PECULIARITIES OF THE NON-RADIATIVE DECAY
OF A SINGLE VIBRONIC LEVEL IN POLYATOMIC MOLECULES

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Optical selection experiments in the first excited singlet state of the benzophenone molecule in solution confirm a theoretical prediction concerning the retardation of the electronic relaxation rate with increasing the excess vibrational energy in excited electronic states of a large molecule characterized by a small electronic energy gap.

Experimental optical selection studies of the non-radiative decay of a single vibronic level of isolated (collision free) large molecules have established that the non-radiative decay probability increases with increasing the excess vibrational energy E_v in the lowest excited electronic singlet state of β-naphthylamine [1] and of benzene [2-5]. Subsequent theoretical studies [6-8] provided a rationalization of these observations. In a recent work [9] a general expression was derived for the electronic relaxation probability of a single vibronic level of a "harmonic molecule", characterized by displaced identical potential hypersurfaces. The electronic relaxation probability, W_{si}, for the decay process $|si\rangle \rightarrow \{|lj\rangle\}$ of a single vibronic level in the $|s\rangle$ electronic manifold to the dissipative quasicontinuum $\{|lj\rangle\}$ was handled by the Feynman operator technique [10], and recasted in terms of a Fourier integral [9]:

$$W_{si} = \hbar^{-2} \exp\left(-\tfrac{1}{2}\sum_{\mu=1}^{N}\Delta_\mu^2\right) \sum_{\kappa=1}^{p} \tfrac{1}{4}|C_{sl}^\kappa|^2 \hbar\omega_\kappa \int_{-\infty}^{\infty} dt \left\{ \left[(v_{s\kappa}+1)\exp\left[-\tfrac{i}{\hbar}(\Delta E - \hbar\omega_\kappa)t\right] \right. \right.$$

$$+ v_{s\kappa}\exp\left[-\tfrac{i}{\hbar}(\Delta E + \hbar\omega_\kappa)t\right] \exp\left[\tfrac{1}{2}\sum_{\mu=1}^{N}\Delta_\mu^2 \exp(i\omega_\mu t)\right] \times$$

$$\prod_{\mu\neq\kappa}\left[(v_{s\mu})!\sum_{r=0}^{v_{s\mu}}(-\Delta_\mu^2)^r \frac{(1-\cos\omega_\mu t)^r}{(v_{s\mu}-r)!\,(r!)^2}\right]\exp\left[-\tfrac{\Gamma}{\hbar}|t|\right]\right\}, \tag{1}$$

where the N vibrational modes, characterized by the frequencies ω_i and the occupation numbers v_{si}, are subdivided into $\kappa = 1\ldots p$ promoting modes and $\mu \neq \kappa$, $\mu = 1\ldots N\text{-}p$ accepting modes. Δ_μ corresponds to the reduced displacement between the two electronic states in the equilibrium position of the μ accepting mode (while for the promoting modes $\Delta_\kappa = 0$), C_{sl}^κ denotes the non-adiabatic coupling matrix element between the two electronic states, ΔE is the electronic energy gap between the origins of the two electronic states while $\Delta E_{eff} = \Delta E - \hbar\omega_\kappa$ is the effective energy gap. Finally, Γ represents the decay width of each level in the $|lj\rangle$ manifold, which in the isolated molecule is due to radiative (infrared or optical) emission, while for a molecule embedded in a medium, the major contribution to Γ will arise from vibrational relaxation. It is further assumed that this width is independent of the particular $|lj\rangle$ level. It can be demonstrated [11] that in the statistical limit in an isolated molecule W_{si} is independent of Γ. A more interesting physical situation is encountered when the effective energy gap in a large molecule is small or, alternatively, for a medium sized molecule which is characterized by a

Recent experimental studies of the intersystem crossing rate from different vibrational levels of the lowest excited states of the benzophenone molecule in solution [12] provide a verification of these theoretical predictions. The electronic energy gap between the lowest excited singlet and triplet states in benzophenone is small, i.e. $\Delta E \approx 2000$ cm^{-1} so that the decay of the lowest singlet state corresponds to the "small molecule case". Large spin orbit coupling results in strong interstate singlet-triplet coupling. When this molecule is embedded in solution, efficient intersystem crossing will occur, being manifested by the "absence" of fluorescence (the fluorescence quantum yield being [12] $\approx 10^{-6}$) and by the near unity quantum yield for phosphorescence. Intramolecular energy dissipation in the benzophenone molecule in solution was monitored [12] in the lowest and in the higher vibrational levels of the first excited singlet state by utilizing picosecond laser pulses of the second harmonic and of the Raman shifted second harmonic of a mode locked ruby laser. The relevant experimental results are [12]:

a) The intersystem crossing rate from the lowest vibronic component of the S_1 state (26 800 cm^{-1}) is $W_0 = 2 \times 10^{11}$ sec^{-1}. This result is consistent with the semiquantitative estimates of Dym and Hochstrasser [13] from optical line broadening data.

b) The intersystem crossing rate from the states at 28 800 cm^{-1} (corresponding to the excitation of two quanta of the O–C stretching mode) is $W_2 = 4 \times 10^{10}$ sec^{-1}.

c) In view of the lower decay rate of the higher state characterized by $E_v = 2000$ cm^{-1}, it can be asserted that the major decay pathway of the 28 800 cm^{-1} levels involves electronic relaxation, rather than vibrational relaxation to the pure electronic origin.

Thus optical selection studies in the lowest excited singlet state of the benzophenone molecule imply that $W_2/W_0 \approx 0.2$. This pattern is drastically different from the characteristics of electronic relaxation of a single vibronic level in the "statistical" limit [1–5], being however in full agreement with the results of the model calculations (for a small energy gap) displayed in table 1. It is gratifying that a unified theoretical scheme is now available which provides a consistent interpretation of optical selection studies in polyatomic molecules.

Finally, we would like to point out, at the risk of triviality, that in view of the small electronic energy gap, electronic relaxation will not take place from the first singlet excited state in the "isolated" benzophenone molecule, and this state will then exhibit the features of the radiative decay of strongly coupled levels in a "small" molecule [14]. Thus in the low pressure gas phase we expect that fluorescence will be observed, being characterized by a radiative decay time which is long relative to the expectations on the basis of the integrated oscillator strength.

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small number of vibrational degrees of freedom. In this "small molecule case" [*] electronic relaxation will not occur within the isolated molecule, as the $|lj\rangle$ manifold cannot act as a dissipative quasicontinuum. When the density of states in the $|l\rangle$ manifold is low, the electronic relaxation characteristics of any $|si\rangle$ level will strongly depend on the decay mechanisms of the $|lj\rangle$ states. Irreversible electronic relaxation can occur in the "small molecule case" provided that this molecule will be embedded in a medium which provides a vibrational relaxation broadening mechanism. In this case W_{si} will be proportional to Γ (except in the rare case of accidental degeneracy).

For the statistical limit which is characterized by a large effective energy gap in a large molecule, the density of states in the $|lj\rangle$ manifold increases roughly exponentially with E_v, much faster than the subsequent decrease of the intramolecular coupling constants, whereupon W_{si} is expected to increase with increasing E_v. On the other hand, in the "small molecule case" the density of states weighted by the non-adiabatic coupling terms, will be dominated by the variation of the Franck-Condon vibrational overlap factors. When such a molecule is embedded in a medium which now insures irreversible electronic relaxation in this case the electronic relaxation probability of a single vibronic level will diminish with increasing E_v. The effect of the "inert" medium does, however, introduce an additional complication, as it will induce an additional decay channel for the $|si\rangle$ states (except for the vibrationless level) which is due to vibrational relaxation within the $|s\rangle$ manifold. Optical selection studies of electronic relaxation will then be feasible only provided that the electronic relaxation rate of each of the states exceeds the vibrational relaxation rate of these levels. We thus expect that fast electronic relaxation processes of a "small molecule case" in an inert medium, which occur on the picosecond time scale, may be sometimes amenable to experimental study by the optical selection technique.

To demonstrate the general qualitative implications of the present theoretical treatment [as summarized in eq. (1)], we display in table 1 some model computations of the dependence of W_{si} (for different values of E_v) on the effective electronic energy gap. The model system used is characterized by two accepting modes $\hbar\omega_1 = 1000$ cm^{-1}; $\Delta_1^2 = 0.5$ and $\hbar\omega_2 = 3000$ cm^{-1}; $\Delta_2^2 = 0.5$, while the width of the final states was taken to be $\Gamma = 1$ cm^{-1}. From the results displayed in table 1 we conclude that for a small effective energy gap the electronic relaxation rate of a single vibronic level decreases with increasing the excess vibrational energy.

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[*] In what follows, we assert that the "small molecule case" is also exhibited by an excited state of a large molecule characterized by a small effective energy gap.

Table 1

Non-radiative decay rate as a function of excess vibrational energy for small effective energy gaps. $\Delta_1^2 = \Delta_2^2 = 0.5$; $\hbar\omega_1 = 1000$ cm^{-1}; $\hbar\omega_2 = 3000$ cm^{-1}; $\Gamma = 1$ cm^{-1}

ΔE_{eff} (cm^{-1})	Excess vibrational energy in quanta of the 1000 cm^{-1} mode	W_{si} (arbitrary units)
	0	1.00
	1	2.64
	2	4.10
4800	3	5.33
	4	6.27
	5	7.00
	6	7.43
	0	5.62
	1	8.50
	2	9.80
3800	3	10.1
	4	9.70
	5	9.05
	6	8.37
	0	21.8
	1	13.3
	2	8.35
2800	3	6.10
	4	5.88
	5	7.05
	6	9.20