.5317	0.3553	−0.2273	0.4427	0.4431

a) $Z(X)$ is always zero, because of the approximation used in calculations (See text).

b) †-Marks denote out-of-plane hydrogen vibrations. The residues are skeletal vibrations, which can be expected to be weak in infrared absorption and are omitted in Table III and Fig. 3.

already in the preceding papers[1,2]. To do this, the ***L*** matrix must be calculated. It is defined as

$$Z = LQ \qquad (2)$$

which can also be expressed as

$$L = M^{-1}B'_J G^{-1} L_J{}^{7)} \qquad (3)$$

where ***M*** is the diagonal matrix, the elements of which are the masses of atoms associated with the Cartesian coordinates. The B_J matrix relates the internal coordinates, J, to the Cartesian coordinates,

$$J = B_J Z \qquad (4)$$

The elements of the B_J matrix are the same

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[7] B. L. Crawford, Jr. and W. H. Fletcher, *J. Chem. Phys.*, **19**, 141 (1951); D. A. Long, *Proc. Roy. Soc.* **A217**, 203 (1953).

TABLE V. ASSIGNMENTS OF OUT-OF-PLANE HYDROGEN VIBRATIONS FOR SEVERAL p-DC_6H_4X TYPE MOLECULES (cm^{-1})

			p-DC_6H_4Br		p-$DC_6H_4CHCH_2$		$[p$-$DC_6H_4CHCH_2]_n$	
			Anal.	Obs.[11]	Anal.	Obs.[11]	Anal.	Obs.[11]
Fundamentals		b	840	841 s	850	856 s	850	852 s
		c	940		950	957 w	950	952 w
		d	830		850		845	
		e	955		965		960	
Combinations	α	$c+e$	1895	1899	1915	1910	1910	1914
	β_1	$d+e$	1785	1783	1815	1820	1805	1803
	β_2	$b+e$	1795		1815		1810	
	β_3	$b+c$	1780		1800	1806	1800	
	γ	$b+d$	1670	1670	1700	1693	1695	1696

as those given in the preceding papers[1]. The L_J matrix relates the internal coordinates to the normal coordinates,

$$J=L_JQ \tag{5}$$

and it is obtained when the secular Eq. 1 is solved.

The calculated reoults of L matrices are shown in Table IV, where the normalization of the L matrix is made by the following equation

$$L'ML=E \tag{6}$$

Absorption Intensities

The in-plane or out-of-plane component of the molecular dipole moment, μ_x, μ_y or μ_z may be expanded in an even or odd power series of the normal coordinates as follows, respectively, neglecting the higher terms:

$$\left.\begin{aligned}\mu_x&=\mu_{x0}+\sum_{i,j}a_{ij}Q_iQ_j,\\ \mu_y&=\mu_{y0}+\sum_{i,j}b_{ij}Q_iQ_j,\\ \mu_z&=\sum_i c_iQ_j,\end{aligned}\right\} \tag{7}$$

where μ_{x0} and μ_{y0} are the constant terms for every molecule. When the vibration is mechanically harmonic, the integrated absorption coefficient of the fundamental band produced by Q_i — (κ_i) — and that of the combination band produced by Q_i and Q_j — (κ_{ij}) — are expressed as follows:

$$\begin{aligned}\kappa_i&=\pi/3c\cdot c_i^2\\ \kappa_{ij}&=\boldsymbol{h}/12c^2\pi\cdot(\nu_i+\nu_{ij})(a_{ij}^2+b_{ij}^2)/\nu_i\nu_j{}^{*1}\end{aligned} \tag{8}$$

respectively, where $\boldsymbol{h}$ is Planck's constant, and ν_i or ν_j is the wave number of the fundamental referring to Q_j or Q_i. Eq. 8 are the same those presented by Wilson et al.[8] and in our earlier papers[2].

When the formal electric charge associated with each atom or atomic group does not change by small vibrational displacement, and some further assumptions referred to in the preceding papers[1,2] are applied, the coefficients of Eq. 7, a_{ij}, b_{ij}, and c_i can be shown to have simple relationships to the elements of L matrices. This enables us to calculate the values of κ_i and κ_{ij}. The results of calculations as relative values of κ_i and κ_{ij} are shown in Table III and illustrated in Fig. 3, where it is assumed that all the C–H bond moments are equal, and the contribution of the motion of the motion of the C–X bond is neglected in the total molecular dipole moment[*2].

Comparison with the Experimental Data

The infrared spectra of *ortho*-, *meta*- and *para*-deuterated toluene have been presented by Turkevich et al.[9] and Tiers et al.[10] These experimental data are shown in Table III and Fig. 3.

Each molecule shows a strong absorption band in the region of 600 to 650 cm^{-1}, which can be assigned with certainty to the first fundamental band of the out-of-plane hydrogen vibrations. The binary combination bands of the out-of-plane hydrogen vibrations can be readily identified in the region of 1600 to 2000 cm^{-1}. These bands can be easily assigned by comparison with the results of calculations for every molecule, as shown in Fig. 3. The "analyzed values" of the fundamental and combination frequencies are determined so as to give the best fit with the above assigned

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[*1] The practical value of κ_{ij} in Eq. 8 must be given as $2\kappa_{ij}=\kappa_{ij}+\kappa_{ji}$ $(i\neq j)$ corresponding to the two terms, $a_{ij}Q_iQ_j$ or $b_{ij}Q_iQ_j$ and $a_{ji}Q_jQ_i$ or $b_{ji}Q_jQ_i$ appearing in Eq. 7.

8) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York (1955), § 7-9.

[*2] The motion of the carbon atom of the C-X bond takes place with small amplitude for the vibrations under consideration, and the X atom does not move at all according to the approximation used in low-frequency splitting.

9) J. Turkevich, H. A. McKenzie, L. Friedman and R. Spurr, *J. Am. Chem. Soc.*, **71**, 4045 (1949).

10) G. V. D. Tiers, *J. Chem. Phys.*, **19**, 1072 (1951). G.V.D. Tiers and J. H. Tiers, ibid., **20**, 761 (1952).

frequencies of fundamentals and their combination bands. As shown in Table III and Fig. 3, the analyzed frequencies are in good agreement with the assigned values.

Recently, Murahashi et al.[11] observed the spectra of *para*-deuterated derivatives of bromobenzene, styrene and polystyrene (atactic) in the region of 700 to 3000 cm^{-1}. Table V shows that our assignments are valid and our theories are applicable also in these cases.

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Department of Chemistry
College of Science
St. Paul's University
Ikebukuro, Tokyo

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[11] S. Murahashi, S. Nozakura and H. Tadokoro, to be published shortly.