Non Radiative Transition Probabilities in the Statistical Limit

Abraham Nitzan and Joshua Jortner

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

In this paper we derive a general computational scheme for the calculation of the non radiative decay probability of a polyatomic molecule in the statistical limit. Within the framework of the Harmonic Approximation the relaxation rate of any polyatomic molecule can be expressed in terms of an infinite sum where each term consists of a medium distribution function and an intramolecular term. In the statistical limit the medium induced vibrational relaxation widths do not affect the non radiative decay characteristics. Numerical calculations are reported for the $T_1 \to S_0$ intersystem crossing in the benzene molecule.

1. Introduction

This paper is concerned with some features of the electronic relaxation of a large molecule in a dense inert medium. Adopting the definition of the inert medium presented in previous work [1, 2] the non radiative decay characteristics of a statistical large molecule can be affected by the medium as follows:

(a) The medium may provide accepting modes for the electronic relaxation.

(b) The medium provides a mechanism for vibrational relaxation in the final intramolecular quasicontinuum.

(c) The medium provides a loss mechanism for vibrational relaxation in the initial electronic manifold.

The coupling between electronic and vibrational relaxation in large molecules has been recently considered by us [3]. We were able to demonstrate that when the vibrational relaxation is slow relative to electronic relaxation (as is the case for some ultrafast processes) the non radiative decay involves the initially excited level, while in the limit of fast vibrational relaxation a Boltzman averaged (over the initial states) non radiative transition probability is obtained. Thus the implications of the vibrational relaxation in the initial electronic manifold [effect (C)] were elucidated. It was pointed out [1, 4] (but not proved) that vibrational relaxation in the final electronic manifold of a statistical molecule is unaffected by vibrational relaxation in the final manifold.

The purpose of this paper is twofold:

(a) From the point of view of general methodology we shall demonstrate that for a molecule which corresponds to the statistical limit the vibrational relaxation in the final vibronic manifold does not affect the non radiative decay characteristics, and does not modify the expressions previously derived [1] which did not include this effect.

(b) From the technical point of view we shall provide a computational scheme for the evaluation of the non radiative decay probability of a statistical molecule by the generating functions method. This method was briefly outlined and applied by us [5]. In view of recent criticism of our approach [6] we would like to provide a complete justification for this technique.

2. Non Radiative Decay Probability

We shall consider the model two electronic level system previously described [1] and invoke the following simplifying assumptions: (a) The medium does not provide accepting modes, and its effect can be subsummed to add a vibrational relaxation width Γ so that the generating function is modified by an exponential damping term [2]. Thus we consider the decay of a zero phonon molecular line. This restriction will be relaxed in Section 3. (b) We consider the fast vibrational relaxation limit whereupon in the low temperature limit the non radiative decay probability corresponds to the relaxation of the vibrationless level in the initial electronic manifold.

The non radiative decay probability of a molecule in a Shpolskii matrix can be expressed in the form

$$W_{so} = \frac{1}{2\hbar^2} \sum_{\varkappa} |C_{sl}^{\varkappa}|^2 \, I_{\varkappa} \tag{2.1}$$

where C_{sl}^{κ} is the electronic coupling matrix element between the two electronic states induced by the promoting mode κ. In the Harmonic molecular model the vibrational integral I_{κ} is determined [1, 5, 7, 8] in terms of a Fourier transform of a function $F(\beta_{\mu}, \Delta_{\mu}, \exp(i\omega_{\mu}t))$ of the molecular frequencies ω_{μ}, the origin displacements of the normal modes Δ_{μ} and the frequency ratios β_{μ} between the two electronic states

$$I_{\varkappa} = \int_{-\infty}^{\infty} dt \, \exp[-i\Delta E_{\varkappa} t/\hbar - \Gamma|t|/2\hbar] \, F(\beta_{\mu}, \Delta_{\mu}, \exp(i\omega_{\mu}t)) \tag{2.2}$$

where $\Delta E_{\varkappa} = \Delta E - \hbar\omega_{\varkappa}$ is the effective energy gap and where Γ is the (average) width of the level in the quasicontinuum manifold [2]. In the simple model of displaced identical energy surfaces

$$F(\beta_{\mu}, \Delta_{\mu}, \exp(i\omega_{\mu}t)) = \exp\left(-\tfrac{1}{2}\sum_{\mu} \Delta_{\mu}^2\right) \exp\left[\tfrac{1}{2}\sum_{\mu} \Delta_{\mu}^2 \exp(i\omega_{\mu}t)\right] \tag{2.3}$$

while in the case of displaced potential surfaces involving frequency changes

$$\begin{aligned}
F = {} & \left[\prod_{\mu} (\beta_{\mu})^{-\frac{1}{2}}\right] \left\{1 + \frac{(1-\beta_{\varkappa})^2}{4\beta_{\varkappa}} [1 - \exp(2i\omega_{\varkappa}t)]\right\}^{-1} \\
& \times \prod_{\mu} \left\{1 + \frac{(1-\beta_{\mu})^2}{4\beta_{\mu}} [1 - \exp(2i\omega_{\mu}t)]\right\}^{-\frac{1}{2}} \\
& \times \exp\left\{-\sum_{\mu} \frac{\beta_{\mu}\Delta_{\mu}^2[1 - \exp(i\omega_{\mu}t)]}{1 + \beta_{\mu} + (\beta_{\mu} - 1)\exp(i\omega_{\mu}t)}\right\}.
\end{aligned} \tag{2.4}$$

The mathematical problem is thus reduced to the evaluation of the integrals $I_\varkappa$. Several attempts have been reported to perform these integrations by the saddle point method [1–7] (assuming that ΔE is sufficiently large). This procedure is valid for the statistical limit only in the case of displaced identical potential surfaces. When frequency changes as well as unharmonicities are included it was found necessary to perform a power expansion in the exponential function of (2.4), in order to apply the saddle point integration [1, 7–9]. It can be demonstrated (see Appendix A) that this expansion method, retaining low order terms is unjustified. This conclusion was also supported by numerical calculations performed by us. Thus when more complicated (and more realistic) physical models are introduced the saddle point method is inapplicable. Furthermore, the saddle point method cannot be applied when the exponential damping term $\exp(-\Gamma|t|)$ is present in the Fourier integral (2.2). Thus we conclude that alternative numerical procedures are required for the evaluation of the non radiative decay probability.

We shall now introduce a normalizing frequency, ω_N, so that the numbers

$$\tilde{\omega}_\mu = \omega_\mu/\omega_N \tag{2.5}$$

are integers for all μ. It should be noted that the definition of ω_N is not unique. In particular it is important to notice that for the set $\{\omega_\mu\}$ (expressed as integers in arbitrary units and given for any available experimental accuracy) we can define the largest common integer divider $\omega_N^{\max}$. We shall also define the reduced quantities

$$\varepsilon_\varkappa = \Delta E_\varkappa/\hbar\omega_N \tag{2.6}$$

$$\gamma = \Gamma/\hbar\omega_N \tag{2.7}$$

and

$$x = \omega_N t. \tag{2.8}$$

Eq. (2.2) may be recast in the form

$$I_\varkappa = \frac{1}{\omega_N} \int_{-\infty}^{\infty} dx \, \exp(-i\varepsilon_\varkappa x - \gamma|x|/2) \, F(\beta_\mu, \Delta_\mu, \exp(i\tilde{\omega}_\mu x)). \tag{2.9}$$

Making use of the relation

$$\exp(-\gamma|x|/2) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \, \exp(-iyx) \frac{\gamma}{y^2 + (\gamma/2)^2}. \tag{2.10}$$

Eq. (2.9) may be rewritten in the form

$$I_\varkappa = \frac{1}{2\pi\omega_N} \int_{-\infty}^{\infty} dy \, \frac{\gamma}{y^2 + (\gamma/2)^2} \int_{-\infty}^{\infty} dx \, \exp[-i(\varepsilon_\varkappa + y)x] \, F(\beta_\mu, \Delta_\mu, e^{i\tilde{\omega}_\mu x}). \tag{2.11}$$

As the numbers $\tilde{\omega}_\mu$ are integers it is easy to perform the integration over x, which yields (Appendix B)

$$\frac{1}{\omega_N} \int_{-\infty}^{\infty} dx \, \exp[-i(\varepsilon_\varkappa + y)x] \, F(\beta_\mu, \Delta_\mu, \exp(i\tilde{\omega}_\mu x)) = I_0(\varepsilon_\varkappa + y) \sum_{s=-\infty}^{\infty} \delta(\varepsilon_\varkappa + y - s) \tag{2.12}$$

where

$$I_0(z) = \frac{1}{\omega_N} \int_0^{2\pi} dx \exp(-izx) F(\beta_\mu, \Delta_\mu, \exp(i\tilde{\omega}_\mu x)). \qquad (2.13)$$

Inserting Eqs. (2.12) and (2.13) into Eq. (2.11) and performing integration over y we obtain

$$I_\varkappa = \frac{1}{2\pi} \sum_{s=-\infty}^{\infty} I_0(s) \frac{\gamma}{(\varepsilon_\varkappa - s)^2 + (\gamma/2)^2}. \qquad (2.14)$$

Thus the non radiative decay probability of a zero phonon line can be expressed in terms of the infinite sum (2.14) where each term involves a medium induced Lorentzian distribution and a (finite) integral of the intramolecular generating function. This result is general, being valid both for the statistical limit and for the small molecule case.

3. The Statistical Limit

Within the framework of the present theoretical scheme the statistical limit is characterized by the inequality

$$\Gamma \gg \omega_N^{\max} \qquad (3.1)$$

where $\omega_N^{\max}$ is the largest common integer divider of the frequencies. Eq. (3.1) is equivalent[1] to the more physically transparent inequality

$$\Gamma \gg \varrho^{-1} \qquad (3.2)$$

in which ϱ is the density of non-degenerate levels in the final manifold. The last inequality is easily recognized to be the condition for the smoothness of the non-radiative line-shape function (with $\Gamma_l = \Gamma$) which is the Freed-Jortner definition [4] of the statistical limit.

If $\Delta E \gg \Gamma$ which is always the case we now have

$$\varepsilon_\varkappa \gg \gamma \gg 1. \qquad (3.3)$$

Eq. (3.3) implies that the summation in Eq. (2.14) may be replaced by an integration, so that

$$I_\varkappa = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds\, I_0(s) \frac{\gamma}{(\varepsilon_\varkappa - s)^2 + (\gamma/2)^2}. \qquad (3.4)$$

Now, if $I_0(s)$ does not change appreciably within the Lorentzian width γ we may take it outside the integral at the point $s = \varepsilon_\varkappa$, getting just $I_\varkappa = I_0(\varepsilon_\varkappa)$. The condition for the slow variation of $I_0(\varepsilon_\varkappa)$ is

$$\left(\frac{1}{I_0} \frac{dI_0}{ds}\right)_{s=\varepsilon_\varkappa} \gamma \ll 1. \qquad (3.5)$$

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[1] Provided that the energy gap ΔE is large enough. (The necessary condition may be shown to be $\Delta E / \hbar \omega_M \gg \omega_M / \overline{\Delta \omega}$ where ω_M is the largest molecular frequency and $\overline{\Delta \omega}$ is the average difference between the molecular frequencies.)

For the sake of an order of magnitude estimate we invoke the approximate result of Engleman, Freed and Jortner [1] for I_0

$$I_0(\varepsilon_\varkappa) \propto \exp(-\varepsilon_\varkappa/\hbar\tilde{\omega}_M) \tag{3.6}$$

where $\tilde{\omega}_M$ is the totally symmetric mode of maximum frequency, the condition (3.5) leads to

$$\Gamma/\hbar\omega_M \ll 1 . \tag{3.7}$$

It may thus be concluded that under the conditions [Eqs. (3.3) and (3.5)]

$$\hbar\omega_N^{\max} \ll \Gamma \ll \hbar\omega_M \ll \Delta E \tag{3.8}$$

the non-radiative decay rate of an excited electronic state in the statistical limit may be computed by expressing the integral (2.2) in the form

$$I_\varkappa = I_0(\varepsilon_\varkappa) = \frac{1}{\omega_N} \int_0^{2\pi} dx \exp(-i\varepsilon_\varkappa x) F(\beta_\mu, \Delta_\mu, \exp(i\tilde{\omega}_\mu x)) . \tag{3.9}$$

It is important to notice that Eq. (3.9) clearly demonstrates that the non-radiative decay rate in the statistical limit is independent of the width Γ of the levels in the dissipative $\{|lj\rangle\}$ intramolecular manifold. Such assumption has been silently invoked in many previous works which dealt with non-radiative transitions in large molecules embedded in an inert medium [1, 5–9].

So far we have been focusing attention on the non-radiative decay of a zero phonon line of a statistical molecule in a matrix. Our conclusion concerning the independence of the non-radiative decay rate on the vibrational relaxation width pertains only to a large molecule in a Shpolskii matrix. We have stated in Section 1 that direct coupling to medium modes is of minor importance in the statistical limit, where the decay rate is dominated by the larger molecular frequencies [1]. This argument may be presented in a more quantitative manner by considering the decay rate of an initial $|sim_s\rangle$ level (where i and m_s denote molecular vibrational state and medium vibrational state, respectively). We assume that the medium provides only promoting modes, so that the non-radiative decay probability is now

$$W_{sim_s} = \frac{1}{2\hbar^2} \sum_\varkappa |C_{sl}^\varkappa|^2 \sum_{j, m_l} |V_{sim_s, ljm_l}|^2$$
$$\times \delta(\Delta E_\varkappa + E_i - E_j + E_{m_s} - E_{m_l}) \tag{3.10}$$

where E_i and E_j are the vibrational energies of the molecule in the s and in the l electronic states, respectively, while E_{m_s} and E_{m_l} denote medium vibrational energies. $|V_{sim_s, ljm_l}|^2$ is the appropriate Franck Condon (FC) factor which may be factorized into a product of a molecular (FC) factor and a medium (FC) factor.

$$|V_{sim_s, ljm_l}|^2 = |V_{si, lj}|^2 |V_{m_s, m_l}|^2 . \tag{3.11}$$

Eq. (3.10) may now be recast a convolution

$$W_{sim_s} = \frac{1}{2\hbar^2} \sum_\varkappa |C_{sl}^\varkappa|^2 \int dE F(\Delta E_\varkappa - E) G(E) . \tag{3.12}$$

The functions $F(E)$ and $G(E)$ are easily recognized as the vibronic line-shape functions which correspond to the intramolecular and the medium modes, respectively.

$$F(\Delta E_\varkappa - E) = \sum_j |V_{si,\,lj}|^2 \,\delta(\Delta E_\varkappa - E + E_i - E_j) \qquad (3.13\,a)$$

$$G(E) = \sum_{m_l} |V_{m_s,\,m_l}|^2 \,\delta(E + E_{m_s} - E_{m_l}) \,. \qquad (3.13\,b)$$

In a Shpolskii matrix $G(E) = \delta(E)$ and we regain the former result (Section 2). Now, also in a non-Shpolskii matrix and even in the strong medium-molecule coupling limit [2] $G(E)$ is a narrow function of E around $E = 0$ relative to $F(E)$. The characteristic width of $G(E)$ is about $< 1000\ \mathrm{cm}^{-1}$ while $F(E)$ is nearly constant (around $E = \Delta E_\varkappa$) within this range. We thus may take $F(\Delta E_\varkappa - E)$ out of the integral in Eq. (3.12) at the point $E = 0$, obtaining

$$W_{sim_s} = W_{s_i} \sum_{m_l} |V_{m_s,\,m_l}|^2 = W_{s_i} \sum_{m_l} |\langle m_s | m_l \rangle|^2 = W_{s_i} \qquad (3.14)$$

where W_{si} is the decay rate of the vibronic level si in a Shpolskii matrix, or rather in an isolated molecule.

We have thus demonstrated that a direct coupling to the medium degrees of freedom does not modify the decay rate of a statistical molecule.

4. Numerical Procedures

We proceed to discuss some mathematical manipulations of the non-radiative decay rate, which in the statistical limit can be expressed in terms of the integral (3.9). When the functional form of $F(\beta_\mu, \Delta_\mu, e^{i\tilde\omega_\mu t})$ allows the application of the saddle point method, Eq. (3.9) provides the mathematical justification for taking the contribution of only one saddle point of the integrand in Eq. (2.2) or (2.9) (where $\Gamma = 0$). To exhibit the difficulty encountered in the original approach we may consider the zero temperature limit of the non-radiative decay rate in the displaced potential surfaces model, where Eq. (2.9) takes the form [neglecting the factor $\exp(-\gamma|x|/2)$]

$$I_\varkappa = \frac{1}{\omega_N} \int_{-\infty}^{\infty} dx \exp\left[-i\varepsilon_\varkappa x + \sum_\mu \tfrac{1}{2} \Delta_\mu^2 \exp(i\tilde\omega_\mu x)\right] \qquad (4.1)$$

where now $\varepsilon_\varkappa = (\Delta E - \hbar\omega_\varkappa)/\hbar\omega_N$. The saddle point approximation up to first order yields

$$\int \exp(z f(x)) \, dx = \sum_n \exp(z f(x_n)) \left[\frac{2\pi}{-z f''(x_n)}\right]^{\frac{1}{2}} \qquad (4.2)$$

where $f(x)$ is an oscillating function of $z \gg 1$ and where x_n are the saddle points of $f(x)$. In Eq. (4.1) we have

$$z = \varepsilon_\varkappa; \quad f(x) = -ix + \frac{1}{\varepsilon_\varkappa} \sum_\mu \tfrac{1}{2} \Delta_\mu^2 \exp(i\tilde\omega_\mu x) \qquad (4.3)$$

so that the equation for the saddle points is [1]

$$\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2 \tilde{\omega}_N \exp(i\tilde{\omega}_{\mu} x) = \varepsilon_{\varkappa}. \tag{4.4}$$

Provided that x_0 is a solution of Eq. (4.4) then every x_n which satisfies

$$x_n = x_0 + 2\pi n; \quad n = 0, \pm 1, \pm 2, \ldots \tag{4.5}$$

is also a solution of this equation. If the normalizing frequency ω_N will be taken as the largest possible one, $\omega_N^{\max}$, then Eq. (4.5) spans all the solutions of Eq. (4.4). Any interval of the length 2π on the real x axis corresponds to one and only one solution x_n whose real part lies in this interval. The solution which corresponds, say, to the interval $(0, 2\pi)$ was obtained by Freed and Jortner [1]. Denoting this solution by x_0 and its contribution to the sum in Eq. (4.2) by $I_0(\varepsilon_{\varkappa})$, it is easy to show that

$$I_{\varkappa} = I_0(\varepsilon_{\varkappa}) \sum_{n=-\infty}^{\infty} \exp(-2\pi i n \varepsilon_{\varkappa}) = I_0(\varepsilon_{\varkappa}) \sum_{s=-\infty}^{\infty} \delta(\varepsilon_{\varkappa} - s) \tag{4.5}$$

which is equivalent to Eq. (2.12). The justification to replacing Eq. (4.5) by the equality $I = I_0(\varepsilon_{\varkappa})$ is provided by Eqs. (3.1–3.9).

Eq. (3.9) constitutes a convenient starting point for numerical computation of the non-radiative decay probability. It is easy to see that as $\varepsilon_{\varkappa}$ in Eq. (3.9) is an integer (as energy conservation is expected[2]), Eq. (3.9) is independent of the chosen normalizing frequency ω_N. This fact suggests the following approximate numerical procedure:

1) $\Delta E_{\varkappa}$ and $\{\omega_{\mu}\}$ will be approximated by integers chosen so that they all have a large common integer divider.

2) The largest common integer divider of $\Delta E_{\varkappa}$ and of $\{\omega_{\mu}\}$ will be applied for the calculation of the integral (3.9).

3) The integral in Eq. (3.9) will be computed numerically using any conventional numerical integration method. As, according to (1) and (2), $\varepsilon_{\varkappa}$ and $\{\tilde{\omega}_{\mu}\}$ are relatively small numbers, (for example, choosing $\omega_N = 50\,\text{cm}^{-1}$ in calculating the intersystem crossing $^3B_{1u} \rightarrow {}^1A_{1g}$ rate in Benzene, performed in the next section, we have $\varepsilon_{\varkappa} = 600$ and $\{\omega_{\mu}\} = 10$–60) the integrand in Eq. (3.9) is not a strongly oscillating function [as, for example, the integrand in Eq. (2.2)] and the integral is easily evaluated by numerical methods.

It should be noted that the choice of a large value of ω_N for the computation of the integral (3.9) should not be confused with the inequality (3.1), as this inequality has provided the ideological basis for deriving the result in the statistical limit [Eq. (3.9)] while now we are just engaged in approximate numerical calculation of the integral in this equation.

We shall now proceed to apply this technique to a real physical system.

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[2] It may be shown, in fact, that if $\varepsilon_{\varkappa}$ is not an integer, $I_0(\varepsilon_{\varkappa}) = 0$. This should not worry us as from Eq. (3.1) it is clear that $\varepsilon_{\varkappa}$ should be taken as the integer closest to the real value of $\Delta E_{\varkappa}/\hbar \omega_N$.

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Table 1. Results of numerical integration of Eq. (4.2) for $T_1 - S_0$ crossing in benzene H_6

$\omega_N = 500$ cm^{-1}			$\omega_N = 50$ cm^{-1}			$\omega_N = 10$ cm^{-1}		
ΔE cm^{-1}	Promoting mode[a]	$\frac{1}{2}\left(\prod_\mu \beta_\mu\right)^{-\frac{1}{2}} I_k$ (cm^{-1})	ΔE cm^{-1}	Promoting mode[a]	$\frac{1}{2}\left(\prod_\mu \beta_\mu\right)^{-\frac{1}{2}} I_k$ (cm^{-1})	ΔE cm^{-1}	Promoting mode[a]	$\frac{1}{2}\left(\prod_\mu \beta_\mu\right)^{-\frac{1}{2}} I_k$ (cm^{-1})
28 500	1	0	29 550	1	6.4×10^{-17}	29 630	1	6.3×10^{-17}
	2	5.7×10^{-16}		2	6.1×10^{-17}		2	1.03×10^{-16}
29 000	1	5.6×10^{-16}	29 600	1	8.6×10^{-17}	29 640	1	7.0×10^{-17}
	2	0		2	4.4×10^{-17}		2	5.0×10^{-17}
29 500	1	0	29 650	1	1.00×10^{-16}	29 650	1	5.9×10^{-17}
	2	1.3×10^{-16}		2	4.3×10^{-17}		2	7.8×10^{-17}
30 000	1	1.3×10^{-16}	29 700	1	6.0×10^{-17}	29 660	1	9.4×10^{-17}
	2	0		2	6.1×10^{-17}		2	5.2×10^{-17}
30 500	1	0	29 750	1	4.2×10^{-17}	29 670	1	7.9×10^{-17}
	2	3.2×10^{-17}		2	9.0×10^{-17}		2	7.8×10^{-17}

[a] 1 denotes the C stretching mode, $\omega_1 = 1313$ cm^{-1}; 2 denotes the H bending mode, $\omega_2 = 1147$ cm^{-1}.

5. Intersystem Crossing ($T_1 \rightarrow S_0$) in the Benzene Molecule

The procedure outlined in the previous section will now be utilized to compute the intersystem crossing rate from the vibrational level of the $^3B_{1u}$ electronic state of the Benzene molecule to the ground electronic A_{1g} state, utilizing Eqs. (2.1), (2.2) and (2.4) for the non-radiative decay rate and making use of the molecular parameters given by Burland and Robinson [10]. This transition is characterized by two promoting modes (C stretching, $\omega_1 = 1313$ cm^{-1} and H bending, $\omega_2 = 1147$ cm^{-1} which are characterized by a b_{2u} symmetry); by two totally symmetric modes of non-vanishing origin displacements (C–H stretching, $\omega = 3063$ cm^{-1}, $\varDelta = 0.3$, and C–C stretching, $\omega = 990$ cm^{-1}, $\varDelta = 1.1$), by the frequency changes tabulated by Burland and Robinson [10] and by an energy gap, $\varDelta E = 29\,650$ cm^{-1}.

Making use of the procedure outlined in Sections (2) and (3) the non-radiative decay probability is [1b]

$$W_{s0} = \frac{1}{2\hbar^2} \sum_{\varkappa} |C_{sl}^{\varkappa}|^2 \left[\prod_{\mu} (\beta_{\mu})^{-\frac{1}{2}} \right] I_{\varkappa} \qquad (5.1)$$

where

$$
\begin{aligned}
I_{\varkappa} = \frac{1}{\omega_N} \int_0^{2\pi} dx \, \exp(-i\varepsilon_{\varkappa} x) \left\{ 1 + \frac{(1-\beta_{\varkappa})^2}{4\beta_{\varkappa}} [1 - \exp(2i\tilde{\omega}_{\varkappa} x)] \right\}^{-1} \\
\times \prod_{\mu} \left\{ 1 + \frac{(1-\beta_{\mu})^2}{4\beta_{\mu}} [1 - \exp(2i\tilde{\omega}_{\mu} x)] \right\}^{-\frac{1}{2}} \\
\times \exp \left\{ - \sum_{\mu} \frac{\beta_{\mu} \varDelta_{\mu}^2 [1 - \exp(i\tilde{\omega}_{\mu} x)]}{\beta_{\mu} + 1 + (\beta_{\mu} - 1)\exp(i\tilde{\omega}_{\mu} x)} \right\}
\end{aligned}
\qquad (5.2)
$$

where now

$$\varepsilon_{\varkappa} = \frac{\varDelta E + \hbar \sum_{\mu} \delta_{\mu}^{(-)} - \hbar \omega_{\varkappa}}{\hbar \omega_N}. \qquad (5.3)$$

in which $\delta_{\mu}^{(-)}$ is the difference in frequencies between the two electronic states.

In order to check our numerical method we have chosen $\omega_N = 500$ cm^{-1}, 50 cm^{-1} and 10 cm^{-1}, modifying each time the molecular frequencies and the effective energy gap so that $\varepsilon_{\varkappa}$ and $\{\tilde{\omega}_{\mu}\}$ are obtained as integers. As a rule, $\varepsilon_{\varkappa}$ and $\{\tilde{\omega}_{\mu}\}$ were chosen to correspond to the integers closest to the values of $\left(\varDelta E - \hbar \sum_{\mu} \delta_{\mu}^{(-)} - \hbar \omega_{\varkappa} \right) / \hbar \omega_N$ and of $\{\omega_{\mu}/\omega_N\}$ respectively.

From the results summarized in Table 1 we may conclude that our mathematical approximation is valid. In particular, we note that the results are

Table 2. Average values for the integral I_k for C_6H_6

ω_N cm^{-1}	500[a]	50	10
Average result for mode 1 (cm^{-1})	1.7×10^{-16}	7.0×10^{-17}	7.3×10^{-17}
Average result for mode 2 (cm^{-1})	1.4×10^{-16}	6.0×10^{-17}	7.2×10^{-17}

[a] The relatively large average in the case of $\omega_N = 500$ evolves from the contribution of the "low" 28\,500 cm^{-1} gap.
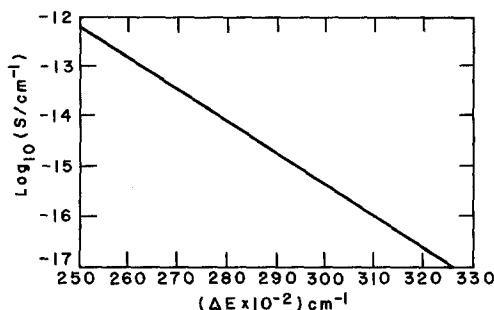
Fig. 1. The energy gap law in the low temperature limit of the $T_1 \rightarrow S_0$ transition in the benzene molecule. These results were obtained by numerical integration of Eqs. (5.1) and (5.2) using the spectroscopic data of Burland and Robinson (Ref. [10])

practically insensitive to the choice[3] of ω_N. Taking for each ω_N the average of the five results (displayed in Table 1) we obtain the final values summarized in Table 2. The physical implications of these numerical computations may be summarized as follows:

a) The inclusion of frequency changes is crucial for a semi-quantitative calculation of the non-radiative decay rate. The numerical results obtained from Eq. (4.2) with β_μ taken as unity for every μ, are three orders of magnitude lower than the results displayed in Table 1.

b) The energy gap law is retained (Fig. 1), but the decrease of the non-radiative decay rate as a function of increasing the energy gap is slightly modified when frequency changes are included. The energy gap law may be approximately represented by the relation

$$W_{s0} \sim A \exp(-\gamma \Delta E/\hbar \omega_M)$$

where from Fig. 1 we obtain $\gamma \approx 4$, while for the displaced undistorted potential surfaces model we have $\gamma = 2$ [1]. This result is reasonable, as with the inclusion of frequency changes the contributions of low frequencies which are strongly modified in the electronic transition, becomes more important.

c) Following Fischer and Schneider [9b] we may add a displacement of $\Delta = 0.9$ for the e_{2g} (1584 cm^{-1}) C–C stretching mode. This modification causes an increase by a numerical factor ~ 40 in the calculated non-radiative decay rate[4].

d) Repeating the calculation of Eq. (4.2) using Burland and Robinson's data [10] for the C_6D_6 molecule we obtain $\frac{1}{2} \prod_\mu \beta_\mu^{-1/2} I_1 = 9 \times 10^{-21}$ cm^{-1}; $\frac{1}{2} \prod_\mu \beta_\mu^{-1/2} I_2 = 4 \times 10^{-21}$ cm^{-1}. We may conclude that the non-radiative decay rate of C_6D_6 is lower by about four orders of magnitude than that of the C_6H_6 molecule.

e) Utilizing the results of Table 2 and taking $C_{sl} = 1.6 \times 10^{-1}$ cm^{-1} [10] we may calculate W_{s0} for the $T_1 - S_0$ intersystem crossing in the benzene molecule.

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[3] The fluctuations of the result as functions of ΔE should not worry us as they just represent the non-uniform distribution of $\{|l_j\rangle\}$ levels resulting from the "round off" approximation. This effect is most profound when we choose $\omega_N = 500$ cm^{-1}.

[4] The increase is much more profound (about three orders of magnitude) in the case of deutrobenzene.

Table 3. Theoretical intersystem crossing rates in the benzene-H_6 and benzene-D_6 molecules

	C_6H_6	C_6D_6
Present work	$7.2 \times 10^{-7} \text{ sec}^{-1}$	$6.6 \times 10^{-11} \text{ sec}^{-1}$
	2.6×10^{-5} [a]	$1.2 \times 10^{-7} \text{ sec}^{-1}$ [a]
Burland and Robinson [10]	$9.04 \times 10^{-5} \text{ sec}^{-1}$	$1.18 \times 10^{-10} \text{ sec}^{-1}$
Fischer and Schneider [9]	$7.4 \times 10^{-4} \text{ sec}^{-1}$	$3.1 \times 10^{-5} \text{ sec}^{-1}$
Experiment [10]	$2.4 \times 10^{-2} \text{ sec}^{-1}$	

[a] Using Fischer's and Schneider's data for the displacement of the e_{2g} deformation mode.

Our numerical results together with previously obtained results of Burland and Robinson [10] and of Fischer and Schneider [9b] are summarized in Table 3. The results of Burland and Robinson are based on an approximate level counting procedure. The results of Fischer and Schneider, which are obtained from a formalism equivalent to ours attempting to incorporate both frequency changes and unharmonicities are doubtful, as they are based on the unjustified expansion discussed in Appendix A.

The results presented in Table 3 should be compared with the experimental result [10] $W_{s0} \approx 2.4 \times 10^{-2} \text{ sec}^{-1}$. The difference of about three to four orders of magnitude is probably caused by the neglect of unharmonicities [13, 10].

We have obtained the worst agreement reported up to date between theory and experiment for the $T_1 \rightarrow S_0$ non-radiative decay probability in the benzene molecule. However, we feel that the numerical results presented herein provide the first correct calculation of the non-radiative decay probability of a harmonic molecule. It is not surprising that the neglect of unharmonicities yields a rather serious underestimate of the decay rate. At present no systematic valid procedure is available for the incorporation of unharmonicities. (The Fischer Schneider procedure [9] is unfortunately invalid in view of unjustified expansions of the generating function.) People interested in this field should attempt to derive the density matrix (i.e., the Green's function [11]) for an unharmonic oscillator and use this result for the evaluation of the generating function.

The goal of theoretical chemistry is not to reproduce experimental results but rather to provide general relations and correlations. In this context, the general formulation of the non-radiative decay of a model harmonic molecule in the statistical limit is of considerable interest.

Appendix A: A Comment on the Convergence Problem

Lin and Berson [8], Freed and Jortner [1b], Fischer [7] and others [6, 9] have used expansions of the form

$$F(\xi \exp(i\omega t)) = 1 + a \xi e^{i\omega t} + b \xi^2 e^{2i\omega t} + \cdots \qquad (A.1)$$

where F is some function and $\xi \ll 1$ is a small parameter, in order to simplify the generating function obtained in the theory of radiationless transitions in the statistical limit. Most of the available expressions [1, 6–8] for the non radiative decay rate of a large molecule characterized by displaced and modified potential surfaces and also Fischer's attempt to include unharmonicities in the theory [9] utilize such expansions and neglect high order terms before evaluating the necessary Fourier transform of the generating function. We now wish to demonstrate that such an approximation which neglects the higher order terms is unfortunately justified. To this end we shall compare the contributions of the low order terms which are usually retained in the approximate expression and of a higher order term which is usually neglected. Suppose, for example, that E/ω is an even integer and we want to compare $\int\limits_{-\infty}^{\infty} dt \exp[-iEt + \xi \exp(i\omega t)]$ and $\int\limits_{-\infty}^{\infty} dt \exp[-iEt + \xi^2 \exp(2i\omega t)]$. Expanding the integrand in the form

$$\exp[\xi \exp(i\omega t)] = \sum_{n=0}^{\infty} \frac{\xi^n}{n!} \exp(in\omega t) \tag{A.2}$$

it is easy to get

$$\int\limits_{-\infty}^{\infty} dt \exp[-iEt + \xi \exp(i\omega t)] = 2\pi \sum_{n=0}^{\infty} \frac{\xi^n}{n!} \delta(E - n\omega). \tag{A.3}$$

In the statistical limit it may be shown that $\delta(E - n\omega)$ may be replaced by $\delta_{E, n\omega}$. This may be proved by utilizing the same procedure which leads to Eq. (3.9) and noting that

$$\int\limits_{0}^{2\pi} dt \exp[-iEt + \xi \exp(i\omega t)] = 2\pi \frac{\xi^n}{n!} \delta_{E, n\omega}. \tag{A.4}$$

Thus we get $2\pi \dfrac{\xi^{E/\omega}}{(E/\omega)!}$ where ξ will be an average over the contributions from many modes.

In the same way, we get

$$\int\limits_{-\infty}^{\infty} dt \exp[-iEt + \xi^2 \exp(2i\omega t)] = 2\pi \frac{(\xi^2)^{E/2\omega}}{(E/2\omega)!} \tag{A.5}$$

which is greater than the first result for every ξ. Of course, higher order terms $0(\xi^n)$ with $n \gg 2$ lead to vanishingly small contributions. Thus one cannot get away by neglecting terms of the order of $0(\xi^2)$ in the expansion (A.1), and one has to retain the terms up to $m = (E/\omega)$. This conclusion is supported by numerical calculations performed by us on Eq. (4.1).

Appendix B: Verification of the Identity [11.12]

Starting from

$$I = \int\limits_{-\infty}^{\infty} dx \exp(-iax) F(x) \tag{B.1}$$

where $F(x)$ is a periodic function of x, characterized by a period of 2π, we proceed as follows [12]:

$$
\begin{aligned}
I &= \sum_{n=-\infty}^{\infty} \int_{2\pi n}^{2\pi(n+1)} dx \exp(-iax) F(x) \\
&= \sum_{n=-\infty}^{\infty} \exp(2\pi ina) \int_{0}^{2\pi} dx \exp(-iax) F(x)
\end{aligned}
\tag{B.2}
$$

where in each integral we have replaced x by $x - 2n\pi$. Relation (2.12) is now easily verified by utilizing the identity

$$
\sum_{n=-\infty}^{\infty} \exp(2\pi ina) = \sum_{s=-\infty}^{\infty} \delta(s-a). \tag{B.3}
$$

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Prof. Dr. J. Jortner
Department of Chemistry
Tel-Aviv University
Tel-Aviv, Israel