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EFFECT OF GEOMETRY CHANGES IN VIBRATIONAL PROMOTING MODES ON THE RATE CONSTANTS OF RADIATIONLESS TRANSITIONS

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The influence of changes in geometry of promoting vibrational modes (due to transitions between electronic states) on the rate constants for radiationless transitions in molecular systems has been analysed. It has been demonstrated that in many-promoting-modes model systems, effects due to interferences between different participating modes can greatly modify the magnitudes of rate constants for radiationless transitions as well as the magnitude of the isotope (deuterium) effect.

1. Introduction

The rate constant for a radiationless transition from the zero-vibronic level $|s0\rangle$, of energy $E_{s0} = E_s + \frac{1}{2}\sum_{i=1}^{N} \hbar\omega_i^{(s)}$, to the quasi-continuum of the final vibronic levels $\{|ln\rangle\}$, of the energies $E_{ln} = E_l + \sum_{i=1}^{N} (\frac{1}{2}+n_i)\hbar\omega_i^{(l)}$, can be expressed within the framework of the radiationless transition theory [1–7] and with all the "conventional" assumptions [4], by the following general expression:

$$k(s \to l) = \frac{2\pi}{\hbar} \sum_{p=1}^{m} \sum_{n_1} \cdots \sum_{n_N} \left| C_{sl}^{p} \left\langle 0 \left| \frac{\partial}{\partial Q_p} \right| n_p \right\rangle \prod_{j \neq p}^{N} \langle 0|n_j\rangle \right|^2$$

$$\times \delta\left(\Delta E_{sl} - \sum_{i=1}^{N} n_i \hbar\omega_i^{(l)} \right) + \frac{2\pi}{\hbar} \sum_{p=1}^{m} \sum_{p'=1}^{m} \sum_{n_1} \cdots \sum_{n_N} C_{sl}^{p} C_{sl}^{p'}$$

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$$\times \left\langle 0 \left| \frac{\partial}{\partial Q_p} \right| n_p \right\rangle \left\langle 0 \left| \frac{\partial}{\partial Q_{p'}} \right| n'_p \right\rangle \langle 0|n_p\rangle \langle 0|n_{p'}\rangle \left| \prod_{j \neq p,p'} \langle 0|n_j\rangle \right|^2$$

$$\times \delta(\Delta E_{sl} - \sum_{i=1}^{N} n_i \hbar \omega_i^{(l)}) = \sum_{p=1}^{m} k(p) + \sum_{p=1}^{m} \sum_{p'=1}^{m} I(p, p'). \quad (1)$$

Here, N is the number of molecular vibrations and p is the number of promoting modes (summation runs over all $p = 1, 2, \ldots, m$, promoting modes, provided they have a non-vanishing electronic matrix element, C_{sl}^{p} [1, 3, 5, 7]). $|0\rangle$ and $|n_j\rangle$ are vibrational wavefunctions of given vibrations in electronic states $|s\rangle$ and $|l\rangle$, respectively: $E_{sl} = E_s - E_l + \frac{\hbar}{2} \sum_{i=1}^{N} (\omega_i^{(s)} - \omega_i^{(l)})$.

The total rate constant, k, given by Eq. (1) is expressed as a sum of partial rate constants, k_p, for each single promoting mode and of "cross-terms", $I(p, p')$ [3].

It is a common practice, in the treatment of radiationless transitions, to assume that there is no change in geometry of promoting modes between the two combining electronic states (i.e. $\Delta_p = 0$, where Δ_p is the reduced displacement and describes the change in the equilibrium position of p-th vibrational mode) [3–6]. In such a case the propensity rule [8] holds involving a single vibrational quantum. This is a natural consequence of the properties of both the overlap and nuclear momentum integrals in Eq. (1) (according to the corresponding formulas $\langle 0|n_p\rangle \sim \delta_{00}$ and $\left\langle 0 \left| \frac{\partial}{\partial Q_p} \right| n_p \right\rangle \sim \delta_{01}$, where $\Delta_p = 0$ [5]). This also means that the "cross-terms" in Eq. (1) vanish and the total rate constant is just a simple sum of partial rate constants. This also holds valid for most of the transitions in symmetric hydrocarbons, which were the most frequently analyzed systems [3–6].

It has been recognized on several occasions, however, that vibrational modes which undergo geometry changes can act as promoting modes [6, 9]. This has been shown to occur for the $S_1 \rightsquigarrow S_0$ internal conversion from the excited charge-transfer state in some electron-donor-acceptor molecular complexes [10, 11]. This can be expected as important for the different radiationless processes in non-symmetric molecules and in some symmetric molecules, for example: internal conversion $S_1(A_1) \rightsquigarrow S_0(A_1)$ in phenantrene [9], internal conversion $S_2(A_1) \rightsquigarrow S_0(A_1)$ in azulene [12], internal conversion between the excited states and the intersystem crossing with the participation of the spin–orbit–vibronic couplings [13, 14]. In all those cases a propensity rule would no longer be valid and therefore the rate constant for a radiationless transition would be given by Eq. (1) with non-vanishing "cross-terms".

In this paper we examine the importance of vibrational modes which change their geometry as promoting modes for radiationless transitions. For model calculations we used the method developed and described by Kuhn, Heller and Gelbart [15] and for reasons discussed by other authors [16, 17] we limit our discussion only to cases with relatively large energy gaps between the electronic states under consideration. The other limitation

of our discussion is the consideration of cases where the excitation does not lead to the mixing of the promoting modes. This is connected with the "conventional" assumption of the model. This problem will be considered by us in the near future.

2. *Results and discussion*

In order to get insight into the role of promoting modes, which change their geometries, one has to consider the effects which are connected with:

(*i*) breakdown of the propensity rule (which brings non-zero $\left\langle 0 \left| \frac{\partial}{\partial Q_p} \right| n_p \right\rangle$ integrals, also when $n_p \neq 1$);

(*ii*) interferences between different promoting modes [described by "cross-terms", $I(p, p')$ in Eq. (1)].

These effects can be examined by inspection of the influence of geometry changes of promoting modes on the energy gap law and on isotope effect for radiationless transitions. Let us first start with the discussion of the system where there is only a single promoting mode active in the radiationless transition.

2.1. Single-promoting-mode model

Let us assume that in the system under consideration there are two vibrational modes of importance, one of which is a promoting and another one can act as an accepting mode only. The results of calculations performed for such a system, with the use of Eq. (1), are

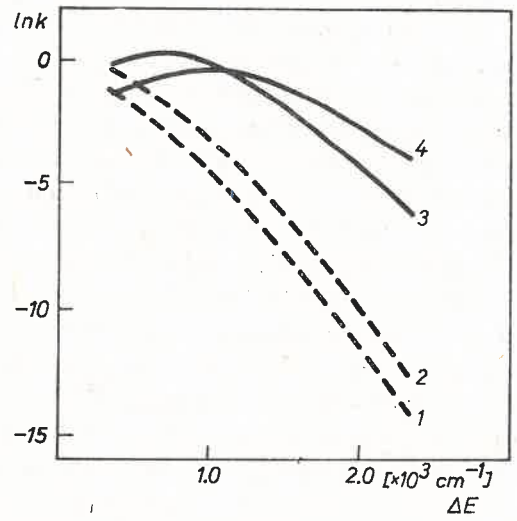

Fig. 1. Single-promoting-mode model. Dependence of rate constant for radiationless transition on the energy gap between electronic states. The vibrational parameters of the promoting mode are: *1* — $\Delta_p = 0$, $\hbar\omega_p = 1500\ \mathrm{cm}^{-1}$; *2* — $\Delta_p = 0$, $\hbar\omega_p = 2700\ \mathrm{cm}^{-1}$; *3* — $\Delta_p = 1.5$, $\hbar\omega_p = 1500\ \mathrm{cm}^{-1}$; *4* — $\Delta_p = 1.5$, $\hbar\omega_p = 2700\ \mathrm{cm}^{-1}$. In all cases the accepting mode is characterized by $\Delta_a = 0.71$ and $\hbar\omega_a = 3000\ \mathrm{cm}^{-1}$

given in Fig. 1. They can be summarized as follows:

(*i*) The energy gap law [1–8] is obeyed also in the system in which a single promoting mode is subject to a change in geometry. However, the validity of the energy gap law is limited to larger energy gaps than in the case of the promoting mode which does not change its geometry upon transition (Fig. 1).

(*ii*) With increasing change in geometry (an increase in reduced displacement parameter, Δ_p) the rate constant for radiationless transitions rapidly increases (Fig. 1).

(*iii*) A change in the geometry of the promoting mode can modify the magnitude of the isotope effect as compared to the case where the same promoting mode does not change its geometry (in Fig. 1: k(case 4)/k(case 3) ratio as compared to the k(case 2)/k(case 1) ratio).

It is seen from Fig. 1 that for large energy gaps this effect increases with energy gap while for small energy gaps the isotope effect is small and it can be reversed.

2.2. Many-promoting-modes model

When the radiationless transition is governed and controlled by more than one promoting mode, the interference effects between different pairs of promoting modes must be taken into account. If there are two vibrations, 1 and 2, active as promoting modes, then the total rate constant for a radiationless transition can be expressed in the general form $k(1,2) = k(1)+k(2)+2I(1,2)$.

The sign of the "cross-term" $I(1,2)$ is determined by the signs of the displacement parameters Δ_1 and Δ_2 and by the sign of the electronic matrix elements C_1 and C_2, i.e.: either sign $C_1 \cdot$ sign $C_2 \cdot$ sign $\Delta_1 \cdot$ sign $\Delta_2 > 0$ and $I(1,2) > 0$ or sign $C_1 \cdot$ sign $C_2 \cdot$ sign $\Delta_1 \cdot$ sign $\Delta_2 < 0$ and $I(1,2) < 0$. Hence, the contribution of the "cross-term" to the total rate constant can be either positive or negative.

The results of calculations of the rate constant for two promoting modes are given in Fig. 2 together with the calculated partial rate constant. It is easily seen that for sufficiently large energy gaps, where the energy gap law holds valid, the positive interference of promoting modes increases the total rate constant and the negative interference decreases the rate constant. It is also seen that the contribution of the "cross-term" is dependent on the ratio of the partial rate constants. The magnitude of this contribution can be estimated by taking into consideration the ratio $k(1,2)/(k(1)+k(2)) = 1+2I(1,2)/(k(1)+k(2))$. It is seen from Fig. 2 that the contribution of the "cross-term" is larger when the values of $k(1)$ and $k(2)$ are close to each other (Fig. 2a). If the partial rate constants are greatly different the contribution of "cross-term" is very small (Fig. 2b).

The relative participation of partial rate constants $k(1)$ and $k(2)$ in the total rate $k(1,2)$ is determined also by the ratio of relevant electronic matrix elements C_1/C_2. When the ratio of $k(1,2)/(k(1)+k(2))$ is plotted against $\ln C_1/C_2$ (see Fig. 3) it passes either through a minimum in the case of negative "cross-terms" or through a maximum in the case of positive "cross-terms". These extrema correspond to the cases when the partial rates are comparable. The position and the magnitude of these extrema are dependent on parameters of all the contributing vibrations.

In general it might be expected that upon isotopic substitution (deuteration) the relative contributions of partial rate constants to the total rate constant would change. It is difficult, however, to make predictions concerning modifications of the magnitude of the isotope effect, in the case where two or more promoting modes are active, without exact knowledge of the character of the interference signs of "cross-terms" between participating modes.

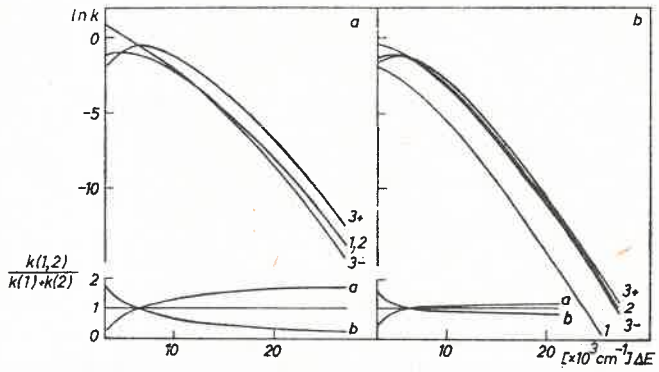

Fig. 2. Many-promoting-modes model. Dependence of the rate constants for radiationless transition on the energy gap between electronic states. The vibrational parameters of promoting and accepting modes are: Fig. 2a. $\hbar\omega_1 = \hbar\omega_2 = 3000\ \mathrm{cm}^{-1}$, $\Delta_1 = \Delta_2 = 0.77$, $C_1 = C_2$; Fig. 2b. $\hbar\omega_1 = 1500\ \mathrm{cm}^{-1}$, $\hbar\omega_2 = 3000\ \mathrm{cm}^{-1}$, $\Delta_1 = \Delta_2 = 0.77$, $C_1 = C_2$. The particular curves correspond to the cases: $I(2) - \hbar\omega_p = \hbar\omega_1$; $\hbar\omega_a = \hbar\omega_2 (\hbar\omega_p = \hbar\omega_2, \hbar\omega_a = \hbar\omega_1)$;, $3+ - \hbar\omega_{p1} = \hbar\omega_1, \hbar\omega_{p2} = \hbar\omega_2$, positive interference; $3- - \hbar\omega_{p1} = \hbar\omega_1, \hbar\omega_{p2} = \hbar\omega_2$, negative interference. At the bottom the contribution of "cross-term" to the total rate constant. The cases "a" and "b" correspond to the positive and the negative interference respectiveiy

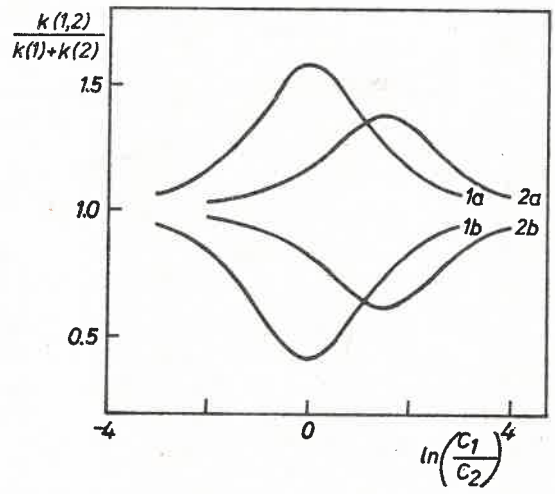

Fig. 3. Many-promoting-modes model. Dependence of the contributions of "cross-terms" $I(1,2)$, to the total rate constant, on the relative ratio of contributing promoting modes (measured by C_1/C_2 ratio). The energy gap is 15000 cm^{-1}. The vibrational parameters of promoting modes are: $1 - \Delta_{p1} = \Delta_{p2} = 077$, $\hbar\omega_{p1} = \hbar\omega_{p2} = 3000\ \mathrm{cm}^{-1}$; $2 - \Delta_{p1} = \Delta_{p2} = 0.77$, $\hbar\omega_{p1} = 1500\ \mathrm{cm}^{-1}$, $\hbar\omega_{p2} = 3000\ \mathrm{cm}^{-1}$. The index a corresponds to the case of positive interference, the index b corresponds to the negative interference

TABLE I

The predicted modifications of isotope effects by "cross-terms" for the different relations between the "partial" rate constants [a,b]

	$k(1) \neq k(2)$	$k(1) \approx k(2)$
$k'(1) \neq k'(2)$	$\chi^+ \approx \chi \approx \chi^-$	$\chi^+ > \chi > \chi^-$
$k'(1) \approx k'(2)$	$\chi^+ < \chi < \chi^-$	$\chi^+ \approx \chi \approx \chi^-$

[a] $\chi = \dfrac{k(1)+k(2)}{k'(1)+k'(2)} \qquad \chi^{\pm} = \dfrac{k(1)+k(2)\pm 2I(1,2)}{k'(1)+k'(2)\pm 2I'(1,2)}$

[b] prime characterises the system after the isotopic substitution.

In Table I the expected modifications of a deuterium isotope effect for different relations between partial rate constants before and after deuteration and for different signs of contributions of "cross-terms" are listed. In Fig. 4 a magnitude of the isotope effect is given as a function of energy gap. It is seen that for larger energy gaps, modifications of the isotope

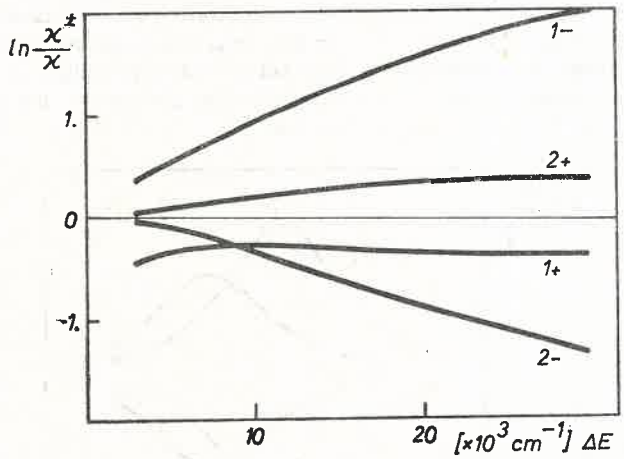

Fig. 4. Many-promoting-modes model. Dependence of the magnitude of the deuterium isotope effect on energy gap, calculated for different contributions of "cross-terms". For definition of $\chi^{\pm}$ and χ, see Table I. The vibrational parameters of promoting modes are: *1* — $\hbar\omega_{p1} = 3000$ cm^{-1}, $\hbar\omega_{p2} = 1500$ cm^{-1}, $\Delta_1 = 0.5$, $\Delta_2 = 0.7$ before the isotopic substitution and $\hbar\omega_{p1} = 1500$ cm^{-1}, $\hbar\omega_{p2} = 1500$ cm^{-1}, $\Delta_1 = 0.7$, $\Delta_2 = 0.7$ after the isotopic substitution. *2* — $\hbar\omega_{p1} = 3000$ cm^{-1}, $\hbar\omega_{p2} = 3000$ cm^{-1}, $\Delta_1 = 0.5$, $\Delta_2 = 0.5$ before the isotopic substitution, $\hbar\omega_{p1} = 1500$ cm^{-1}, $\hbar\omega_{p2} = 3000$ cm^{-1}, $\Delta_1 = 0.7$, $\Delta_2 = 0.5$ after the isotopic substitution. The indices + and − correspond to positive and negative interference

effects can appreciably differ, depending on the sign of the "cross-term". It is seen also that the effects corresponding to the negative interference case are larger in comparison to the effects for the case of positive interference.

3. Concluding remarks

We think that the above discussion has clearly demonstrated the importance of geometry changes of promoting modes in the description of radiationless transitions. This fact may be of extreme importance in all those systems where there are two or more such promoting modes active in radiationless transitions. Unfortunately, in such cases, no general prediction can be made concerning the magnitude of rate constants and of the magnitude of the isotope effect, unless the relative importance of each of the contributing vibrational modes as well as the detailed knowledge of changes in vibrational and of relevant electronic parameters are established. This is due to the fact that positive and negative interferences between contributing modes can either enhance or effectively damp the nonradiative decay channel. In addition, the description of these effects is more complicated when the changes in the frequency of the promoting mode upon transition are taken into consideration [18]. Moreover, the problem of introduction of a non-linear treatment should be discussed in cases where electronic excitation leads to a mixing of the molecular normal modes in analogy to the Dushinsky effect for the radiative transitions [19]. Therefore, it seems that systematic studies, experimental and theoretical, are needed for radiationless transitions with many promoting modes.

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