Electronic States of p-Benzoquinone. III. Calculation of the Out-of-plane Vibrational Frequencies in the Ground Electronic State

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(Received March 31, 1958)

In the first[1] and the second[2] part of this series the present authors, in collaboration with Matubara, have calculated the energy levels of *p*-benzoquinone using the semiempirical molecular orbital method proposed by Pariser and Parr[3], taking account of non-bonding electrons explicitly as well as π electrons. Experimental checking of the theoretical results requires the vibrational analysis of the electronic band spectrum of this molecule. To this end, the assignment of fundamental frequencies to modes of vibrations in the ground electronic state should be made at first.

Although the calculation of the fundamental frequencies using the force constants carried over from similar molecules would help those assignments using infrared and Raman data, the force constants to be carried over for *p*-benzoquinone are nearly unknown, since the normal coordinate treatments of quinones have not been performed yet.

In a recent paper[4] by one of the present authors, a method of obtaining some of the out-of-plane force constants in conjugated hydrocarbons from bond orders and of borrowing the remaining kinds of these constants from similar molecules was described. In the present paper the result of calculation of the non-planar frequencies of *p*-benzoquinone using this method will be reported.

Group-Theoretical Considerations

The molecular structure of *p*-benzoquinone has been studied by both the X-ray and electron-diffraction[6] experiments and it is known that this molecule belongs to the point group V_h. We take the axis connecting the two oxygen atoms as y axis and the molecular plane as xy plane. Then, the symmetry notations are the same as those given by Herzberg[7].

The fundamental vibrations of this molecule are distributed among symmetry species as follows; $6A_g+5B_{1g}+1B_{2g}+3B_{3g}+2A_u+3B_{1u}+5B_{2u}+5B_{3u}$. Vibrations in species B_{2g}, B_{3g}, A_u and B_{1u} are non-planar ones and the remaining vibrations are of planar modes.

Internal Coordinates and G Matrix

Notations for internal and symmetry coordinates are chosen to be as consistent as possible with those of benzene[8,9].

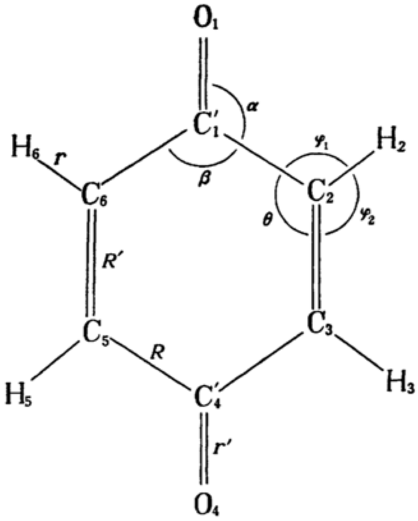

Fig. 1. Notations expressing bond angles and bond distances and the numbering of atoms for *p*-benzoquinone.

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1) T. Anno, I. Matubara and A. Sadô, This Bulletin, **30**, 168 (1957).

2) T. Anno, A. Sadô and I. Matubara, *J. Chem. Phys.*, **26**, 967 (1957).

3) R. Pariser and R. G. Parr, ibid., **21**, 466, 767 (1953).

4) T. Anno, ibid., **28**, 944 (1958).

5) J. M. Robertson, *Proc. Roy. Soc.* (London), **A150**, 106 (1935).

6) S. M. Swingle, *J. Am. Chem. Soc.*, **76**, 1409 (1954).

7) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. van Nostrand Co., New York (1945), p. 108.

8) F. A. Miller and B. L. Crawford, Jr., *J. Chem. Phys.*, **14**, 282 (1946).

9) Y. Kakiuti and T. Shimanouchi, ibid., **25**, 1252 (1956).

Thus, as shown in Fig. 1 the carbon atoms are numbered consecutively, and the oxygen and the hydrogen atoms are numbered altogether consecutively. The carbon atom to which an oxygen atom attaches is distinguished by being primed. Equilibrium internuclear distances are represented by: $C_1'O_1=r'$, $C_2H_2=r$, $C_1'C_2=R$, and $C_2C_3=R'$, as also shown in Fig. 1, together with the notations for bond angles. The internal coordinates used are chosen as follows: the perpendicular displacement of the *i*th hydrogen(oxygen) atom out of the plane defined by the three nearest carbon atoms is termed $r\gamma_i$ ($r'\gamma_i'$); the out-of-plane ring bendings are regarded as torsions around carbon-carbon bonds; carbon atoms 1, 2, and 3 define one plane and carbon atoms 2, 3, and 4 define another; these planes intersect along the C_2C_3 bond; the angle between them is designated δ_2', prime denoting that the angle refers to a nominal double bond; for the corresponding quantities referring to a " single bond " the prime is dropped.

Table I contains symmetry coordinates formed from internal coordinates described above. In benzene, symmetry coordinates corresponding to S_A, S_B, and S_C are redundant. In the case of *p*-benzoquinone, however, S_A and S_C are not redundant by themselves. Therefore, we retain them in the following calculation and a frequency of zero is found in each of the cases of species A_u and B_{3g}.

Following Wilson's[10] procedure we obtain the factorized **G** matrix whose elements are given in Table II. Although **G**-matrix elements given in Table II are expressed as generally as possible in conformity with V_h structure, we need the internuclear distances and bond angles in order to calculate the numerical values of these elements. The following values are used: $r=1.08$ Å, $r'=1.23$ Å, $R=1.461$ Å, $R'=1.349$ Å, $\alpha=\theta=122°$, and $\beta=116°$. These are the values determined by electron-diffraction experiment[6] except R, R', and r. The values of CC distances are those calculated from bond order rather than experimental values, because when we later estimate the frequencies in the excited electronic states, the CC length will also be obtained from bond order. The CH distance assumed is taken from benzene[11]. Moreover, the C_2H_2 bond, for example, is assumed to bisect the external angle between bonds $C_1'C_2$ and C_2C_3. Therefore, it follows $\varphi_1=\varphi_2=119°$. The values of bond orders used are those calculated by a semiempirical MO method taking CI into account. Just as in the case of the calculation of the energy levels[2] not only the singly-excited configurations but also the doubly-excited configurations were considered, although only the " more important configurations" were taken into the secular equation and the neglected configurations were considered by the second-order perturbation theory. Bond orders obtained are:

$$p_{C_1'C_2}=0.226 \text{ and } p_{C_2C_3}=0.945\,.$$

Potential Function

Notations for valence force constants are also chosen as consistently as possible with those for benzene[8,9]. Fig. 2 shows **F** matrix in terms of internal coordinates.

	$r'\gamma_1'$	$r\gamma_2$	$r\gamma_3$	$r'\gamma_4'$	$r\gamma_5$	$r\gamma_6$	$R\delta_1$	$R'\delta_2'$	$R\delta_3$	$R\delta_4$	$R'\delta_5'$	$R\delta_6$
$r'\gamma_1'$	A''	a_o'	a_m'	a_p''	a_m'	a_o'	c_o'	c_m''	c_p'	$-c_p'$	$-c_m''$	$-c_o'$
$r\gamma_2$		A	a_o	a_m'	a_p	a_m	$-c_o$	$\bar{c}_o$	c_m^d	c_p	$-\bar{c}_p$	$-c_m^s$
$r\gamma_3$			A	a_o'	a_m	a_p	$-c_m^d$	$-\bar{c}_o$	c_o	c_m^s	$\bar{c}_p$	$-c_p$
$r'\gamma_4'$				A''	a_o'	a_m'	$-c_p'$	$-c_m''$	$-c_o'$	c_o'	c_m''	c_p'
$r\gamma_5$					A	a_o	c_p	$-\bar{c}_p$	$-c_m^s$	$-c_o$	$\bar{c}_o$	c_m^d
rr_6						A	c_m^s	$\bar{c}_p$	$-c_p$	$-c_m^d$	$-\bar{c}_o$	c_o
$R\delta_1$							B	b_o'	b_m	b_p	b_m'	b_o
$R'\delta_2'$			(Symmetric)					B''	b_o'	b_m'	b_p''	b_m'
$R\delta_3$									B	b_o	b_m'	b_p
$R\delta_4$										B	b_o'	b_m
$R'\delta_5'$											B''	b_o'
$R\delta_6$												B

Fig. 2. **F** matrix in terms of internal coordinate.

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[10] E. B. Wilson, Jr., ibid., **7**, 1047 (1939); **9**, 76 (1941).

[11] P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

TABLE
SYMMETRY COORDINATES IN TERMS

$$\begin{pmatrix} S_{16a} \\ S_{17a} \\ S_A \\ S_{11} \\ S_{16b} \\ S_{17b} \\ S_{10a} \\ S_B \\ S_4 \\ S_5 \\ S_{10b} \\ S_G \end{pmatrix} = \left(\begin{array}{cccccc} & & & & & \\ & -1/2 & 1/2 & & -1/2 & 1/2 \\ & & & & & \\ 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \\ & & & & & \\ -2/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} & -2/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} \\ & 1/2 & 1/2 & & -1/2 & -1/2 \\ & & & & & \\ & & & & & \\ 1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} \\ -2/\sqrt{12} & -1/\sqrt{12} & 1/\sqrt{12} & 2/\sqrt{12} & 1/\sqrt{12} & -1/\sqrt{12} \\ & & & & & \end{array} \right.$$

TABLE II
G-MATRIX ELEMENTS FOR THE OUT-OF-PLANE VIBRATIONS OF *p*-BENZOQUINONE

(Species A_u)

$G_{16a,16a}=(4\mu_C/3)(D+E-2F)^2$

$G_{17a,17a}=\mu_H+\mu_C(1+B+2C)^2$

$G_{A,A}=(2\mu_C/3)(D-2E-2F)^2$

$G_{16a,17a}=(2\sqrt{3}\mu_C/3)(D+E-2F)(1+B+2C)$

$G_{16a.A}=(2\sqrt{2}\mu_C/3)(D+E-2F)(D-2E-2F)$

$G_{17a,A}=(\sqrt{6}\mu_C/3)(1+B+2C)(D-2E-2F)$

(Species B_{1u})

$G_{11\ 11}=(\mu_O/3)+(2\mu_H/3)+(\mu_C/3)[(1+2A-2B)^2+2(1+B-A)^2]$

$G_{16b,16b}=3\mu_C(F+G-H)^2$

$G_{17b,17b}=(2\mu_O/3)+(\mu_H/3)+\mu_C(1+2A+B)^2$

$G_{11,16b}=(\sqrt{6}\mu_C)(F+G-H)(A-B)$

$G_{11,17b}=(\sqrt{2}/3)(\mu_H-\mu)_O-(\sqrt{2}\mu_C)(1+2A+B)(A-B)$

$G_{16b,17b}=-(\sqrt{3}\mu_C)(1+2A+B)(F+G-H)$

(Species B_{2g})

$G_{10a,10a}=\mu_H+\mu_C(1+B)^2$

$G_{B,B}=\mu_C(F+G+H)^2=0$

$G_{10a,B}=-\mu_C(1+B)(F+G+H)=0$

(Species B_{3g})

$G_{4,4}=(2\mu_C/3)[2(D-F-G+H)^2+(-D-2E+3F+G-H)^2]$

$G_{5,5}=(\mu_O/3)+(2\mu_H/3)+(\mu_C/3)[(1+2A+2B)^2+2(1+A+B+2C)^2]$

$G_{10b,10b}=(2\mu_O/3)+(\mu_H/3)+(\mu_C/3)[2(1+2A-B)^2+(1-2A+B+2C)^2]$

$G_{G,G}=(\mu_C/3)[2(H-G-F-2D)^2+(2D-2E-3F+G-H)^2]$

$G_{4,5}=(2\mu_C/3)[(D-F-G+H)(-1-2A-2B)+(-D-2E+3F+G-H)(1+A+B+2C)]$

$G_{4,10b}=(\sqrt{2}\mu_C/3)[2(D-F-G+H)(1+2A-B)+(-D-2E+G+3F-H)(1-2A+B+2C)]$

$$G_{4,G}=(\sqrt{2}\mu_C/3)[2(D-F-G+H)(-2D-F-G+H) \\ +(-D-2E+3F+G-H)(2D-2E-3F+G-H)]$$

$$G_{5,10b}=(\sqrt{2}/3)(\mu_H-\mu_O)+(\sqrt{2}\mu_C/3)[(1-2A-2B)(1+2A-B) \\ +(1+A+B+2C)(1-2A+B+2C)]$$

$G_{5,G}=(\sqrt{2}\mu_C/3)[(1+2A+2B)(2D+F+G-H)+(1+A+B+2C)(2D-2E-3F+G-H)]$

$G_{10b,G}=(\mu_C/3)[2(1+2A-B)(-2D-F-G+H)+(1-2A+B+2C)(2D-2E-3F+G-H)]$

$A=(r'\sin\alpha/R\sin\beta)$ $B=(r\sin\varphi_2/R\sin\theta)$ $C=(r\sin\varphi_1/R'\sin\theta)$ $D=R'/R\sin\theta$

$E=R/R'\sin\theta$ $F=\cos\theta/\sin\theta$ $G=\cos\beta/\sin\beta$ $H=1/\sin\beta$

μ_H, μ_C and μ_O are the reciprocal masses of the hydrogen, the carbon and the oxygen atom, respectively.

I
OF INTERNAL COORDINATES

$$\left.\begin{matrix}
-1/\sqrt{12} & 2/\sqrt{12} & -1/\sqrt{12} & -1/\sqrt{12} & 2/\sqrt{12} & -1/\sqrt{12} \\
 & & & & & \\
1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \\
 & & & & & \\
1/2 & & -1/2 & 1/2 & & -1/2 \\
 & & & & & \\
 & & & & & \\
1/2 & & -1/2 & -1/2 & & 1/2 \\
1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} \\
 & & & & & \\
 & & & & & \\
1/\sqrt{12} & 2/\sqrt{12} & 1/\sqrt{12} & -1/\sqrt{12} & -2/\sqrt{12} & -1/\sqrt{12}
\end{matrix}\right)
\left(\begin{matrix}
r'\gamma_1' \\ r\gamma_2 \\ r\gamma_3 \\ r'\gamma_4' \\ r\gamma_5 \\ r\gamma_6 \\ R\delta_1 \\ R'\delta_2' \\ R\delta_3 \\ R\delta_4 \\ R'\delta_5' \\ R\delta_6
\end{matrix}\right)$$

TABLE III
FACTORIZED **F**-MATRIX ELEMENTS

(Species A_u)

$F_{16a,16a}=(1/3)(B+2B''-4b_o'+b_o-4b_m'+b_m+2b_p''+b_p)$
$F_{17a,17a}=A-a_o-a_m+a_p$
$F_{A,A}=(1/3)[2B+B''+2(b_o+2b_o')+2(b_m+2b_m')+2b_p+b_p'']$
$F_{16a,17a}=(1/\sqrt{3})(-c_o-2\bar{c}_o+c_m^d-c_m^s+c_p+2\bar{c}_p)$
$F_{16a,A}=(\sqrt{2}/3)(B''-B+b_o'-b_o+b_m'-b_m+b_p''-b_p)$
$F_{17a,A}=\sqrt{2/3}\,(c_o-\bar{c}_o-c_m^d+c_m^s-c_p+\bar{c}_p)$

(Species B_{1u})

$F_{11,11}=(1/3)[A''+2A+2(2a_o'+a_o)+2(2a_m'+a_m)+a_p''+2a_p]$
$F_{16b,16b}=B-b_o-b_m+b_p$
$F_{17b,17b}=(1/3)(2A''+A+a_o-4a_o'+a_m-4a_m'+a_p+2a_p'')$
$F_{11,16b}=\sqrt{2/3}\,(c_0'-c_o+c_m^s-c_m^d+c_p-c_p')$
$F_{11,17b}=(\sqrt{2}/3)(A-A''+a_o-a_o'+a_m-a_m'+a_p-a_p'')$
$F_{16b\ 17b}=(1/\sqrt{3})(-2c_o'-c_o-c_m^d+c_m^s+2c_p'+c_p)$

(Species B_{2g})

$F_{10a,10a}=A+a_o-a_m-a_p$

(Species B_{3g})

$F_{4.4}=(1/3)[2B+B''-2(2b_o'+b_o)+2(2b_m'+b_m)-(2b_p+b_p'')]$
$F_{5,5}=(1/3)[A''+2A-2(2a_o'+a_o)+2(2a_m'+a_m)-(a_p''+2a_p)]$
$F_{10b,10b}=(1/3)(2A''+A+4a_o'-a_o-4a_m'+a_m-2a_p''-a_p)$
$F_{C,C}=(1/3)(B+2B''+4b_o'-b_o-4b_m'+b_m-b_p-2b_p'')$
$F_{4,5}=(2/3)[(c_o'+c_o+\bar{c}_o)-(c_m''+c_m^d+c_m^s)+(c_p'+c_p+\bar{c}_p)]$
$F_{4,10b}=(\sqrt{2}/3)[(c_o+\bar{c}_o-2c_o')-(c_m^d+c_m^s-2c_m'')+(c_p+\bar{c}_p-2c_p')]$
$F_{4,C}=(\sqrt{2}/3)(B-B''+b_o'-b_o-b_m'+b_m+b_p''-b_p)$
$F_{5,10b}=(\sqrt{2}/3)(A-A''+a_o'-a_o-a_m'+a_m+a_p''-a_p)$
$F_{5,C}=(\sqrt{2}/3)[(c_o'+c_o-2\bar{c}_o)-(c_m^d+c_m^s-2c_m'')+(c_p'+c_p-2\bar{c}_p)]$
$F_{10b,C}=(1/3)[(-2c_o'-2\bar{c}_o+c_o)-(c_m^d+c_m^s+4c_m'')-(2c_p'-c_p+2\bar{c}_p)]$

The transformation from internal to symmetry coordinates yields the factorized **F** matrix whose elements are shown in Table III. Following the work on benzene by Kakiuti and Shimanouchi[9] only the interaction constants referring to such internal coordinates that are "ortho" with each other are considered in the actual calculation. Moreover, interaction constants referring to the wagging motion of C=O bonds are also neglected because of difficulties in their estimation. Descriptions will be made of the retained force constants in succession.

Force constants for the torsions around CC bonds are obtained using the relation proposed in a previous paper[4]. Bond orders used were explained above. Overlap integrals used correspond to the CC distances obtained from bond orders. Using these torsional constants interaction constants c_0 and $\bar{c}_0$ are obtained using the method which has also been described in a previous paper[4]. Potential constants A, a_0, b_0 and b_0' are taken from benzene. The remaining constant A'' is determined in such a way that the calculated value of the lowest B_{3g} fundamental coincides with the smallest Raman shift of 243 cm^{-1} which can be assigned to the B_{3g} mode of lowest frequency, as will be discussed in a subsequent paper[12]. A summary of the value of force constants is given in Table IV.

TABLE IV

VALUES OF FORCE CONSTANTS

(in 10^5 dyn./cm.)

$A'' = 0.201$ $\quad c_0 = +0.038$

$A = 0.402$ $\quad \bar{c}_0 = +0.205$

$a_0 = -0.073$ $\quad c_0' = 0$

$a_0' = 0$ $\quad B = 0.048$

$b_0' = -0.012$ $\quad B'' = 0.287$

$b_0 = -0.011$

Calculation of the Frequencies and Discussions

Now that all the necessary values of potential constants are determined, it is possible to calculate the frequencies. The calculated values are shown in Table V.

TABLE V

CALCULATED AND OBSERVED FREQUENCIES OF OUT-OF-PLANE VIBRATIONS OF *p*-BENZOQUINONE (cm^{-1})

mode	A_u		B_{1u}		B_{2g}		B_{3g}	
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
C=O bending			533	—			(243)	243
C-H bending	962	—	871	876	839	794	959	932
ring bending	403	533	98	99			790	—

In this table experimental frequencies are also given for comparison. All the experimental frequencies, except those belonging to species A_u, are obtained from the analysis of the infrared and Raman data as will be discussed in part IV[12] of this series. Of the two vibrations belonging to species A_u experimental frequency is available only for the lower one (hereafter denoted as $\nu_2(A_u)$) and this frequency is obtained from the vibrational analysis of the electronic spectrum of *p*-benzoquinone vapor.

The agreement between calculated and observed frequencies is fairly good except for $\nu_2(A_u)$. Since the potential constants (both the diagonal and the interaction constants) referring to the wagging of C=O bond do not appear in the **F** matrix for species A_u, the neglect of or the inadequate values of these constants are not the reasons why the calculated $\nu_2(A_u)$ does not agree with the experiment.

In the vibrational analysis of the electronic spectrum lying around 4500 Å to be discussed in a separate article, two bands assigned to vibronic transitions in which $\nu_2(A_u)$ is superimposed by one quantum on the forbidden 0, 0 transition in the ground and the excited state, respectively, are found 1066 cm^{-1} apart from each other. This separation should represent the sum of ground- and excited-state value of $\nu_2(A_u)$. On the other hand it is found in a calculation of the nonplanar frequencies for the excited state using the scheme similar to that used for the ground state that $\nu_2(A_u)$ is almost completely insensitive to the electronic excitation concerned. Therefore, one-half of the above-mentioned separation may be considered to represent the value of $\nu_2(A_u)$ in the ground state. Hence, we take 533 cm^{-1} as the "experimental" value of $\nu_2(A_u)$ in the ground state. It is to be noted that the bond angles assumed for the calculation of upper-state frequencies are the same as those used for the ground state, although the change of bond length and torsional force constants are taken into consideration from the bond order. As can been seen in Eq. 20 of reference 4, c_0 and $\bar{c}_0$ depend on the bond angles which may be changed by the electronic excitation. Therefore, the reason for the disagreement between calculated and "experimental" values of $\nu_2(A_u)$ should be searched for not only in the calculated but also on the "experimental" side. This point will be discussed more fully in a later paper.

The authors express their sincere thanks to Professor S. Imanishi and to Dr. Y.

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[12] T. Anno and A. Sadô, This Bulletin, **31**, 734 (1958).

TABLE VI

L MATRIX[a]

A_u	$\lambda_1 (\nu=962\ \mathrm{cm}^{-1})$	$\lambda_2 (\nu=403\ \mathrm{cm}^{-1})$	$\lambda_3 (\nu=0\ \mathrm{cm}^{-1})$
S_{16a}	1.169 417	2.717 244	0
S_{17a}	3.210 802	1.251 510	0
S_A	−0.049 317	−0.114 592	0

B_{1u}	$\lambda_1 (\nu=871\ \mathrm{cm}^{-1})$	$\lambda_2 (\nu=533\ \mathrm{cm}^{-1})$	$\lambda_3 (\nu=98\ \mathrm{cm}^{-1})$
S_{11}	1.661 739	1.360 246	−0.182 856
S_{16b}	1.602 491	−2.110 660	−0.659 572
S_{17b}	2.543 457	−1.186 288	0.144 455

B_{2g}	$\lambda (\nu=839\ \mathrm{cm}^{-1})$
S_{10a}	2.753 927

B_{3g}	$\lambda_1 (\nu=959\ \mathrm{cm}^{-1})$	$\lambda_2 (\nu=790\ \mathrm{cm}^{-1})$	$\lambda_3 (\nu=243\ \mathrm{cm}^{-1})$	$\lambda_4 (\nu=0\ \mathrm{cm}^{-1})$
S_4	−1.879 766	4.447 465	−0.998 018	0
S_5	2.914 687	−2.090 424	−0.188 288	0
S_{10b}	1.570 902	0.817 234	0.893 017	0
S_G	−0.019 107	0.045 207	−0.010 144	0

a) Numerical values in these tables are based on the length in 10^{-8} cm. and the mass in 10^{-23} gram.

Kanda for their encouragement throughout this work and their kind suggestions in preparing the manuscript.

Appendix: L Matrix

Following Wilson[10] **L** matrix is defined as

$$\mathbf{S} = \mathbf{L}\mathbf{Q}$$

where **S** and **Q** are the column matrices formed by the internal (or internal symmetry) and the normal coordinates, respectively. Normalization condition is

$$\mathbf{L}\mathbf{L}' = \mathbf{G}$$

in which prime denotes the transpose of the matrix.

Since **L** matrix elements may be used to estimate the change of the frequencies owing to some small changes of the various force constants by the perturbation method[13] we have calculated normalized **L** matrix which is shown in Table VI. Numerical values in this table are based on the length in Å and the mass in 10^{-23} gram.

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[13] T. Anno, A. Sadô and I. Matubara, This Bulletin, **29**, 703 (1956).