

# Effects of Anharmonicity on Non-Radiative Transitions in Polyatomic Molecules

Noriyuki Shimakura, Yuichi Fujimura, and Takeshi Nakajima

Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan

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The effect of anharmonicity on the non-radiative transition in large molecules is examined within the Morse potential surface model. The vibrational wavefunctions are assumed to be the product of the harmonic and Morse oscillator wavefunctions. The method of factorization introduced by Gelbart *et al.* is used for the evaluation of a density weighted Franck-Condon factor. As an example, we choose the intersystem crossing  ${}^3B_{1u} \rightarrow {}^1A_{1g}$  in benzene. The numerical calculation shows that the anharmonicity causes an increase by a numerical factor  $\sim 10^3$  in the non-radiative transition rate. The electronic energy distribution over the vibrational modes in the final state is determined and compared with that obtained using the harmonic potential surface model.

*Key words:* Radiationless transitions – Electronic relaxation – Polyatomic molecules

## 1. Introduction

Although a considerable amount of theoretical investigations on intramolecular non-radiative transitions has been made and various formulas for the non-radiative transition rate have been proposed, there have so far been few actual calculations of the absolute non-radiative transition rates in a particular molecule which allow a direct comparison with the available experimental data. It seems that there remain many problems which must be clarified from the theoretical point of view in order to obtain the absolute non-radiative transition rates. The problem of effects of anharmonicity on the non-radiative transition is the important one among these problems.

Burland and Robinson [1] have calculated the non-radiative transition rates for the internal conversion between the  ${}^1B_{2u}(S_1)$  and  ${}^1A_{1g}(S_0)$  states and the intersystem crossing between the  ${}^3B_{1u}(T_1)$  and  ${}^1A_{1g}(S_0)$  states in benzene and deuterobenzene using a so-called density of states model. They assumed both harmonic and anharmonic vibrational potentials. The anharmonicity was restricted to either cubic or quartic terms in the potential energy. The large polyacenes have a large number of accepting modes operating effectively and we can calculate the rate using such a model. In the case of the molecules classified as the intermediate case like benzene, however, the number of accepting modes to be considered is restricted and the density of states model is not expected to give satisfactory results.

Nitzan and Jortner [2] have also calculated the relaxation rate for the  ${}^3B_{1u} \rightarrow {}^1A_{1g}$  intersystem crossing in benzene and deuterobenzene using a dynamic

model. In their treatment, the vibrational wavefunctions were approximated by the harmonic oscillator wavefunctions.

Fischer's [3] is the only theory of non-radiative transition rate in which the inclusion of the effects of anharmonicity is attempted within the dynamical model. However, the theory was criticized from the viewpoint of unjustified expansion of the generating function [2]. Furthermore, he considered only cubic anharmonicity [4].

In this paper, we attempt to circumvent these difficulties by the use of Morse potentials. We neglect the anharmonic coupling between normal modes. The method of factorization introduced by Gelbart *et al.* [5] for the evaluation of the density weighted Franck-Condon factor is used to examine the effect of anharmonicity on the non-radiative transition. We also determine the electronic energy distribution over the different normal modes and discuss the validity of the most probable path method. As an example we choose the intersystem crossing  ${}^3B_{1u} \rightarrow {}^1A_{1g}$  in benzene since in this case all the parameters needed in determining the Franck-Condon factors are well known and we can easily compare the results with the experimental information.

## 2. The Non-Radiative Transition Rate

In the statistical limit the non-radiative transition rate from the vibrationless state of the electronic state  $s$ ,  $|s_0\rangle$ , to the manifold of the vibronic states,  $\{|l_j\rangle\}$ , can be written in the form of the Fermi golden rule [6]

$$W_{s \rightarrow l} = (2\pi/\hbar) \sum_j |\langle l_j | V | s_0 \rangle|^2 \delta(E_{s_0} - E_{l_j}), \quad (1)$$

where  $V$  is the interaction Hamiltonian. Assuming that the vibrational modes are mutually independent we employ the partitioning technique to separate any modes of interest from other modes and rewrite Eq. (1) as follows:

$$W_{s \rightarrow l} = (|C_{si}^\kappa|^2/\hbar^2) \sum_{\{v_i\}} |\langle v_1 | 0 \rangle|^2 \cdots |\langle v_i | 0 \rangle|^2 I[\Delta E], \quad (2)$$

where  $C_{si}^\kappa$  is the electronic coupling matrix element induced by the promoting mode  $\kappa$  and  $v_i$  is the vibrational quantum number of the separated mode  $i$ . The integral  $I[\Delta E]$ , which corresponds to a density weighted Franck-Condon factor for the remaining vibrational modes, is given by

$$I[\Delta E] = \int_{-\infty}^{\infty} dt f(t) \exp(-i\Delta E t/\hbar), \quad (3a)$$

where

$$\Delta E = \Delta E^0 + \frac{1}{2}\hbar \sum_j (\omega_{sj} - \omega_{lj}) - \sum_i v_i \hbar \omega_{li}, \quad (3b)$$

and

$$f(t) = f_\kappa(t) \prod_{j \neq \kappa, (i)} f_j(t). \quad (3c)$$

$\Delta E^0$  is the energy difference between the potential minima of the two electronic states and  $\omega_{sj}$  and  $\omega_{lj}$  are vibrational frequencies of the  $j^{\text{th}}$  mode in the initial and final electronic states, respectively. The generating functions for  $\kappa^{\text{th}}$  and  $j^{\text{th}}$

modes are given by

$$f_x(t) = \beta_x^{\frac{1}{2}} [A_x(t)]^3 \exp(i\omega_{ix}t), \quad (4a)$$

and

$$f_j(t) = A_j(t) \exp[-H_j(t)]. \quad (4b)$$

Here

$$A_j(t) = \left\{ \beta_j + \frac{(1 - \beta_j)^2}{4} [1 - \exp(2i\omega_{ij}t)] \right\}^{-\frac{1}{2}}, \quad (5a)$$

and

$$H_j(t) = \frac{\beta_j \Delta_j^2 [1 - \exp(i\omega_{ij}t)]}{1 + \beta_j + (\beta_j - 1) \exp(i\omega_{ij}t)}, \quad (5b)$$

where

$$\Delta_j = \left( \frac{M_j \omega_{ij}}{\hbar} \right)^{\frac{1}{2}} \Delta Q_j. \quad (5c)$$

The parameters,  $\Delta Q_j (= Q_{sj}^o - Q_{lj}^o)$  and  $\beta_j$ , indicate the displacement and frequency ratio between initial and final states.

### 3. The Intersystem Crossing ${}^3B_{1u} \rightarrow {}^1A_{1g}$ in Benzene

For the intersystem crossing  ${}^3B_{1u} \rightarrow {}^1A_{1g}$  in benzene, the C–H and C–C totally symmetric stretching modes and the  $b_{2g}$  out-of-plane mode ( $\omega_{1b_{2g}} = 705 \text{ cm}^{-1}$ ) are considered as effective accepting modes. In this case, totally symmetric modes have non-zero displacement between the two electronic states<sup>1</sup> and the  $b_{2g}$  out-of-plane mode has the largest frequency change<sup>2</sup>. We separate the C–H and C–C totally symmetric stretching modes from the  $b_{2g}$  mode, since anharmonicities of the former are considered to be markedly effective as compared with that of the latter. Thus, Eq. (1) is transformed as follows:

$$W_{T_1 \rightarrow S_0} = (|C_{T_1, S_0}^x|^2 / \hbar^2) \sum_{v_1} \sum_{v_2} |\langle v_1 | 0 \rangle|^2 \times |\langle v_2 | 0 \rangle|^2 \cdot I[\Delta E^x(b_{2g})], \quad (6)$$

where  $v_1$  and  $v_2$  are the vibrational quantum numbers of the C–H and C–C totally symmetric modes in the final electronic state,  $S_0$ , and  $\Delta E^x(b_{2g})$  is the effective energy gap to be accepted by the  $b_{2g}$  mode. Also we neglect the frequency change for the nontotally symmetric promoting mode, the  $b_{2u}$  C–C stretching mode, and the integral  $I[\Delta E(b_{2g})]$  is given by

$$I[\Delta E(b_{2g})] = \int_{-\infty}^{\infty} dt f_{b_{2g}}(t) \exp[-i \Delta E^x(b_{2g})t/\hbar], \quad (7)$$

where

$$\Delta E^x(b_{2g}) = \Delta E - \hbar\omega_{ix}.$$

Thus, the effects of anharmonicity can simply be accounted for by pulling out the Franck-Condon factors of C–H and C–C totally symmetric modes<sup>3</sup>. However, since the effective energy gap  $\Delta E^x(b_{2g})$  may be small because of the possible large energy acceptance of the separated modes, we must evaluate the vibrational integral Eq. (7) exactly. The density weighted Franck-Condon factor

<sup>1</sup> In this paper we neglect the displacement of the  $e_{2g}$  mode.

<sup>2</sup> If it is proved that the  $b_{2g}$  mode is more effective accepting mode than totally symmetric modes, other distorted modes must be considered. In general, however, the C–H totally symmetric mode is the most effective accepting mode.

<sup>3</sup> Only totally symmetric modes act as Morse oscillators.

for the  $b_{2g}$  mode whose potential is considered to be distorted can be written as follows:

$$I[\Delta E^\times(b_{2g})] = (2\pi^{\frac{1}{2}}/\omega_{1b_{2g}}) \left( \frac{1}{1+\beta} \right) \left( \frac{1-\beta}{1+\beta} \right)^{\Delta E^\times(b_{2g})/\hbar\omega_{1b_{2g}}} \times \frac{\Gamma[1/2 + \Delta E^\times(b_{2g})/2\hbar\omega_{1b_{2g}}]}{\Gamma[1 + \Delta E^\times(b_{2g})/2\hbar\omega_{1b_{2g}}]}. \quad (8)$$

#### 4. Evaluation of Franck-Condon Factors Using the Morse Function

In order to evaluate the Franck-Condon factors of the totally symmetric vibrational modes, we assume that the potential curves of the two electronic states are in the form of the Morse potential

$$U_{n\mu}(R_\mu) = D_{n\mu} \{1 - \exp[-\alpha_{n\mu}(R_\mu - R_{n\mu}^o)]\}^2. \quad (9)$$

Here  $D_{n\mu}$  is a dissociation energy and  $\alpha_{n\mu}$  is a constant referred to the  $\mu$ -th mode in the electronic state  $n$ . The corresponding vibrational wavefunction  $\chi_{n\mu}$  takes the following form [7]:

$$\chi_{n\mu} = \left[ \frac{\alpha_{n\mu}(K_{n\mu} - 2v_{n\mu} - 1)}{v_{n\mu}! \Gamma(K_{n\mu} - v_{n\mu})} \right]^{1/2} \exp(-Z_{n\mu}/2) Z_{n\mu}^{(K_{n\mu} - 2v_{n\mu} - 1)/2} \times \sum_k^{v_{n\mu}} (-1)^{k+v_{n\mu}} \binom{v_{n\mu}}{k} \frac{\Gamma(K_{n\mu} - v_{n\mu})}{\Gamma(K_{n\mu} - v_{n\mu} - k)} (Z_{n\mu})^{v_{n\mu} - k}, \quad (10)$$

where  $\Gamma(x)$  is the gamma function and  $Z_{n\mu} = K_{n\mu} \exp[-\alpha_{n\mu}(R_\mu - R_{n\mu}^o)]$ .  $K_{n\mu}$  and  $D_{n\mu}$  are related to the constants appeared in the expression for the vibrational energy

$$E_{n\mu}(v_{n\mu}) = \hbar\omega_{n\mu}(v_{n\mu} + \frac{1}{2}) - \hbar\omega_{n\mu}x_{n\mu}(v_{n\mu} + \frac{1}{2})^2, \quad (11a)$$

$$K_{n\mu} = \frac{\hbar\omega_{n\mu}}{\hbar\omega_{n\mu}x_{n\mu}}, \quad D_{n\mu} = \frac{(\hbar\omega_{n\mu})^2}{4\hbar\omega_{n\mu}x_{n\mu}}, \quad \hbar\omega_{n\mu}x_{n\mu} = \frac{\hbar^2}{4\pi c M_{n\mu}} \alpha_{n\mu}^2, \quad (11b)$$

where  $M_{n\mu}$  is the effective mass and  $\omega_{n\mu}x_{n\mu}$  is the anharmonic parameter of the  $\mu$ th normal mode in the  $n$  electronic state. The vibrational overlap integral between the initial and final electronic states,  $s$  and  $l$ , is

$$S(v_{s\mu}, v_{l\mu}) = \int dR_\mu \chi_{l\mu}^* \chi_{s\mu}, \quad (12a)$$

and the Franck-Condon factor is

$$F(v_{s\mu}, v_{l\mu}) = |S(v_{s\mu}, v_{l\mu})|^2, \quad (12b)$$

where  $v_{s\mu}$  and  $v_{l\mu}$  are the vibrational quantum numbers of the  $\mu$ th mode in the  $s$  and  $l$  electronic states, respectively. Since for  $\alpha_{s\mu} \neq \alpha_{l\mu}$  the integral in Eq. (12a) cannot be performed analytically, it is necessary to resort to an approximate analytical formula for the overlap integral. The approximation used by Makshantsev and Pertnev [8] is to replace the potential of the initial electronic state by the potential

$$U_{s\mu}(R_\mu) \approx D' \{1 - \exp[-\alpha_{l\mu}(R_\mu - R_{s\mu}^o)]\}^2, \quad (13a)$$

where

$$D' = D_{s\mu} (\alpha_{s\mu}/\alpha_{l\mu})^2. \quad (13b)$$

Then, we have

$$K' = K_{s\mu} (\alpha_{s\mu}/\alpha_{l\mu})^2. \quad (13c)$$

It is possible to examine the error caused by the replacement of Eq. (9) by Eq. (13a); Eqs. (9) and (13a) can be expanded as follows:

$$U_{s\mu}(R_\mu) = D_{s\mu} \alpha_{s\mu}^2 (R_\mu - R_{s\mu}^o)^2 - D_{s\mu} \alpha_{s\mu}^3 (R_\mu - R_{s\mu}^o)^3 + \dots \quad (14a)$$

$$U_{s\mu}(R_\mu) \approx D_{s\mu} \alpha_{s\mu}^2 (R_\mu - R_{s\mu}^o)^2 - D_{s\mu} \alpha_{s\mu}^2 \alpha_{l\mu} (R_\mu - R_{s\mu}^o)^3 + \dots \quad (14b)$$

The first term of Eq. (14b) is just that of Eq. (14a). The expansion coefficients in Eq. (14b) involve the power of  $\alpha_{l\mu}$  except for the first term. The deviation of the approximate potential from the original one is larger in higher terms than in lower terms.

Further Makshantsev and Perstnev assumed that the main contribution to the sum in Eq. (10) is made by terms with small  $k$  or with  $k$  values close to  $v_{n\mu}$ . However, this approximation gave satisfactory results only for the case in which the difference of frequency is large between the initial and final electronic states. In the case of small frequency changes (observed generally in polyatomic molecules), we must sum every terms.

The integration in Eq. (12a) gives the expression:

$$\begin{aligned} S(v_{s\mu}, v_{l\mu}) &= \left[ \frac{(K' - 2v_{s\mu} - 1)(K_{l\mu} - 2v_{l\mu} - 1)}{v_{s\mu}! v_{l\mu}!} \right]^{\frac{1}{2}} \\ &\times (-1)^{v_{s\mu} + v_{l\mu}} \exp[-\alpha_{l\mu} \Delta Q_\mu (K_{l\mu} - 1)/2] \\ &\times (K')^{(K' - 1)/2} (K_{l\mu})^{(K_{l\mu})/2} \\ &\times \left( \frac{2}{K' + K_{l\mu} \exp(-\alpha_{l\mu} \Delta Q_\mu)} \right)^{(K' - K_{l\mu} - 2)/2} \\ &\times \sum_k^{v_{s\mu}} \sum_{k'}^{v_{l\mu}} (-1)^{k+k'} \binom{v_{s\mu}}{k} \binom{v_{l\mu}}{k'} \\ &\times \exp(k' \alpha_{l\mu} \Delta Q_\mu) (K')^{-k} (K_{l\mu})^{-k'} \\ &\times \left( \frac{2}{K' + K_{l\mu} \exp(-\alpha_{l\mu} \Delta Q_\mu)} \right)^{-(k+k')} \\ &\times \left[ \frac{1}{\Gamma(K' - v_{s\mu}) \Gamma(K_{l\mu} - v_{l\mu})} \right]^{\frac{1}{2}} \\ &\times \frac{\Gamma(K' - v_{s\mu}) \Gamma(K_{l\mu} - v_{l\mu})}{\Gamma(K' - v_{s\mu} - k) \Gamma(K_{l\mu} - v_{l\mu} - k')} \\ &\times \Gamma([K' + K_{l\mu} - 2k - 2k' - 2]/2), \end{aligned} \quad (15a)$$

where

$$\Delta Q_\mu = R_{s\mu}^o - R_{l\mu}^o. \quad (15b)$$

The anharmonic parameter for the initial state vanishes in Eq. (15a) because  $K'$  is written as follows:

$$\begin{aligned} K' &= K_{s\mu} (\alpha_{s\mu}/\alpha_{l\mu})^2 = (\hbar\omega_{s\mu}/\hbar\omega_{s\mu} x_{s\mu}) (\hbar\omega_{s\mu} x_{s\mu}/\hbar\omega_{l\mu} x_{l\mu}) \\ &= (\hbar\omega_{s\mu}/\hbar\omega_{l\mu} x_{l\mu}). \end{aligned} \quad (16)$$

The parameters necessary for calculating the Franck-Condon factors are thus reduced to  $K'$ ,  $K_{l\mu}$ ,  $\alpha_{l\mu}$ , and  $\Delta Q_\mu$ . It is a marked characteristic of our method that the anharmonic parameter is necessary only for the lower electronic state.

Table 1. Franck-Condon factors for the  $A^2\Sigma \rightarrow X^2\Pi$  transition in the NO molecule<sup>a</sup>

$v_{s\mu}^b$ \ / \ $v_{l\mu}^c$	0	1	2	3
0	0.16139 (0.16345) <sup>d</sup>	0.32236 (0.32560)	0.28914 (0.29009)	0.15472 (0.15275)
1	0.26290 (0.26351)	0.10856 (0.10683)	0.01107 (0.01279)	0.17687 (0.18377)
2	0.23948 (0.23900)	0.00046 (0.00064)	0.15143 (0.15308)	0.05540 (0.05176)
3	0.16230 (0.16159)	0.07098 (0.07209)	0.07883 (0.07667)	0.03163 (0.03480)
4	0.09160 (0.09110)	0.13611 (0.13629)	0.00093 (0.00064)	
5	0.04572 (0.04546)	0.13608 (0.13540)	0.03340 (0.03467)	
6	0.02094 (0.02082)	0.10011 (0.09928)	0.08941 (0.09007)	
7	0.00901 (0.00897)	0.06135 (0.06072)	0.10781 (0.10741)	
8	0.00371 (0.00369)	0.03332 (0.03294)	0.09180 (0.09090)	
9	0.00148 (0.00147)	0.01665 (0.01644)	0.06387 (0.06298)	
10	0.00058 (0.00057)	0.00783 (0.00772)	0.03892 (0.03826)	
11	0.00022 (0.00022)	0.00353 (0.00347)	0.02163 (0.02121)	
12	0.00008 (0.00008)			
13	0.00003 (0.00003)			

<sup>a</sup> Eq. (15a) with the following parameters [9]:  $\omega_{s\mu} = 2371.3 \text{ cm}^{-1}$ ,  $\omega_{s\mu} x_{s\mu} = 14.48 \text{ cm}^{-1}$ ,  $\omega_{l\mu} = 1903.9 \text{ cm}^{-1}$ ,  $\omega_{l\mu} x_{l\mu} = 13.97 \text{ cm}^{-1}$ ,  $\Delta Q_{\mu} = 0.0871 \text{ \AA}$ ,  $\alpha_{l\mu} = 2.489 \text{ \AA}^{-1}$ ,  $K_{s\mu} = 136$ .

<sup>b</sup> Vibrational quantum number in  $A^2\Sigma$  state.

<sup>c</sup> Vibrational quantum number in  $X^2\Pi$  state.

<sup>d</sup> Values of the Franck-Condon factor, taken from [9], are given in parentheses.

## 5. Results and Discussion

In order to examine the validity of the present method, we first calculate Franck-Condon factors for the  $A^2\Sigma \rightarrow X^2\Pi$  transition in the NO molecule using Eq. (15a). Assuming a Morse potential, Ortenberg has calculated the Franck-Condon factors for this transition by the numerical integration. The present results obtained using the same parameter values as used by Ortenberg are given in Table 1, together with the previous results. The Franck-Condon factors are in good agreement with those calculated by the numerical integration. We notice that Eq. (15a) obtained with the approximate potential Eq. (13a) is applicable

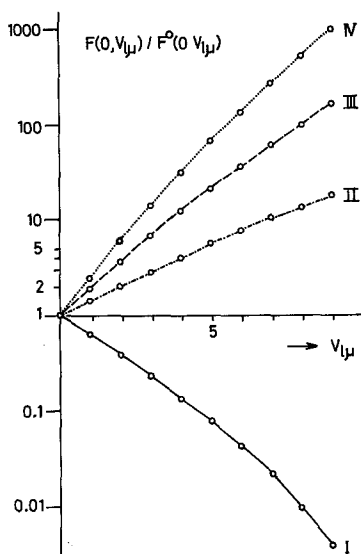


Fig. 1. Dependence of relative Franck-Condon factors on displacement. Results obtained using Eq. (15a) with the following parameters:  $\omega_{lu} = 3063 \text{ cm}^{-1}$ ,  $\omega_{su} = 3130 \text{ cm}^{-1}$ ,  $\alpha_{lu} = 0.714 \text{ \AA}^{-1}$ ,  $\omega_{lu} x_{lu} = 9.2 \text{ cm}^{-1}$ .  $F^0(0, v_{l\mu})$ :  $\Delta Q_{\mu} = -0.0343 \text{ \AA}$ .  $F(0, v_{l\mu})$  I:  $\Delta Q_{\mu} = -0.0269 \text{ \AA}$ .  $F(0, v_{l\mu})$  II:  $\Delta Q_{\mu} = -0.0416 \text{ \AA}$ .  $F(0, v_{l\mu})$  III:  $\Delta Q_{\mu} = -0.0490 \text{ \AA}$ .  $F(0, v_{l\mu})$  IV:  $\Delta Q_{\mu} = -0.0563 \text{ \AA}$ .

even to the cases in which the vibrational quantum numbers in the initial electronic state are fairly large.

It is obvious from Eq. (15a) that for  $K' = K_{l\mu}$ , the Franck-Condon factor satisfies the following relation.

$$F(v_{s\mu}, v_{l\mu}; \Delta Q_{\mu}) = F(v_{l\mu}, v_{s\mu}; -\Delta Q_{\mu})$$

That is to say, the Franck-Condon factors,  $F(v_{s\mu}, v_{l\mu})$ , and  $F(v_{l\mu}, v_{s\mu})$ , are equal, when the displacements are equal in magnitude and opposite in sign.

In Figs. 1, 2, and 3, we display the dependence of the Franck-Condon factors on the vibrational quantum numbers of the final state and, at the same time, on the displacements, vibrational frequencies, and anharmonic parameters. We choose the C-H totally symmetric mode in benzene as a relevant mode and vary the parameter values around the reference ones corresponding to the  $T_1 \rightarrow S_0$  transition. From these figures we can remark the following points about the Franck-Condon factors of the Morse function.

1) The Franck-Condon factor depends on the displacement in a monotonous manner (see Fig. 1).

2) Both the decrease in the initial state (see Fig. 2a) and the increase in the final state (see Fig. 2d) of the vibrational frequency strongly influence the Franck-Condon factor in a similar way. On the other hand, the increase in the initial state (see Fig. 2b) and the decrease in the final state (see Fig. 2c) affect the Franck-Condon factor in a complicated manner.

3) The variation of the anharmonic parameter from 5.2 to 14.2 does not produce a significant effect on the Franck-Condon factor (see Figs. 3a and 3b).

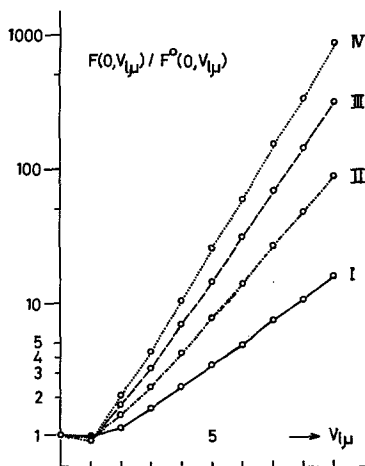


Fig. 2a

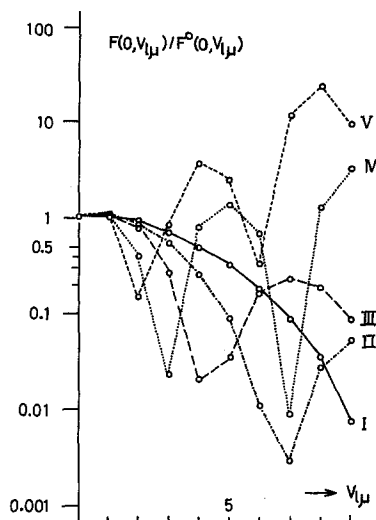


Fig. 2b

Fig. 2a. Dependence of relative Franck-Condon factors on the vibrational frequency in the initial state. Results obtained using Eq. (15a) with the following parameters:  $\omega_{l\mu} = 3063 \text{ cm}^{-1}$ ,  $\Delta Q_{\mu} = -0.0343 \text{ \AA}$ ,  $\alpha_{l\mu} = 0.714 \text{ \AA}^{-1}$ ,  $\omega_{l\mu} x_{l\mu} = 9.2 \text{ cm}^{-1}$ .  $F^0(0, v_{l\mu})$ :  $\omega_{s\mu} = 3130 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  I:  $\omega_{s\mu} = 3082 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  II:  $\omega_{s\mu} = 3036 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  III:  $\omega_{s\mu} = 2990 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  IV:  $\omega_{s\mu} = 2944 \text{ cm}^{-1}$

Fig. 2b. Dependence of relative Franck-Condon factors on the vibrational frequency in the initial state. Results obtained using Eq. (15a) with the following parameters:  $\omega_{l\mu} = 3063 \text{ cm}^{-1}$ ,  $\Delta Q_{\mu} = -0.0343 \text{ \AA}$ ,  $\alpha_{l\mu} = 0.714 \text{ \AA}^{-1}$ ,  $\omega_{l\mu} x_{l\mu} = 9.2 \text{ cm}^{-1}$ .  $F^0(0, v_{l\mu})$ :  $\omega_{s\mu} = 3130 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  I:  $\omega_{s\mu} = 3156 \text{ cm}^{-1}$ .  $F^0(0, v_{l\mu})$  II:  $\omega_{s\mu} = 3174 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  III:  $\omega_{s\mu} = 3210 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  IV:  $\omega_{s\mu} = 3321 \text{ cm}^{-1}$ .  $F(0, v_{sl\mu})$  V:  $\omega_{s\mu} = 3450 \text{ cm}^{-1}$

This means that the Franck-Condon factor is rather insensitive to the variation of the value of the anharmonic parameter around the reference value. On the other hand, the variation of the vibrational frequency gives a relatively remarkable effect on the Franck-Condon factor.

We will now calculate the intersystem crossing rate from the vibrationless level of the  ${}^3B_{1u}$  state to the ground state in benzene, using Eqs. (6) and (8) for the non-radiative transition rate and Eqs. (12b) and (15a) for the Franck-Condon factor of the Morse potential. We consider the  $b_{2u}$  C-C stretching mode ( $\omega_{b_{2u}} = 1313 \text{ cm}^{-1}$ ) as the promoting mode. We use the same parameter values as those used by Burland and Robinson except for anharmonic parameters of the C-H totally symmetric mode. They analyzed the phosphorescence and fluorescence intensities of benzene in the crystal phase and found a value of  $\omega_1 x_1 = 12.6 \text{ cm}^{-1}$  for the anharmonic parameter of the C-H mode in the ground state. The analysis of the infrared spectra by Henry and Siebrand suggests the value of  $\omega_1 x_1 = 9.2 \text{ cm}^{-1}$ . We feel that the latter is better. The anharmonic parameter for the C-C breathing mode is found to be  $\omega_2 x_2 = 1.28 \text{ cm}^{-1}$  in crystal phase and  $\omega_2 x_2 = 0.98 \text{ cm}^{-1}$  in gas phase by Burland and Robinson. These values are fairly small, so that, in our calculation, the anharmonicity of the C-C breathing mode is neglected.



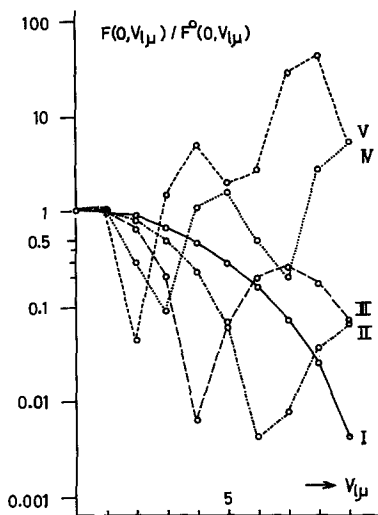


Fig. 2c

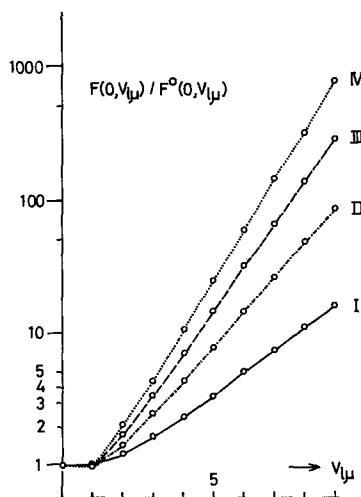


Fig. 2d

Fig. 2c. Dependence of relative Franck-Condon factors on the vibrational frequency in the final state. Results obtained using Eq. (15a) with the following parameters:  $\omega_{s\mu} = 3130 \text{ cm}^{-1}$ ,  $\Delta Q_{\mu} = -0.0343 \text{ \AA}$ ,  $\alpha_{l\mu} = 0.714 \text{ \AA}^{-1}$ ,  $\omega_{l\mu} x_{l\mu} = 9.2 \text{ cm}^{-1}$ .  $F^0(0, v_{l\mu})$ :  $\omega_{l\mu} = 3063 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  I:  $\omega_{l\mu} = 3027 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  II:  $\omega_{l\mu} = 3008 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  III:  $\omega_{l\mu} = 2972 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  IV:  $\omega_{l\mu} = 2861 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  V:  $\omega_{l\mu} = 2732 \text{ cm}^{-1}$

Fig. 2d. Dependence of relative Franck-Condon factors on the vibrational frequency in the final state. Results obtained using Eq. (15a) with the following parameters:  $\omega_{s\mu} = 3130 \text{ cm}^{-1}$ ,  $\Delta Q_{\mu} = -0.0343 \text{ \AA}$ ,  $\alpha_{l\mu} = 0.714 \text{ \AA}^{-1}$ ,  $\omega_{l\mu} x_{l\mu} = 9.2 \text{ cm}^{-1}$ .  $F^0(0, v_{l\mu})$ :  $\omega_{l\mu} = 3063 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  I:  $\omega_{l\mu} = 3100 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  II:  $\omega_{l\mu} = 3146 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  III:  $\omega_{l\mu} = 3192 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  IV:  $\omega_{l\mu} = 3238 \text{ cm}^{-1}$

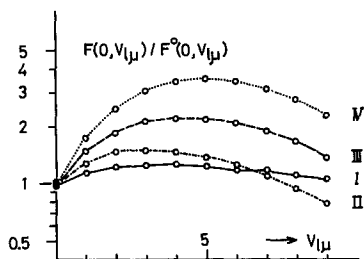


Fig. 3a

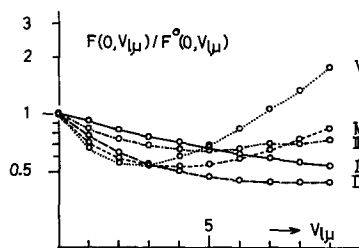


Fig. 3b

Fig. 3a. Dependence of relative Franck-Condon factors on anharmonic parameters. Results obtained using Eq. (15a) with the following parameters:  $\omega_{s\mu} = 3130 \text{ cm}^{-1}$ ,  $\omega_{l\mu} = 3063 \text{ cm}^{-1}$ ,  $\Delta Q_{\mu} = -0.0343 \text{ \AA}$ .  $F^0(0, v_{l\mu})$ :  $\omega_{l\mu} x_{l\mu} = 9.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  I:  $\omega_{l\mu} x_{l\mu} = 8.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  II:  $\omega_{l\mu} x_{l\mu} = 7.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  III:  $\omega_{l\mu} x_{l\mu} = 6.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  IV:  $\omega_{l\mu} x_{l\mu} = 5.2 \text{ cm}^{-1}$

Fig. 3b. Dependence of relative Franck-Condon factors on anharmonic parameters. Results obtained using Eq. (15a) with the following parameters:  $\omega_{s\mu} = 3130 \text{ cm}^{-1}$ ,  $\omega_{l\mu} = 3063 \text{ cm}^{-1}$ ,  $\Delta Q_{\mu} = -0.343 \text{ \AA}$ .  $F^0(0, v_{l\mu})$ :  $\omega_{l\mu} x_{l\mu} = 9.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  I:  $\omega_{l\mu} x_{l\mu} = 10.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  II:  $\omega_{l\mu} x_{l\mu} = 11.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  III:  $\omega_{l\mu} x_{l\mu} = 12.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  IV:  $\omega_{l\mu} x_{l\mu} = 13.2 \text{ cm}^{-1}$ .  $F(0, v_{l\mu})$  V:  $\omega_{l\mu} x_{l\mu} = 14.2 \text{ cm}^{-1}$

Table 2. Contributions of the energy distributions in the final electronic state to the total non-radiative transition rate<sup>a</sup>. Case A: Harmonic oscillator approximation<sup>b</sup>

CH-T <sub>s</sub> <sup>c</sup>		CC-T <sub>s</sub>		Out-of-plane	W <sub>T<sub>1</sub>→S<sub>0</sub></sub> (sec <sup>-1</sup> )		
v <sub>1</sub>	$ \langle v_1 0\rangle ^2$ <sup>d</sup>	v <sub>2</sub>	$ \langle v_2 0\rangle ^2$ <sup>e</sup>	I'[ΔE(b <sub>2g</sub> )] <sup>f</sup>			
8	$5.29 \times 10^{-16}$	1	$3.53 \times 10^{-1}$	$6.30 \times 10^{-3}$	$1.77 \times 10^{-10}$		
		2	$2.02 \times 10^{-1}$	$3.80 \times 10^{-2}$	$6.08 \times 10^{-10}$		
		3	$8.14 \times 10^{-2}$	$2.53 \times 10^{-1}$	$1.63 \times 10^{-9}$		
7	$1.33 \times 10^{-14}$	3	$8.14 \times 10^{-2}$	$9.31 \times 10^{-4}$	$1.51 \times 10^{-10}$		
		4	$2.60 \times 10^{-2}$	$5.31 \times 10^{-3}$	$2.75 \times 10^{-10}$		
		5	$6.99 \times 10^{-3}$	$3.20 \times 10^{-2}$	$4.45 \times 10^{-10}$		
		6	$1.64 \times 10^{-3}$	$2.10 \times 10^{-1}$	$6.86 \times 10^{-9}$		
6	$1.87 \times 10^{-12}$	4	$2.60 \times 10^{-2}$	$2.60 \times 10^{-5}$	$1.89 \times 10^{-10}$		
		5	$6.99 \times 10^{-3}$	$1.41 \times 10^{-4}$	$2.75 \times 10^{-10}$		
		6	$1.64 \times 10^{-3}$	$7.92 \times 10^{-4}$	$3.64 \times 10^{-10}$		
		7	$3.46 \times 10^{-4}$	$4.51 \times 10^{-3}$	$4.37 \times 10^{-10}$		
		8	$6.59 \times 10^{-5}$	$2.71 \times 10^{-2}$	$5.00 \times 10^{-10}$		
		9	$1.17 \times 10^{-5}$	$1.75 \times 10^{-1}$	$5.73 \times 10^{-10}$		
		10	$1.93 \times 10^{-6}$	1.48	$7.99 \times 10^{-10}$		
5	$5.34 \times 10^{-10}$	3	$8.14 \times 10^{-2}$	$2.72 \times 10^{-8}$	$1.77 \times 10^{-10}$		
		4	$2.60 \times 10^{-2}$	$1.43 \times 10^{-7}$	$2.98 \times 10^{-10}$		
		5	$6.99 \times 10^{-3}$	$7.65 \times 10^{-7}$	$4.28 \times 10^{-10}$		
		6	$1.64 \times 10^{-3}$	$4.12 \times 10^{-6}$	$5.40 \times 10^{-10}$		
		7	$3.46 \times 10^{-4}$	$2.21 \times 10^{-5}$	$6.11 \times 10^{-10}$		
		8	$6.59 \times 10^{-5}$	$1.21 \times 10^{-4}$	$6.38 \times 10^{-10}$		
		9	$1.17 \times 10^{-5}$	$6.76 \times 10^{-4}$	$6.32 \times 10^{-10}$		
		10	$1.93 \times 10^{-6}$	$3.82 \times 10^{-3}$	$5.90 \times 10^{-10}$		
		11	$3.00 \times 10^{-7}$	$2.28 \times 10^{-2}$	$5.46 \times 10^{-10}$		
		12	$4.41 \times 10^{-8}$	$1.47 \times 10^{-1}$	$5.18 \times 10^{-10}$		
		13	$6.20 \times 10^{-9}$	1.19	$5.90 \times 10^{-10}$		
		Total					$1.89 \times 10^{-8}$

<sup>a</sup> The contributions smaller than 2% of the most effective one (corresponding to the most probable path) are neglected.

<sup>b</sup> Every vibrational wavefunctions, C–H and C–C totally symmetric stretching mode and b<sub>2g</sub> out of plane mode, are approximated by harmonic oscillator wavefunctions.

<sup>c</sup> T<sub>s</sub> = carbon or hydrogen totally symmetric stretching mode.

<sup>d</sup> Franck-Condon factors calculated by using Eq. (16) in reference [10] with the following parameters: ω<sub>1</sub><sup>S<sub>0</sub></sup> = 3 063 cm<sup>-1</sup>, ω<sub>1</sub><sup>T<sub>1</sub></sup> = 3 130 cm<sup>-1</sup>, ΔQ<sub>1</sub> = -0.034 Å, ΔE = 29.658 cm<sup>-1</sup>.

<sup>e</sup> Franck-Condon factors calculated by using Eq. (16) in reference [10] with the following parameters: ω<sub>2</sub><sup>S<sub>0</sub></sup> = 990 cm<sup>-1</sup>, ω<sub>2</sub><sup>T<sub>1</sub></sup> = 923 cm<sup>-1</sup>, ΔQ<sub>2</sub> = 0.071 Å.

<sup>f</sup> I'[ΔE(b<sub>2g</sub>)] = (2π<sup>1/2</sup>/ω<sub>b<sub>2g</sub></sub><sup>S<sub>0</sub></sup>) I'[ΔE(b<sub>2g</sub>)].

Comparing Table 2 with Table 3, we notice that the anharmonicity results in an increase by a numerical factor  $\sim 3.7 \times 10^3$  in the calculated non-radiative transition rate. It should be also noticed that, owing to the anharmonicity, the C–H totally symmetric mode becomes more effective as the accepting mode. The vibrational quantum numbers of the C–H totally symmetric and the C–C breathing modes in the final state corresponding to the most probable path are v<sub>1</sub> = 7, v<sub>2</sub> = 6 for the case of the harmonic oscillator approximation and v<sub>1</sub> = 8, v<sub>2</sub> = 4 for the case of the Morse oscillator approximation.

Table 3. Contributions of the energy distributions in the final electronic state to the total non-radiative transition rate<sup>a</sup>. Case B: Morse oscillator approximation<sup>b</sup>

CH- $T_s^c$		CC- $T_s$		Out-of-plane	$W_{T_1 \rightarrow S_0}(\text{sec}^{-1})$
$v_1$	$ \langle v_1   0 \rangle ^2{}^d$	$v_2$	$ \langle v_2   0 \rangle ^2{}^e$	$I[\Delta E(b_{2g})]{}^f$	
9	$1.057 \times 10^{-12}$	0	$3.29 \times 10^{-1}$	$3.26 \times 10^{-2}$	$1.70 \times 10^{-6}$
		1	$3.53 \times 10^{-1}$	$2.14 \times 10^{-1}$	$1.19 \times 10^{-5}$
8	$1.854 \times 10^{-11}$	1	$3.53 \times 10^{-1}$	$1.35 \times 10^{-3}$	$1.32 \times 10^{-6}$
		2	$2.02 \times 10^{-1}$	$6.92 \times 10^{-3}$	$3.88 \times 10^{-6}$
		3	$8.14 \times 10^{-1}$	$4.22 \times 10^{-2}$	$9.54 \times 10^{-6}$
		4	$2.60 \times 10^{-1}$	$2.83 \times 10^{-1}$	$2.04 \times 10^{-5}$
7	$3.455 \times 10^{-10}$	2	$2.02 \times 10^{-1}$	$4.72 \times 10^{-5}$	$4.91 \times 10^{-7}$
		3	$8.14 \times 10^{-2}$	$2.63 \times 10^{-4}$	$1.11 \times 10^{-6}$
		4	$2.60 \times 10^{-2}$	$1.47 \times 10^{-3}$	$1.98 \times 10^{-6}$
		5	$6.99 \times 10^{-3}$	$8.58 \times 10^{-3}$	$3.12 \times 10^{-6}$
		6	$1.64 \times 10^{-3}$	$5.21 \times 10^{-2}$	$4.41 \times 10^{-6}$
		7	$3.46 \times 10^{-4}$	$3.57 \times 10^{-1}$	$6.37 \times 10^{-6}$
		6	$6.856 \times 10^{-9}$	5	$6.99 \times 10^{-3}$
		6	$1.64 \times 10^{-3}$	$3.05 \times 10^{-4}$	$5.15 \times 10^{-7}$
		7	$3.64 \times 10^{-4}$	$1.73 \times 10^{-3}$	$6.15 \times 10^{-3}$
		8	$6.59 \times 10^{-5}$	$9.94 \times 10^{-3}$	$6.72 \times 10^{-7}$
		9	$1.17 \times 10^{-5}$	$6.20 \times 10^{-2}$	$7.46 \times 10^{-7}$
		10	$1.93 \times 10^{-6}$	$4.32 \times 10^{-1}$	$8.55 \times 10^{-7}$
Total					$7.00 \times 10^{-5}$

<sup>a</sup> The contributions smaller than 2% of the most effective one (corresponding to the most probable path) are neglected.

<sup>b</sup> C-H totally symmetric stretching mode is approximated by the Morse oscillator wavefunction. Other modes, the C-C totally symmetric mode and  $b_{2g}$  out plane mode, are approximated by harmonic oscillator wavefunctions.

<sup>c</sup>  $T_s$  = carbon or hydrogen totally symmetric stretching mode.

<sup>d</sup> Franck-Condon factors calculated by using Eq. (15a) with the following parameters:  $\omega_1^{S_0} = 3063 \text{ cm}^{-1}$ ,  $\omega_1^{T_0} = 3130 \text{ cm}^{-1}$ ,  $\omega_1^{S_0} x_1^{S_0} = 9.2 \text{ cm}^{-1}$ ,  $\alpha_1 = 0.714 \text{ \AA}^{-1}$ ,  $\Delta Q_1 = -0.034 \text{ \AA}$ ,  $\Delta E = 29658 \text{ cm}^{-1}$ .

<sup>e</sup> Franck-Condon factors calculated by using Eq. (16) in Ref. [10] with the following parameters:  $\omega_2^{S_0} = 990 \text{ cm}^{-1}$ ,  $\omega_2^{T_1} = 923 \text{ cm}^{-1}$ ,  $\Delta Q_2 = 0.071 \text{ \AA}$ .

<sup>f</sup>  $I[\Delta E(b_{2g})] = (2\pi^{1/2}/\omega_{b_{2g}}^{S_0}) I[\Delta E(b_{2g})]$ .

Using the results of Table 3 and assuming  $C_{T_1, S_0} = 1.6 \times 10^{-1} \text{ cm}^{-1}$  [1] we may calculate the absolute rate for the  ${}^3B_{1u} \rightarrow {}^1A_{1g}$  intersystem crossing in the benzene molecule. Our numerical results together with previous ones are summarized in Table 4. The value in parentheses corresponds to the rate obtained considering only the most probable path. The numerical result obtained using the most probable path method is about a fourth part of the value obtained using the present method. The predicted results in Table 4 should be compared with the experimental result  $W_{T_1 \rightarrow S_0} \simeq 2.4 \times 10^{-2}$ . According to Nitzan and Jortner [2], the inclusion of frequency changes for other modes increases the rate by an order of about 3. Considering this effect, we feel that our result is in better agreement with the experimental one than any other calculated result obtained previously.

Table 4. Calculated intersystem crossing rate in benzene

	Rate (sec <sup>-1</sup> )
Present work	7.00 × 10 <sup>-5</sup> (2.04 × 10 <sup>-5</sup> ) <sup>a</sup>
Nitzan and Jortner [2]	7.2 × 10 <sup>-7</sup>
Burland and Robinson [1]	9.04 × 10 <sup>-5</sup>
Fischer and Schneider [11]	7.4 × 10 <sup>-4</sup>
Experiment [1]	2.4 × 10 <sup>-2</sup>

<sup>a</sup> The value obtained from the most probable path method.

In this paper we have neglected the displacement for the  $e_{2g}$  mode. Fischer and Schneider [11] have calculated the rate taking into account the displacement of  $\Delta Q = 0.021 \text{ \AA}$  for the  $e_{2g}$  C-C stretching mode (1606 cm<sup>-1</sup>). The inclusion of the displacement augments the rate by a numerical factor  $\sim 40$ . However, the magnitude of the displacement for the  $e_{2g}$  mode depends strongly upon solvents and cannot be determined definitely. The semi-empirical calculation by Nieman [12] shows that the displacement is less than 0.01  $\text{\AA}$ .

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Prof. Dr. T. Nakajima  
Department of Chemistry  
Faculty of Science  
Tohoku University  
Sendai, Japan