Calculation of the Nonradiative Transition Rate for the $^1B_{1u} \rightarrow {}^1B_{2u}$ Transition in Benzene

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The nonradiative transition rate for the $^1B_{1u} \rightarrow {}^1B_{2u}$ transition in benzene was calculated taking into account the pseudo-Jahn-Teller distortion in the $^1B_{1u}$ state and using a crude adiabatic approximation. The calculated rate constant is compared with the experimental one reported by Katz *et al.*

In a previous paper,[1] we dealt with a theoretical estimate of the intramolecular nonradiative transition rates for various interstates of benzene as considered from a breakdown of the Born-Oppenheimer approximation. The calculations were carried out on many assumptions which were thought to be justified within statistical limit. Apart from the exact reproduction of experimental data for the nonadiabatic transition rate of $^1B_{1u} \rightarrow {}^1B_{2u}$ transition, there was a significant discrepancy between theory and experiment even in a qualitative sense.

Katz *et al.*[2] have experimentally determined the absorption widths of the $^1E_{1u}$, $^1B_{1u}$, and $^1B_{2u}$ excited states of benzene in solid rare-gas matrices to be about 300, 300, and 0 cm^{-1} respectively. In our calculation, the nonradiative transition rates for $^1E_{1u} \rightarrow {}^1B_{1u}$, $^1B_{2u}$ transitions were predicted to be appreciable, but it turned out that the rate for the $^1B_{1u} \rightarrow {}^1B_{2u}$ transition vanishes.

So far as the $^1B_{1u}$ state is assumed to be of D_{6h} symmetry and expressed by a wavefunction including only singly excited configurations, the transition density between the $^1B_{1u}$ and $^1B_{2u}$ states is exactly zero in π-electron approximation and consequently the nonradiative transition rate vanishes. When the excited states are given in terms of configurations including doubly excited states, the transition density does not vanish. However, the use of wavefunctions including doubly excited configurations as the electronic part of the zeroth-order Born-Oppenheimer vibronic state does not seem to have any significant influence on the nonradiative transition rate.

On the other hand, it is known[3-5] that the $^1B_{1u}$ excited state of benzene is subjected to the pseudo-Jahn-Teller interaction with the $^1E_{1u}$ excited state through vibrations of e_{2g} symmetry, and as a result takes D_{2h} conformations with a quinoidal form or an antiquinoidal. In order to refine the estimation of the nonradiative transition rate for the $^1B_{1u} \rightarrow {}^1B_{2u}$ transition, we should adopt the distorted conformations of D_{2h} symmetry as the zeroth-order Born-Oppenheimer state for the $^1B_{1u}$ state.

Using a simplified, virtual model Sharf and Silbey[6] estimated the line broadening due to interaction between the non-diagonal Born-Oppenheimer states in higher excited electronic states of polyatomic molecules. They used an approximate adiabatic wavefunction for the zeroth-order Born-Oppenheimer vibronic state, and showed that the estimated linewidth obtained with the use of the above wavefunction is of the order of 1 cm^{-1}, whereas experimentally observed linewidths are of several hundred cm^{-1}. Recently they discussed this discrepancy[7] and showed that the vibronic broadening can be properly described through the "crude adiabatic approximation,"[8] whereas the procedure based on the adiabatic wavefunction can be misleading if proper care is not taken. Since both the adiabatic and crude adiabatic Born-Oppenheimer approximations employ complete sets of states, an exact calculation of the nonradiative decay rate could start from either procedure and produce the same, correct result. Nevertheless, since we use the perturbation theory and consider only the lower-order contributions, it is no longer required for the values of the nonradiative transition rate calculated in the crude adiabatic and adiabatic Born-Oppenheimer schemes to be the same or for either scheme to agree with its exact values. It is therefore important to ascertain which scheme would give rise to the smallest higher-order corrections and lead to the fastest convergence. Choice of the zeroth-order wavefunction is related to the problem of which description is more convenient rather than more correct.

In this paper we calculate the nonradiative transition rate for $^1B_{1u} \rightarrow {}^1B_{2u}$, taking into account the pseudo-Jahn-Teller distortion in the $^1B_{1u}$ state and using the crude adiabatic approximation.

Method of Calculation

Let $|s\rangle$ and $\{|l\rangle\}$ denote the optically excited initial Born-Oppenheimer vibronic state and the manifold of isoenergetic Born-Oppenheimer vibronic levels belonging to a lower electronic state, respectively. These vibronic states are the eigenfunctions of a zeroth-order Hamiltonian, H_0, and nonradiative transition is induced by the perturbation term

$$V = H - H_0, \tag{1}$$

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[1] N. Shimakura, Y. Fujimura, and T. Nakajima, This Bulletin, **45**, 695 (1972).

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

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

[4] A. D. Liehr, *J. Phys. Chem.*, **67**, 389 (1963).

[5] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," Benjamin, New York (1966).

[6] B. Sharf and R. Silbey, *Chem. Phys. Lett.*, **4**, 423 (1969).

[7] B. Sharf and R. Silbey, *ibid.*, **4**, 561 (1970).

[8] H. C. Longuet-Higgins, *Advan. Spectry.*, **2**, 429 (1961).

where

$$H = T(q) + V(q, Q) + T(Q), \tag{2}$$

$$H_0 = T(q) + V(q, Q_0) + T(Q). \tag{3}$$

$T(q)$ and $T(Q)$ denote the kinetic-energy operator for electronic motion and nuclear motion, respectively, and $V(q, Q)$ is the potential energy operator of the molecular Hamiltonian. Subscript 0 to Q indicates that the corresponding quantity should be evaluated at the ground-state equilibrium nuclear arrangement.

Using resolvent operator R,⁹⁾ the exact nonradiative transition rate can be expressed as

$$k_{nr} = \frac{2\pi}{\hbar}\sum_l |\langle s|R|l\rangle|^2 \delta(E_s{}^0 - E_l{}^0), \tag{4}$$

where

$$H_0|s\rangle = E_s{}^0|s\rangle,$$

$$H_0|l\rangle = E_l{}^0|l\rangle. \tag{5}$$

In the statistical limit, Eq. (4) may be rewritten as⁹⁾

$$k_{nr} = \frac{2\pi}{\hbar}\sum_l |\langle s|V|l\rangle|^2 \delta(E_s{}^0 - E_l{}^0) \tag{6}$$

If the most probable path¹⁰⁾ (*vide infra*) can be found for the nonradiative transition, we can represent the nonradiative transition rate by the most dominant term corresponding to the most probable path in the summation in Eq. (6). The nonradiative transition rate from the initial vibronic state $\Psi(^1\mathrm{B}_{1u})$ to the final vibronic state $\Psi(^1\mathrm{B}_{2u})$, is then written as follows.

$$k_{nr} = \frac{2\pi}{\hbar}|v_{\mathrm{MPP}}|^2, \tag{7}$$

where the coupling matrix element v_{MPP} is given by

$$v_{\mathrm{MPP}} = \langle \Psi(\mathrm{B}_{1u})|\{V(q, Q) - V(q, Q_0)\}|\Psi(\mathrm{B}_{2u})\rangle. \tag{8}$$

Let us choose the equilibrium nuclear position for the ground electronic state as an origin and expand the potential energy operator in normal coordinates to the first order. Equation (8) is then rewritten as

$$v_{\mathrm{MPP}} = \langle \Psi(\mathrm{B}_{1u})|\sum_{i=1}^{3N-6}\{\partial V(q, Q)/\partial Q_i\}_0 Q_i|\Psi(\mathrm{B}_{2u})\rangle. \tag{9}$$

Since energy difference between the $^1\mathrm{B}_{1u}$ and $^1\mathrm{E}_{1u}$ state of benzene is very small, the conventional perturbation scheme for the Herzberg-Teller intensity-borrowing mechanism is not a good approximation in describing the $^1\mathrm{B}_{1u}$ state subjected to pseudo-Jahn-Teller interactions with the $^1\mathrm{E}_{1u}$ level, and a more refined treatment should be applied. Such calculations for the $^1\mathrm{B}_{1u}$ state coupled with the $^1\mathrm{E}_{1u}$ state have been carried out by van der Waals *et al.*,¹¹⁾ who maintained that a single e_{2g} vibration dominates the vibronic mixing. They expanded a proper variational vibronic wavefunction in terms of the crude adiabatic electronic wavefunction, $\Phi^0(=\Phi(q, Q_0))$, which is the electronic wavefunction at the equilibrium configuration in the ground state as in the following.

$$\Psi(\mathrm{B}_{1u}) = \eta \prod_{j\neq \mathrm{e}_{2g}^{\mathrm{c}}}^{3N-8} \chi''(n, j), \tag{10}$$

$$\eta = \Phi^0(\mathrm{E}_{1u}^-)\sum_n L_n \chi''(n, \mathrm{e}_{2g}^{\mathrm{c}}) + \Phi^0(\mathrm{B}_{1u})\sum_n M_n \chi''(n, \mathrm{e}_{2g}^{\mathrm{c}})$$
$$+ \Phi^0(\mathrm{E}_{1u}^+)\sum_n N_n \chi''(n, \mathrm{e}_{2g}^{\mathrm{c}}), \tag{11}$$

where the double prime denotes vibrational wavefunctions belonging to the $^1\mathrm{B}_{1u}$ state, superscript c to e_{2g} the C–C stretching vibrations, and $\chi''(n, j)$ refers to the harmonic nuclear vibrational function in the jth normal mode in its nth quantum state. L_n, M_n, and N_n are the expansion coefficients to be determined. The summation in Eq. (11) indicates that, to calculate η exactly, we should carry out summation infinitely, but for computational purposes it will have to be truncated. The following points can be inferred from Eqs. (10) and (11). (1) The total wavefunction for the $^1\mathrm{B}_{1u}$ state is the product of the vibronic wavefunction which contains only the e_{2g} skeletal stretching mode and the vibrational wavefunction. (2) The vibrational wavefunction is the product of harmonic-oscillator wavefunctions. (3) Only the e_{2g}-type carbon skeleton stretching vibration ($\mathrm{e}_{2g}^{\mathrm{c}}$) is considered since it dominates the vibronic mixing between $^1\mathrm{B}_{1u}$ and $^1\mathrm{E}_{1u}$ states in benzene. (4) For the $^1\mathrm{B}_{1u}$ state we construct a new trial vibronic wavefunction, which is expanded in terms of the crude adiabatic electronic

TABLE 1. FIRST 8 EXPANSION COEFFICIENTS OF L_n AND N_n IN Eq. (11) CORRESPONDING TO THE LOWEST EIGENVALUES[a]

Quantum number of e_{2g} mode	Expansion coefficient L_i and N_k
1	−0.1774786
3	−0.0372783
5	−0.0052206
7	−0.0005606
9	−0.0000491
11	−0.0000036
13	−0.0000002
15	−0.0000000

a) Expansion coefficients vanish if the quantum numbers are even.

TABLE 2. FIRST 8 EXPANSION COEFFICIENTS OF M_n IN Eq. (11) CORRESPONDING TO THE LOWEST EIGENVALUE[a]

Quantum number of e_{2g} mode	Expansion coefficient M_n
0	0.9464586
2	0.1938479
4	0.0282337
6	0.0031885
8	0.0002940
10	0.0000229
12	0.0000015
14	0.0000001

a) Expansion coefficients vanish if the quantum numbers are odd.

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9) The off-diagonal components of R contain terms to all orders in perturbation theory.

$$\langle s|R|l\rangle = \langle s|V|l\rangle + \sum_{c\neq s}\frac{\langle s|V|c\rangle\langle c|V|l\rangle}{(E_s - E_c)}$$
$$+ \sum_{c\neq s}\sum_{c'\neq s}\frac{\langle s|V|c\rangle\langle c|V|c'\rangle\langle c'|V|l\rangle}{(E_s - E_c)(E_s - E_{c'})} + \cdots$$

Cf. M. Goldberger and K. Watson, "Collision Theory," Wiley, New York (1964) for more details of the resolvent operator.

10) W. M. Gelbart, K. G. Spears, K. F. Freed, J. Jortner, and S. A. Rice, *Chem. Phys. Lett.*, **6**, 345 (1970).

11) J. H. van der Waals, A. M. D. Berghius, and M. S. De Groot, *Mol. Phys.*, **13**, 301 (1967).

Table 3. Calculated electronic parts

Electronic state Initial	 Final	Accepting mode (k)	$\langle \Phi^0(f)\|\{\partial V(q, Q)/\partial Q_k\}_0\|\Phi^0(i)\rangle$ (eV/Å)
$^1B_{1u}$	$^1B_{2u}$	a_{2g}	0
$^1E_{1u}^+ + {}^1E_{1u}^-$	$^1B_{2u}$	e_{2g}	0.3057

wavefunctions of the $^1E_{1u}^+$, $^1B_{1u}$, and $^1E_{1u}^-$ states. The expansion coefficients are further expanded in terms of the vibrational wavefunctions of e_{2g}-type, $\chi(n, e_{2g})$. Some calculated expansion coefficients, L_n, M_n, and N_n, for the vibrational wavefunctions corresponding to the lowest energy are summarized in Tables 1 and 2.

The wavefunction for the $^1B_{2u}$ state is written as follows,

$$\Psi(B_{2u}) = \Phi^0(B_{2u}) \prod_{j \neq 1}^{3N-6} \chi'(n,j) \tag{12}$$

where the prime denotes vibrational wavefunctions belonging to the $^1B_{2u}$ state. Thus we obtain for the coupling matrix element:

$$\begin{aligned} v = {} & \langle \Phi^0(B_{2u})|\{\partial V(q, Q)/\partial Q(e_{2g}^c)\}_0|\Phi^0(E_{1u}^-)\rangle \\ & \times \langle \chi(e_{2g}, n)|Q(e_{2g})|\sum_n L_n \chi(n, e_{2g}^c)\rangle \prod_{j \neq e_{2g}^c}^{3N-8} \langle \chi(n,j)|\chi(0,j)\rangle \\ & + \langle \Phi^0(B_{2u})|\{\partial V(q, Q)/\partial Q(a_{2g})\}_0|\Phi^0(B_{1u})\rangle \\ & \times \langle \chi(n, e_{2g}^c)|\sum_n M_n \chi(n, e_{2g}^c)\rangle \\ & \times \langle \chi(a_{2g}, 1)|Q(a_{2g})|\chi(a_{2g}, 0)\rangle \prod_{j \neq e_{2g}^c, a_{2g}}^{3N-9} \langle \chi(n,j)|\chi(0,j)\rangle \\ & + \langle \Phi^0(B_{2u})|\{\partial V(q, Q)/\partial Q(e_{2g}^c)\}_0|\Phi^0(E_{1u}^+)\rangle \\ & \times \langle \chi(e_{2g}, n)|Q(e_{2g})|\sum_n N_n \chi(n, e_{2g}^c)\rangle \prod_{j \neq e_{2g}^c}^{3N-8} \langle \chi(n,j)|\chi(0,j)\rangle. \end{aligned} \tag{13}$$

Here we have assumed that the vibrational wavefunctions for the $^1B_{1u}$ and $^1B_{2u}$ states are the same as those in the ground state.

We shall now treat the electronic and vibrational parts separately. The electronic parts can be calculated by the same method as that used previously.[1] The values of the calculated electronic parts are summarized in Table 3. Of the electronic parts

$$\langle \Phi^0(B_{2u})|\{\partial V(q, Q)/\partial Q(a_{2g})\}_0|\Phi^0(B_{1u})\rangle,$$

and

$$\langle \Phi^0(B_{2u})|\{\partial V(q, Q)/\partial Q(e_{2g})\}_0|\{\Phi^0(E_{1u}^+) + \Phi(E_{1u}^-)\}\rangle,$$

the former is zero, and the latter appreciable.

We must now decide the mode which accepts the excess energy. It is assumed that the e_{2g}-type C–C stretching vibration (1606 cm^{-1}) is the most probable path for accepting excess energy for the following reason. Equilibrium configuration differs for the ground and excited states of aromatic hydrocarbons only in the totally symmetric normal coordinate. Therefore, only the progression of totally symmetric vibration is observed in absorption and emission spectra of aromatic hydrocarbons. It is known that as the difference in equilibrium configuration and that in vibrational frequency between the initial and final electronic states become larger, the Franck-Condon factor becomes larger at the higher vibrational quantum number of the final states. We assume the vibrational frequencies of each excited electronic state to be the same as those of the ground state. To accept the same excess energy, the oscillator of the high vibrational frequency requires a small vibrational quantum number compared with that of the low vibrational frequency. Thus, the Franck-Condon factor also becomes larger for the higher vibrational frequency of the final state (see Ref. 12 for more details). The difference in the equilibrium configuration between the $^1B_{1u}$ and $^1B_{2u}$ states in benzene is large along the direction of the e_{2g} normal coordinate. In the present model, the nonradiative transition is considered to occur from the $^1B_{1u}$ state subjected to the pseudo-Jahn-Teller interaction with the $^1E_{1u}$ state. Only the e_{2g}-type carbon skeleton stretching vibration is effective in the above interaction and, is thus the most probable accepting mode.

Results and Discussion

The transition densities necessary for calculating the electronic parts of the coupling matrix element are shown in Fig. 1. The calculated nonradiative transition rate constant is given in Table 4 together with

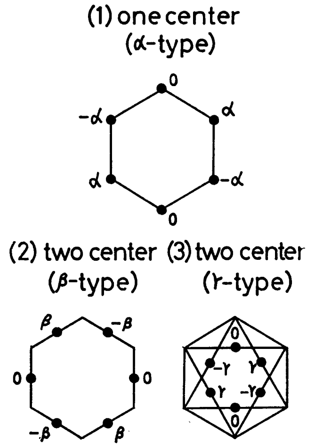

Fig. 1. The electronic energy surface of the lower singlet state of benzene as the function of a_{1g} and e_{2g} normal coordinate displacements.[a]

E_1[b]=4.9 eV E_2[b]=6.2 eV E_3[b]=7.0 eV

[a] The same equilibrium points in the $^1E_{1u}$, $^1B_{1u}$, and $^1B_{2u}$ states along totally symmetric C–C stretching coordinate are assumed.

[b] D. K. Kearns, *J. Chem. Phys.*, **36**, 1608 (1960).

Table 4. Nonradiative transition rate constant

Transition	Calculated rate constant (Calculated half width)	Experimental rate constant (Experimental half width)
$^1B_{1u} \rightarrow {}^1B_{2u}$	3×10^{13} sec^{-1} (150 cm^{-1})	6×10^{13} sec^{-1} (300 cm^{-1})

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12) W. Siebrand, *J. Chem. Phys.*, **46**, 440 (1967).

the experimental one, the former being in good agreement with the latter. There may be some cancellations among the various types of error arising from the approximations we employed.

We calculated the nonradiative transition rate from the $^1B_{1u}$ state, which undergoes the pseudo-Jahn-Teller interaction with $^1E_{1u}$ state, to the $^1B_{2u}$ state. We assume that the initial and final states can be expressed by the vibronic wavefunctions with a crude adiabatic wavefunction as an electronic factor. When we use the crude adiabatic wavefunction, the off-equilibrium electronic Hamiltonian is the dominant operator responsible for the line broadening or for the decay of the initial state.

The present calculation shows how the lowest order of the potential energy operator contributes to the nonradiative transition rate in the crude adiabatic approximation.

The procedure should be applied to other cases where the state to be dealt with is very near other states. In such cases, we must take into account the vibronic interaction (the pseudo-Jahn-Teller interaction) between these states, because the interaction between each state is very large.

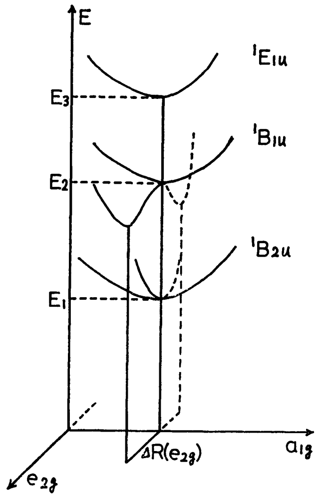

Fig. 2. Calculated transition density between the $^1B_{1u}$ and $(E^+_{1u}+E^-_{1u})$ states.
(1) $\alpha=0$ (2) $\beta=1/3$ (3) $\gamma=0$

The electronic energy surfaces of the $^1E_{1u}$, $^1B_{1u}$, and $^1B_{2u}$ states of benzene as the functions of the a_{1u} and e_{2g} normal coordinate displacements are shown in Fig. 2. The first strong vibrational component in the progressions of the absorption spectrum of the $^1B_{1u}$ state was assigned to $0\text{-}0+\nu_{18}(e_{2g})$.[2] Using these data and the assumed harmonic potential, we estimated the magnitude of difference in equilibrium configuration ΔR (e_{2g}) between the $^1B_{1u}$ and the $^1B_{2u}$ states, arising from the pseudo-Jahn-Teller interaction with the $^1E_{1u}$ state, to be about 0.1 Å.

Fisher and Schneider[13] analyzed the time dependent correlation function about the rate constant and calculated the rate for intersystem crossing from the $^3B_{1u}$ state to the ground state in benzene. They used the saddle point method[14,15] in order to find the most probable path for the intersystem crossing in benzene. They found that 66% (55%) of the energy goes into the C–H (C–D) breathing mode for benzene (deuterobenzene) and the other major energy sinks involve the totally symmetric skeletal breathing mode (990 cm^{-1}), the e_{2g} stretching mode (1584 cm^{-1}) and, to a smaller extent, the out-of-plane vibrations. It is apparent that a certain vibration accepts most of the excess energy. We took into consideration all the possible combinations of the vibrational overlap integrals under the constraint of conservation of the excess electronic energy of the final state.[1] The non-adiabatic Franck-Condon factor was taken as the average value of vibrational coupling matrix elements for computational purposes. We have employed the most probable path method and chosen the e_{2g} C–C stretching vibration as the most probable path. The difference in C–H bond length between the $^1B_{1u}$ and $^1B_{2u}$ states would be small and the C–H normal vibration could not serve as a good accepting mode.[16]

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13) S. Fischer and S. Schneider, *Chem. Phys. Lett.*, **10**, 392 (1971).

14) K. F. Freed and J. Jortner, *J. Chem. Phys.*, **52**, 6272 (1970).

15) S. Fischer, *ibid.*, **53**, 3195 (1970).

16) J. P. Byrne, E. F. McCoy, and I. G. Ross, *Aust. J. Chem.*, **18**, 1589 (1965).