Electronic Relaxation of Small Molecules in a Dense Medium

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In this paper we present a theoretical study of radiationless transitions in a small molecule embedded in a dense inert medium. Two extreme situations of the molecule-medium coupling were considered, involving the case of zero displacements of the medium modes between the two electronic states (i.e. the Shpolskii matrix) and the limit of strong molecule-medium coupling. The Fourier transform of the non radiative decay probability of a small molecule in a Shpolskii matrix involves exponential damping, while for the strong coupling situation Gaussian damping is involved. In the case of the Shpolskii matrix the decay rate of a small molecule can be expressed in terms of an infinite series where each term corresponds to a product of an (intramolecular) Poisson distribution and a (medium induced) Lorentzian distribution. The Lorentzian widths were explicitly expressed in terms of the vibrational relaxation widths. The Robinson-Frosch formula can be obtained for the extreme case of near degeneracy in a Shpolskii matrix. In the limit of strong molecule-medium coupling the decay rate of a small molecule can be recast in terms of an infinite sum where each term involves a superposition of a Poisson distribution and a Gaussian distribution. The medium induced Gaussian distribution is determined by intramolecular phonon broadening. We have elucidated some new features of the electronic relaxation of a small molecule in a dense medium pertaining to the problem of off-resonance intramolecular coupling which modifies the energy gap law and the deuterium isotope effect.

Strahlungslose Übergänge in einem kleinen Molekül, das von einem dichten inerten Medium umgeben ist, werden untersucht, wobei zwei Grenzfälle bei der Kopplung Molekül/Medium zugrunde gelegt werden: keine Verschiebungen der Medium-Bewegungen beim Übergang (d.h. der Shpolskii-Matrix) einerseits und starke Kopplung Molekül/Medium andererseits. Die Fouriertransformierte für die Wahrscheinlichkeit des strahlungslosen Zerfalls eines kleinen Moleküls in Form einer Shpolskii-Matrix schließt exponentielle Dämpfung ein, wohingegen bei starker Kopplung die Dämpfung einer Gauss-Funktion entspricht. Im ersteren Fall läßt sich der Zerfall als unendliche Reihe von Produkten einer intramolekularen Poisson-Verteilung mit einer vom Medium induzierten Lorentz-Verteilung formulieren, wobei die Lorentz-Breite explizit mittels der Schwingungsrelaxationsbreiten angegeben wird. Die Robin-Frosch-Formel ergibt sich für den Grenzfall der Fastentartung der Shpolskii-Matrix. Bei starker Molekül-Medium-Kopplung läßt sich der Zerfallsverlauf als unendliche Summe von Überlagerungen von Poisson- und Gaussverteilungen angeben. Dabei wird die Medium-induzierte Gauss-Verteilung durch die intramolekulare Phononen-Verbreiterung bestimmt. In diesem Zusammenhang zeigten sich einige neue Gesichtspunkte für die elektronische Relaxation kleiner Moleküle in dichten Medien, wie z. B. das Problem von Nicht-Resonanz bei intramolekularer Kopplung, wo der Satz vom Energie-Sprung und der Deuterium-Isotopie-Effekt modifiziert werden müssen.

1. Introduction

In considering the implications of intramolecular interstate coupling on the radiative decay of electronically excited states of polyatomic molecules, it is important to realize that the existence of interstate coupling provides a necessary but by no means a sufficient condition for the occurrence of an intramolecular electronic relaxation process. Intramolecular non-radiative decay is exhibited in

the statistical limit for excited state of "isolated" large molecular which are characterized by a large energy gap ($\sim$ 1 eV) [1]. In the case of small molecules in the low pressure gas phase no intramolecular relaxation occurs, while the effects of intramolecular coupling are exhibited as follows: a) A complex molecular absorption spectrum of some triatomic molecules [2] (i.e. NO_2) is observed, which may be sensitive to external fields ($^2\Sigma - {}^2\Pi$ mixing in the CN molecule [3]). b) Anomalously long radiative decay times of the first spin allowed excited states of some triatomic molecules (i.e. NO_2, SO_2 and CS_2) [4] are observed, while the emission quantum yields are unity.

One can extend the concept of the decay of electronically excited states of a "small molecule" to include the following two categories:

1. Electronically excited states of diatomic and triatomic molecules (i.e. NO_2, SO_2 and CS_2), which are characterized by a small number of vibrational degrees of freedom.

2. Electronically excited states of some large molecules which are characterized by a small electronic energy gap. Such excited states will exhibit the small molecule case encountered within a large molecule [5]. Experimental verification of this theoretical prediction was recently obtained for the radiative decay of the second excited singlet state of 3,4 Benzopyrene [6] and of naphthalene [7] (where the $S_2 - S_1$ energy gap is $\sim 3000\,\text{cm}^{-1}$) and of the lowest excited singlet state of Benzophenone [8, 9] (where the $S_1 - T_1$ energy gap is $2800\,\text{cm}^{-1}$) in the low pressure gas phase, which exhibit anomalously long radiative decay times (relative to the expectations on the basis of the integrated oscillator strength).

Most of previous theoretical work on electronic relaxation in large molecules focused attention on the "isolated" molecule in the statistical limit [1]. Little theoretical attention has been devoted to medium effects on electronic relaxation of a guest molecule. Consider the simplest model for an "inert" medium which is characterized by the following features:

1. It does not modify the relevant energy levels.

2. It does not affect the interstate coupling matrix elements.

3. It does not provide promoting modes for electronic relaxation.

Thus the electronic wave functions of the guest molecule are practically invariant with respect to charges in the medium nuclear coordinates.

Such an "inert" medium may affect the electronic relaxation of a guest molecule as follows: a) It may provide accepting modes for the intramolecular decay process. The equilibrium configurations of the medium phonon modes (and their frequencies) usually vary between different electronic states of the impurity molecule. Indirect information concerning this effect may be obtained from the phonon broadening of optical lines of impurity molecules in inert matrices [10]. It is well known that the low lying excited electronic states (where the contribution of intramolecular decay to the linewidth is small) in mixed crystals and in hydrocarbon matrices exhibit appreciable phonon broadening, and only in special cases [11] (which are referred to as Shpolskii matrices) the equilibrium configurations of the medium phonons do not vary between the ground and the electronically excited states. We may conclude that in many cases of physical interest low frequency medium vibrations may act as accepting modes in the electronic relaxation process. b) The medium provides a heat bath for vibrational

relaxation of the intramolecular vibrations. This vibrational relaxation (and vibrational excitation) processes may occur both in the initial and in the final electronic manifold.

In the statistical limit the non-radiative decay probability (in the weak electronic vibrational coupling limit) is dominated by the high frequency vibrational modes [12], whereupon the contribution of the low frequency medium accepting modes is negligible. Furthermore, it is asserted that in the statistical limit the vibrational relaxation in the final dense electronic manifold does not affect the non-radiative transition [13]. Thus the non-radiative decay of an individual vibronic level in the statistical limit is unaffected by an inert medium. From the experimental point of view provided that the vibrational relaxation process (in the initial electronic manifold) is fast on the time scale of the electronic transition, the non-radiative decay probability in an inert medium is obtained in terms of a thermal average over the decay of the individual vibronic levels of the isolated molecule.

The situation is drastically different in the small molecule case. As is well established both experimentally and theoretically an isolated small molecule does not exhibit intramolecular electronic relaxation [4], while external perturbations (in the gas phase or by a dense host matrix) may induce a non-radiative decay process [14–22]. The relevant experimental evidence may be summarized as follows: a) From the study of the emission spectra of NO in rare gas solid matrices experimental evidence was obtained for the $a^4\Pi - x^2\Pi$ intersystem crossing [14]. The lifetime of the quartet state in Ne, Ar and Kr was found to be 156, 93 and 35 msec respectively, and this shortening of the lifetime can be assigned to externally induced spin orbit coupling which enhances the non-radiative decay. It should be noted however that this interpretation is not conclusive as the enhanced spin orbit coupling can also reduce the pure radiative decay time of the $a^4\Pi$ state, and quantum yield experiments are required to resolve this point. b) A strong temperature dependence of the phosphorescence $(T_1 \to S_0)$ intensity of SO_2 in inert rare gas and molecular matrices intitially excited to the S_1 state was reported [15], while the $T_1 \to S_0$ radiative decay times were temperature independent. These results were interpreted in terms of the temperature and medium effects on the rate of the $T_1 \to S_0$ intersystem crossing. c) The S_1 state of the benzophenone molecule, which is separated by a small $(\sim 2800\,\mathrm{cm}^{-1})$ gap from the T_1 state, exhibits ultrafast $S_1 - T_1$ intersystem crossing in solution [16] (fluorescence quantum yield $\sim 10^{-6}$, non-radiative decay rate from the vibrationless S_1 level $\sim 5\,\mathrm{psec}$). On the other hand efficient fluorescence from the S_1 state is observed from the isolated benzophenone molecule [8], which exhibits predominantly the features of strong interstate $S_1 - T_1$ coupling as is the case for small molecules.

The theoretical treatment of the non-radiative decay of a small molecule embedded in a medium pertains to the following theoretical problems: a) The conventional golden rule rate formula, or related expressions, which are adequate for the treatment of the statistical limit, are not of general applicability for the electronic relaxation of a small molecule embedded in a medium. This point was not always realized and some authors [17, 18] have used second order perturbation theory to handle non-radiative processes in small molecules with-
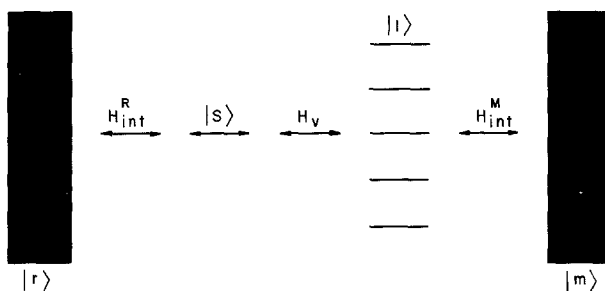
Fig. 1. Scheme for consecutive decay. $|s\rangle$ – initial molecular state; $|r\rangle$ – radiative continuum; $|l\rangle$ – sparse intramolecular manifold; $|m\rangle$ – medium states

out proper modifications. It should be pointed out that the pioneering work of Robinson and Frosch handled the vibrational relaxation in the final manifold. The Robinson-Frisch formula [19] for the non-radiative decay probability $W = (2\pi/\hbar\alpha)\sum_n \beta_n^2$ (where β_n are the intramolecular coupling matrix elements, while α is the vibrational relaxation width in the final manifold) is valid only for special cases and is inadequate for the small molecule case. Recently Takahashi and Yokota [20] attempted to consider the decay of small molecules by an ad-hoc inclusion of a vibrational relaxation rate into the Kubo-Toyozawa generating functions formalism, and provided a distinction between the small molecule and the large molecule case in terms of the corresponding vibrational relaxation width. b) When the medium does not supply accepting modes, the non-radiative decay rate of a small molecule may be considered in terms of a consecutive decay precess. Here the initial molecular state is intramolecularly coupled to final molecular states which in turn decay by vibrational relaxation which originates from intermolecular coupling to the medium states. c) The consecutive decay process for a small molecule can be described phenomenologically (see Fig. 1) by assigning a vibrational relaxation width to the final molecular states. A more elaborate model should involve the details of the vibrational relaxation process [21].

   In this paper we explore the problem of electronic relaxation of small molecules in a dense medium. In the first stage of this treatment we consider the idealized situation of a Shpolskii medium [10] whereupon the medium vibrations do not provide accepting modes. In this context we shall attempt to resolve the following problems: a) To establish the criteria for the validity of an exponential decay law (described in terms of the golden rule rate constant) for a small molecule subjected to a consecutive decay process. b) To elucidate the effects of vibrational relaxation on electronic relaxation of small molecules. We shall demonstrate that in general the decay rate of a small molecule will exhibit a linear dependence on the (medium induced) vibrational relaxation width. c) To clarify the connection between the consecutive decay scheme and the Robinson and Frosch expression [19]. Only in the rare and special case of accidental degeneracy between the initial and the final molecular vibronic states, a reciprocal relation is expected to exist between the decay rate and the vibrational relaxation width. d) To study the contribution of the vibrational relaxation width to the non-

radiative decay rate of a small molecule in terms of a harmonic model which considers vibrational relaxation as a ladder process.

In the second stage of the present treatment we shall relax the restinction of a Spolskii medium and consider the role of medium modes as accepting modes for the electronic relaxation of a small molecule. This physical situation will bring back the features of the statistical limit whereupon the electronic relaxation rate will be independent of the vibrational relaxation rate for intramolecular and intermolecular vibrations.

2. Model System

We consider non-radiative relaxation of a molecule embedded in an inert dense host matrix. We do not need to concern ourselves with the relatively complex description of relaxation by collisions but rather consider coupling of the guest molecule to the medium phonons. The Hamiltonian of the system may be conveniently factorized into the molecular Hamiltonian (which in itself consists of the Born Oppenheimer Hamiltonian, H_{BO}, and a term H_V responsible for the non-adiabatic coupling), the medium Hamiltonian H_{Med}, an interaction term, H_{int}^M, between the medium and the molecule

$$H = H_{BO} + H_V + H_{Med} + H_{int}^M \tag{2.1}$$

Our molecular model will be similar to that presented in previous work. We shall also apply the same notations (see Ref. [21], Section 2).

Utilizing some approximate symmetry arguments it may be demonstrated that within our model: a) Interference effect resulting from the coupling of different levels to the same medium levels, are negligible. b) Intramolecular interference effects will be neglected. c) We consider the fast vibrational relaxation limit, whereupon electronic relaxation is slow on the time scale of vibrational relaxation.

These basic assumptions will be utilized to handle the phenomenology of the non-radiative decay of a (large or small) molecule in an inert medium which does not provide accepting modes (Section 3). These results are then applied in Section 4 for the non-radiative decay of a small molecule in a Shpolskii matrix. In Section 5 we consider the details of the vibrational relaxation (induced by the H_{int}^M term) and its effect on the electronic relaxation of a small molecule in a Shpolskii medium. Finally we consider (Section 6) a medium which provides accepting modes, whereupon the electronic relaxation of a small molecule is now reminescent of the statistical limit.

3. Theory of Consecutive Decay

In this section we shall briefly consider the problem of the time evolution of an "initially prepared" state $|si\rangle$ subjected to a coupling scheme represented by Fig. 1, which has been previously handled by Freed and Jortner [22] who utilized the Green's function technique, and more recently by Nitzan et al. [5], using the Wigner-Weisskopf method. The Green's function method is based on the observation that the time evolution of an initially prepared state $|si\rangle$ is given by the Fourier transform of the diagonal element $\langle si|G|si\rangle$ of the Green's operator for the system, $G = (E - H + i\eta)^{-1}$, $\eta \rightarrow 0^+$, and that the decay characteristics

of this state are determined by the complex poles of this diagonal matrix element, whose explicit form in our model is (see Appendix A)

$$\langle si|G|si\rangle = \left(E - \tilde{E}_{si} + \frac{i}{2}\Gamma_{si}(E) + \frac{i}{2}\Delta_{si}(E)\right)^{-1} \tag{3.1}$$

where $\Gamma_{si}(E)$ is a smooth function of the energy E which is nearly a constant in the vicinity of $E \approx E_{si}$ and whose magnitude for $E = E_{si}$ corresponds to the radiative width of the state $|si\rangle$; and where $\Delta_{si}(E)$ is given by

$$\Delta_{si}(E) = 2\sum_j \frac{\frac{1}{2}\Gamma_{lj}|(H_v)_{si,lj}|^2}{(E - \tilde{E}_{lj})^2 + \frac{1}{4}\Gamma_{lj}^2} \tag{3.2}$$

Γ_{lj} is the width of the state $|l_j\rangle$ due to its coupling with the medium states (strictly speaking this is a smooth and nearly constant function of E, near $E = E_{lj}$). E_{si} and E_{lj} are the modified (by the appropriate level shifts) energies of the states $|si\rangle$ and $|l_j\rangle$ respectively.

The crucial point is now the form of $\Delta_{si}(E)$ as a function of E. Freed and Jortner [22] have demonstrated that the statistical limit corresponds to the case in which this function is a smooth and nearly constant function of E. In this case it may be shown that the function $G_{si,si}$, Eq. (3.1) has only a single pole $E = E_s - \frac{1}{2}i(\Gamma_{si} + \Delta_{si})$. In this case the decay will be smoothly exponential in time, and Δ_{si} is the non-radiative contribution to the decay rate.

A more interesting behaviour results in the situation where $\Delta_{si}(E)$ is not a smooth function of E, which corresponds to the case where the density of states in the manifold $\{|l_j\rangle\}$ is low. This case is much more difficult to mathematical treatment (a general exact solution has been obtained [5] only for the case where the manifold $\{|l_j\rangle\}$ consists of one state only). However it will be sufficient to consider the time evolution of the system in two important limits. a) The strong intramolecular coupling limit characterized by

$$(H_v)_{si,lj}| \gg |E_{lj} - E_{lj'}| \tag{3.3a}$$

where $|l_j\rangle$ and $|l_{j'}\rangle$ are two adjacent levels in the $\{|li\rangle\}$ manifold. b) The weak intramolecular coupling limit which is defined by the inequality for all j,

$$|(H_v)_{si,lj}| \ll \left|E_{si} - E_{lj} + \frac{i}{2}(\Gamma_{si} - \Gamma_{lj})\right|. \tag{3.3b}$$

A small molecule embedded in a dense medium where fast vibrational relaxation occurs can be often described by the weak coupling limit. If the density of states in the $\{|l_j\rangle\}$ manifold is low (for example in a diatomic or in a triatomic molecule), the term $|E_{si} - E_{lj}|$ is sufficiently large to satisfy condition (3.3b) (excluding cases of accidental degeneracy). Even if this is not the case, the other term $|\Gamma_{si} - \Gamma_{lj}|$ in which $\Gamma_{lj} \sim 1 - 10\,\mathrm{cm}^{-1} \gg \Gamma_{si}$ will in most cases be much greater than $|(H_v)_{si,li}|$. We may thus conclude that the relaxation of a molecule in a medium will correspond in most cases to the weak coupling situation.[1]

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[1] In the case of a strong coupling situation a prediagonalization of the strongly coupled levels should be performed. A discussion of this situation is provided in Refs. [5, 9].

The time evolution of a prepared $|si\rangle$ state in our model has been evaluated by Nitzan et al. [5], and is given by

$$|\langle\psi(t)|si\rangle|^2 = \exp(-\gamma^s t) + \sum_j \frac{|(H_v)_{si,lj}|^2 \exp(-\gamma^{lj} t)}{(E_{si} - E_{lj})^2 + \frac{1}{4}(\Gamma_{si} - \Gamma_{lj})^2} + \text{interference terms} \quad (3.4)$$

where $\psi(t)$ is the state vector of the system at time t given that $\psi(0) = |si\rangle \cdot \gamma^{si}$ is given by

$$\gamma^{si} = \Gamma_{si} + \sum_j \frac{|(H_v)_{si,lj}|^2 (\Gamma_{lj} - \Gamma_{si})}{(E_{si} - E_{lj})^2 + \frac{1}{4}(\Gamma_{lj} - \Gamma_{si})^2} \quad (3.5a)$$

(see also Eq. (A.11)), while γ^{lj} takes the form

$$\gamma^{lj} = \Gamma_{lj} - \frac{|(H_v)_{si,lj}|^2 (\Gamma_{lj} - \Gamma_{si})}{(E_s - E_l)^2 + \frac{1}{4}(\Gamma_{lj} - \Gamma_{si})^2} . \quad (3.5b)$$

The interference terms in Eq. (3.4) decay as $\exp(-\frac{1}{2}\gamma^{lj} t)$. Now in the weak coupling limit, we have

$$\gamma^{lj} \cong \Gamma_{lj} \gg \gamma^{si} \quad (3.6)$$

which is also consistent with the restriction that vibrational relaxation is faster than the electronic transitions. In this case the time evolution of our system will be essentially characterized by the exponentially decaying term $\exp(-\gamma^{si} t)$, as the other terms in Eq. (3.3) are characterized by much smaller amplitudes and also decay much more rapidly.

We conclude that our model molecule subjected to weak coupling conditions and to the restriction that relaxation due to the coupling with the medium is much faster than the radiative decay, i.e. $\Gamma_{lj} \gg \Gamma_{si}$ for all j, if prepared initially in the state $|si\rangle$ will decay exponentially with a decay rate given by Eq. (3.5a). The non-radiative decay rate is thus

$$W_{si} = \frac{1}{\hbar} \sum_j \frac{|(H_v)_{si,lj}|^2 \Gamma_{lj}}{(E_{si} - E_{lj})^2 + (\Gamma_{lj}/2)^2} \quad (3.7)$$

where Γ_{si} has been neglected relative to Γ_{lj}. The result (3.7) is a slight generalization of Fermi's golden rule. The latter is obtained in the limit $\Gamma_{lj} \to 0$ and when $\{|lj\rangle\}$ is a continuous manifold of states. An alternative derivation of (3.7) using sum rules for non-radiative decay is given in Appendix B.

Returning to Eq. (3.7), it is easy to show that with the simplifying assumption that Γ_{li} is a constant over the manifold $\{|lj\rangle\}$

$$\Gamma_{lj} = \Gamma_l \quad \text{for all } j. \quad (3.8)$$

Eq. (3.7) may be expressed as a Fourier transform of a generating function. To achieve this goal we note that a Lorentzian may be expressed as a Fourier transform in the following way

$$\frac{\Gamma}{(E_{si} - E_{lj})^2 + (\Gamma/2)^2} = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \exp\left[\frac{it}{\hbar}(E_{lj} - E_{si}) - \frac{\Gamma}{2\hbar}|t|\right]$$

where the variable t has dimensions of time. Thus Eq. (3.7) may be recast in the form

$$W_{si} = \frac{1}{\hbar^2} \int\limits_{-\infty}^{\infty} dt \exp\left(-\frac{\Gamma}{2\hbar}|t|\right) \sum_j |(H_v)_{si,lj}|^2 \exp\left[\frac{it}{\hbar}(E_{lj} - E_{si})\right]$$

$$= \frac{1}{\hbar^2} \int\limits_{-\infty}^{\infty} dt \exp\left(-\frac{i\Delta E}{\hbar}t - \frac{\Gamma}{2\hbar}|t|\right) \sum_j |(H_v)_{si,lj}|^2 \exp\left[\frac{it}{\hbar}(E_j^l - E_i^s)\right] \qquad (3.9)$$

where

$$\Delta E = E_{s0} - E_{l0} \qquad (3.10)$$

corresponds to the energy gap between the pure electronic origins of the two electronic manifolds, and where E_j^l and E_i^s are vibrational energies above the corresponding electronic origins.

Averaging now over the initial distribution, we obtain

$$\langle W_s \rangle_T = \frac{1}{\hbar^2} \int\limits_{-\infty}^{\infty} dt \exp\left(-\frac{i\Delta E t}{\hbar} - \frac{\Gamma}{2\hbar}|t|\right)$$

$$\otimes \sum_i P_i \sum_j |(H_v)_{si,lj}|^2 \exp\left[\frac{it}{\hbar}(E_j^l - E_i^s)\right] \qquad (3.11)$$

where

$$p_i = Z^{-1} \exp(-\beta E_i^s)$$

$$Z = \sum_i \exp(-\beta E_i^s); \qquad \beta = (k_B T)^{-1}. \qquad (3.12)$$

We note that Eqs. (3.9) and (3.11) yield rigorous expressions for the non-radiative decay rate also for the statistical limit case. It also applies for the isolated molecule case, where now Γ will correspond to the infrared and or radiative width of the levels $|lj\rangle$. The results previously obtained [12, 23–24] which have not included the factor $\exp\left(-\frac{\Gamma}{2\hbar}|t|\right)$ in the generating function where conceptually deficient as, bearing in mind that we actually handle a quasicontinuum and not a real continuum, the result with $\Gamma = 0$ will diverge at any point where exact conservation of energy occurs, as is easy to see from Eq. (3.7). However, as we shall demonstrate elsewhere, the non-radiative transition probability in the statistical limit does not depend on Γ and reduces to the previously obtained results of Lin and Bersohn [24], Engleman, Freed and Jortner [12] and Fisher [23].

The sum over i in Eq. (3.9), and over i and j in Eq. (3.11) may now be evaluated using the Green's function (or density matrix) expression for the harmonic oscillator, or alternatively the Feynman's operator calculus together with a simple closure relation.

The result may be written generally in the form

$$W_{si} = \frac{1}{\hbar^2} \int\limits_{-\infty}^{\infty} dt \exp\left(-i\frac{\Delta E}{\hbar}t - \frac{\Gamma}{2\hbar}|t|\right) F(t), \qquad (3.13a)$$

$$\langle W_s \rangle_T = \frac{1}{\hbar^2} \int\limits_{-\infty}^{\infty} dt \exp\left(-i\frac{\Delta E}{\hbar}t - \frac{\Gamma}{2\hbar}|t|\right) \langle F(t) \rangle_T \qquad (3.13b)$$

where expressions for $F(t)$ and $F(t)$ have been previously obtained [12b, 25] for a molecule characterized by identical displaced potential surfaces:

$$F(t) = \frac{1}{2} \sum_{\varkappa} |C_{sl}^{\varkappa}|^2 \exp\left(-\sum_{\mu} (\Delta_{\mu}^2/2)\right) \int_{-\infty}^{\infty} dt$$

$$\cdot \{[(v_{s\varkappa} + 1)\exp(i\omega_{\varkappa}t) + v_{s\varkappa}\exp(-i\omega_{\varkappa}t)]\} \exp\left[\sum_{\mu}(\Delta_{\mu}^2/2)\exp(i\omega_{\mu}t)\right] \quad (3.14a)$$

$$\otimes \prod_{\mu \neq \varkappa}(v_{s\mu})! \sum_{r=0}^{v_{s\mu}}(-\Delta\mu)^{2r} \frac{[1-\cos(\omega_{\mu}t)]^r}{(v_{s\mu}-r)!\,(r!)^2}$$

$$\langle F(t)\rangle_T = \frac{1}{4}\sum_{\varkappa}|C_{sl}^{\varkappa}|^2 \exp\left\{-\frac{1}{2}\sum_{\mu}\Delta_{\mu}^2(2\langle v_{\mu}\rangle_T + 1)\right\} \quad (3.14b)$$

$$\otimes \int_{-\infty}^{\infty} dt \left\{\{[\coth(\beta\hbar\omega_{\varkappa/2}) + 1]\exp(i\omega_{\varkappa}t) + [\coth(\beta\hbar\omega_{\varkappa}) - 1]\exp(-i\omega_{\varkappa}t)\}\right.$$

$$\left. \otimes \exp\left[\frac{1}{2}\sum_{\mu}\Delta_{\mu}^2(\langle v_{\mu}\rangle + 1)\exp(i\omega_{\mu}t) + \frac{1}{2}\sum_{\mu}\Delta\mu^2\langle v_{\mu}\rangle\exp(-i\omega_{\mu}t)\right]\right\}$$

and for a molecule characterized by displaced potential surfaces which differ also in the frequencies of the normal modes [12b, 26]. The result for this case in the zero temperature limit is

$$\langle F(t)\rangle_0 = \frac{1}{2}\sum_{\varkappa}|C_{sl}^{\varkappa}|^2 \prod_{\mu}(\beta_{\mu})^{-1/2} \exp[i\omega_{l\varkappa}t - i\delta_{\mu}t]$$

$$\otimes \left\{1 + \frac{(1-\beta_{\varkappa})^2}{4\beta_{\varkappa}}[1 - \exp(i\omega_{l\varkappa}t)]\right\}^{-1}$$

$$\otimes \prod_{\mu}\left\{1 + \frac{(1-\beta_{\mu})^2}{4\beta_{\mu}}[1 - \exp(2i\omega_{l\mu}t)]\right\}^{-1/2} \qquad (3.15)$$

$$\otimes \exp\left\{-\sum_{\mu \neq \varkappa}\frac{\beta_{\mu}\Delta_{\mu}^2[1 - \exp(i\omega_{l\mu}t)]}{1 + \beta_{\mu} + (\beta_{\mu} - 1)\exp(i\omega_{l\mu}t)}\right\}.$$

An approximate result for W_{si} for any i is given in Ref. [26]. In these expressions $v_{s\mu}$ is the initial population in the mode μ while $\langle v_{\mu}\rangle_T = [\exp(\beta\hbar\omega_{\mu}) - 1]$, $C_{sl}^{\varkappa}$ is the electronic matrix element [12], $\omega_{l\mu}$ and $\omega_{s\mu}$ are the frequencies of the mode μ in the l-th and s-th electronic states respectively. Finally, δ_{μ} and β_{μ} are defined by

$$\delta_{\mu} = \frac{1}{2}(\omega_{s\mu} - \omega_{l\mu})$$

$$\beta_{\mu} = (\omega_{s\mu}/\omega_{l\mu}).$$

It is important to note that expressions (3.14) and (3.15) are valid for both large and small molecules interacting with an inert medium and subjected to the conditions (3.8) and (3.3b) (the last condition is not important for the large molecule case). We now turn to study the particular characteristics of the small molecule case.

4. The Small Molecule Case

It has been asserted in Section 3 that within the restrictions imposed by the weak coupling limit, a small molecule embedded in a medium, if initially prepared in some excited electronic-vibrational state will exhibit an exponential non-radiative decay (basides its radiative decay). The non-radiative decay rate is given by Eq. (3.13b).

In order to handle Eq. (3.13b) analytically we shall consider the simple molecular model system characterized by identical frequencies in the two electronic states which just differ in their origins. The non-radiative decay probability in the zero temperature limit is (taking for the sake of simplicity the contribution of only one promoting mode)

$$\langle W \rangle_T = \frac{1}{2\hbar^2} |C_{sl}^x|^2 \exp\left(-\sum_\mu a_\mu\right) J \tag{4.1}$$

where the vibrational integral has the form

$$
\begin{aligned}
J &= \int_{-\infty}^{\infty} dt \exp\left\{-\frac{i}{\hbar}(\Delta E - \hbar\omega_x)t + \sum_\mu a_\mu \exp(i\omega_\mu t) - \frac{\Gamma}{2\hbar}|t|\right\} \\
&= \frac{1}{\omega_N} \int_{-\infty}^{\infty} dx \exp\left\{-i\varepsilon x + \sum_\mu a_\mu \exp(i\bar{\omega}_\mu x) - \frac{1}{2}\gamma|x|\right\}
\end{aligned}
\tag{4.2}
$$

here we have set $a_\mu = \frac{1}{2} \sum_\mu \Delta_\mu^2$. The intramolecular frequencies have been normalized by a common divider ω_N so that $\bar{\omega}_\mu = \dfrac{\omega_\mu}{\omega_N}$ are integers and where $\gamma = \Gamma/\omega_N$ while $\varepsilon = E - \hbar\omega_x/\omega_N$.

In the small molecule case the exponential damping factor in the integral (4.2) cannot be neglected and thus the saddle point method which was popular in the statistical limit is now inapplicable. To proceed we now expand the exponent in (4.2) in the form

$$
\begin{aligned}
\exp\left\{\sum_\mu a_\mu \exp(i\bar{\omega}_\mu x)\right\} &= \prod_{\mu=1}^{N} \exp\left[a_\mu \exp(i\bar{\omega}_\mu x)\right] \\
&= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \prod_{\mu=1}^{N} \frac{(a_\mu)^{n_\mu}}{(n_\mu)!} \exp(i\bar{\omega}_\mu n_\mu x) \\
&= \sum_{\{n\}} \exp\left[i\left(\sum_{\mu=1}^{N} n_\mu \bar{\omega}_\mu\right)x\right] \prod_{\mu=1}^{N} \frac{(a_\mu)^{n_\mu}}{(n_\mu)!}
\end{aligned}
\tag{4.3}
$$

where N is the number of vibrational degrees of freedom and $\sum_{\{n\}}$ is a sum over all the sets of any N integers (including zero). We thus obtain

$$J = \frac{1}{\omega_N} \sum_{\{n\}} \left[\left(\prod_{\mu=1}^{N} \frac{(a_\mu)^{n_\mu}}{n_\mu!}\right) \int_{-\infty}^{\infty} dx \exp\left\{i\varepsilon x + i \sum_{\mu=1}^{N} n_\mu \bar{\omega}_\mu x - \frac{\gamma}{2}|x|\right\}\right]. \tag{4.4}$$

The integral in Eq. (4.4) is easily performed to give a Lorentzian of width γ, so that J takes the form of a superposition of Lorentzians

$$J = \frac{1}{\omega_N} \sum_{\{n\}} \frac{\gamma}{\left(\varepsilon - \sum_{\mu=1}^{N} n_\mu \bar{\omega}_\mu\right)^2 + \left(\frac{\gamma}{2}\right)^2} \prod_{\mu=1}^{N} \frac{(a_\mu)^{n_\mu}}{(n_\mu)!} . \qquad (4.5a)$$

This expression can be easily transformed to an alternative form which contains the conventional energy parameters. Multiplying the numerator and the denominator by $\hbar^2 \omega_N^2$ Eq. (4.5a) then takes the form

$$J = \hbar \sum_{\{n\}} \frac{\Gamma}{\left(\Delta E - \hbar \omega_\varkappa - \hbar \sum_{\mu=1}^{N} n_\mu \omega_\mu\right)^2 + (\Gamma/2)^2} \prod_{\mu} \frac{(a_\mu)^{n_\mu}}{n_\mu!} . \qquad (4.5b)$$

Eqs. (4.1) and (4.5b) provide an explicit expression for the non-radiative transition probability (Eq. (3.7)), where the widths Γ_{li} are assumed to be independent of the particular vibronic levels $|lj\rangle$, and where the coupling matrix elements have been evaluated for the simple model at hand. These expressions are still general being applicable for both the small molecule case and for the statistical limit. The statistical limit is characterized by the relation $\Gamma \ll \varrho^{-1}$ (where ϱ is the density of states in the $|li\rangle$ manifold). In this case the overlapping Lorentzian peaks in (4.5b) yield a smooth function of the energy so that J (and $\langle W \rangle$) is a smooth function of the energy, being independent of Γ [13].

Turning now the small molecule case we specialize in the simple situation where only a single intramolecular vibrational mode acts as an accepting mode. This physical situation prevails for spin orbit coupling in a diatomic molecule (i.e. $^4\Pi - {}^2\Pi$ coupling in NO). Eq. (4.5b) takes the form

$$J = \hbar \sum_{n} \frac{\Gamma}{(\Delta E - n\hbar\omega)^2 + (\Gamma/2)^2} \left(\frac{a^n}{n!}\right) . \qquad (4.6)$$

Provided that the widths of the final states originate from vibrational relaxation then for the low temperature limit the vibrationless level $n = 0$ does not contribute to the final result and the sum in (4.6) has to be taken over $n = 1 \cdots \infty$.

The following comments are now in order: a) The decay rate of a small molecule in a dense medium is expressed in terms of an infinite series where each term corresponds to a product of a Lorentzian distribution and of a Poisson (Pekerian) distribution. b) In the simple case considered herein the density of vibronic states in the final electronic manifold is constant, whereupon only the magnitudes of the Lorentzian and of the Pekerian will determine the relative contributions of the various terms in Eq. (4.6). For $a \lesssim 1$ it may happen that the largest contribution to the decay rate of the $|s0\rangle$ level will not originate from the close lying $|lj\rangle$ levels, but rather from low lying $|lj\rangle$ states which contribute via the tails of their Lorentzian (uncertainty) distributions. c) In the case of accidental degeneracy when $(\Delta E - \hbar\omega) \ll \Gamma$, and provided that a is not too small[2], the dominating

---

[2] Reasonable order of magnitude estimates are $\Delta E = 10^4 \text{cm}^{-1}$, $\hbar\omega = 10^3 \text{cm}^{-1}$, $a \sim 1$ and $\Gamma \sim 1 \text{cm}^{-1}$. This value of Γ corresponds to fast vibrational relaxation.

contribution to J originates from a single level, whereupon one gets

$$J = \frac{4\hbar}{\Gamma} \left[a^{(\Delta E/\hbar\omega)}/(\Delta E/\hbar\omega)! \right] \tag{4.7a}$$

and

$$w_{s0} = \frac{2}{\hbar\Gamma} |c_{sl}|^2 e^{-a} \left[a^{\Delta E/\hbar\omega}/(\Delta E/\hbar\omega)! \right]. \tag{4.7b}$$

Eq. (4.7) corresponds to the Robinson-Frosch formula, obtained for our simplified model system. The main feature of this result is the dependence of w_{s0} on the reciprocal of the width Γ. It is also easy to verify that the result (4.7) is model independent, for the case of accidental degeneracy one gets

$$J = 4\hbar |(H_v)_{si,1j}|^2/\Gamma_{1j}. \tag{4.8}$$

Thus the Robinson-Frosch formula is applicable only for the case of near degeneracy in a small molecule embedded in a Shpolskii matrix. This theoretical result is of little use in real life. d) When accidental degeneracy is not encountered i.e. $\Delta E - n\hbar\omega \gg \Gamma$, we have

$$J = \hbar\Gamma \sum_n \frac{1}{(\Delta E - n\hbar\omega)^2} \frac{a^n}{n!} \tag{4.9}$$

so that the non-radiative probability is linear with the coupling to the medium, expressed in terms of the width Γ. This physical situation may be encountered in real life for small molecules in a Shpolskii matrix. e) The energy gap law for the non-radiative decay of a small molecule in a dense medium is not expected to be of general validity, as in the case for large molecules. If the major contribution to J (and to W) originates from off resonance low lying levels, W will vary as $(\Delta E)^{-2}$. On the other hand only when the major contribution will originate from near resonance coupling the usual energy law $W \sim a^{(\Delta E/\hbar\omega)}/(\Delta E/\hbar\omega)!$ will apply.

5. Details of Vibrational Relaxation

Up to this point we have been concerned with a phenomenological description of the vibrational relaxation widths of the final molecular states involved in the electronic relaxation process. The details of the vibrational relaxation process and its effect on the electronic relaxation of a small molecule can be handled by considering a simplified model of a harmonic molecule interacting with a harmonic medium via interaction terms which are linear in the molecular nuclear coordinates and of arbitrary order (within the rotating wave approximation) in the medium phonons [21, 27]. The limit of fast vibrational relaxation which is of interest for us can be defined in terms of the relation [21]

$$\gamma_\mu t \gg 1$$

for all $\mu = 1 \cdots N$.

Where t is the time scale and the indices μ refer to the vibrational mode. The thermally averaged non-radiative transition probability for spin allowed internal

conversion in the fast vibrational relaxation limit is [21]

$$
\langle W_s \rangle_T = \frac{2}{\hbar^2} \sum_\varkappa |C_{sl}^\varkappa|^2 \ \exp\left[-\frac{1}{2} \sum_\mu \varDelta_\mu^2 (2\langle v_\mu \rangle_T + 1) \right]
$$

$$
\otimes \left\{ \left[\coth\left(\frac{\beta\hbar\omega_\varkappa}{2}\right) + 1 \right] \int_{-\infty}^{\infty} dt \exp\left[-i\left(\frac{\varDelta E}{\hbar} - \omega_\varkappa\right) t + \sum_\mu \left(\frac{\varDelta_\mu^2}{2}\right) \right. \right.
$$

$$
\cdot (\langle v_\mu \rangle_T + 1) \exp\left(i\omega_\mu t - \frac{\gamma_\mu}{2\hbar}|t| \right) + \frac{1}{2} \sum_\mu \varDelta_\mu^2 \langle v_\mu \rangle_T \exp\left(-i\omega_\mu t - \frac{\gamma_\mu}{2\hbar}|t| \right) \Big]
$$

$$
+ \left[\coth\left(\frac{\beta\hbar\omega_\varkappa}{2}\right) - 1 \right] \otimes \int_{-\infty}^{\infty} dt \exp\left[-i\left(\frac{\varDelta E}{\hbar} + \omega_\varkappa\right) t + \sum_\mu \left(\frac{\varDelta_\mu^2}{2}\right) \right. \tag{5.1}
$$

$$
\cdot (\langle v_\mu \rangle_T + 1) \exp\left(i\omega_\mu t - \frac{\gamma_\mu}{2\hbar}|t| \right) + \frac{1}{2} \sum_\mu \varDelta_\mu^2 \langle v_\mu \rangle_T \exp\left(-i\omega_\mu t - \frac{\gamma}{2\hbar}|t| \right) \Big].
$$

Where $C_{sl}^\varkappa$ is the intramolecular electronic coupling matrix element induced by the $\varkappa$ promoting mode. ω_μ is the frequency of the μ-th vibrational mode characterized by the displacement $\varDelta_\mu$ and by the thermal occupation number $\langle v_\mu \rangle_T$. The effective electronic energy gap $\varDelta E_\varkappa = \varDelta E - \hbar\omega_\varkappa$ is reduced by the promoting mode frequency. Eq. (5.1) bears a close resemblance to the thermally averaged non-radiative transition probability in the statistical limit except that each frequency is now replaced by the complex frequency $\omega_\mu + i\gamma_\mu$.

To simplify matters we consider the electronic relaxation probability of the vibrationless level (corresponding to the zero temperature limit of Eq. (5.1)) which is given by

$$
W_{s0} = \frac{1}{2\hbar^2} \sum_\varkappa |C_{sl}^\varkappa|^2 \exp\left(-\frac{1}{2} \sum_\mu \varDelta_\mu^2 \right) \int_{-\infty}^{\infty} dx \left\{ \exp\left[-\frac{i\varDelta E_\varkappa x}{\hbar} - \gamma_\varkappa |x| \right] \right.
$$

$$
\otimes \exp\left[\frac{1}{2} \sum_\mu \varDelta_\mu^2 \exp(i\omega_\mu x - \gamma_\mu |x|) \right] \right\}. \tag{5.2}
$$

Utilizing the expansion of the exponential function

$$
\exp\left[\frac{1}{2} \sum_\mu \varDelta_\mu^2 \exp(i\omega_\mu x - \gamma_\mu |x|) \right]
$$

$$
= \sum_{\{n\}} \exp\left[i\left(\sum_\mu n_\mu \omega_\mu x\right) - \sum_\mu n_\mu \gamma_\mu |x| \right] \prod_\mu \frac{(\frac{1}{2}\varDelta_\mu^2)^{n_\mu}}{n_\mu!} \tag{5.3}
$$

Eq. (5.2) takes the form

$$
W_{s0} = \frac{1}{2\hbar^2} \sum_\varkappa |C_{sl}^\varkappa|^2 \exp\left[-\frac{1}{2} \sum_\mu \varDelta_\mu^2 \right]
$$

$$
\otimes \sum_{\{n\}} \frac{\gamma_\varkappa + \sum_{\mu \neq \varkappa} n_\mu \gamma_\mu}{\left(\varDelta E - \hbar\omega_\varkappa - \hbar \sum_{\mu \neq \varkappa} n_\mu \omega_\mu\right)^2 + \frac{1}{4}\left(\gamma_\varkappa + \sum_{\mu \neq \varkappa} n_\mu \omega_\mu\right)^2}. \tag{5.4}
$$

We have thus obtained a generalized microscopic expression for the non-radiative decay probability in the fast vibrational relaxation limit. The width of the lj level characterized by the vibrational occupation numbers $j \equiv \{M\}$ (for the harmonic model) is given by

$$\Gamma_{lj} = \gamma_\varkappa + \sum_{\mu \neq \varkappa} n_\mu \gamma_\mu \qquad (5.5)$$

The linear dependence of the thermal relaxation widths of the multimode harmonic oscillator on the population number is well known [28]. It should be noted that Eq. (5.4) is equivalent to the phomelogical equation (3.2) except that now an explicit expression has been obtained (Eq. (5.5)) for the level widths. Thus in the small molecule case when a small number of vibrational modes contributes to (5.4) the conclusions derived in section 4 are of general applicability.

6. The Contribution of Medium Modes

Up to this point we have disregarded the displacement of the origins of the medium modes, assuming that the inert medium does not contribute accepting modes for electronic relaxation. In order to extend the relaxation theory of a small molecule in a medium we shall consider the small number of intramolecular vibrations and the intermolecular vibrations on the same footing. Our model system consists of a supermolecule with a single intramolecular vibrational mode (specified by the frequency ω and the reduced displacement Δ) and N intermolecular modes (characterized by frequencies ω_α and reduced displacements Δ_α; $\alpha = 1 \cdots N$). The physical situation now corresponds to the statistical limit, whereupon the non-radiative decay probability is independent of the vibrational relaxation widths γ_μ. Separating the intramolecular and the intermolecular contributions the transition probability (Eq. (3.13)) takes the form

$$
\begin{aligned}
W_{s0} = \ & \frac{1}{2\hbar^2} \sum_\varkappa |C_{sl}^\varkappa|^2 \exp\left[-\frac{1}{2}\Delta^2 - \frac{1}{2}\sum_\alpha \Delta_\alpha^2 \right] \\
& \otimes \int_{-\infty}^{\infty} dx \exp\left(-\frac{iE_\varkappa}{\hbar}x \right) \otimes \exp\left[\frac{1}{2}\Delta^2 \exp(i\omega x) \right] \\
& \otimes \exp\left[\frac{1}{2}\sum_\alpha \Delta_\alpha \exp(i\omega_\alpha x) \right].
\end{aligned}
\qquad (6.1)
$$

The non-radiative decay probability can be expressed in terms of separate contributions of the intramolecular high frequency mode and intermolecule low frequency modes. Utilizing the expansion (4.3) we now have

$$W_{s0} = \frac{1}{2\hbar^2} \sum_\varkappa |C_{sl}^\varkappa|^2 \sum_n \exp\left(-\frac{1}{2}\Delta^2 \right) \frac{(\Delta^2/2)^n}{n!} F(\Delta E_\varkappa - n\omega) \qquad (6.2)$$

where

$$
\begin{aligned}
F(\Delta E_\varkappa - n\omega) = \ & \exp\left[-\frac{1}{2}\sum_\alpha \Delta_\alpha^2 \right] \int_{-\infty}^{\infty} dx \exp\left[\frac{i}{\hbar}(\Delta E_\varkappa - n\omega)x \right] \\
& \otimes \exp\left[\frac{1}{2}\sum_\alpha \Delta_\alpha^2 \exp(i\omega_\alpha x) \right].
\end{aligned}
\qquad (6.3)
$$

Thus the non-radiative transition probability can be recast as a sum of products of the intramolecular Franck Condon factors and the medium contributions (5.3). The F functions (5.3) just correspond to the line shape functions at the energies $(\Delta E_x - n\omega)$, which were previously treated in detail [29]. Thus the effect of the accepting medium modes, amounts to the replacement of the Lorentzian distributions Eq. (5.4) by the equivalent medium line shape functions.

As is well known from the theory of radiative and non-radiative processes in molecules and solids Eq. (6.3) can be considerably simplified in the limit of strong coupling to the medium phonons whereupon

$$\sum_\alpha (\Delta_\alpha^2/2) \gg 1 \,. \tag{6.4}$$

In this case the exponential function in the integral can be expanded in a power series of X retaining terms up to X^3 [12]. This procedure leads to the well known Gaussian line shape

$$F(\varepsilon) = \int_{-\infty}^{\infty} dx \exp(i\varepsilon x/\hbar) \exp(-D^2 X^2) = \left(\frac{2\pi}{D^2}\right)^{1/2} \exp\left[-(\varepsilon - E_M)^2/D^2\right] \tag{6.5}$$

where

$$D^2 = \tfrac{1}{2} \sum_\alpha \hbar \omega_\alpha^2 \Delta_\alpha^2 \tag{6.6a}$$

is the second moment of the distribution, while the Stokes shift is

$$E_M = \tfrac{1}{2} \sum_\alpha \hbar \omega_\alpha \Delta_\alpha^2 \,. \tag{6.6b}$$

Utilizing Eqs. (6.2), (6.3) and (6.5) the transition probability in the strong molecule-medium coupling limit takes the form

$$W_{s0} = \left(\frac{\pi}{2}\right)^{1/2} \left(\frac{1}{\hbar^2 D}\right) \sum_\varkappa |C_{si}^\varkappa|^2 \sum_n \exp(-\Delta^2/2) \frac{(\Delta^2/2)^n}{n!}$$
$$\otimes \exp\left[-(\Delta E - n\hbar\omega - E_M)^2/D^2\right] \,. \tag{6.7}$$

Thus the non-radiative decay of a small molecule strongly coupled to the medium can be recast in terms of a superposition of a Poisson and a Gaussian distribution. It is important to notice that as in the case of the Shpolskii matrix the non-radiative decay probability (6.7) may be dominated by off resonance coupling to the tails of the distributions of low lying states in the final manifold.

To conclude this discussion we would like to point out that a phenomenological model can be provided which accounts simultaneously for the medium broadening D (Eq. (6.6a)) and for vibrational relaxation broadening γ_μ (Eq. (4.1)). Provided that medium accepting modes are not active in intramolecular and intermolecular vibrational relaxation the non-radiative decay probability is given by Eq. (6.2) which includes both the intramolecular mode and the intermolecular mode. It is easy to demonstrate that when the γ_μ terms are retained Eq. (6.3) will include additional contribution of the form $\exp\left(-\sum_\alpha \gamma_\alpha |x|\right)$ in

the integral. In the case of strong molecule medium coupling the Gaussian distri-

bution (6.5) is replaced by a Voigt line shape function [30]. Now in this limit the phonon broadening will appreciably exceed the vibrational relaxation broadening, i.e. $D \gg \gamma_\mu$ for all μ, the Gaussian distribution (6.5) will be regained.

7. Discussion

In this paper we have considered the features of the electronic relaxation of a small molecule in a dense medium. We have focused attention on two limiting cases and considered the limit of zero displacements of the medium modes between the two electronic states (i.e. a Shpolskii matrix) and the case of strong molecule-medium coupling. In both cases we were able to recost the non-radiative decay probability in terms of a sum, where each term is a product of an intra-molecular Franck Condon factor and a medium assisted distribution function. In the case of the Shpolskii matrix the latter term involves a Lorentzian distribution while in the limit of strong molecule medium coupling this term involves a Gaussian distribution. From the mathematical point of view we can assert that the Fourier transform of the non-radiative decay probability of a small molecule in a Shpolskii matrix involves exponential damping while in the strong molecule medium coupling Gaussian damping is involved.

The main new features of the decay of a small molecule can be summarized as follows:

a) Interaction of the small molecule with a medium via vibrational relaxation or phonon broadening is a prerequisite for the occurrence of non-radiative relaxation.

b) The non-radiative relaxation probability of the small molecule in a medium is dominated by the coupling to the medium, being determined by the vibrational relaxation width γ_μ in the Shpolskii matrix or by the distribution width, D, in the strong coupling case.

c) The electronic relaxation of a small molecule may involve non-resonant coupling originating from overlapping widths of low lying final state.

d) The popular energy gap law will not hold when off resonance coupling dominates.

e) In the case of dominating of resonance coupling the deuterium isotope effect in the electronic relaxation will be negligibly small.

These features drastically differ from the decay characteristics in the statistical limit occurs via near resonance coupling, which are independent of the medium induced widths (γ_μ or D), which exhibit the energy gap law and the large deuterium isotope effect.

Appendix A.
Sequential Decay by the Green's Function Method

To verify Eqs. (3.1) and (3.2) we start from a model (see Fig. 1) where a single molecular vibronic level $|s\rangle$ is coupled to a radioactive continuum $|r\rangle$ and to a discrete molecular manifold $|l\rangle$. The $|l\rangle$ manifold is in turn coupled to a continuum of level states $|m\rangle$, assuming that the levels $\{|l\rangle\}$ do not interfere through their interaction with the medium, so that each $|l\rangle$ level is coupled to a different

set of $\{|m\rangle\}$ states. Making use of the Dyson equation

$$G + G_0 + G_0 VG \tag{A. 1}$$

we obtain the following forms for the matrix elements of the Green's function

$$G_{ss} = \frac{1}{E - E_s} + \frac{1}{E - E_s} \sum_r (H_{\text{int}}^R)_{sr} G_{rs} + \frac{1}{E - E_s} \sum_l (H_v)_{ls} G_{ls}, \tag{A. 2}$$

$$G_{rs} = \frac{1}{E - E_r} (H_{\text{int}}^R)_{rs} G_{ss}, \tag{A. 3}$$

$$G_{ls} = \frac{1}{E - E_l} (H_v)_{ls} G_{ss} + \frac{1}{E - E_l} \sum_m (H_{\text{int}}^M)_{lm} G_{ms}, \tag{A.4}$$

$$G_{ms} = \frac{1}{E - E_m} \sum_l (H_{\text{int}}^M)_{ml} G_{ls}. \tag{A.5}$$

Inserting Eq. (A.5) into Eq. (A.4) we get

$$G_{ls} = \frac{1}{E - E_l} \left[(H_v)_{ls} G_{ss} + \sum_{l'} G_{l's} \sum_m (H_{\text{int}}^M)_{lm} (H_{\text{int}}^M)_{ml'} \otimes \frac{1}{E - E_m} \right]. \tag{A.6}$$

If interference between different 1 and 1' states is neglected we obtain

$$G_{ls} = \frac{1}{E - E_m} \left[(H_v)_{ls} G_{ss} + G_{ls} \sum_m \frac{|(H_{\text{int}}^M)_{lm}|^2}{E - E_l} \right] \tag{A.7}$$

which after some algebraic manipulations results in

$$G_{ls} = \frac{(H_v)_{ls}}{E - \tilde{E}_l + \frac{i}{2} \Gamma_l} G_{ss} \tag{A.8}$$

where the modified energy

$$\tilde{E}_l = E_l + pp \sum_m \frac{|(H_{\text{int}}^M)_{lm}|^2}{E - E_m} \tag{A.9}$$

and the width

$$\Gamma_l = 2\pi \sum_m |(H_{\text{int}}^M)|^2 \, \delta(E - E_m) \tag{A.10}$$

are assumed to be weakly dependent on the energy variable E. Inserting now Eqs. (A.8) and (A.3) into Eq. (A.2) we obtain after some further algebraic manipulation

$$G_{ss} = \frac{1}{E - \tilde{E}_s + \frac{i}{2} \Gamma_s(E) + \Delta_s(E))} \tag{A.11}$$

where

$$\Delta_s = \sum_l \frac{\Gamma_l |(H_v)_{sl}|^2}{(E - \tilde{E}_l)^2 + (\Gamma_{l/2})^2}, \tag{A.11a}$$

$$\Gamma_s = 2\pi \sum_r |(H_{\text{int}}^R)_{sr}|^2 \, \delta(E - E_r) \tag{A.11b}$$

and where

$$E_s = \tilde{E}_s + pp \sum_r \frac{|(H^R_{int})_{sr}|^2}{E - E_r} + \sum_l \frac{2(E - \tilde{E}_l)\,|(H_v)_{sl}|^2}{(E - \tilde{E}_l)^2 + (\Gamma_{l/2})^2}. \qquad (A.12)$$

The radiative contributions to the width and level shift of the state s are usually nearly constant functions of the energy variable E. Eqs. (3.1) and (3.2) are now obtained by replacing the notations $|s\rangle$ and $|l\rangle$ by $|si\rangle$ and $|lj\rangle$ respectively.

Appendix B. Sum Rules for Non Radiative Decay

The effect of the broadening of the "final" molecular levels $|lj\rangle$ on the non radiative decay rate may be obtained in the following less concise but simpler procedure. As a starting point we take the well known expression [31] for the probability distribution in the dissipative manifold. The probability to be at time $t = \infty$ in a particular state $|f\rangle$ of this manifold is given by

$$P_f = \frac{|V_{kf}|^2}{(E_f - \tilde{E}_k)^2 + (\Gamma_{k/2})^2} \qquad (B.1)$$

where $|k\rangle$ is the initial metastable state, with the corresponding decay width Γ_k and the (shifted) energy $\tilde{E}_k \cdot V_{kf}$ denotes the coupling between the states k and f. Summing over all the final states f we obtain (assuming that f is the only decay channel)[3]

$$\sum_f P_f = \sum_f \frac{|V_{kf}|^2}{(E_f - \tilde{E}_k)^2 + (\Gamma_{k/2})^2} = 1. \qquad (B.2)$$

This trivial sum rule may be applied to derive an expression for Γ_k provided that is may be assumed that Γ_k is weakly dependent on E_f. This restriction should be recognized as the condition for an exponential decay of the state $|k\rangle$. Assuming that this condition is satisfied we may apply Eq. (B.2) to our model taking $|k\rangle$ to be our initial state $|si\rangle$ and taking the states $\{|f\rangle\}$ to be the states which result from a partial diagonalization of the "final" molecular levels $\{|lj\rangle\}$ and the continuous manifold of medium levels. Denoting the (continuous) medium levels by $\{|m\rangle\}$ we have

$$|f\rangle = a^f_{lj}|lj\rangle + \sum_m b^f_m |m\rangle \qquad (B.3)$$

where the absolute square of the amplitudes a^f_{lj} is given by Fano [32] to be

$$|a^f_{lj}|^2 = \frac{|V_{lj,m}|^2_{E_m = E_f}}{(E_f - E_{lj})^2 + (\Gamma_{lj/2})^2} \qquad (B.4)$$

where $\Gamma_{lj} = 2\pi\varrho_m |V_{lj,m}|^2$ is the width of the level $|lj\rangle$ and where level shifts have been neglected. To derive these results one should invoke the assumption that each molecular level $|lj\rangle$ decays into its own set of levels $\{|m\rangle\}$, namely, that the levels $|lj\rangle$ do not interfere through their interaction with the medium levels. The same assumption has been invoked in deriving Eq. (3.7).

---

[3] Other independent decay channels will contribute in an additive manner.

Assuming further that there is no direct interaction between the initial molecular state $|si\rangle$ and the medium levels $\{|m\rangle\}$ (so that the only interaction occurs through the molecular levels $|lj\rangle$) and utilizing Eq. (B.3) we obtain[4]

$$V_{si,f} = a_{lj}^f (H_v)_{si,lj} \,. \tag{B.5}$$

Inserting this result into Eq. (B.2) we now have

$$\sum_{lj} \sum_f \frac{|(H_v)_{si,lj}|^2 \, |a_{lj}^f|^2}{(E_f - \tilde{E}_{si})^2 + (\gamma^{si/2})^2} = 1 \tag{B.6}$$

where γ^{si} now replaces Γ_k in order to match the notation in Section 3.

Utilizing Eq. (B.4) and replacing the summation over f by an integration over E_f with the corresponding density of states, Eq. (B.6) takes the form

$$\frac{1}{2\pi} \sum_{lj} \int dE_f \frac{|(H_v)_{si,lj}|^2 \, \Gamma_{lj}}{[(E_f - \tilde{E}_{si})^2 + (\gamma^{si}/2)^2] \, [(E_f - E_{lj})^2 + (\Gamma_{lj/2})^2]} = 1 \,. \tag{B.7}$$

The integral over E_f is easily evaluated assuming that Γ_{lj} does not depend on this variable leading to

$$W_{si} = \frac{\Gamma_{si}}{\hbar} = \frac{1}{\hbar} \sum_{lj} \frac{|(H_v)_{si,lj}|^2 \, (\gamma^{si} + \Gamma_{lj})}{(E_{si} - E_{lj})^2 + [\frac{1}{2}(\gamma^{si} + \Gamma_{lj})^2]} \,. \tag{B.8}$$

This result corresponds to the physical situation only in the limit $\Gamma_{lj} \ll \gamma^{si}$. Neglecting γ^{si} relative to Γ_{lj} in the r.h.s. of Eq. (B.8) we regain Eq. (3.7). It should be noted that if γ^{si} and Γ_{lj} were comparable in magnitude, the present procedure which is based on the condition (3.6) leads to an incorrect result as is seen by comparing Eqs. (B.8) and (3.5a).

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[4] In Eq. (B.5) only one level $|lj\rangle$ contributes as we have assumed that only one such level participates in a particular $|f\rangle$ state.

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