BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 695—700(1972)

The Calculation of the Rates of Intramolecular Nonradiative Transitions in Benzene

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(Received August 16, 1971)

Intramolecular nonradiative transition rates for various interstates of benzene were calculated from the standpoint of the breakdown of the Born-Oppenheimer approximation. The electronic parts of the coupling matrix elements were explicitly evaluated. These parts vary in the range of $10^{-1}-10^{-3}$ Å^{-1}. The nonradiative transition rates for the ${}^1E_{1u}\rightarrow{}^1B_{1u}$, ${}^1B_{2u}$ transitions were predicted to be appreciable. The rate for the ${}^1B_{1u}\rightarrow{}^1B_{2u}$ transition vanishes as long as the geometrical structure of the ${}^1B_{1u}$ state is assumed to be of the D_{6h} symmetry. These results are compared with the experimental nonradiative transition widths recently reported by Jortner *et al.*

The ocurrence of intramolecular radiationless transitions in polyatomic molecules in the gas phase is now a well-established experimental fact.[1-10] Previous theoretical investigations concerning radiationless transitions have been based on the implicit assumption that the coupling between the molecule and the medium is essential for the occurrence of the nonradiative process. The theory for intramolecular radiationless transitions in an isolated molecule was set forward by Lin[11] and by Bixon and Jortner,[12] who derived the necessary restricting conditions for the occurrence of a radiationless transition in an isolated molecule in the gas phase from the standpoint of the breakdown of the Born-Oppenheimer approximation.

Information on the rates of the radiationless transi-

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1) M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).
2) N. Stevens and E. Hutton, *Mol. Phys.*, **3**, 71 (1960).
3) M. Kasha, *Radiat. Res. Suppl.*, **2**, 243 (1960).
4) K. F. Greenough and A. B. F. Duncan, *J. Amer. Chem. Soc.*, **83**, 555 (1961).
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6) P. Seybold and M. Gouterman, *Chem. Rev.*, **65**, 413 (1963).
7) G. W. Kistiakowsky and C. S. Parmenter, *J. Chem. Phys.*, **42**, 2942 (1963).
8) R. J. Watts and S. J. Strickler, *ibid.*, **44**, 2423 (1966).
9) R. E. Kollogg, *ibid.*, **44**, 411 (1966).
10) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, New York (1949), p. 271.
11) S. H. Lin, *J. Chem. Phys.*, **44**, 3759 (1966).
12) M. Bixon and J. Jortner, *ibid.*, **48**, 715 (1968); *ibid.*, **50**, 3284 (1969); *ibid.*, **50**, 4061 (1969).

tions may be inferred from the linewidths in the absorption spectrum. In gas-phase spectra, it is difficult to determine the rates experimentally because of the trivial diffuseness of the linewidths as a result of the molecular rotation, the molecular vibration, and the sequence spectral congestion, but these difficulties are eliminated at low temperature in solid matrices. Recently Jortner *et al.*[13] have observed the linewidths in the absorption spectra of benzene at low temperatures in the rare-gas matrices and have estimated the line broadenings arising from the intramolecular radiationless decay in the lower three excited states ($^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$) of benzene.

Our main purpose in this paper is to calculate the radiationless transition rates in the lower three $\pi \rightarrow \pi^*$ excited states of benzene on the basis of the theory for intramolecular radiationless transitions in an isolated molecule and to compare the results with the above experimental information reported by Jortner *et al.*

Robinson and Burland[14] have calculated the radiationless transition probabilities for the internal conversion between the $^1B_{2u}$ and $^1A_{1g}$ states and the intersystem crossing between the $^3B_{1u}$ and $^1A_{1g}$ states in benzene. In their treatment, however, the explicit forms of the perturbation terms which cause the zero-order states to be nonstationary were not given, and the physical meaning of the perturbation terms is somewhat obscure.

Our calculation of the radiationless transition rates in benzene is made on the basis of the following assumptions:

(1) The radiationless transition is regarded as the transition from the lowest zero-order Born-Oppenheimer vibronic level, Ψ_i, in the higher electronic state to a dense manifold of the (zero-order) vibronic levels, Ψ_f, corresponding to a lower electronic state, and the breakdown of the adiabatic approximation is taken as the perturbation which brings about the radiationless decay.

(2) The coupling matrix elements, v, between the Ψ_i and Ψ_f states are assumed to be constant, independent of the channels which connect the initial state with a manifold of the vibronic levels, Ψ_f.

(3) The density, ρ, of the zero-order vibronic states, Ψ_f, is sufficiently high to exceed the reciprocal of the vibronic coupling term, v. This is nothing but a condition for the statistical limit of the intramolecular vibronic coupling and is expressed as:

$$\rho v \gg 1. \tag{1}$$

(4) The vibrational wave functions are approximated by a product of the harmonic oscillator wave functions.

Method of Calculation

In the excited electronic states of a large molecule, the Born-Oppenheimer separability condition for electronic and nuclear motion breaks down, and the intramolecular coupling between the zero-order vibronic level, Ψ_i, and a dense manifold of vibronic levels, Ψ_f, corresponding to a lower electronic state, both of which are eigenstates of the Born-Oppenheimer Hamiltonian, H_0, is induced by the nonadiabatic interaction term (the nuclear kinetic-energy operator), V:

$$V = H - H_0 \tag{2}$$

By considering the time evolution of a coherently-excited molecular state, which can be displayed as a time-dependent superposition of molecular eigenstates, each of which is a time-independent superposition of zero-order vibronic states, Bixon and Jortner showed that, with the statistical limits, the rate constant, k, for the nonradiative transition is given by:

$$k = (2\pi/\hbar)\rho v^2 \tag{3}$$

where v is the coupling matrix element and is expressed by:

$$v = \langle \Psi_f | V | \Psi_i \rangle. \tag{4}$$

The adiabatic (zero-order) molecular wave functions, Ψ, are represented in the simple product form:

$$\Psi_i = \Phi_b \theta_{b\beta} \tag{5}$$

and:

$$\Psi_f = \Phi_a \theta_{a\alpha} \tag{5'}$$

where Φ is the electronic wave function and where θ is the vibrational wave function. The non-adiabatic interaction term, V, is given explicitly by the following equation:

$$V\Psi_i = T\Phi_b\theta_{b\beta} - \Phi_b T\theta_{b\beta} \tag{6}$$

where T denotes the kinetic-energy operator for nuclear motion. The coupling matrix element, v, can now be displayed in terms of normal coordinates, Q_i:

$$v = -\hbar^2 \langle \Phi_a | (\partial/\partial Q_i) | \Phi_b \rangle \langle \theta_{a\alpha} | (\partial/\partial Q_i) | \theta_{b\beta} \rangle \tag{7}$$

where the Condon approximation[15] has been employed.

We are now in a position to treat the electronic and vibrational parts of Eq. (7) separately. First, the reduction of the electronic part will be considered. Expanding the Hamiltonian in normal coordinates to the first order, we obtain:

$$H = H_0{}^0 + H_{so}^0 + \sum_i \{(\partial H_0/\partial Q_i)_0 + (\partial H_{so}/\partial Q_i)_0\} Q_i \tag{8}$$

where H_{so} is the spin-orbit coupling Hamiltonian and where the two superscripts of H_0 and H_{so} and the two subscripts of $(\partial H_0/\partial Q_i)$ and $(\partial H_{so}/\partial Q_i)$ indicate that the corresponding quantities should be evaluated at the ground-state equilibrium nuclear arrangement. Further, the Φ_a and Φ_b wave functions are expanded into the series of Φ_c^0, and the expansion coefficients, correct to the second order, can be determined using the second-order perturbation theory. We thus obtain for the internal conversion.

$$\langle \Phi_a | (\partial/\partial Q_i) | \Phi_b \rangle = \frac{\langle \Phi_a{}^0 | (\partial H_0/\partial Q_i)_0 | \Phi_b{}^0 \rangle}{(E_b{}^0 - E_a{}^0)}, \tag{9}$$

and for the intersystem crossing:

$$\begin{aligned} \langle \Phi_a | (\partial/\partial Q_i) | \Phi_b \rangle = {} & \frac{\langle \Phi_a{}^0 | (\partial H_{so}/\partial Q_i)_0 | \Phi_b{}^0 \rangle}{(E_b{}^0 - E_a{}^0)} \\ & + \sum_{c \neq b} \sum_{c \neq a} \left\{ \frac{\langle \Phi_a{}^0 | H_{so}^0 | \Phi_c{}^0 \rangle \langle \Phi_c{}^0 | (\partial H_0/\partial Q_i)_0 | \Phi_b{}^0 \rangle}{(E_a{}^0 - E_c{}^0)(E_b{}^0 - E_a{}^0)} \right. \\ & \left. + \frac{\langle \Phi_a{}^0 | (\partial H_0/\partial Q_i)_0 | \Phi_c{}^0 \rangle \langle \Phi_c{}^0 | H_{so}^0 | \Phi_b{}^0 \rangle}{(E_b{}^0 - E_a{}^0)(E_b{}^0 - E_c{}^0)} \right\}. \end{aligned} \tag{9'}$$

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[13] B. Katz, M. Brith, B. Sharf, and J. Jortner, *J. Chem. Phys.*, **52**, 88 (1970).

[14] D. M. Burland and G. W. Robinson, *ibid.*, **51**, 4548 (1969).

[15] M. Lax, *ibid.*, **20**, 1752 (1952).

The problem is thus reduced to the calculation of the matrix element:

$$\langle \Phi_a{}^o | (\partial H_o/\partial Q_i)_o | \Phi_b{}^o \rangle.$$

According to Albrecht[16] and Liehr,[17] this matrix element is to be written as follows:

$$\langle \Phi_a{}^o | (\partial H_o/\partial Q_i)_o | \Phi_b{}^o \rangle = \sum_{f=1}^{3} \sum_{\sigma=1}^{N} (\partial \xi_\sigma{}^f/\partial Q_i)_o \times \int \rho_{ab}(p)(\partial H_{o,p\sigma}/\partial r_{p\sigma})_o (\partial r_{p\sigma}/\partial \xi_\sigma{}^f)_o \mathrm{d}x_p \quad (10)$$

where σ runs over the N nuclei, where p denotes the pth electron, where $\xi_\sigma{}^f$ is the coordinate of the nuclei in the Wilsonian type (Fig. 1), and where the integration of right-hand side of Eq. (10) is over the pth electron. $(\partial \xi_\sigma{}^f/\partial Q_i)_o$ is a matrix element which transforms the normal coordinates into the local cartesian coordinates, and $(\partial r_{p\sigma}/\partial \xi_\sigma{}^f)_o$ is the appropriate direction cosine of the vector, $r_{p\sigma}$, connecting the p electron and the σ nucleus with respect to the local cartesian coordinate, f. ρ_{ab} is the one-electron transition density given by:

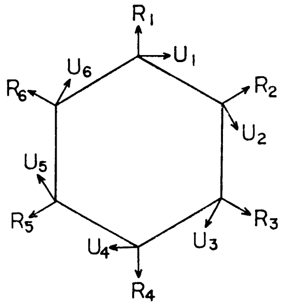

Fig. 1. Wilsonian type coordinate.
R: radial displacement of Wilsonian type coordinate
U: tangential displacement of Wilsonian type coordinate

$$\rho_{ab}(p) = n \int \Phi_a{}^o \Phi_b{}^o \mathrm{d}x' \quad (11)$$

where n is the number of electrons and the integration is over all but the pth electron. It should be noted that $H_{o,p\sigma}$ is just $(-Z_\sigma e^2/r_{p\sigma})$, because the only nuclear dependent part of the Hamiltonian is the Coulomb potential between the electron and the nucleus. As an example, the electronic part $({}^1B_{2u} \rightarrow {}^1A_{1g})$ will be calculated in the Appendix.

Next, the vibrational part in Eq. (7) will be considered. The vibrational wave functions are approximated in terms of the products of the harmonic-oscillator wave functions, $\chi_{ami}(Q_i)$ and $\chi_{bni}(Q_i')$, where mi and ni correspond to the vibrational quantum numbers:

$$\theta_{bn} = \prod_i \chi_{bni}(Q_i') \quad (12)$$

and

$$\theta_{am} = \prod_i \chi_{ami}(Q_i) \quad (13)$$

where $Q_i' = Q_i + R_i$, R_i being the displacement of the equilibrium points of the its harmonic oscillator between the initial and final states. Using Eqs. (12) and (13), we get the following expression for the vibrational part of the coupling matrix element:

$$\langle \theta_{am} | \partial/\partial Q_i | \theta_{bn} \rangle = \langle \chi_{ami}(Q_i) | (\partial/\partial Q_i) | \chi_{bni}(Q_i') \rangle \times \prod_{j \neq i} \langle \chi_{amj}(Q_j) | \chi_{bnj}(Q_j') \rangle. \quad (14)$$

$\langle \chi_{ami}(Q_i) | (\partial/\partial Q_i) | \chi_{bni}(Q_i') \rangle$ is the non-adiabatic overlap integral; this term can also be expressed in terms of the usual overlap integrals as follows:[11,18]

$$\langle \chi_{ami}(Q_i) | (\partial/\partial Q_i) | \chi_{bni}(Q_i') \rangle = ni^{1/2} \langle \chi_{ami}(Q_i) | \chi_{b,ni-1}(Q_i') \rangle - (ni+1)^{1/2} \langle \chi_{ami}(Q_i) | \chi_{b,ni+1}(Q_i') \rangle \quad (15)$$

All the vibrational wave functions in the initial electronic state are assumed to correspond to the zero-quantum vibrational level.

In Eq. (14), we must take into consideration all the possible combinations of the vibrational overlap integrals under the constraint of the conservation of the excess electronic energy of the final state. Because of the difficulties of the above procedure, the first term on the right-hand side of Eq. (14), which corresponds to a non-adiabatic Franck-Condon overlap, is taken as the average value of the vibrational coupling matrix elements.

The evaluation of the vibrational part of the coupling-matrix element is thus reduced to the calculation of the overlap integral, $S_{mi,ni} (= \langle \chi_{ami}(Q_i) | \chi_{bni}(Q_i') \rangle)$. The analytical expression of $S_{mi,ni}$ as a function of the K_{mi} and K_{ni} constants and the displacement of the equilibrium point, R_i, is given as follows:

$$S_{mi,ni} = \mathrm{c} \sum_{j=0}^{[mi/2]} \frac{(\alpha^2-1)^j}{j!} \sum_{k=0}^{ni} \frac{(2\alpha\beta)^{ni-k}(2\gamma)^{mi-2j-ni+k}}{(ni-k)!(mi-2j-ni+k)!} \times \sum_{L=0}^{[k/2]} \frac{(\beta^2-1)^L (2\delta)^{k-2L}}{L!(k-2L)!} \quad (16)$$

where:

$$\mathrm{c} = (2^{mi+ni})^{-1/2}(mi!)(ni!)\sqrt{\frac{2K_{mi}K_{ni}}{(K_{mi}^2+K_{ni}^2)}} \times \exp\left\{-\frac{K_{mi}^2 K_{ni}^2 r^2}{2(K_{mi}^2+K_{ni}^2)}\right\}$$

$$\alpha = \frac{2^{1/2}\rho}{(1+\rho^2)^{1/2}},\ \beta = \frac{\alpha}{\rho},\ \gamma = \frac{K_{mi}r}{1+\rho^2},\ \delta = -\rho r$$

$$\rho = \left(\frac{\nu_{mi}}{\nu_{ni}}\right)^{1/2},\ K_{mi} = \left(\frac{\mu\nu_{mi}}{\hbar}\right)^{1/2},\ K_{ni} = \left(\frac{\mu\nu_{ni}}{\hbar}\right)^{1/2}$$

where ν_{mi} and ν_{ni} are the vibrational frequencies for the initial and final states and where μ is the effective mass. This formula for $S_{mi,ni}$ applies only to a one-dimensional harmonic oscillator. For a two-dimensional case, we use the formula derived by Bell and Warsop.[19]

For the vibrational frequencies in both the ${}^1A_{1g}$ and ${}^1B_{2u}$ states of benzene, we employ the values proposed by Bernstein *et al.*[20] and by Garforth *et al.*[21] For the other states, the vibrational frequencies are unknown. Recently the differences in the zero-point vibrational energy between the ground state and excited states in benzene have been obtained by observing the deuteration effects on the transition energies.[13] We assume

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[16] A. C. Albrecht, *J. Chem. Phys.*, **33**, 156 (1960); *ibid.*, **50**, 169 (1960).

[17] A. D. Liehr, *Z. Naturforsch.*, *A*, **13**, 596 (1960).

[18] T. Matsushita, Doctoral Dissertation, Univ. of Tokyo (1967).

[19] S. Bell and P.A. Warsop, *J. Mol. Spectrosc.*, **20**, 425 (1966).

[20] E. R. Bernstein, S. D. Colson, D. S. Tinti, and G. W. Robinson, *J. Chem. Phys.*, **48**, 4632 (1968).

[21] F. M. Garforth, C. K. Ingold, and H. G. Poole, *J. Chem. Soc.*, **1948**, 491.

that the vibrational frequencies for the $^1B_{1u}$ and $^1E_{1u}$ states can be estimated from these data.

Apart from the coupling matrix element, the remaining parameter determining the radiationless transition rate is the density, ρ, of the vibrational energy levels. The classical approximation[22-24] for the density of vibrational states is not sufficiently accurate, the main reason for the inaccuracy being the neglect of the zero-point energy. We adopt in this paper the semiclassical approximation proposed by Haarhoff,[25] where the density is expressed as follows:

$$\rho = [(E+E_z^o)^{n-1}/(n-1)!](\prod_i^n h\nu_i)^{-1} \tag{17}$$

and where ν_i is the frequency of the ith oscillator, n is the number of the vibrational freedom, E is the energy difference between the initial and final electronic states, and E_z^o is defined by the equation:

$$E_z^o = \sum_i^n (h\nu_i/2). \tag{18}$$

Results and Discussion

The nonradiative transition rates between the various states shown in Fig. 2 have been calculated by the method described in the preceeding section. The vibrational level densities calculated for the various electronic states are shown in Table 1. The calculated matrix elements are summarized in Tables 2, 3, and 4. As can be seen from Table 3, the electronic parts of the vibronic matrix elements for the nonradiative transitions vary over a wide range, from about 10^{-1} to 10^{-3} (Å^{-1}). The electronic part for the $^1B_{1u}\rightarrow{}^1B_{2u}$ nonradiative transition vanishes, because all types of the transition density give zero. These results indicate that the electronic parts cannot be taken as constants in calculating the nonradiative transition rates. The calculated nonradiative transition rates are summarized in Table 4.

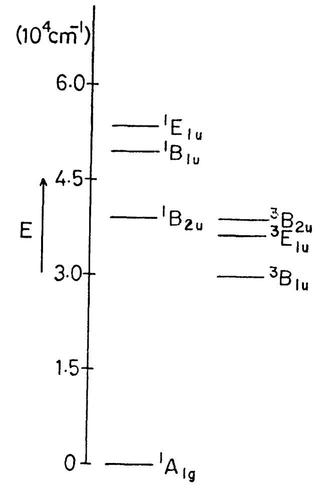

Fig. 2. Energy-level diagram showing the low-lying states of benzene.

TABLE 1. CALCULATED LEVEL DENSITIES

Electronic state		Level density[a)] $\frac{1}{\text{cm}^{-1}}$
Initial	Final	
$^1B_{2u}$	$^1A_{1g}$	9.26×10^{15}
$^1B_{1u}$	$^1A_{1g}$	1.13×10^{17}
$^1B_{1u}$	$^1B_{2u}$	6.50×10^{8}
$^1E_{1u}$	$^1A_{1g}$	4.25×10^{17}
$^1E_{1u}$	$^1B_{2u}$	9.60×10^{9}
$^1E_{1u}$	$^1B_{1u}$	1.17×10^{5}
$^1B_{2u}$	$^3E_{1u}$	2.25×10^{4}
$^1B_{2u}$	$^3B_{1u}$	1.90×10^{6}

a) The level densities are given by Eq. (17).

TABLE 2. CALCULATED ELECTRONIC PARTS

Electronic state		$\left\langle \Phi_a \left\| \frac{\partial}{\partial Q_i} \right\| \Phi_b \right\rangle$	Inducing mode (cm^{-1})
Initial	Final		
$^1B_{2u}$	$^1A_{1g}$	1.3×10^{-1} (Å^{-1})	b_{2u} (1313)
		2.8×10^{-2}	b_{2u} (1147)
$^1B_{1u}$	$^1A_{1g}$	2.0×10^{-3}	b_{1u} (3069)
		1.9×10^{-2}	b_{1u} (1011)
$^1B_{1u}$	$^1B_{2u}$	0	a_{2g} (1340)
$^1E_{1u}$	$^1A_{1g}$	7.0×10^{-6}	e_{1u} (3063)
		7.5×10^{-2}	e_{1u} (1478)
		2.6×10^{-2}	e_{1u} (1035)
$^1E_{1u}$	$^1B_{2u}$	8.0×10^{-3}	e_{2g} (3042)
		1.9×10^{-2}	e_{2g} (1584)
		8.6×10^{-3}	e_{2g} (1174)
		5.6×10^{-2}	e_{2g} (606)
$^1E_{1u}$	$^1B_{1u}$	7.5×10^{-2}	e_{2g} (3042)
		2.1×10^{-1}	e_{2g} (1584)
		8.4×10^{-2}	e_{2g} (1174)
		3.7×10^{-1}	e_{2g} (606)

TABLE 3. CALCULATED NON-ADIABATIC FRANCK-CONDON FACTORS

Electronic state		Non-adiabatic Franck-Condon factor[a)]	Inducing mode (cm^{-1})
Initial	Final		
$^1B_{2u}$	$^1A_{1g}$	9.5×10^{-52}	b_{2u} (1313)
		$<10^{-60}$[b)]	b_{2u} (1147)
$^1B_{1u}$	$^1A_{1g}$	9.1×10^{-34}	b_{1u} (3069)
		$<10^{-60}$[b)]	b_{1u} (1011)
$^1B_{1u}$	$^1B_{2u}$	1.3×10^{-11}	a_{2g} (1340)
$^1E_{1u}$	$^1A_{1g}$	3.2×10^{-31}	e_{1u} (3063)
		$<10^{-60}$[b)]	e_{1u} (1478)
		$<10^{-60}$[b)]	e_{1u} (1035)
$^1E_{1u}$	$^1B_{2u}$	1.1×10^{-7}	e_{2g} (3042)
		9.3×10^{-12}	e_{2g} (1584)
		1.8×10^{-19}	e_{2g} (1174)
		1.5×10^{-37}	e_{2g} (606)
$^1E_{1u}$	$^1B_{1u}$	9.9×10^{-1}	e_{2g} (3042)
		4.6×10^{-2}	e_{2g} (1584)
		3.6×10^{-3}	e_{2g} (1174)
		6.0×10^{-5}	e_{2g} (606)

a) The non-adiabatic Franck-Condon factors are given by Eq. (15).
b) These values are less than 10^{-60}.

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[22] R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952), *ibid.*, **43**, 2658 (1965).

[23] R. A. Marcus and O. K. Rice, *J. Phys. Colloid. Chem.*, **55**, 894 (1951).

[24] M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *J. Chem. Phys.*, **37**, 1276 (1962).

[25] P. C. Haarhoff, *Mol. Phys.*, **7**, 101 (1963).

TABLE 4. CALCULATED NONRADIATIVE RATE CONSTANTS

Electronic state		Nonradiative rate constant k (sec^{-1})
Initial	Final	
$^1B_{2u}$	$^1A_{1g}$	1.1×10^{-27}
$^1B_{1u}$	$^1A_{1g}$	1.2×10^{-6}
$^1B_{1u}$	$^1B_{2u}$	0
$^1E_{1u}$	$^1A_{1g}$	5.5×10^{-6}
$^1E_{1u}$	$^1B_{2u}$	1.1×10^{-11}
$^1E_{1u}$	$^1B_{1u}$	1.7×10^{-15}

It is interesting to compare the calculated widths with the experimental ones. As the present results have been obtained on the basis of many assumptions which can be thought to be justified within the statistical limits, we cannot expect to reproduce the experimental widths exactly. Katz *et al.*[13] have experimentally determined the absorption widths of the $^1E_{1u}$, $^1B_{1u}$, and $^1B_{2u}$ excited states in solid rare-gas matrices and reported that they are about 300, 300, and 0 cm^{-1} respectively. The calculated width of the $^1E_{1u}$ state is about twenty times as large as the experimental one. This discrepancy between the calculated width and the experimental one may be ascribed in part to the evaluation of the level density by means of the semiclassical method. Frost *et al.*[26] have concluded, from a comparison of the semiclassical method with other methods, that the value of the level density based on the semiclassical method is about ten to twenty times as large as the true value in the case of a relatively low energy.

The calculated width of the $^1B_{1u}$ state is zero, in contrast to the experimental one. The width can be expected, from a consideration of the Franck-Condon factor, to have an appreciable order. The zero width stems from the basic assumption that the zero-order wave function, $\Psi(B_{1u})$, is constructed from the adiabatic wave function. In the present calculations, the vibronic coupling between the $^1B_{1u}$ and $^1E_{1u}$ states is not considered. It is well known [13,17,27,28] that the $^1B_{1u}$ state is subjected to the pseudo-Jahn-Teller interaction with the $^1E_{1u}$ state through vibrations of the e_{2g} symmetry. It can be expected, therefore, that, if $\Psi(B_{1u})$ is constructed by means of the configurational mixing, the calculated width will have a non-zero value. In a subsequent paper, the vibronic-coupling matrix element between the $^1E_{1u}$ and $^1B_{1u}$ states *via* e_{2g} vibrations will be evaluated on the basis of the crude adiabatic approximation.[29–31]

TABLE 5. RELATIVE MAGNITUDES OF LOCAL CARTESIAN COEFFICIENTS $\xi_\sigma{}^R(b_{2u})$ AND $\xi_\sigma{}^U(b_{2u})$ AND RELATIVE MAGNITUDES OF ELECTRONIC INTEGRALS $I_\sigma{}^R\ (B_{2u}, A_{1g}, b_{2u})$ AND $I_\sigma{}^U(B_{2u}, A_{1g}, b_{2u})$

Wilsonian coordinate	Center number					
	1	2	3	4	5	6
R	O	O	O	O	O	O
U	x	$-x$	x	$-x$	x	$-x$

The width of the $^1B_{2u}$ state remains to be confirmed. It is shown in Table 4 that the calculated width of the nonradiative transition is negligibly small. We have calculated the width of the intersystem crossing from the $^1B_{2u}$ state to the $^3E_{1u}$ and $^3B_{1u}$ states. The results of the calculation are as follows:

$$\Gamma(^1B_{2u}\rightarrow{}^3E_{1u}) = 1.2\times10^{-6}\ \mathrm{cm}^{-1},$$

$$\Gamma(^1B_{2u}\rightarrow{}^3B_{1u}) = 5.0\times10^{-13}\ \mathrm{cm}^{-1}.$$

It may be concluded that the most favorable energy dissipation of the $^1B_{2u}$ state is the intersystem crossing to the $^3E_{1u}$ state. The width from other works gives 2.0×10^{-6} cm^{-1}.[7,32]

Appendix

The evaluation of the matrix element, Eq. (10), for the radiationless transition ($^1B_{2u}\rightarrow{}^1A_{1u}$) will be outlined as an example. Q_i should belong to the b_{2u} mode, judging from the selection rule for the nonradiative transition.

It is often convenient to symbolize the normal coordinate coefficient by $\xi_\sigma{}^f(b_{2u})$, and the electronic integral, by $I_\sigma{}^f(B_{2u}, A_{1g}, b_{2u})$, and to rewrite Eq. (10) as follows:

$$\langle\Phi(B_{2u})^o|\{\partial H_o/\partial Q(b_{2u})\}_o|\Phi(A_{1g})^o\rangle = \sum_f^3\sum_\sigma^N \xi_\sigma{}^f(b_{2u}) I_\sigma{}^f(B_{2u}, A_{1g}, b_{2u}), \quad \text{(A1)}$$

where:

$$\xi_\sigma{}^f(b_{2u}) = \{\partial\xi_\sigma{}^f/\partial Q(b_{2u})\}_o, \quad \text{(A2)}$$

$$I_\sigma{}^f(B_{2u}, A_{1g}, b_{2u}) = \int\rho(B_{2u}, A_{1g})(\partial H_{o,p\sigma}/\partial r_{p\sigma}) \times (\partial r_{p\sigma}/\partial\xi_\sigma{}^f)\mathrm{d}x_p. \quad \text{(A3)}$$

All the types of the transition density, $\rho(B_{2u}, A_{1g})$, are shown in Fig. 3. Applying a group theoretical reduction[16] (Table 5) shows how Eq. (A1) may be greatly simplified. It is proven that the identical relationships holding among the $\xi_\sigma{}^f(b_{2u})$ values hold among the $I_\sigma{}^f(B_{2u}, A_{1g}, b_{2u})$ values, thus

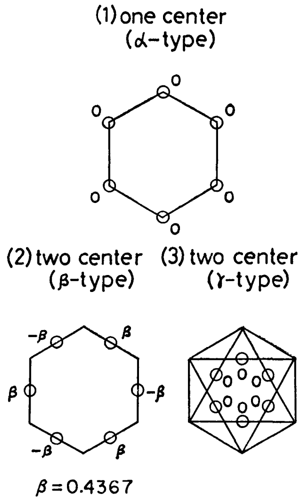

Fig. 3. Calculated transition density.

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permitting one to write:

$$\langle\Phi(B_{2u})^o|\{\partial H_o/\partial Q(b_{2u})\}_o|\Phi(A_{1g})^o\rangle$$
$$=\sum_{f^*}\sum_{\sigma^*}\xi_{\sigma^*}^{f^*}(b_{2u})I_{\sigma^*}^{f^*}(B_{2u},A_{1g},b_{2u})\sum_{f}^{3}\sum_{\sigma}^{N}\eta_{\sigma f}^2(b_{2u},\sigma^*,f^*)\quad\text{(A4)}$$

where the sum over f^* and σ^* goes over a minimum number of atomic centers and the corresponding cartesian coordinates. The expression in brackets is group-theoretically determined, where:

$$\eta_{\sigma f}(b_{2u},\sigma^*,f^*)=I_\sigma{}^f(B_{2u},A_{1g},b_{2u})/I_{\sigma^*}^{f^*}(B_{2u},A_{1g},b_{2u})$$
$$=\xi_\sigma{}^f(b_{2u})/\xi_{\sigma^*}^{f^*}(b_{2u}).\quad\text{(A5)}$$

Thus, we may write:

$$\langle\Phi(B_{2u})^o|\{\partial H_o/\partial Q(b_{2u})\}_o|\Phi(A_{1g})^o\rangle$$
$$=6\xi_1{}^U(b_{2u})I_1{}^U(B_{2u},A_{1g},b_{2u}).\quad\text{(A6)}$$

$I_1{}^U$ can be expanded as follows:

$$I_1{}^U=\beta[I_o(d_1)\cos(d_1,U_1)-I_o(d_2)\cos(d_2,U_1)$$
$$+I_o(d_3)\cos(d_3,U_1)-I_o(d_4)\cos(d_4,U_1)$$
$$+I_o(d_5)\cos(d_5,U_1)-I_o(d_6)\cos(d_6,U_1)]\quad\text{(A7)}$$

where d_1, d_2,$\cdots$and d_6 represent the distance between the atomic center, 1, and the six centers of the transition density. We assume that the geometry of benzene is a hexagon whose bond distance is 1.397 Å. The following values, which have been calculated by Liehr, are then substituted on the right-hand side in Eq. (A7):

$$\beta=0.4367$$

$$\cos(d_1,U_1)=\frac{7}{2},\qquad \cos(d_2,U_1)=\frac{21}{7},$$

$$\cos(d_3,U_1)=\frac{39}{26},\qquad \cos(d_4,U_1)=-\frac{39}{26},$$

$$\cos(d_5,U_1)=-\frac{21}{7},\qquad \cos(d_6,U_1)=-\frac{7}{2},$$

$$I_o(d_1)=I_o(d_6)=0.8239,\quad I_o(d_2)=I_o(d_5)=0.1834,$$
$$I_o(d_3)=I_o(d_4)=0.0950.$$

Thus, we obtain:

$$I_1{}^U(\beta)=0.5378/5.201\ (\text{eV/Å}).\quad\text{(A8)}$$

There are two normal modes in b_{2u} species, whose vibrational frequencies are 1147.7 and 1306.7 (cm^{-1}) respectively. The $\xi_1{}^U$ value corresponding to each normal mode is obtained as follows:

$$\left.\begin{aligned}\xi_1{}^U(b_{2u}-1306.8)&=-0.10716\\ \xi_1{}^U(b_{2u}-1147.7)&=0.04894.\end{aligned}\right.\quad\text{(A9)}$$

By inserting Eq. (A8) and Eq. (A9) into Eq. (A1), we obtain $<\Phi(A_{1g})^o|(\partial/\partial Q_i)|\Phi(B_{2u})^o>=0.136$ and 0.0281 (Å^{-1}) for the modes of 1306.8 and 1147.7 (cm^{-1}) respectively.