

THEORY OF NONRADIATIVE DECAY FROM THE LOWEST SINGLET STATE OF BENZENE: EXCESS ENERGY DEPENDENCE

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

A time-independent Green function formalism is developed to study the excess energy dependence on the nonradiative decay in the S_1 state of benzene. Effects of purely electronic relaxation (internal conversion, IC) and intramolecular vibrational redistribution, IVR, are taken into account at the same time. Model calculations show that the drastic increase in the nonradiative decay rate at around $3\,000\text{ cm}^{-1}$ excess energy is due to the same onset of both IC and IVR rates. Our theory can explain the difference in rate constant between IVR and IC observed by Moss and Parmenter.

In 1977 Prof. Zahradnik visited Japan for the first time and had stayed for one month and a half in our Laboratory of Tohoku University. His intelligible scientific talks as well as his sociable personality have deeply impressed all of us, who say that he has left with us many pleasant memories.

Investigation of the nonradiative decay in the lowest excited singlet state (S_1) of benzene is still one of the hot subjects of the dynamics in electronically excited molecules. The mechanisms of the onset of the fast nonradiative decay of single vibronic levels at about $3\,000\text{ cm}^{-1}$ above the S_1 origin has not yet been clarified though many experimental works¹⁻¹⁰ such as measurements of the line widths in absorption spectra, and in multiphoton ionizations, fluorescence decay rates, and fluorescence quantum yields have been reported so far.

There are basically two possibilities about the origin of the onset of the fast nonradiative decay: one originates from the electronic relaxation from the S_1 state to the ground state (internal conversion, abbreviated by IC), and the other originates from the intramolecular vibrational energy redistribution (IVR) in the S_1 state. The internal conversion and IVR may take place independently or simultaneously. Recently applying the technique of chemical timing to the observation of time-

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-resolved fluorescence spectra from the S_1 state, Moss and Parmenter¹⁰ have found that IVR makes an important role in the nonradiative decay rates from some levels in the S_1 state, the IVR rates being faster than the IC rates by about two orders of magnitude.

The purpose of this paper is to study theoretically the excess energy dependence on the nonradiative decay in the S_1 state of benzene taking into account both the IVR and IC processes.

Theoretical works on the excess energy dependence reported so far are classified into two limiting cases. In one case, the excess energy dependence is assumed to arise from the IC process without taking into account the IVR (ref.¹¹) process. In the other case, the IVR process is considered to take place before the IC process occurs, and a microcanonical ensemble with certain internal temperature in an isolated system is assumed.¹²⁻¹³ This model is called the communicating state one.¹⁴ In this model, the communicating state is assumed to be created even in low excess energy regions in which the IVR does not take place. The effects of IVR on the onset of the nonradiative decay observed by Moss and Parmenter¹⁰ cannot explicitly be explained on the basis of the communicating state model. In this paper we treat the IVR and IC processes for the nonradiative decay at the same time. For this purpose we use the Green function (resolvent) formalism.

In the next section the Green function formalism is applied to the derivation of the rate constant expression. In the following section, the calculations of the rate constant as a function of the excess energy are carried out and a comparison with experiment is discussed.

THEORETICAL

We consider a model for the nonradiative decay in the S_1 state in benzene as shown in Fig. 1. The level a denotes a zero-order state optically allowed from the initial level. Manifolds $\{b\}$ and $\{l\}$ represent dark vibronic levels in the S_1 and ground states, respectively. The matrix element inducing either the IC or the IVR process between relevant states α and β is denoted by $V_{\alpha\beta}$.

The nonradiative decay rate constant from the optically allowed state a is given in terms of the diagonal matrix element of the time-independent Green function $G_{aa}(E)$ as¹⁵

$$k = -(4\pi/\hbar) \text{Im } G_{aa}^{-1}(E), \quad E \rightarrow E_a, \quad (1)$$

where the Green function is defined by

$$\mathbf{G}(E) = (E - \mathbf{H})^{-1}. \quad (2)$$

The molecular Hamiltonian \mathbf{H} in Eq. (2) is divided into two parts as

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}, \quad (3)$$

where \mathbf{H}_0 is the zero-order Hamiltonian, and the perturbation \mathbf{V} is given by

$$\mathbf{V} = \mathbf{T}_N + \mathbf{V}', \quad (4)$$

in which \mathbf{T}_N , kinetic energy operator for nuclei, denotes the nonadiabatic interaction operator inducing IC, and \mathbf{V}' the anharmonic or the Coriolis interaction inducing IVR.

The Green function satisfies the Dyson equation

$$\mathbf{G}(E) = \mathbf{G}^0(E) + \mathbf{G}^0(E) \mathbf{V} \mathbf{G}(E), \quad (5)$$

where

$$\mathbf{G}^0(E) = \lim_{\eta \rightarrow 0^+} (E - \mathbf{H}_0 + i\eta)^{-1}. \quad (6)$$

By using the Dyson equation and Eq. (6), the matrix elements of the Green function relevant to the nonradiative decay are expressed as

$$G_{aa} = G_{aa}^0 \left(1 + \sum_l V_{al} G_{la} + \sum_b V_{ab} G_{ba} \right), \quad (7a)$$

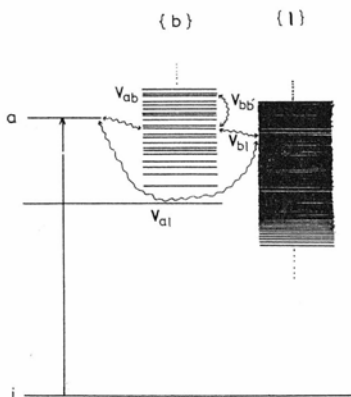


FIG. 1

Model for a nonradiative decay in the S_1 state of benzene. a and $\{b\}$ refer to an optically allowed state from the initial state i and the dark states in the S_1 electronic state, respectively. Manifold $\{l\}$ denotes the vibronic states in the electronic ground state. The terms V_{al} and $V_{bl'}$ and V_{ab} and $V_{bb'}$ represent the matrix elements inducing internal conversion (IC) and those inducing intramolecular vibrational redistribution (IVR), respectively

$$G_{1a} = G_{1l}^0(V_{1a}G_{aa} + \sum_b V_{1b}G_{ba}), \quad (7b)$$

and

$$G_{ba} = G_{bb}^0(V_{ba}G_{aa} + \sum_l V_{bl}G_{la} + \sum_{b'} V_{bb'}G_{b'a}), \quad (7c)$$

with $G_{aa} \equiv G_{aa}(E)$, etc.

Solving the coupled equations for the Green function, Eqs (7a)–(7c), we obtain the diagonal matrix element of the Green function G_{aa} as

$$G_{aa}(E) = \left(E - E_a + i\Gamma_a - \sum_b \frac{|V_{ab}|^2}{E - E_b + i\Gamma_b - \sum_{b' \neq b} \frac{|V_{bb'}|^2}{E - E_{b'} + i\Gamma_{b'}}} \right)^{-1}, \quad (8)$$

where

$$E_k = E_k^0 + \sum_{(l)} \frac{|V_{kl}|^2}{E - E_l^0}, \quad (k = a, b, b'), \quad (9)$$

and the half-width at half-maximum originating from the nonadiabatic perturbation is given

$$\Gamma_k = \pi \sum_l |(\mathbf{T}_N)_{kl}|^2 \delta(E - E_l^0), \quad (k = a, b, b'). \quad (10)$$

Substituting Eq. (8) into Eq. (1), the nonradiative decay rate constant from level a , k_{nr} , is given as

$$k_{nr} = (4\pi/\hbar) \left[\Gamma_a + \sum_b \frac{|V_{ab}|^2 \Gamma_b(E_a^0)}{\{E_a^0 - E_b(E_a^0)\}^2 + \Gamma_b^2(E_a^0)} \right], \quad (11)$$

where

$$E_b(E) = E_b + \sum_{b' \neq b} \frac{|V_{bb'}|^2 (E - E_{b'})}{(E - E_{b'})^2 + \Gamma_{b'}^2}, \quad (12)$$

and

$$\Gamma_b(E) = \Gamma_b + \sum_{b' \neq b} \frac{|V_{bb'}|^2 \Gamma_{b'}}{(E - E_{b'})^2 + \Gamma_{b'}^2}. \quad (13)$$

RESULTS AND DISCUSSION

In calculating the half width Γ_k given by Eq. (10), we consider five vibrational modes, ν_1 , ν_2 , ν_4 , ν_{14} and ν_{16} . The modes ν_1 and ν_2 belong to the skeletal and C—H stretching vibrations of the a_{1g} symmetry, respectively, and these are taken to be the displaced modes in this paper. The C—H vibration is assumed to be characterized by a Morse potential.¹⁶ The mode ν_4 is an out-of-plane bending vibration with the b_{2g} symmetry, and characterized by a distorted mode whose frequencies in S_1 and

S_0 are of 365 cm^{-1} and 707 cm^{-1} , respectively. The mode ν_{16} of the e_{2u} symmetry is characterized by a distorted mode whose frequencies in S_1 and S_0 are of 399 cm^{-1} and 237 cm^{-1} , respectively. The mode ν_{14} of the b_{2u} symmetry is a promoting mode for the IC from S_1 to S_0 .

We use the factorization method for evaluating the half width Γ_k (refs^{16,17}). The width within the Condon approximation is then expressed as

$$\Gamma_k = \pi |v_{e1}|^2 \sum_{\{i\}} |\langle \chi_{\nu_{14}} | \frac{\partial}{\partial Q_{14}} | \chi_{\nu'_{14}} \rangle|^2 \prod_{i \neq 1, 14} |\langle \chi_{\nu_i} | \chi_{\nu'_i} \rangle|^2 I_{\nu_i}[\delta E'], \quad (14)$$

where χ_{ν_i} and $\chi_{\nu'_i}$ denote the vibrational wavefunction of the quantum state ν_i and that of ν'_i belonging to the i -th mode, respectively. The matrix element v_{e1} represents the electronic part of the nonadiabatic coupling matrix element. The magnitude of the matrix element is assumed to be $v_{e1} = 2.25 \cdot 10^5 \text{ cm}^{-1}$ which is one order larger than that of the usual vibronic coupling because the non-Condon effect is indirectly taken into account.¹⁸ The term $I_{\nu_i}[\delta E']$ in Eq. (14) is given by

$$I_{\nu_1}(\delta E') = \sum_{n=0}^{\nu_1} \sum_{m=0}^n \sum_{r=0}^m \frac{(-1)^{n+m} 2^{n-m} \nu_1! g^n}{n!(\nu-n)!(n-m)!(m-r)! r!} \times \\ \times \frac{2\pi \exp(-g) g^{(2\pi\delta E'/\hbar\omega_1 - \nu_1 - 1/2 - m + 2r)}}{\hbar\omega_1 \Gamma[1 + (2\pi\delta E'/\hbar\omega_1 - \nu_1 - 1/2 - m + 2r)]}, \quad (15)$$

where g is the coupling strength between S_1 and S_0 defined in terms of the dimensionless displacement of the ν_1 mode, Δ_1 , as $g = \Delta_1^2/2$ (ref.¹⁹). The constant $\delta E'$ is the energy accepted by the ν_1 mode in the course of IC. The term $\Gamma[]$ denotes the Gamma function.

Figure 2 shows the excess energy dependence of the IC rate constants, k_{IC} , defined by $k_{\text{IC}} = 4\pi\Gamma_k/\hbar$. Five quantum states are taken as the initial state a : $6^11^216^1$, $6^11^216^2$, 7^1 , 6^11^3 and $6^11^316^1$, ν_7 being an in-plane vibration with the e_{2g} symmetry. The rate constants from the quantum states $\{b\}$ within the excitation band width of $\pm 1.5 \text{ cm}^{-1}$ around each initial state have been considered in Fig. 2. From this figure we can see that the magnitude of k_{IC} increases on the average as the excess energy does, and there is no drastic increase in k_{IC} around the excess energy of 3000 cm^{-1} . The variation of $10^5 \sim 10^8 \text{ s}^{-1}$ in k_{IC} around each initial state mainly originates from consideration of a restricted number of the vibrational modes adopted in the calculation of Γ_k . As already shown by Hornburger and Brand,^{12,13} the IC rate from the states involving distorted modes such as ν_4 and ν_{16} have a large magnitude of k_{IC} .

Figure 3 shows the excess energy dependence of the nonradiative decay constant calculated by using Eq. (11). The five quantum states mentioned above are taken as

the initial state. The points denoted by the cross sign represent k_{nr} calculated by neglecting the IVR effect. The points denoted by circle and star signs represent, respectively, the rate constants calculated by using the IVR coupling matrix elements $V_{ab} = 0.1 \text{ cm}^{-1}$ and $V_{bb'} = 0$, and $V_{ab} = V_{bb'} = 0.1 \text{ cm}^{-1}$. In the former case the effects of IVR are partially considered. The value of the coupling matrix element for IVR has been estimated from the experimental values by Moss and Parmenter.¹⁰ We use this value as an average magnitude of the coupling matrix element between the quantum states in S_1 within a frequency range excited by a pulse laser. The quantum states are directly counted by taking into account all the vibrational modes within the harmonic approximation. The values of Γ_b and $\Gamma_{b'}$ are taken from by averaging over the IC rates from the levels within the laser band width. The drastic decrease of the nonradiative decay constant from 7^1 level comes from the fact that the line width of 7^1 level is equal to that of the zero point level in S_1 if the potential of the ν_7 mode is assumed to be identical in S_1 and S_0 states.

Figure 4 shows the excess energy dependence on the nonradiative decay constant calculated by using the fluorescence life-times which have been measured by Yoshihara's group²⁰. The various marks in this figure are the same as those in Fig. 3, that is, the crosses denote the rate constants calculated by neglecting the IVR process, the circles and stars refer to the k_{nr} evaluated with $V_{ab} = 0.1 \text{ cm}^{-1}$ and $V_{bb'} = 0$ and those with $V_{ab} = V_{bb'} = 0.1 \text{ cm}^{-1}$, respectively. The values of k_{nr} obtained from the absorption line width measured by Callomon et al.³ are represented by triangles. The k_{nr} calculated including the IVR effects has the excess energy dependence similar to the observed values by Callomon et al.³ with respect to onset of the drastic increase and saturation phenomena in k_{nr} .

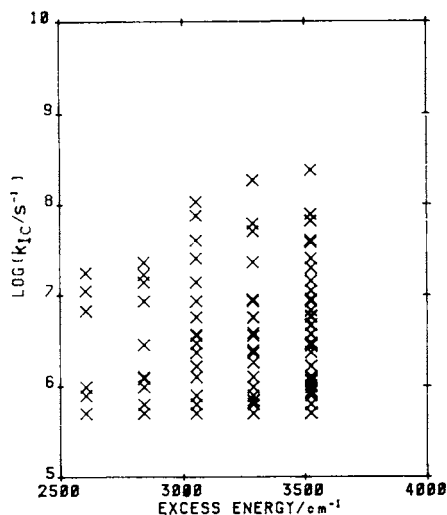


FIG. 2

Calculated excess energy dependence on the internal conversion rate k_{IC}

Figure 4 demonstrates that there exists a difference of two orders of magnitude in k_{nr} depending on the methods of the measurement of the excited states, for example, fluorescence decay or absorption measurement. This is experimentally shown by Moss and Parmenter.¹⁰ The above trend of k_{nr} indicates the similar excess energy threshold for the IC and IVR processes. This causes the drastic increase in k_{nr} at about $3\,000\text{ cm}^{-1}$ excess energy.

It is interesting to investigate the mechanism of the drastic increase of k_{IC} . One possibility is due to a surface crossing between S_1 and S_0 states. We have calculated the potential surfaces of both states by using the *ab initio* SCFMO method with the 4-31G basis set combined with the Brillouin–Wigner many body perturbative CI procedure, and have obtained a crossing point at the excess energy of about $20\,000\text{ cm}^{-1}$ in S_1 state which is much higher than the excess energy of $3\,000\text{ cm}^{-1}$. Therefore, a simple internal conversion in the strong coupling case is ruled out.

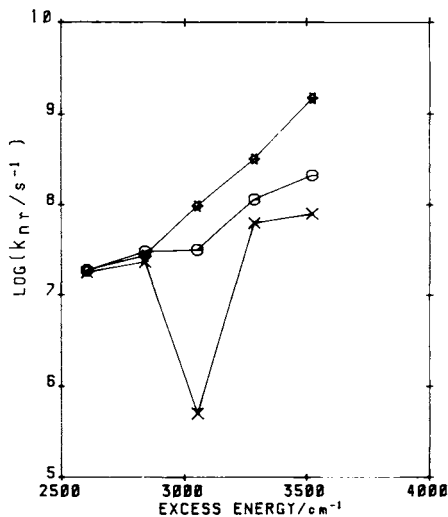


FIG. 3

Excess energy dependence on the nonradiative decay constant k_{nr} calculated using k_{IC} presented in Fig. 2. The cross sign denotes the k_{IC} . Circles and stars refer to k_{nr} calculated with IVR matrix elements, $V_{ab} = 0.1\text{ cm}^{-1}$ and $V_{bb'} = 0$, and $V_{ab} = 0.1\text{ cm}^{-1}$ and $V_{bb'} = 0.1\text{ cm}^{-1}$, respectively

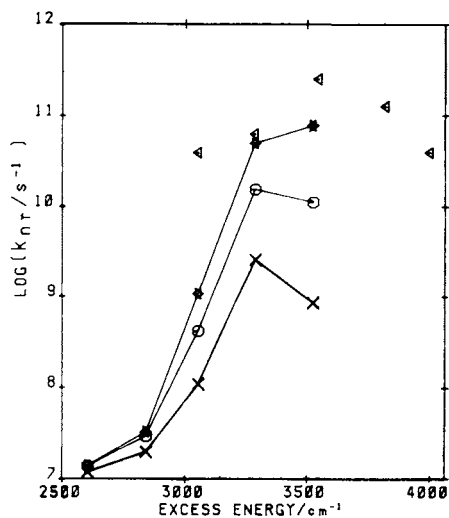


FIG. 4

Excess energy dependence on k_{nr} calculated with k_{IC} estimated from the experimental data. The cross sign denotes the k_{IC} . Circles and stars refer to k_{nr} calculated with IVR matrix elements $V_{ab} = 0.1\text{ cm}^{-1}$ and $V_{bb'} = 0$, and $V_{ab} = V_{bb'} = 0.1\text{ cm}^{-1}$, respectively. For comparison, experimental values of k_{nr} evaluated from the absorption line shape are shown by triangles

Other mechanisms such as photochemical isomerizations in S_1 state reaction may be included.

In summary, in this paper, we have applied the time-independent Green function formalism to the calculation of the excess energy dependence on k_{nr} in the S_1 state of benzene. In this formulation effects of both IC and IVR processes are taken into account at the same time. It is demonstrated from the model calculations of the nonradiative decay constant that the drastic increase in k_{nr} at around $3\,000\text{ cm}^{-1}$ excess energy originates from the same onset for both IC and IVR rate constants. The existence of the two order difference between the IVR and IC rate constants observed by Moss and Parmenter¹⁰ is also theoretically explained by using the rate expression for k_{nr} derived in this paper.

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