Electronic States of p-Benzoquinone. VII. Intensity of the Symmetry-forbidden Electronic Absorption Bands of p-Benzoquinone

By Akira SADÔ

(Received July 26, 1961)

In Parts I[1] and II[2] of this series, we calculated the energy levels of the *p*-benzoquinone molecule and showed that the absorption bands of this molecule, appearing around 2900Å, are a superposition of three transitions, the $^1B_{1g} \leftarrow {}^1A_g$ transition, which corresponds to the π-π transition, and ^1A_u and $^1B_{2g} \leftarrow {}^1A_g$ transitions, which correspond to the n-π transitions. These transitions are all forbidden by the molecular symmetry, but are allowed through the vibronic interaction with the allowed $^1B_{2u} \leftarrow {}^1Ag$ transition. If this assignment is correct, the spectrum will appear with its transition moment along the long axis of the molecule (connecting two oxygen atoms). This is in agreement with the results of the spectroscopic studies of crystalline *p*-benzoquinone by Fixl and Schauenstein[3], Brand and Goodwin[4], and Sidman[5]. The absorption intensity around

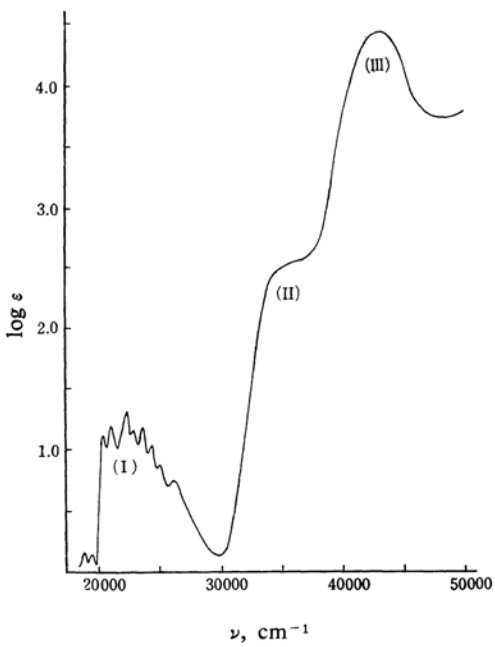

Fig. 1. The absorption spectrum of *p*-benzoquinone in *n*-hexane.

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) J. O. Fixl and E. Schauenstein, *Monatsh.*, **81**, 598 (1950); *Chem. Abstr.*, **45**, 4136f (1951).
4) J. C. D. Brand and T. H. Goodwin, *Trans. Faraday Soc.*, **53**, 295 (1951).
5) J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 2363 (1956); *J. Chem. Phys.*, **27**, 820 (1957).

2900Å in a *n*-hexane solution is greater than the absorption intensity around 4500Å,

$$f_{\mathrm{I}}/f_{\mathrm{II}} \fallingdotseq 1/10 \tag{1}$$

where

$$f=\int \varepsilon_\nu \mathrm{d}\nu \tag{2}$$

and where subscripts I and II refer to the absorption systems around the 4500Å and 2900Å regions respectively. Therefore, we may calculate the absorption intensity as a means of determining the nature of the absorption. In the description of vibronic interaction, spatially-fixed electronic wave functions are assumed.

Theoretical Considerations

The symmetry-forbidden electronic transitions are allowed by vibronic interaction with the allowed transition. This vibronic interaction has been treated by several authors[6-8]. According to the first-order perturbation method, the oscillator strength, f, for the forbidden electronic transition is described by the following formula:

$$f_{0\to k}=\sum_s (E_{0\to k}/E_{0\to s})C_{sk}(\boldsymbol{s})^2 f_{0\to s} \tag{3}$$

and

$$C_{sk}(\boldsymbol{s})=(W_{sk})/(E_{0\to s}-E_{0\to k}) \tag{4}$$

where $\boldsymbol{s}$ is the displacement from the equilibrium configuration in the ground electronic state, where subscript $0\to k$ indicates that the transition is from the ground state to the k state, where $0\to k$ and $0\to s$ transitions correspond to the forbidden and the allowed transitions respectively, and where $E_{0\to k}$ is the energy of the $0\to k$ transition. If we write

$$(W_{sk})_Q=\int \Theta_s^*(\boldsymbol{r})\sum_i\sum_a\{Z_a e^2 \boldsymbol{r}_a(i)\boldsymbol{s}_{Qa}/|\boldsymbol{r}_a(i)|^3\} \times\Theta_k(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{5}$$

then,

$$(W_{sk})^2=\sum_Q (W_{sk})_Q \tag{6}$$

where $\boldsymbol{s}_{Qa}$ is the displacement of the atom a in the normal mode Q, $\Theta_s(\boldsymbol{r})$ is the molecular electronic wave function of the quantum state, s, for the equilibrium configuration in the ground electronic state, $\boldsymbol{r}$, the symbol for the electronic coordinate, Z_a, the effective nuclear charge, and $|\boldsymbol{r}_a(i)|$, the distance from atom a to electron i. The introduction of the molecular orbital theory to give an approximate form for the electronic wave functions $\Theta_s(\boldsymbol{r})$ and $\Theta_k(\boldsymbol{r})$ leads to a considerable simplification of Eq. 5:

$$(W_{sk})_Q=\pm e^2\int \phi_1(\boldsymbol{r})\sum_a(Z_a\boldsymbol{r}_a\boldsymbol{s}_{Qa}/|\boldsymbol{r}_a|^3) \times\phi_2(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{7}$$

where ϕ_1 and ϕ_2 are the ummatched molecular orbitals in $\Theta_k(\boldsymbol{r})$ and $\Theta_s(\boldsymbol{r})$, respectively. This expression is now a one-electron integral and represents the electrostatic energy of the interaction between a set of dipoles, μ_a, and the electronic distribution, $e\phi_1\phi_2$.

If MO is constructed by the LCAO approximation, we can write

$$\phi_1=\sum_b c_{1b}\chi_b(\boldsymbol{r}) \tag{8}$$

where χ_b is the atomic orbital for atom b and c_{1b} is the coefficient of χ_b in ϕ_1. From Eqs. 7 and 8,

$$(W_{sk})_Q=\pm e^2\int\sum_a\sum_b c_{1b}\chi_b(\boldsymbol{r})(\boldsymbol{r}_a\boldsymbol{s}_{Qa}/|\boldsymbol{r}_a|^3) \times\sum_c c_{2c}\chi_c(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{9}$$

since,

$$\boldsymbol{r}_a=\boldsymbol{r}_b+\boldsymbol{r}_{ab} \tag{10}$$

where $|\boldsymbol{r}_{ab}|$ is the distance from atom a to atom b and where it is constant, and if we neglect the differential overlap formally, we obtain,

$$(W_{sk})_Q=\pm e^2\int\sum_a\sum_b c_{1b}\chi_b(\boldsymbol{r}) \times\{(\boldsymbol{r}_b+\boldsymbol{r}_{ab})\boldsymbol{s}_{Qa}/|\boldsymbol{r}_a|^3\}c_{2b}\chi_b(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{11}$$

but

$$\int\chi_b(\boldsymbol{r})(\boldsymbol{r}_b\boldsymbol{s}_{Qa}/|\boldsymbol{r}_a|^3)\chi_b(\boldsymbol{r})\mathrm{d}\boldsymbol{r}=0 \tag{12}$$

and if we assume

$$\boldsymbol{r}_{ab}=\boldsymbol{r}_a \tag{13}$$

Eq. 11 becomes

$$(W_{sk})_Q=\pm e^2\int\sum_a\sum_b Z_a c_{1b}c_{2b}\chi_b(\boldsymbol{r})\boldsymbol{r}_{ab}\boldsymbol{s}_{Qa} \times\chi_b(\boldsymbol{r})\mathrm{d}\boldsymbol{r}/|\boldsymbol{r}_{ab}|^3 \tag{14}$$

Using Eq. 14, we can calculate Eq. 7 numerically.

The quantities μ_a can be evaluated by the standard method[9]:

$$\mu_a=\boldsymbol{s}_a Z_a e \tag{15}$$

Thus,

$$\boldsymbol{s}=\boldsymbol{M}^{-1}\boldsymbol{B}'(\boldsymbol{L}^{-1})'\boldsymbol{Q} \tag{16}$$

6) J. N. Murrell and J. A. Pople, *Proc. Phys. Soc.*, A61, 245 (1956).
7) J. A. Pople and J. W. Sidman, *J. Chem. Phys.*, 27, 1270 (1957).
8) A. D. Liehr, *Can. J. Phys.*, 35, 1123 (1957).
9) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations", McGraw-Hill Book Co., Inc., New York (1955), Chap. 4.

where $\boldsymbol{M}^{-1}$ is a diagonal matrix whose elements are the reciprocal masses of the appropriate atoms. $\boldsymbol{B}'$ is the transpose of the matrix $\boldsymbol{B}$, which transforms the Cartesian displacement coordinates $\boldsymbol{s}$ into the symmetry coordinates $\boldsymbol{S}$. $(\boldsymbol{L}^{-1})'$ is the transpose of the matrix $(\boldsymbol{L}^{-1})$, which transforms the symmetry coordinates, $\boldsymbol{S}$, into the normal coordinates, $\boldsymbol{Q}$. The $\boldsymbol{B}$ matrix can be evaluated from the geometry and atomic mass of *p*-benzoquinone.

Normal Coordinates

Assuming the $\boldsymbol{V}_h$ structure of the *p*-benzoquinone molecule, the transitions from the ground A_g state to the B_{2u} and B_{3u} states can appear with the transition moments along the y and x axes (both lying in the molecular plane; see Fig. 1) respectively, while the transitions to the B_{1u} state appear with moment along the z axis (perpendicular to the molecular plane)[1,2]. As is shown by Eqs. 3 and 4, the contribution of a perturbing state to the absorption intensity is inversely proportional to the energy difference between the perturbing state and the perturbed state. The absorption spectrum[3-5] of the *p*-benzoquinone crystal, using a low temperature of 20°K, appears around 2900Å with its transition moment along the y axis. Therefore, the perturbing state belongs to species B_{2u}, and we can consider vibrations belonging to b_{3u} ($B_{1g}\times b_{3u}=B_{2u}$), b_{2g}($A_u\times b_{2g}=B_{2u}$) and a_u($B_{2g}\times a_u=B_{2u}$). Since vibrations belonging to species b_{2g} and a_u have been calculated[10], we can calculate the vibration belonging to species b_{3u}.

The normal coordinate was calculated by using the method of Wilson[9]. Thereby, a matrix equation

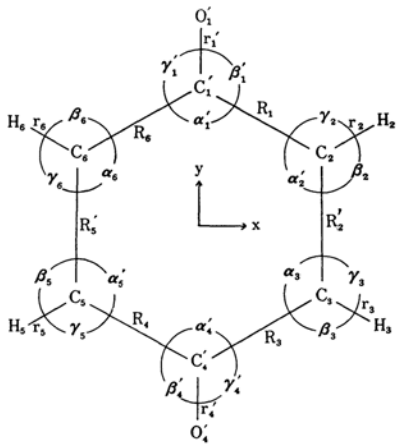

Fig. 2. Notations expressing bond angles and bond lengths and the numbering of atoms for the *p*-benzoquinone molecule.

$$(\boldsymbol{GF}-\lambda\boldsymbol{I})\boldsymbol{S}=0 \qquad (17)$$

was obtained. The $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices are the inverse kinetic energy matrix and the force constant matrix respectively, and $\boldsymbol{I}$ is the unit matrix.

The symbols used to describe various atoms, bond lengths and bond angles in the *p*-benzoquinone molecule are shown in Fig. 2. Denoting the increase in bond lengths and angles by placing Δ in front of the symbols for these quantities, the internal symmetry coordinates, whose symbols are chosen to be as consistent as possible with those of benzene[11], are

$$\left.\begin{aligned}
S_{14} &= (1/\sqrt{6})(-\Delta R_1+\Delta R_2'-\Delta R_3+\Delta R_4\\
&\quad -\Delta R_5'+\Delta R_6)\\
S_{15} &= (1/\sqrt{6})(-\Delta\phi_1'+\Delta\phi_2-\Delta\phi_3+\Delta\phi_4'\\
&\quad -\Delta\phi_5+\Delta\phi_6)\\
S_{18b} &= (1/\sqrt{12})(2\Delta\phi_1'+\Delta\phi_2-\Delta\phi_3\\
&\quad -2\Delta\phi_4'-\Delta\phi_5+\Delta\phi_6)\\
S_{19b} &= (1/\sqrt{12})(\Delta R_1+2\Delta R_2'+\Delta R_3\\
&\quad -\Delta R_4-2\Delta R_5'-\Delta R_6)\\
S_{20b} &= (1/2)(\Delta r_2+\Delta r_3-\Delta r_5-\Delta r_6)\\
S_D &= (1/2)(\Delta\alpha_2+\Delta\alpha_3-\Delta\alpha_5-\Delta\alpha_6)
\end{aligned}\right\} \qquad (18)$$

where $\Delta\phi_i=(1/2)(\Delta\gamma_i-\Delta\beta_i)$ ($i=1$, 2, 3, 4, 5 and 6).

In calculating the numerical values of $\boldsymbol{G}$ and $\boldsymbol{B}$ matrix elements, the following values of

Table I. Values of force constants of *p*-benzoquinone

$D=5.548\times10^5$ dyn./cm.
$D''=9.313\times10^5$ dyn./cm.
$F=5.065\times10^5$ dyn./cm.
$I=1.0142\times10^{-11}$ erg./rad²
$(I''=1.7086\times10^{-11}$ erg./rad²) a)
$H=(1/3)(H+2H'')$
$=1.3418\times10^{-11}$ erg./rad²

a) Evaluated value, see text.

Table II. Calculated and observed frequencies of b_{3u} vibrations of *p*-benzoquinone (cm^{-1})

	Normal coordinate	Calcd.	Obs.[a]
C-H stretching	Q_1	3068	3049
C-C stretching	Q_4	1142	944
C-C breathing	Q_3	1402	1064
C=O bending	Q_5	(370)[b]	370
C-H bending	Q_2	1836	1356

a) T. Anno and A. Sadô, This Bulletin, **31**, 734 (1958).
b) The value in parentheses is used to calculate the C=O bending force constant.

10) T. Anno and A. Sadô, This Bulletin, **31**, 728 (1958).

11) B. L. Crawford, Jr., and F. A. Miller, *J. Chem. Phys.*, **17**, 249 (1949).

TABLE III

N matrix[a)]

b_{3u}	X_1	X_2	X_3	X_4	X_5	X_6
S_{14}	$2A/\sqrt{6}$	$-A/\sqrt{6}$	0	0	$(1-B)/\sqrt{6}$	0
S_{15}	$1/\sqrt{6}r'$	$D/\sqrt{6}r$	$-1/\sqrt{6}r'$	$-D/\sqrt{6}r$	$A/\sqrt{6}r$	$-(2C/r+A/R)/\sqrt{6}$
S_{18b}	$3B/\sqrt{12}R$ $-1/\sqrt{3}r'$	$-\sqrt{3}B/4R$ $+D/\sqrt{12}r$	$1/\sqrt{3}r'$	$-D/\sqrt{12}r$	$\sqrt{3}C/4R$ $+C/\sqrt{12}r$	$-(2C/r+A/R)/\sqrt{12}$
S_{19b}	$-A/\sqrt{3}$	$A/\sqrt{12}$	0	0	$B/\sqrt{12}+1/\sqrt{3}$	0
S_{20b}	0	$-C/2$	0	$C/2$	$D/2$	$-D/2$
S_D	B/R	$B/2R$	0	0	$-A/R$	0

a) $A=\sin\alpha$, $B=\cos\alpha$, $C=\sin\beta$, $D=\cos\beta$

TABLE IV

L^{-1} matrix

b_{3u}	S_{14}	S_{15}	S_{18b}	S_{19b}	S_{20b}	S_D
Q_1	−0.005174	0.000178	−0.002246	−0.016444	0.122330	0.001894
Q_2	0.110382	0.026871	0.020412	0.124886	0.014495	−0.008061
Q_3	−0.123996	−0.003126	0.079654	0.196126	0.021796	−0.029465
Q_4	−0.079997	0.122540	0.046664	0.190321	−0.013264	0.021185
Q_5	0.524840	−0.977320	1.348043	−1.519523	−0.054969	0.212170

the interatomic distances and the bond angles for the ground electronic state are used:

$r_i'=1.23$ Å $\quad r_i=1.08$ Å

$R_i=1.461$ Å $\quad R_i'=1.349$ Å

$\alpha_i'=116°$ $\quad \alpha_i=\beta_i'=\gamma_i'=122°$

and $\beta_i=\gamma_i=119°$

The source of these data may be found in a previous paper[10].

The potential function assumed was a simple valence-force field type,

$$\begin{aligned}2V=&D\{(\Delta R_1)^2+(\Delta R_3)^2+(\Delta R_4)^2+(\Delta R_6)^2\}\\&+D''\{(\Delta R_2')^2+(\Delta R_5')^2\}\\&+F\{(\Delta r_2)^2+(\Delta r_3)^2+(\Delta r_5)^2+(\Delta r_6)^2\}\\&+H\{(\Delta\alpha_2)^2+(\Delta\alpha_3)^2+(\Delta\alpha_5)^2+(\alpha\Delta_6)^2\}\\&+I\{(\Delta\phi_2)^2+(\Delta\phi_3)^2+(\Delta\phi_5)^2+(\Delta\phi_6)^2\}\\&+I''\{(\Delta\phi_1')^2+(\Delta\phi_4')^2\}\end{aligned}\tag{19}$$

The numerical values of the force constant, the same as those used in a previous paper[12] except for I'', are given in Table I. I'' is determined in such a way that a calculated value of the frequency agrees with the experimental frequency assigned to the b_{3u} C=O bending vibration ($\nu=370\,\mathrm{cm}^{-1}$ in the ground state). The calculated and the observed frequencies are shown in Table II. The Cartesian coordinate system at each atom is defined in such a way that the positive direction of the y axis runs parallel to a line running from atom O_4 to atom O_1 and the xy plane coincides with the molecular plane. In Table III, the N' matrix is shown; it is defined by the following relation:

$$S=NX \tag{20}$$

and N' is the transpose of the matrix N. The matrix X represents the external symmetry coordinates, which are defined by using the Cartesian displacement coordinates:

$$\left.\begin{aligned}X_1&=x_{C_1'}+x_{C_4'}\\X_2&=x_{C_2}+x_{C_3}+x_{C_5}+x_{C_6}\\X_3&=x_{O_1'}+x_{O_4'}\\X_4&=x_{H_2}+x_{H_3}+x_{H_5}+x_{H_6}\\X_5&=y_{C_2}-y_{C_3}+y_{C_5}-y_{C_6}\\X_6&=y_{H_2}-y_{H_3}+y_{H_5}-y_{H_6}\end{aligned}\right\}\tag{21}$$

The L^{-1} matrix is given in Table IV.

Intensity Calculation

A dipole moment is calculated from the following formulae:

$$\mu_a=Z_a e(\overline{s_a^2})^{1/2} \tag{22}$$

and

$$\overline{s_a^2}=(\overline{x_a^2}+\overline{y_a^2}+\overline{z_a^2})\frac{h}{8\pi^2\nu_Q} \tag{23}$$

where Z_a is the "effective charge" at atom a and we use three kinds of value: (i) Z_a is the one which has been used by Murrell and Pople[11] and by Sidman[7]; (ii) each atomic displacement acts towards the π-electrons and the non-bonding electrons on its non-neighbors as a small dipole, but it is completely screened by the combined σ-electron, π-electron and non-bonding electron density from the

12) T. Anno and A. Sadô, ibid., 32, 1611 (1960).

π-electrons and non-bonding electron on its neighbors[13]. Therefore, Z_a is given the value of zero for its neighbor electron, but it is given Slater's effective nuclear charge for the 3p orbital in a negative ion of atom a ($Z_C=0.6$ and $Z_O=0.9$) for its non-neighbors. (iii) Since the *p*-benzoquinone molecule has an unbalanced electron density, screening constants are calculated by considering the electron density. The electron densities used are given in Table V; they have been determined by the method of Moffitt[14]. The molecular orbital used for the calculation was determined in a previous paper[1]. The electronic wave functions for the equilibrium configuration were determined by a semi-empirical MO method, taking CI into account, but for the B_{2g} state only one configuration was used.

TABLE V. FORMAL CHARGE OF *p*-BENZOQUINONE (AS A RESULT OF EXCITATION)

	O_1'	C_1'	C_2
$A_u(I)$[a] $B_{2g}(I)$	+0.0121	—[b]	—[b]
$A_u(II)$[a] $B_{2g}(II)$	+0.0209	—[b]	—[b]
B_{1g}	−0.7456	+0.2314	+0.2576

a) (I) and (II) show the lowest and the second lower states.
b) In the present calculation, these values are unnecessary.

Results and Discussion

For observing the absorption spectrum, a model EPS-2 Hitachi recording spectrophotometer was used, the oscillator strength was obtained graphically with a planimeter. The *p*-benzoquinone sample was prepared in the same manner as in Part V of this series[15] from hydroquinone. *n*-Hexane was used for the solvent, which was purified in the usual manner[16]. The experimental results are shown in Fig. 1.

The Cartesian displacement coordinates are given in Table VI. The calculated values of intensities are shown in Tables VII and VIII for the 4500 Å and 2900 Å regions respectively. From these results, we may conclude that the band around 2900 Å corresponds to the transition belonging to $^1B_{1g}\leftarrow{}^1A_g$, and that the perturbing vibration is almost the b_{3u} C=O bending vibration (370 cm^{-1} in the ground state).

For the absorption band around 4500 Å, the calculated intensity is very small. This is due to the facts that the interaction between the non-bonding electron of oxygen and the electronic dipole corresponds to the interaction

TABLE VI. CARTESIAN DISPLACEMENT OF b_{3u} VIBRATION (in 10^{-2} Å)

	Q_1	Q_2	Q_3	Q_4	Q_5
$x_{C_1'}$[a]	0.00194	0.03111	−0.12066	−0.06844	−0.15682
x_{C_2}	−0.01564	−0.02150	0.04219	0.02755	−0.28131
$x_{O_1'}$	−0.00023	0.00021	0.01358	−0.00704	0.57370
x_{H_2}	0.18758	0.06967	0.10904	0.13631	−0.27291
y_{C_2}	−0.01154	0.08433	0.02199	0.04554	−0.02752
y_{H_2}	0.10612	−0.05081	−0.06958	0.32805	−0.05135

a) Other displacements are evaluated from symmetrical character.

TABLE VII. OBSERVED AND CALCULATED VALUES OF THE INTENSITY OF ABSORPTION BAND APPEARING AROUND 4500 Å AND THE CONTRIBUTION OF NORMAL VIBRATIONS

	$Z_a=1$	Z_a by method (ii)	Z_a by method (iii)
$f_{Au(I)}/f_{B_{2u}}$[a]	1.44×10^{-10}	0.52×10^{-10}	0.53×10^{-10}
$f_{B_{2g}(I)}/f_{B_{2u}}$	6.96×10^{-10}	2.50×10^{-10}	2.59×10^{-10}
Q_1[b]	0.50×10^{-10}	0.18×10^{-10}	0.19×10^{-10}
Q_2	6.46×10^{-10}	2.32×10^{-10}	2.40×10^{-10}
f_I/f_{III}[c]		8.77×10^{-4}	

a) $f_{Au(I)}$ shows the oscillator strength of $^1A_u(I)\leftarrow{}^1A_g$ transition, (I) showing the lowest excited state belonging to the species.
b) Contribution of Q_1 vibration belonging to a_u species, and so on.
c) f_I and f_{III} show observed oscillator strengths of the first and the third longest wavelength absorptions, respectively.

13) D. P. Craig, *J. Chem. Soc.*, **1950**, 59.
14) W. Moffitt, *J. Chem. Phys.*, **22**, 1820 (1954).
15) T. Anno and A. Sadô, ibid., **32**, 1602 (1960).
16) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold (Publishers), Ltd. London (1954), p. 262.

TABLE VIII. OBSERVED AND CALCULATED VALUES OF THE INTENSITY OF ABSORPTION BAND APPEARING AROUND 2900 Å AND THE CONTRIBUTION OF NORMAL VIBRATIONS

	$Z_a=1$	Z_a by method (ii)	Z_a by method (iii)
$f_{Au(II)}/f_{B_{2u}}$[a]	8.58×10^{-11}	3.09×10^{-11}	3.27×10^{-11}
$f_{B_{2g}(II)}/f_{B_{2u}}$	4.16×10^{-10}	1.49×10^{-10}	1.59×10^{-10}
Q_1[b]	0.30×10^{-10}	0.11×10^{-10}	0.11×10^{-10}
Q_2	3.86×10^{-10}	1.39×10^{-10}	1.46×10^{-10}
$f_{B_{1g}}/f_{B_{2u}}$	3.39×10^{-3}	3.39×10^{-5}	1.07×10^{-3}
Q_1	0.00×10^{-3}	0.22×10^{-5}	$0.00_4\times10^{-4}$
Q_2	0.03×10^{-3}	0.13×10^{-5}	$0.00_3\times10^{-3}$
Q_3	0.71×10^{-3}	0.20×10^{-5}	$0.00_1\times10^{-3}$
Q_4	0.24×10^{-3}	0.00×10^{-5}	$0.00_0\times10^{-3}$
Q_5	2.40×10^{-3}	2.84×10^{-5}	1.06×10^{-3}
f_{II}/f_{III}[c]		1.77×10^{-2}	

a) $f_{Au(II)}$ shows oscillator strength of $^1A_u(II)\leftarrow{}^1A_g$ transition, (II) showing the second lowest excited state belonging to the species.
b) Contribution of Q_1 vibration belonging to a_u species, and so on.
c) f_{II} and f_{III} show observed oscillator strengths of the second and the third longest wavelength absorptions, respectively.

between an electric quadrupole and a dipole and that in the present calculation only this interaction contributes to the "n-π transition". Therefore, we considered the s-character of the non-bonding electron, but this effect was excluded from a consideration of the molecular symmetry. Assuming a V_h structure of *p*-benzoquinone[17,18], the non-bonding orbital of oxygene cannot be a hybridized s- and p_x-orbital, because the "s-p_x hybrid orbital" is symmetric to the yz plane. If the non-bonding orbital in oxygen is the s-orbital or the s-p_y hybrid orbital, according to the notations in Part I of this series[1], the non-bonding orbitals of *p*-benzoquinone ϕ_{n1} and ϕ_{n2} belong to the A_g and B_{2u} species respectively, and the $(n_1\rightarrow5)$ and $(n_2\rightarrow5)$ states belong to species B_{3g} and B_{1u}. Therefore, one of the "n-π transitions" should be an allowed transition. This fact is inconsistent with the vibrational analysis of the absorption of *p*-benzoquinone vapor around 4500 Å[15]. We must consider other effects or other higher-order interactions.

17) J. M. Robertson, *Proc. Roy. Soc.*, **A150**, 106 (1955).
18) S. M. Swingle, *J. Am. Chem. Soc.*, **76**, 1409 (1954).

Summary

The intensity of the symmetry-forbidden electronic absorption band of *p*-benzoquinone, whose excited states belong to $^1B_{2g}$, ^1A_u and $^1B_{1g}$, has been calculated by the perturbation method. It has been concluded that the absorption band around 2900 Å corresponds to the $^1B_{1g}\leftarrow{}^1A_g$ transition, which is allowed through vibronic interaction with the allowed $^1B_{2u}\leftarrow{}^1A_g$ transition. The interaction is contributed to almost entirely by b_{3u} C=O bending vibration, whose frequency is 370 cm^{-1} in the ground state.

The author wishes to express his deep thanks to Professor Sunao Imanishi and Dr. Yoshiya Kanda of Kyushu University for their encouragement throughout this research, and to Dr. Tosinobu Anno for his helpful guidance and discussions.

Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa