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The energy gap law for radiationless transitions in large molecules

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In this paper we present a unified treatment of non-radiative decay processes in large molecules which involve either electronic relaxation between two electronic states or unimolecular rearrangement reactions in excited electronic states. The present treatment is analogous to the formalism previously applied for the line shape problem in nuclear recoil and in the optical spectra of solids. We were able to derive theoretical expressions for the non-radiative decay probability so that an arbitrary number of different molecular vibrations can be incorporated in the vibrational overlap factors. The general expressions obtained herein can be reduced to analytical form for two limiting cases, which we call the strong coupling case (which corresponds to a substantial horizontal displacement of the potential energy surfaces of the two electronic states) and the weak coupling limit (whereupon the relative horizontal displacement of the two potential energy surfaces is small). Quantitative criteria for the applicability of these two coupling limits are provided. In the strong coupling limit the transition probability is determined by a gaussian function of the energy parameter $(\Delta E - E_M)$, where ΔE is the energy gap between the origins of the two electronic states and $2E_M$ is the Stokes shift. This limit exhibits a generalized Arrhenius type temperature behaviour whereupon the transition probability depends exponentially on the energy barrier for the intersection of the two potential surfaces. At low temperatures the transition probability is determined by the mean vibrational frequency and is thus expected to reveal only a moderately weak deuterium isotope effect. The weak coupling limit reveals an exponential (or rather superexponential) dependence of the transition probability on the energy gap ΔE. In this limit the transition probability is dominated by the highest vibrational frequency (e.g. the C–H or C–D vibrations) and thus will reveal a marked isotope effect. When semi-empirical estimates of the pre-exponential factors are provided, the approximate theoretical expression for the weak coupling limit is found to be consistent with the available experimental data on electronic relaxation in large organic molecules.

1. FEATURES OF RADIATIONLESS TRANSITION IN THE STATISTICAL LIMIT

Radiationless transitions in large molecules constitute a class of molecular relaxation processes which are electronic in nature. Two general classes of such processes may be considered:

(*a*) Electronic relaxation processes [1–21] which involve transitions between different electronic states in a large molecule (e.g. internal conversion and intersystem crossing).

(*b*) Unimolecular photochemical rearrangement reactions [22–44] in excited electronic states of large molecules.

Electronic relaxation processes in large molecules, such as naphthalene, anthracene and tetracene correspond to the statistical limit [15–17], which is completely analogous to the corresponding case in nuclear physics [45]. In this limit the density of vibronic states is extremely high, resulting in intramolecular line broadening [6, 16–21]. Electronic relaxation takes place on a time scale shorter than a typical recurrence time [16–21]. To consider in some detail the physical situation encountered in the statistical limit let us focus our attention on the two-level system presented in figure 1. The higher excited electronic state, *s*, is characterized by the zero-order B.O.† levels $\psi_{si}(\mathbf{r}, \mathbf{Q}^{(s)}) = \phi_s(\mathbf{r}, \mathbf{Q}^{(s)})\,\chi_{si}(\mathbf{Q}^{(s)})$ which are coarsely spaced, each of which is coupled to the dense quasicontinuum of vibronic levels $\psi_{lj}(\mathbf{r}, \mathbf{Q}^{(l)}) = \phi_l(\mathbf{r}, \mathbf{Q}^{(l)})\,\chi_{lj}(\mathbf{Q}^{(l)})$. Here $\mathbf{r}$ represents the electronic coordinates, while $\mathbf{Q}^{(s)}$ and $\mathbf{Q}^{(l)}$ correspond to the normal coordinates in the electronic states *s* and *l*, respectively. ϕ and χ represent electronic and vibrational wavefunctions.

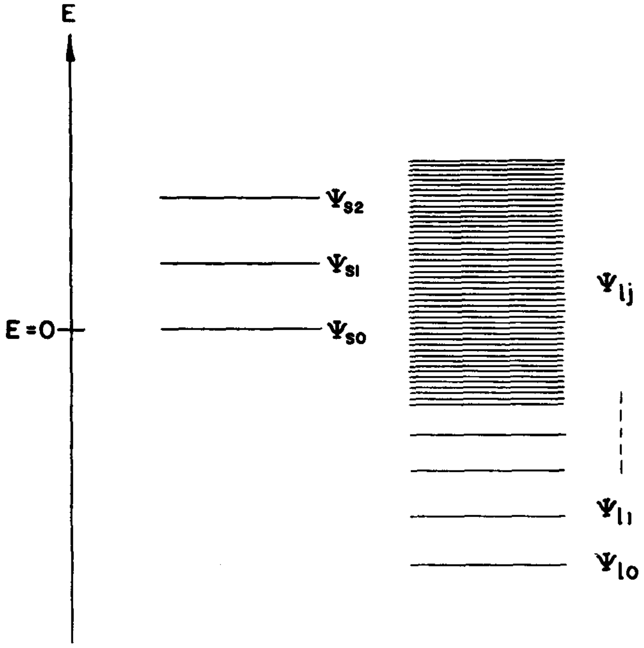

Figure 1. A schematic energy levels diagram for a two-electronic levels system.

We shall now focus our attention on the simultaneous decay of a number of resonances. An excited state is ‘ prepared ’ at the time $\tau = 0$ in the form of the superposition [16–21].

$$\Psi(\tau = 0) = \sum_i \omega(si)\,\psi_{si}, \tag{1.1}$$

$\omega(si)$ is the amplitude of the zero-order state ψ_{si} in the total wavefunction at $\tau = 0$. The probability of the system being initially in the zero-order state ψ_{si} is given by $p(si) = |\omega(si)|^2$ and obviously $\sum_i p(si) = 1$.

$$\Psi(t) = \sum_i A_i(t)\,\psi_{si} + \sum_j B_{lj}(t)\,\psi_{lj}. \tag{1.2}$$

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† Born–Oppenheimer (B.O.).

The equation of motion for the vector $\mathbf{A}$ of the coefficients $A_i(t)$ can be displayed in the form [46]:

$$i\hbar \frac{d}{dt}\mathbf{A} = \left(\mathbf{H}_{\mathrm{el}} - \frac{i\hbar}{2}\mathbf{\Gamma}\right)\mathbf{A}, \tag{1.3}$$

where $\mathbf{H}_{\mathrm{el}}$ is the matrix of the electronic hamiltonian $H_{\mathrm{el}} = H_{\mathrm{BO}} + V$ while the damping matrix $\mathbf{\Gamma}$ is recast in the form [20, 46].

$$\Gamma_{si,\, si'} = \frac{2\pi}{\hbar}\sum_j V_{si,\, lj} V_{lj,\, si'}\, \delta(E - E_{lj}), \tag{1.4}$$

where the coupling matrix elements are $V_{si,\, lj} = \langle \psi_{si} | V | \psi_{lj} \rangle$. When the spacing of the zero-order energy levels E_{si} exceeds the widths of the resonances or, more quantitatively stated, when [20, 46]

$$\hbar\Gamma_{si,\, si'} \ll \left| E_{si} - E_{si'} - \frac{i\hbar}{2}(\Gamma_{si,\, si} - \Gamma_{si',\, si'}) \right|$$

the damping matrix is diagonal and each resonance decays with its own lifetime [20, 46]. The initial transition probability (at $\tau = 0$) for the non-radiative decay to the dissipative quasicontinuum $\{\psi_{lj}\}$ can be recast in the conventional form [10, 11, 47]:

$$W = \frac{2\pi}{\hbar}\sum_i \sum_j p(si) |V_{si,\, lj}|^2\, \delta(E_{si} - E_{lj}). \tag{1.5}$$

Equation (1.5) is well known, however, it is useful to bear in mind that it is valid only when interference effects between resonances are negligible. Up to this point the effect of the radiative decay was not considered; however, in the statistical limit the radiative decay can be included by considering an additional decay channel [19–21].

The final stage of most quantum chemical calculations usually involves the evaluation of the pertinent matrix elements. The coupling matrix element between the zero-order components which correspond to two electronic states can be displayed in the form [10, 16]†:

$$V_{si,\, lj} = C \sum_{t \neq k} \langle X_{st}(Q_t^{(s)}, v_{sk}) | X_{lt}(Q_t^{(l)}, v_{lt}) \rangle, \tag{1.6}$$

where

$$C^{(\mathrm{co})} = \sum_{k \in p} J_{sl}^{k} \left(X_{sk}(Q_k^{(s)}, v_{sk}) \left| \frac{\partial}{\partial Q_k} \right| X_{lk}(Q_k^{(l)}, v_{lk}) \right), \tag{1.7 a}$$

$$C^{(\mathrm{cr})} = \sum_{k \in p} \sum_{\gamma \neq l,\, s} (K_{s\gamma} J_{\gamma s}^{k} + J_{s\gamma}^{k} K_{\gamma l}) \left(X_{sk}(Q_k^{(s)}, v_{sk}) \left| \frac{\partial}{\partial Q_k} \right| X_{lk}(Q_k^{(l)} v_{lk}) \right). \tag{1.7 b}$$

The superscripts (co) and (cr) correspond to internal conversion and to intersystem crossing, respectively. These expressions involve the electronic matrix elements‡ J_{sl}^{k} for the kinetic energy operator $\partial/\partial Q_k$ of the kth normal mode and the spin–orbit terms‡ $K_{s\gamma}$ and $K_{\gamma l}$ which combine the electronic states ϕ_s and ϕ_l with intermediate

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† There is a typographical error in equation (85) of [16]. The correct version is given by equation (1.7 *b*).

‡ We are using the same notation as in [16].

states ϕ_γ. The molecular vibrational wavefunctions χ_{si} and χ_{lj} have been displayed as products of harmonic oscillator wavefunctions

$$\prod_{\mu} X_{s\mu}(Q_\mu^{(s)}, v_{s\mu}) \quad \text{and} \quad \prod_{\nu} X_{l\nu}(Q_\nu^{(l)}, v_{l\nu}),$$

where $v_{s\mu}$ and $v_{s\nu}$ correspond to the vibrational quantum numbers. The index $t = 1, \ldots, N$ corresponds to all the normal modes, while the index $k = 1, \ldots, p$ refers to the promoting modes for which the J^k terms are appreciable. From the theory of vibronic coupling [48] it is apparent that the promoting modes [11] involve skeletal bending [10, 11]. The normal coordinates for these promoting modes are thus not displaced between different electronic states of aromatic hydrocarbons. In the case of a large molecule whereupon $p \ll N$ and for the case when the electronic energy gap ΔE between the two electronic states considerably exceeds the frequency of the promoting modes, it appears that the removal of the $t \neq k$ restriction in equation (1.6), i.e. the omission of a single vibrational overlap factor from equation (1.6) is of minor importance. One can therefore rewrite equation (1.6) in the approximate form [8, 9, 12].

$$V_{si,\, lj} \approx C S_{si,\, lj}, \tag{1.8}$$

where $S_{si,\, lj}$ is the Franck–Condon vibrational overlap factor:

$$S_{si,\, lj} = \prod_{\text{all } t} \langle X_{st}(Q_t^{(s)}, v_{st}) | X_{lt}(Q_t^{(l)}, v_{lt}) \rangle \tag{1.9}$$

and the energy parameters C for internal conversion and for intersystem crossing is given by equations (1.7 *a*) and (1.7 *b*). The energy parameters [8] $C^{(\mathrm{co})}$ and $C^{(\mathrm{cr})}$ will not be evaluated. The main new feature of our treatment involves the handling of the sums which involve the S integrals.

Using the approximation concerning the constancy of the C terms the general form of the non-radiative decay probability is given by:

$$W = \frac{2\pi}{\hbar} C^2 \sum_i \sum_j p(si) |S_{si,\, lj}|^2 \delta(E_{si} - E_{lj}). \tag{1.10}$$

Two physically interesting cases can be now considered:

(*a*) When the molecule is inserted in an inert medium which acts as a heat bath, thermal equilibration among the si levels can be assumed. Provided that the vibrational relaxation (and excitation) rates considerably exceed the non-radiative decay time we can set:

$$p(si) = \exp(-\beta E_{si}) / \sum_i \exp(-\beta E_{si}) \tag{1.11}$$

where $\beta = 1/(k_B T)$.

(*b*) For the case of an isolated molecule (in the vacuum or even better in outer space) we can consider a coherent excitation of a single vibronic state $\psi_{si'}$ whereupon $p(si) = \delta_{ii'}$. When this zero-order vibronic level si, corresponds to the lowest vibronic level, so, the transition probability is given by equations (1.10) and (1.11) in the zero temperature limit (or rather for $\beta \to \infty$).

It is important to notice at this point that the general theory of radiationless transitions in the statistical limit outlined above should be applicable not only for electronic relaxation process but also for other intramolecular radiationless processes which involve photo-chemical rearrangements in excited electronic states of large molecules.

2. AIMS AND CLAIMS

Although the theory outlined above provides a unified formal interpretation of radiationless processes in the statistical limit, reliable predictions of the non-radiative transition probability are not available at present. Several attempts were made to handle the vibronic coupling matrix elements which determine the transition probability for electronic relaxation. Ross *et al.* [7, 9], Robinson and Frosch [8], and Bersohn and Lin [10, 11] and Siebrand [12–14] have substantially contributed to an understanding of the intramolecular coupling terms. Some rough estimates of the density of states were also performed [15–17]. However, these attempts based on conventional computational methods cannot be expected to yield reliable information for a large molecule which is characterized by a large number, N, of vibrational degrees of freedom. In view of the complexity of the problem encountered in the calculation of W (equation (1.10)) in the statistical limit conventional ' quantum chemistry ' type methods seem to be inadequate. General problems related to the calculation of expressions of the form of equations (1.5) and (1.10) were encountered in solid state physics. Such a task was considered by Lamb [49] and by others [50, 51] for the Mössbauer effect. The nuclear recoil problem for the displacements in the momentum space requires the same treatment as a harmonic lattice. Indeed, analogous problems were encountered in the theory of line shapes and zero phonon lines in the absorption spectra of impurity centres in solids [52–58]. Finally, similar methods were introduced by Kubo [47, 55] for the study of radiationless transition (e.g. thermal ionization) in solids. We shall attempt to consider the problem of radiationless transitions in a large molecule from the point of view of multi-phonon processes. Indeed, for a large molecule when $N \gg 1$ it seems a logical step to transfer the problem from the field of molecular physics† to the realm of solid state physics and to consider the problem of ' phonons in large molecules '.

We were able to derive theoretical expressions for the non-radiative decay probability from the lower vibronic level of an excited electronic state in an isolated molecule and for a molecule in a dense inert medium. When an inert medium (which does not modify the energy levels or the spin–orbit coupling terms [59, 60]) is considered, there is currently convincing evidence for the absence of drastic medium effects [61–64] on electronic relaxation in large molecules (e.g. larger than the benzene molecule [65]) which correspond to the statistical limit, so that the inert medium just acts as a heat bath. The advantage of this new formalism is that we do not have to factor out the general expressions (1.5) or (1.10) into a product of a coupling term and a density of states and then an arbitrary number of different molecular vibrational frequencies can be incorporated in the vibrational overlap factor. The general structure of the theoretical formulas obtained herein makes it possible to ascertain the gross features of the electronic level structure and to determine what are the relevant molecular parameters which dominate the probability for non-radiative decay. The general expressions can be reduced to an analytical form for two limiting cases which we shall call the strong and the weak coupling limits. In the strong coupling limit the relative horizontal displacement of the multidimensional potential energy surfaces which correspond to two electronic states is large and the energy surfaces are expected to cross not far from the

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† The formalism presented herein is valid for any N. Although in the first treatment of this problem [49] it was assumed that $N \gg 1$, this assumption is not necessary.

minimum of the higher electronic state. This situation corresponds to the model proposed many years ago by Teller [66] to account for electronic relaxation. This limit is not appropriate in most cases for the latter class of relaxation processes. However, large configurational changes between two electronic states are encountered in the field of rearrangements reaction in organic photochemistry [22] such as cis–trans isomerization [23–33] or electrocyclic reactions [34–44]. In the weak coupling the relative displacement of the potential energy surfaces is small and this situation corresponds to the Robinson–Frosch–McCoy–Ross picture for electronic relaxation. Indeed, the weak coupling limit prevails for electronic relaxation in large aromatic molecules, while the study of the strong coupling case is of interest for the understanding of unimolecular photochemical reactions which take place in excited electronic states of large molecules. It was felt for a long time that electronic relaxation and photochemical rearrangement processes should be amenable to a theoretical treatment from a unified point of view. The present work provides the first step in that direction.

3. GENERATING FUNCTIONS

The approximate expression for the non-radiative transition probability (equation (1.10)) is completely analogous to the formal expressions for the line shape in optical absorption in solids [52–58]. Indeed, in this approximation the non-radiative process can be formally regarded as optical excitation in the limit of zero excitation energy. Equations (1.5) and (1.10) seem at first sight as useless theoretical expressions which contain intractable summations. These expressions can be handled by the application of the generating function method [47]. The main advantage of this technique is that it handles the generalized density of states function of the form (1.5) (e.g. the density of states weighted by an arbitrary operator) without the necessity to factor out these expressions into products of matrix elements and the vibronic density of states.

In what follows this technique is briefly considered. Our purpose is to evaluate a line shape function of the general form:

$$F(E))=\left[\sum_i\sum_j |S_{si,\,lj}|^2 \exp(-\beta E_{si})\,\delta(E_{lj}-E_{si}-E)\right]\Big/\sum_i \exp(-\beta E_{si}), \qquad (3.1)$$

so that obviously:

$$W=\frac{2\pi}{\hbar}C^2F(0). \qquad (3.2)$$

The Fourier transform of equation (3.1) is given by:

$$f(t)=\int_{-\infty}^{\infty} F(E)\exp(iEt/\hbar)\,dE. \qquad (3.3)$$

Application of equation (3.1) leads to the form:

$$f(t)=\sum_i\sum_j S_{si,\,lj}\exp(iE_{lj}t/\hbar)\,S_{lj,si}\exp\left[-\left(\beta+\frac{it}{\hbar}\right)E_{si}\right] \times\left[\sum_i \exp(-\beta E_{si})\right]. \qquad (3.4)$$

It is easier to calculate the generating function $f(t)$. The line shape function is then given by the inverse Fourier transform:

$$F(E)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} f(t)\exp(-iEt/\hbar)\,dt. \tag{3.5}$$

We now have to specify the model system in detail. We shall consider two adiabatic energy surfaces for the electronic states s and l. It will be assumed that the major effect on the line shape function arises from terms linear in relative nuclear displacements. We shall thus ignore the effects arising from changes in normal modes and in their frequencies in the two electronic states. Finally, the harmonic approximation will be applied.

Let the normal coordinates be denoted by Q_j $(j=1, \ldots, N)$ with the effective masses M_j and frequencies ω_j. The equilibrium configuration of the electronic state s is characterized by the configuration $Q_j^{0(s)}$ $(j=1, \ldots, N)$. Let $\Delta Q_j^0=Q_j^{0(l)}-Q_j^{0(s)}$ correspond to the displacement of the Q_j normal coordinate in the equilibrium configuration of the electronic state l relative to the electronic state s. It will be also useful to define a set of dimensionless coordinates and displacements:

$$q_j=\left(\frac{M_j\omega_j}{\hbar}\right)^{1/2}(Q_j-Q_j^{0(s)}) \tag{3.6}$$

$$\Delta_j=\left(\frac{M_j\omega_j}{\hbar}\right)^{1/2}\Delta Q_j^0. \tag{3.7}$$

The adiabatic potentials E_s and E_l for the two electronic states are given in the form:

$$E_s=\tfrac{1}{2}\sum_j\hbar\omega_j q_j^2, \tag{3.8 a}$$

$$\begin{aligned}E_l&=\tfrac{1}{2}\sum_j\hbar\omega_j(q_j-\Delta_j)^2-\Delta E\\&=E_s-\sum_j\gamma_j q_j-\Delta E+E_M,\end{aligned} \tag{3.8 b}$$

where $\gamma_j=\hbar\omega_j\Delta_j$ corresponds to the linear coupling term for the jth mode. The energy term:

$$E_M=\tfrac{1}{2}\sum_j\hbar\omega_j\Delta_j^2 \tag{3.9}$$

represents the molecular nuclear relaxation energy, or rather half the Stokes shift, due to the reduced displacements Δ_j (see figure 2).

From equations (3.4), (3.8), and (3.9) the following relation for the generating function is obtained [29–36]:

$$\log f(t)=-\frac{i\Delta Et}{\hbar}-G+G_+(t)+G_-(t), \tag{3.10}$$

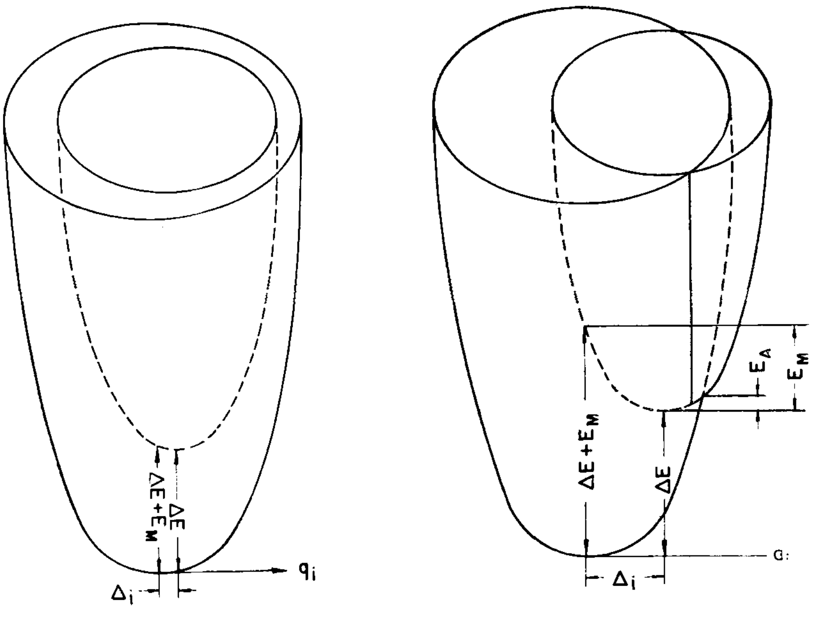
where the functions $G_\pm(t)$ are given by:

$$\left.\begin{aligned}G_+(t)&=\tfrac{1}{2}\sum_j|\Delta_j|^2(\bar{n}_j+1)\exp(i\omega_j t),\\G_-(t)&=\tfrac{1}{2}\sum_j|\Delta_j|^2\,\bar{n}_j\exp(-i\omega_j t)\end{aligned}\right\} \tag{3.11}$$

and

$$\bar{n}_j=[\exp(\beta\hbar\omega_j)-1]^{-1}, \tag{3.12}$$

$\bar{n}_j$ is the number of excited vibrations with frequency ω_j at thermal equilibrium.



(*a*) (*b*)

Figure 2. Schematic representation of the two adiabatic potential surfaces E_s and E_l in two-dimensional vibrational space. (*a*) The weak coupling limit. (*b*) The strong coupling case.

The dimensionless quantity G is defined in the form:

$$G = G_+(0) + G_-(0) = \tfrac{1}{2}\sum_j |\Delta_j|^2(2\bar{n}_j + 1), \tag{3.13}$$

which corresponds to the change in the number of vibrational quantum in the radiationless transition. This quantity is referred to as the coupling strength. Thus when thermal equilibration within the manifold ψ_{si} is faster than all other molecular decay processes, and provided that the approximate form for the adiabatic energy surfaces (equations (3.8) and (3.9)) are acceptable, the non-radiative transition probability is given by:

$$W = \frac{C^2}{\hbar^2}\exp(-G)\int_{-\infty}^{\infty}\exp\left[-\frac{i\Delta E t}{\hbar} + G_+(t) + G_-(t)\right]dt. \tag{3.14}$$

This expression for W seems at first sight abstract and rather impractical; however, even in its present form it is quite an advance over current methods for the evaluation of the Franck–Condon factors for more than a single mode with different frequencies. Note that this result exhibits the dependence of W on the energy gap ΔE. The general result derived herein can be recast in a more transparent form for certain limiting cases, which are determined by the magnitude of the coupling strength G (equation (3.13)). In order to obtain an approximate estimate for the coupling strength we make use of equation (3.9) and write the approximate relation:

$$G \approx \frac{E_M}{\hbar\langle\omega\rangle}\coth\left(\frac{\beta\hbar\langle\omega\rangle}{2}\right), \tag{3.15}$$

where $\langle\omega\rangle = N^{-1}\sum_j \omega_j$ is the mean vibrational frequency. The low and high temperature limits are:

$$G \approx E_M/\hbar\langle\omega\rangle\,; \qquad \beta\hbar\langle\omega\rangle \gg 1, \tag{3.16 a}$$

$$G \approx 2E_M(\hbar\langle\omega\rangle)^{-2}\,\beta^{-1}\,; \qquad \beta\hbar\langle\omega\rangle \ll 1. \tag{3.16 b}$$

Considering a large molecule at room temperature we expect to encounter the low temperature limit (3.16 *a*). The various coupling limits can be defined as follows:

(*a*) In the strong coupling limit $G \gg 1$ or alternatively $E_M \gg \hbar\langle\omega\rangle \tanh(\frac{1}{2}\beta\hbar\langle\omega\rangle)$. At low temperatures the strong coupling limit will be encountered whereupon E_M exceeds the mean vibrational frequency so that the relative displacement of the potential energy surfaces are large, and the Stokes shift will considerably exceed the vibrational frequency. Under these circumstances it is possible for the energy surfaces of the two electronic states to cross or to intersect in the vicinity of the minimum of the upper surface. Such a situation was examined 30 years ago by Teller [66].

(*b*) The weak coupling limit is encountered when $G \lesssim 1$ or (at low temperatures) $E_M \sim \hbar\langle\omega\rangle$. Thus the relative displacement for each normal mode is relatively small.

We shall now demonstrate that our general expression (3.14) can be reduced to a tractable form for these two limiting cases.

4. THE STRONG COUPLING LIMIT

When $G \gg 1$ it is reasonable to try to expand the functions $G_+(t)$ and $G_-(t)$ (equation (3.11)) in a power series in t retaining only terms up to the t^2 term:

$$G_+(t) + G_-(t) = G + \frac{it}{2}\sum_j \omega_j\Delta_j^2 - \tfrac{1}{2}D^2t^2 + O(t^3), \tag{4.1}$$

where

$$D^2 = \tfrac{1}{2}\sum_j \omega_j^2\Delta_j^2(2\bar{n}_j + 1). \tag{4.2}$$

Thus the coefficient of the quadratic is roughly $D^2 \approx G\langle\omega\rangle^2$. Provided that G is large we then expect that the generating function $f(t)$ (equation (3.10)) will decay exponentially (as $\exp(-\langle\omega\rangle^2t^2/2)$) to a small value before the power expansion of $G_\pm(t)$ becomes invalid (e.g. when $\langle\omega\rangle\, t \gtrsim 1$). Thus in the strong coupling limit we obtain, from equations (3.9), (3.10), and (4.1):

$$f(t) = \exp\left[-\frac{it}{\hbar}(\Delta E - E_M) - D^2t^2/2\right]; \tag{4.3}$$

and the transition probability is given in the gaussian form:

$$W = \frac{C^2\sqrt{(2\pi)}}{D\hbar^2}\exp\left[-(\Delta E - E_M)^2/2D^2\hbar^2\right]. \tag{4.4}$$

Finally making use of the approximate relations for G and for D one can recast this result in the form:

$$W = \frac{C^2\sqrt{(2\pi)}\exp\left[-(\Delta E - E_M)^2/2E_M\hbar\langle\omega\rangle\coth(\beta\hbar\langle\omega\rangle/2)\right]}{\left[E_M\hbar\langle\omega\rangle\coth(\beta\hbar\langle\omega\rangle/2)\right]}. \tag{4.5}$$

The gaussian dependence on the energy parameter $(\Delta E - E_M)$ in the strong coupling limit is of course analogous to the gaussian line shape (near the band maximum) devoid of phonon structure for impurity centres [53–58]. However, equation (4.5) contains some further interesting information. Inspection of equations (3.8 *a*) and (3.8 *b*) reveals that the potential surfaces E_s and E_l intersect on the hypercurve (actually on the $(N-1)$-dimensional surface) which satisfies the relation:

$$\sum_j \gamma_j q_j = -\Delta E + E_M. \tag{4.6}$$

The point of minimum energy on this hypercurve is given by the conditions $(\partial E_s/\partial q_i) = 0$ subjected to the restriction (4.6). Thus the intersection point of minimum energy, E_A, measured from the energy origin $E_{s0} = 0$ (see figure 2), is obtained from the relation $E_A = \alpha^2 E_M$, where $\alpha = (\Delta E - E_M)/2E_M$ so that

$$E_A = (\Delta E - E_M)^2/4E_M. \tag{4.7}$$

We obtain the following result:

$$W = \frac{C^2\sqrt{(2\pi)}}{\hbar(E_M k_B T^*)^{1/2}} \exp(-E_A/k_B T^*), \tag{4.8}$$

where the effective temperature is defined in the form:

$$k_B T^* = \tfrac{1}{2}\hbar\langle\omega\rangle \coth(\beta\hbar\langle\omega\rangle/2). \tag{4.9}$$

The following conclusions are now in order:

(*a*) In the strong coupling limit at 'low' temperatures (e.g. $\beta\hbar\langle\omega\rangle \gg 1$) the following rate equation results:

$$W = \frac{C^2\sqrt{(4\pi)}}{\sqrt{(E_M\hbar\langle\omega\rangle)}} \exp(-2E_A/\hbar\langle\omega\rangle). \tag{4.10}$$

This equation is valid both for a molecule in an inert medium and for an isolated molecule when only one level was excited. Thus the transition probability is determined by the mean vibrational frequency $\langle\omega\rangle$ and by the energy E_A. From equation (4.7) we may conclude that as in the strong coupling limit $\Delta E \sim E_M$ and hence $E_A < \Delta E$.

(*b*) Considering a molecule which corresponds to the strong coupling limit immersed in a heat bath at high temperatures ($\beta\hbar\langle\omega\rangle \ll 1$) one obtains:

$$W = \frac{k_B T}{\hbar} \frac{C^2\sqrt{(2\pi)}}{\sqrt{[E_M(k_B T)^3]}} \exp(-E_A/k_B T). \tag{4.11}$$

This equation has a general appearance of a conventional rate equation, where the energy E_A plays the role of the activation energy as might have been guessed by the intelligent chemist on intuitive grounds. Unfortunately, high temperatures (only to be achieved in a shock tube) are required for approaching this limit.

(*c*) In the intermediate temperature region ($\beta\hbar\langle\omega\rangle \gtrsim 1$) the activated rate equation is characterized by the effective temperature $\tfrac{1}{2}\hbar\langle\omega\rangle \coth(\tfrac{1}{2}\beta\hbar\langle\omega\rangle)$. This relation is only approximate in view of the averaging involved in the derivation of equation (3.16).

(*d*) As W in the strong coupling limit is determined by the mean vibrational frequency $\langle\omega\rangle$ only a moderate isotope effect on the transition probability will be observed in this case. This should be compared with the large isotope effect obtained in the weak coupling limit (see §6).

The theoretical treatment of the strong coupling limit is gratifying as a closed expression for the transition probability can be provided. This limit is expected to be encountered even at low temperatures when the relative displacements of the two potential energy surfaces are large so that crossing on intersection of these energy surfaces will occur close to the minimum point of E_s. From the experimental point of view the criteria mentioned above should be utilized to characterize this limit. We are not aware of a molecular system where a radiationless (e.g. electronic relaxation) process between two electronic states (which takes place without a chemical modification of the molecule) corresponds to the strong coupling case. This limit may be of considerable interest for the understanding of photochemical rearrangement processes in large molecules.

5. THE WEAK COUPLING LIMIT

When $G \lesssim 1$, whereupon $E_M \lesssim \hbar\langle\omega\rangle$, so that the relative displacement of the potential energy surfaces is small, and the weak coupling limit is encountered. This is essentially the physical situation described by Robinson, Frosch, McCoy and Ross and others. To treat this problem, we must go back to equation (3.14) and we shall initially focus our attention on the low temperature limit setting $\bar{n}_j = 0$ for all j. The integral in (3.14) will be evaluated by the method of steepest descent. The saddle point in the complex t plane is easily seen to be given by the root (or roots) of

$$\tfrac{1}{2}\sum_j \Delta_j^2 \hbar\omega_j \exp(i\omega_j t) - \Delta E = 0. \tag{5.1}$$

Let the index M refer to the mode (or modes) of maximum frequency (and for which $\Delta_M^2 \neq 0$), and let d be the number of degenerate (or nearly degenerate) modes of this maximum frequency. For large ΔE (e.g. $\Delta E \gg \hbar\langle\omega\rangle$) the physically meaningful root of (5.1) appears to be:

$$t = -\frac{i}{\omega_M} \log\left(\frac{2\Delta E}{\sum_{M=1}^{d} \hbar\omega_M \Delta_M^2}\right). \tag{5.2}$$

The relative error involved in this approximation can be estimated as follows: let ω_m be the next high frequency smaller than ω_M, and suppose that $\Delta_m \sim \Delta_M$. Then the relative error in the approximation (5.2) is of the order:

$$\left(\frac{\hbar\omega_M \Delta_M^2}{\Delta E}\right)(\omega_M - \omega_m)/\omega_M, \tag{5.3}$$

which is small for large ΔE and for values of $(\omega_M - \omega_m)/\omega_M$ which are not too small. Carrying through the computation the following result is obtained:

$$W = \frac{C^2\sqrt{(2\pi)}}{\hbar\sqrt{(\hbar\omega_M \Delta E)}} \exp\left(-\frac{1}{2}\sum_j \Delta_j^2\right) \exp\left\{-\frac{\Delta E}{\hbar\omega_M}\left[\log\left(\frac{2\Delta E}{\sum_M \hbar\omega_M \Delta_M^2}\right) - 1\right]\right\}. \tag{5.4}$$

Let

$$d e_M = \tfrac{1}{2} \sum_{M=1,\ldots,d} \hbar\omega_M \Delta_M^2$$

be the contribution of the modes of maximum frequency to E_M, and we assume that there is the same contribution from each of the d normal modes so that $e_M = \frac{1}{2}\hbar\omega_M\Delta_M^2$. Then equation (5.4) can be rewritten in the form:

$$W = \frac{C^2\sqrt{(2\pi)}}{\hbar\sqrt{(\hbar\omega_M\Delta E)}} \exp\left(-E_M/\hbar\langle\omega\rangle\right) \exp\left\{-\frac{\Delta E}{\hbar\omega_M}\left[\log\left(\frac{\Delta E}{de_M}\right)-1\right]\right\}. \tag{5.5}$$

This low temperature result is adequate either for the isolated molecule or for a molecule in an inert medium. The following conclusions are in order:

(*a*) Equation (5.4) exhibits the energy gap law for the weak coupling limit. As $G \lesssim 1$ we set $\exp(-G) \sim 1$. Furthermore, as in equation (5.5) $\log(\Delta E/de_M) > 1$, we expect that the parameter:

$$\gamma \equiv \gamma(\Delta E, e_M, d) = \log\left(\frac{\Delta E}{de_M}\right) - 1 \tag{5.6}$$

is positive so that W assumes the form:

$$W = \frac{C^2\sqrt{(2\pi)}}{\hbar\sqrt{(\hbar\omega_M\Delta E)}} \exp\left(-\gamma\Delta E/\hbar\omega_M\right). \tag{5.7}$$

This result exhibits a rough exponential (or rather somewhat stronger than exponential) dependence of the transition probability on the energy gap.

(*b*) The parameter γ contains the pertinent structural information concerning the relative displacement of the potential energy surfaces in the two electronic states. It should be noted that the (weak) dependence of γ on ΔE has to be taken into account when ‘ second-order ’ effects such as the isotope effect on radiationless transitions are considered. We shall return later to this point in §6.

(*c*) The transition probability is now dominated by the frequency ω_M which corresponds to the normal vibration of maximum frequency. For aromatic hydrocarbons the relevant frequencies are the C–H (or C–D) stretching frequencies so that $\hbar\omega_{\text{C–H}} \approx 3000$ cm^{-1} and $\hbar\omega_{\text{C–D}} \approx 2200$ cm^{-1}. Note that this result was not derived on the basis of a single frequency model or by any *ad hoc* assumptions, but rather constitutes a reasonable approximation for the general many mode formula (3.14) in the weak coupling limit. This result is entirely reasonable as the calculations of individual Franck–Condon factors of Ross *et al.* [9] and the arguments of Lin and Bersohn [10, 11] indicate that the high frequency vibrations (e.g. C–H or C–D stretching modes) are favoured as acceptor modes.

(*d*) A physically transparent interpretation of the isotope effect in the weak coupling limit is obtained. As pointed out above the maximum frequency of the molecular vibrations involves the C–H($\omega_{\text{C–H}}$) or C–D($\omega_{\text{C–D}}$) modes. As the parameter $G \sim E_M/h\langle\omega\rangle$ in equation (5.5) is weakly dependent on the isotopic composition, the isotopic effect is determined by the energy gap ΔE and by the parameter $\gamma(\Delta E, d)$ (equation (5.6)). The ratio of the non-radiative transition probabilities for the perhydrated (W_{H}) and for the corresponding perdeuterated (W_{D}) molecule is given by:

$$\frac{W_{\text{H}}}{W_{\text{D}}} = \exp\left[\frac{\Delta E}{\hbar}\left(\frac{\gamma_{\text{D}}}{\omega_{\text{C–D}}} - \frac{\gamma_{\text{H}}}{\omega_{\text{C–H}}}\right)\right], \tag{5.8}$$

where γ_{H} and γ_{D} are obtained from equation (5.6) where the appropriate dependence of γ on the frequency ω_M has been incorporated. In view of the uncertainty in the parameters involved in the calculation of γ the approximate relation:

$$\frac{W_{\mathrm{H}}}{W_{\mathrm{D}}}=\exp\left[\frac{\gamma\Delta E}{\hbar}\left(\frac{1}{\omega_{\mathrm{C-D}}}-\frac{1}{\omega_{\mathrm{C-H}}}\right)\right] \tag{5.9}$$

will be sometimes recommended.

Up to this point we have considered the low temperature case in the weak coupling limit. To derive the temperature dependence in the weak coupling limit, we have to replace equation (5.1) for the point in the complex t plane by the more general relation (obtained from equation (3.14)):

$$\frac{1}{2}\sum_j \frac{\Delta_j{}^2\hbar\omega_j}{\exp(\beta\hbar\omega_j/2)-\exp(-\beta\hbar\omega_j/2)}\left\{\exp\left[i\omega_j\left(t+\frac{\beta\hbar}{2i}\right)\right]-\exp\left[-i\omega_j\left(t+\frac{\beta\hbar}{2i}\right)\right]\right\}-\Delta E=0, \tag{5.10}$$

which leads to the solution:

$$t\approx-\frac{i}{\omega_M}\log\left(\frac{2\Delta E}{\sum\limits_{M=1,\ldots,d}\hbar\omega_M\Delta_M{}^2(\bar{n}_M+1)}\right), \tag{5.11}$$

where

$$\bar{n}_M+1=[1-\exp(-\beta\hbar\omega_M)]^{-1}.$$

The transition probability is now given in the form:

$$W=\frac{C^2}{\hbar}\sqrt{\left(\frac{2\pi}{\hbar\omega_M\Delta E}\right)}\exp\left(-\frac{1}{2}\sum_j\Delta_j{}^2\left(2\bar{n}_j+1\right)\right)\times\exp\left\{-\frac{\Delta E}{\hbar\omega_M}\left[\log\left(\frac{2\Delta E}{\sum\limits_M\hbar\omega_M\Delta_M{}^2(\bar{n}_M+1)}\right)-1\right]\right\}. \tag{5.12}$$

Thus the temperature dependent result in the weak coupling limit just incorporates the temperature dependence of the coupling parameter G and will multiply the energy term e_M in equations (5.5) and (5.6) by the coefficient $(\bar{n}_M+1)$. In view of the high frequency of the ω_M vibrations the low temperature limit in the weak coupling case seems to be adequate for most practical purposes.

Finally, we would like to point out that the general ' low temperature ' result (equations (5.4)–(5.7)) in the weak coupling limit is adequate both for a molecule in an inert medium (provided that $\beta\hbar\langle\omega\rangle\gg 1$) and for the radiationless decay of the lowest vibronic component in an ' isolated ' molecule. As the coupling strength G is temperature dependent (see equation (3.15)), one expects that large molecules which correspond to the weak coupling limit at room (or lower) temperatures will be transferred to the strong coupling limit at high temperatures (when $\beta\hbar\langle\omega\rangle\ll 1$). However, such high temperatures may not be realized in practice.

6. INSPECTION OF SOME EXPERIMENTAL DATA FOR THE WEAK COUPLING LIMIT

Adopting the terminology of the strong and weak coupling limits for non-radiative decay we can easily convince ourselves that electronic relaxation processes in large aromatic molecules correspond indeed to the weak coupling limit as proposed by Hunt *et al.* [7] and by Robinson and Frosch [8]. Byrne *et al.* [9] have estimated the reduced displacement parameters Δ_i (equation (3.7)) for different types of vibration from the analysis of spectroscopic data and from semi-empirical molecular calculations. Grouping the normal molecular vibrations into the following groups (1) C–H (or C–D) stretches, (2) skeletal stretches, (3) skeletal bends, (4) C–H (or C–D) bends and (5) out of plane modes, the reduced displacements estimated by Byrne *et al.* [9] for these five types of groups of normal vibrations are as follows: $0{\cdot}13 < 0{\cdot}71\ \Delta_1 < 0{\cdot}3$ (where $\omega_1 \sim 3000\ \mathrm{cm}^{-1}$ for C–H and $\omega_1 \sim 2200\ \mathrm{cm}^{-1}$ for C–D and $(\Delta_1 \equiv \Delta_M)$, $0{\cdot}71\ \Delta_2 \sim 0{\cdot}2$ $(\omega_2 \sim 1400\ \mathrm{cm}^{-1})$, and $\Delta_3 = \Delta_4 = \Delta_5 = 0$. (We have used this rather strange notation as the parameter X calculated by Ross *et al.* [9] is $X_i = \Delta_i/\sqrt{2}$.) At the risk of triviality let us point out that indeed $G \sim E_M/\hbar\langle\omega\rangle \sim 1$ and the weak coupling limit is applicable. We shall consider the weak coupling low temperature limit, whereupon the non-radiative decay takes place from the lowest vibronic component of the higher electronic state. Within our approximate theoretical framework the non-radiative transition probability is determined by the following parameters:

(*a*) *The pre-exponential factor* in equation (5.7) exhibits only a weak dependence on the energy gap, and contains the coupling parameter C^2. We have not attempted to evaluate the electronic matrix elements which mediate the non-radiative decay channel. Following the classical arguments Kasha [67] and of Robinson and Frosch [8] rough order of magnitude estimates for the matrix elements (1.7 *a*) and (1.7 *b*) are $C^{(\mathrm{co})} = \langle H_\mathrm{v}\rangle$ and $C^{(\mathrm{cr})} = \langle H_\mathrm{v}\rangle \langle H_\mathrm{so}\rangle/(E_\mathrm{so} - E_{\gamma\mathrm{o}})$, where $\langle H_\mathrm{v}\rangle$ and $\langle H_\mathrm{so}\rangle$ correspond to typical vibronic coupling [48] and spin–orbit coupling matrix elements, respectively, while $(E_\mathrm{so} - E_{\gamma\mathrm{o}})$ is a typical energy gap between two spin–orbit coupled states. Vibronic coupling matrix elements were recently established by Hochstrasser and Marzzacco [68] for several aromatic hydrocarbons from the intensity of symmetry forbidden components in the optical spectrum. For benzene [8, 48, 68] $\langle H_\mathrm{v}\rangle\,({}^1B_{2u}, {}^1E_{1u}) = 780\ \mathrm{cm}^{-1}$, for naphthalene [68] $\langle H_\mathrm{v}\rangle\,({}^1B_{3u}^-, {}^1B_{2u}) = 200\ \mathrm{cm}^{-1}$ and $195\ \mathrm{cm}^{-1}$, for phenanthrene [68] $\langle H_\mathrm{v}\rangle\,({}^1A_1, {}^1A_1) = 145\ \mathrm{cm}^{-1}$ and $\langle H_\mathrm{v}\rangle\,({}^1A_1, {}^1B_2) = 85\ \mathrm{cm}^{-1}$, while for anthracene [68] $\langle H_\mathrm{v}\rangle\,({}^1B_{2u}, {}^1B_{3u}) = 1030\ \mathrm{cm}^{-1}$, $726\ \mathrm{cm}^{-1}$ and $726\ \mathrm{cm}^{-1}$. From this analysis [68] we may conclude that the $\langle H_\mathrm{v}\rangle$ term varies over one order of magnitude for different molecules. This variation of the vibronic coupling term may introduce an uncertainty of about two orders of magnitude in the ‘ semiquantitative ’ theoretical predictions for non-radiative decay probabilities. We believe that a better agreement with experiment obtained for the W values, which are based on ‘ empirical fittings ’ of the pre-exponential factor [13, 14] should be regarded with some suspicion. To obtain a rough estimate for the pre-exponential factor for intersystem crossing we use again the estimate of Robinson and Frosch [8] for the ratio of the oscillator strength for spin forbidden orbitally allowed $S \rightarrow T$ transition and the spin and symmetry allowed $S \rightarrow S$ transition [8, 69] which leads to $(\langle H_\mathrm{so}\rangle/(E_\mathrm{so} - E_{\gamma\mathrm{o}}))^2 \sim 10^{-10}$. As reliable theoretical or experimental information concerning the $\langle H_\mathrm{so}\rangle$ matrix elements is still lacking one is unable to ascertain the variation of these terms between different states of different aromatic molecules. From these qualitative considerations one may conclude that within confidence range of two orders of magnitude $(C^{(\mathrm{co})})^2 \sim 10^6\ \mathrm{cm}^{-2}$ and $(C^{(\mathrm{cr})})^2 \sim 10^{-4}\ \mathrm{cm}^{-2}$. Using now a mean value for the energy gap $\Delta E \sim 10^4\ \mathrm{cm}^{-1}$ and $h\omega_M \sim 3000\ \mathrm{cm}^{-1}$ one obtains the following rough estimates for the transition probability:

$$W^{(\mathrm{co})} \sim 10^{13 \pm 2} \exp\left(-\gamma \Delta E/\hbar\omega_M\right), \tag{6.1}$$

$$W^{(\mathrm{cr})} \sim 10^{3 \pm 2} \exp\left(-\gamma \Delta E/\hbar\omega_M\right). \tag{6.2}$$

(*b*) *The exponential factor*, equations (5.6) and (5.7), reveals of course an exponential dependence of W on the energy gap. Our approximate weak coupling theory contains the parameters which specify the changes in molecular geometry (Δ_M) and the number (d) of the degenerate vibrations of maximum frequency in a rather disguised manner as they are included in the logarithmic factor γ. For radiationless transitions to the ground state the estimates of Δ_M in the range of $0{\cdot}42 > \Delta_M > 0{\cdot}19$ derived by Byrne *et al.* [9] from the analysis of the optical spectrum of benzene and other hydrocarbons are adopted. For radiationless transitions between two excited electronic states we expect that Δ_M (excited→ground) > Δ_M (excited→excited) as the changes in molecular geometry are expected to be smaller between two $\pi \rightarrow \pi^*$ excited states, especially when one electron jump is involved. Finally, we adopt the idea of Ross *et al.* [9] and set d to be equal to the number of C–H bonds in the molecule.

Several problems of physical interest will be now briefly considered:

(*a*) *Triplet to ground state radiationless transitions.* We have analysed the data compiled by Siebrand [9, 14] for C_xH_y and C_xD_y type hydrocarbons. These data provide the best example for the energy gap law [8, 14]. In order to estimate the parameter γ we have used the value of $\Delta_M = 0{\cdot}42$ for C–H and C–D modes which corresponds to the McCoy–Ross parameter [5] $X_M = X_1 = 0{\cdot}3$. As pointed out by Byrne *et al.* [9] this value provides an upper limit for the X parameter for the C–H and C–D stretching vibrations. The γ parameters for various hydrocarbons thus estimated vary in the range 1·31–0·50. Using Siebrand's estimates [9, 14] of the non-transition decay probabilities in C_xH_y hydrocarbons the resulting pre-exponential factors in equation (5.6) were then found to vary in the range 10–1000 s^{-1}. This is not surprising in view of the previous discussion of the pre-exponential factors. Another related set of data which are practically independent of the pre-exponential factor involve the isotope effect W_H/W_D on intersystem crossing to the ground state. Using the γ values calculated again with $\Delta_M = 0{\cdot}42$, equation (5.8) yields reasonable agreement with experiment [9, 14] in most cases. Finally, we would like to point out that the benzene data [65] for intersystem crossing from the $^3B_{1u}$ state to the ground state do not fit the theoretical correlation (5.7). It was pointed out by van der Waals *et al.* [70] that the benzene $^3B_{1u}$ state is subjected to strong pseudo Jahn–Teller coupling effects with the $^3E_{1u}$ state which is located just 4000 cm^{-1} above it. Hence the harmonic approximation is not applicable in this case.

(*b*) *Singlet to ground state internal conversion.* The meagre experimental information currently available was carefully analysed by Siebrand and Williams [13]. Using $0{\cdot}19 \leqslant \Delta_M \leqslant 0{\cdot}42$, equation (5.7) leads to a very low value for the non-radiative $^1B_{2u} \rightarrow {}^1A_{1g}$ transition probability for benzene in variance with the experimental data [13]. For other hydrocarbons the γ factors were calculated again using $\Delta_M = 0{\cdot}42$. The resulting upper limits for the pre-exponential factors for naphthalene, anthracene, phenanthrene, pyrene and triphenylene and the pre-exponential factor for tetracene fall in the region 10^{13}–10^{10} s^{-1} and are consistent with our estimate of the pre-exponential factor. On the other hand, the upper limits obtained for the pre-exponential factors for chrysene, 1,2 benzanthracene, perylene and coronene are lower than 10^{10} s^{-1}. These upper limits for W were obtained [13] assuming that the branching ratio for the non-radiative decay of the excited singlet to the ground state does not exceed 1 per cent. The analysis indicates that for these latter molecules the non-radiative decay probability from the excited singlet to the ground state should be of the order of 10 per cent of the radiative decay probability, and may thus be amenable to experimental observation.

It should be noted that in view of the relatively large energy gaps and as $\gamma > 1$ in these cases, an appreciable isotope effect is expected for this class of radiationless transitions.

(*c*) *The azulene problem.* A qualitative interpretation for the anomalous fluorescence of the azulene molecule and its derivatives [71–74] was provided by Robinson and Frosch [8] and by Ross *et al.* [7, 9] who pointed out that the radiative lifetimes for the $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$ transitions differ by two orders of magnitude. The non-radiative decay probability of the first singlet state of the azulene molecule can be estimated from two sources: optical relaxation experiments of Rentzepis [74] provide an upper limit for the non-radiative decay probability $W(S_1 \rightarrow S_0) < 10^{11}\,\mathrm{s}^{-1}$. Line broadening in the first excited singlet state led to the estimate [4] $W(S_1 \rightarrow S_0) > 10^{10}\,\mathrm{s}^{-1}$ while a careful analysis of line widths in mixed crystals by Hochstrasser [75] sets a value of $W(S_1 \rightarrow S_0) \approx 3 \times 10^{10}\,\mathrm{s}^{-1}$ for azulene. On the other hand, quantum yield measurements lead to $W(S_2 \rightarrow S_1) = 6 \times 10^8\,\mathrm{s}^{-1}$. The difference between the two non-radiative decay probabilities for the same energy gap can be immediately rationalized by equation (5.7) considering the different Δ_M values for these two processes. Denoting the appropriate γ values for the $S_1 \rightarrow S_0$ and for the $S_2 \rightarrow S_1$ by γ_1 and by γ_2, respectively, we now have

$$W(S_1 \rightarrow S_0)/W(S_2 \rightarrow S_1) = \exp\,[(\Delta E/h\omega_M)\,(\gamma_2 - \gamma_1)]$$

where the common energy gap between S_1 and S_0 and between S_2 and S_1 is taken as $\Delta E = 14\,000\,\mathrm{cm}^{-1}$. For the $S_1 \rightarrow S_0$ non-radiative decay we utilize again the value of $\Delta_M = 0{\cdot}42$, which for $d = 8$ and $\Delta E = 14\,000\,\mathrm{cm}^{-1}$ leads to $\gamma_1 = 0{\cdot}89$ and to a pre-exponential factor of $2 \times 10^{12}\,\mathrm{s}^{-1}$. The value of Δ_M for the $S_2 \rightarrow S_1$ non-radiative decay is expected to be smaller than the corresponding value for the excited ground state transition so we expect that $\gamma_2 > \gamma_1$. A value of $\gamma_2 = 1{\cdot}6$ is consistent with the experimental results $W(S_1 \rightarrow S_0)/W(S_2 \rightarrow S_1) \sim 50$. This implies that the value of $\Delta_M{}^2$ for the $S_2 \rightarrow S_1$ coupling is lower by a factor of about 2 relative to the corresponding $\Delta_M{}^2$ value for the $S_1 \rightarrow S_0$ decay, a conclusion which is entirely reasonable. Using this rough estimate for γ_2 we can estimate the isotope effect for the $S_2 \rightarrow S_1$ decay from equation (5.8) which leads to

$$W_{\mathrm{H}}(S_2 \rightarrow S_1)/W_{\mathrm{D}}(S_2 \rightarrow S_1) \sim 30.$$

This result implies that the quantum yield for the fluorescence $S_2 \rightarrow S_0$ in azulene-d_8 will be close to unity, not in disagreement with the experimental observation of Johnson *et al.* [76]. On the other hand, the isotope effect for the $S_1 \rightarrow S_0$ decay is expected to be lower. Equation (5.8) leads to $W_{\mathrm{H}}(S_1 \rightarrow S_0)/W_{\mathrm{D}}(S_1 \rightarrow S_0) \sim 4$.

To conclude this discussion we would like to stress that the theoretical analysis presented herein rests on several rather severe approximations. Furthermore it was assumed that the Δ_M terms are constant for a given class of radiationless transitions. Thus the numerical estimates are not intended to reproduce experimental data which are at present much more reliable than theoretical computations but rather to predict a general pattern of behaviour for a given class of electronic relaxation processes.

7. DISCUSSION

In this paper we have attempted to provide a semiquantitative treatment of the transition probability for non-radiative decay in large molecules which provides an advance over previous theoretical studies of this problem. Any arbitrary number of different molecular vibrations can be incorporated and the resonance widths can be directly calculated without referring to crude factorization procedures [16] which attempt to separate the resonance width into a product of a mean coupling term and the mean density of states [16, 17].

The present treatment rests on the following assumptions:

(*a*) Interference effects are disregarded as discussed in §1.

(*b*) A two-electronic level system is considered.

(*c*) The vibrational factors in the $V_{si,\, lj}$ matrix elements are approximated in terms of a product of an electronic coupling matrix element and Franck–Condon vibrational overlap terms.

(*d*) We assume that the normal modes and their frequencies are the same in the two electronic states except for displacements in the origins of the normal coordinates.

(*e*) We assume that the molecular vibrations are harmonic, disregarding anharmonicity effects.

Some of the drastic approximations involved in the present treatment can be removed. Thus, for example, it is not necessary to factor out the individual coupling terms $V_{si,\, lj}$ into a product of an electronic term and a Franck–Condon overlap factor, as the generating function method can be applied for the general expression (equation (1.10)) for the non-radiative transition probability. In a similar fashion the effect of the changes of vibrational frequencies between the two electronic states can be incorporated. Unfortunately, such modifications result in rather cumbersome expressions which can be handled only by numerical methods. The anharmonicity problem [13, 14] which was omitted from the present treatment is more complex as in this case the normal mode analysis breaks down. A way of overcoming this difficulty will involve replacing the harmonic potential surfaces in equation (3.8) by superposition of more general type potentials (which include anharmonicity effects) at least for the C–H (or C–D) stretching modes. Again, numerical techniques will be required in this case.

We must admit that in the present treatment we have sacrificed the detailed consideration of some of the physical factors for the sake of a simple and elegant representation of the problem. We believe, however, that the present treatment elucidates the gross features of the non-radiative decay processes.

The main accomplishments of the present study can be summarized as follows:

(*a*) From the general structure of the theoretical formulas we can ascertain that the relative displacement of the two potential energy surfaces expressed in terms of the coupling parameter G determines whether the molecular system corresponds to the strong or to the weak coupling limit. This classification provides a link between the Teller picture [66] and the conventional Robinson–Frosch–McCoy–Ross [7–9] model for radiationless transitions. As it is well established, the weak (and possibly sometimes the intermediate) coupling scheme is appropriate for the description of a large number of electronic relaxation processes in aromatic molecules.

(*b*) In the strong coupling limit the transition probability is determined by the mean molecular frequency, provided of course that the Δ_i values for a substantial number of different frequencies are non-vanishing. On the other hand, in the weak coupling case the non-radiative transition probability is dominated by the highest molecular frequency ω_M.

(*c*) In the strong coupling limit the transition probability is determined by the energy E_A corresponding to the point of minimum intersection energy located above the origin of the higher electronic state, equation (4.7). In the weak coupling limit the transition probability is essentially determined by the energy gap ΔE.

(*d*) A proper theoretical interpretation of the ' energy gap law ' for radiationless transitions in the weak coupling limit is provided. This general energy difference dependent behaviour is characteristic for many molecular relaxation processes, such as vibrational relaxation. Robinson and Frosch [8] and Siebrand [14] attempted to provide empirical or semi-empirical correlations for the energy gap law. However, no theoretical treatment of the problem was provided until now.

(*e*) Following the considerations presented in (*b*) some features of the intramolecular isotope effect on radiationless transitions can be elucidated. A pronounced isotope effect can be encountered only in the weak coupling limit.

(*f*) The present scheme provides the first step in ascertaining the nature of ' trivial ' medium effects on the non-radiative decay probability, whereupon the insert medium acts as a ' heat bath ' [77]. This problem was previously considered by Bersohn and Lin [11]. In general, the temperature dependence of the effective radiationless rate constant should not follow a simple Arrhenius type law. We have demonstrated that in the case of the strong coupling limit, the extended Arrhenius type law (where an effective temperature factor comes in equation (4.8)) is obeyed. In the weak coupling limit we were also able to extract an approximate expression for the transition probability. This temperature dependence (equation (5.12)) is expected to be rather weak. It should, however, be borne in mind that, as the present treatment rests on the approximate relation (1.10), the temperature dependence of the C terms has been omitted from the present treatment. This feature may be of considerable importance, in particular for the weak coupling limit.

(*g*) From the chemist's point of view the different features of the isotope effects, the energy gap law and the temperature dependence encountered in the weak and strong coupling limits can be summarized as follows: the weak coupling limit corresponds to a tunnelling mechanism between zero-order vibronic levels which correspond to different electronic configurations, while in the strong coupling limit we encounter the situation whereupon adiabatic potential surfaces cross or intersect and the non-radiative decay occurs via a conventional adiabatic type unimolecular process. It should be, however, noted that the concept of an ' activated complex ' does not enter in any way in this theory. It is gratifying that both limits result as particular cases of the same general formalism.

Although conventional electronic relaxation processes in large aromatic molecules correspond to the weak coupling situation, we believe that the strong coupling limit is of considerable physical interest for the interpretation of many reactions encountered in the field of organic photochemistry. The reactivity of excited electronic states of organic molecules resulting in unimolecular rearrangement processes involves large configurational changes between two or more electronic states, and thus corresponds to the strong coupling limit. The present treatment has established the link between electronic relaxation and intramolecular rearrangement processes in excited electronic states of large organic molecules.

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