

Radiationless Transitions in Molecules

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Received March 9, 1977

After light absorption, a molecule can undergo a number of different possible radiationless transitions. These include a series of photochemical processes such as unimolecular decompositions, isomerizations, and ionizations. In photochemical processes only the quantum state is changed as in electronic relaxation, vibrational relaxation, and collisional quenching processes. The photophysical processes generally accompany and strongly influence photochemical processes, so there is considerable interest in studying the photophysical processes separately. Here we briefly review^{1,2} some of our recent work and related developments concerning electronic relaxation, its pressure dependence, collision-induced intersystem crossing, and intramolecular vibrational relaxation.

Electronic Relaxation Processes

Early experiments on the luminescence of organic molecules in solutions and rigid media³ determined thermally averaged lifetimes, $\tau^{\text{rad}}(T)$, and quantum yields, $\Phi(T)$, whereupon the thermally averaged pure radiative, $k_{\text{rad}}(T)$, and nonradiative, $k_{\text{nr}}(T)$, rates are obtained as

$$\Phi(T) \equiv k_{\text{rad}}(T) / [k_{\text{rad}}(T) + k_{\text{nr}}(T)] \quad (1)$$

$$\tau^{\text{rad}}(T) \equiv [k_{\text{rad}}(T) + k_{\text{nr}}(T)]^{-1} \quad (2)$$

In general, aromatic molecules were found to have fluorescence quantum yields of less than unity (often $\Phi \ll 1$), and observed radiative lifetimes were considerably shorter than pure radiative values, $[k_{\text{rad}}(T)]^{-1}$, deduced from (1) or (2) or from the integrated absorption intensity for the transition.

These observations were taken to be indicative of an electronic relaxation process, a radiationless transition involving a change in the electronic state. This process is termed intersystem crossing or internal conversion when the spin symmetry of the state changes or not, respectively, in the transition. These radiationless transitions were explained on the basis of the theoretical energy level diagram of Figure 1 that is expected to apply to all polyatomic molecules. The zeroth-order energy levels are those generated by the Born-Oppenheimer approximation.⁴ The molecule is initially in some thermally accessible vibronic level, ϕ_0 , of the ground electronic state. Somewhere in the visible or ultraviolet region the molecule is found to absorb in an electric-dipole-allowed (possibly vibronically induced) transition to an excited electronic state ϕ_s . Isoenergetic with ϕ_s is a dense manifold of vibronic levels, $\{\phi_i\}$, be-

longing to some lower electronic state(s) including high lying levels of the ground electronic state. Radiative transitions between ϕ_0 and $\{\phi_i\}$ are unobserved because of unfavorable Franck-Condon factors, spin selection rules, etc., so the expected optical spectrum is that generated by ϕ_s alone.

The Born-Oppenheimer approximation ignores some small terms in the molecular Hamiltonian, but these nonadiabatic interactions can have profound effects when coupling nearly degenerate zeroth-order levels.⁶ Robinson and Frosch⁷ used simple first-order time-dependent perturbation theory to show how the nonadiabatic couplings between ϕ_s and $\{\phi_i\}$ lead to the observed nonradiative decay in condensed media. The host medium serves as a heat bath to carry away the vibrational excitation of the initially produced $\{\phi_i\}$ levels that are isoenergetic with ϕ_s . This explains, for instance, the observed phosphorescence from the thermally equilibrated lowest triplet state in aromatic hydrocarbons. Robinson and Frosch also noted that the explicit dependence on the host medium is essentially eliminated from the nonradiative decay rate expression, thereby explaining the observed apparent purely intramolecular character of the electronic relaxation. They further asserted that an isolated large molecule could act as its own heat bath to produce nonradiative decay, but the mechanism for this possible process was not understood.

To eliminate the essential perturbation of the host medium (a heat bath for vibrational relaxation) and to exhibit the believed purely intramolecular character of the electronic relaxation, it is necessary to study the nonradiative decay in isolated molecules in gases at very low pressures (≤ 0.01 Torr).

The results of low-pressure experiments could be anticipated on the basis of simple quantum mechanical arguments. When light, having a frequency corresponding to the ϕ_0 - ϕ_s energy difference, is incident on the isolated molecule, the molecule can be excited from ϕ_0 to ϕ_s since ϕ_s is the only level in the region carrying oscillator strength from ϕ_0 . Once in ϕ_s , the molecule can either fluoresce or it can "cross over" to isoenergetic levels of $\{\phi_i\}$ because of the nonadiabatic coupling between ϕ_s and ϕ_i . Since the ϕ_s - $\{\phi_i\}$ couplings mix a finite

(1) For more details and additional references, see: K. F. Freed, *Top. Appl. Phys.*, **15**, 23 (1976).

(2) For extensions to photochemistry, see: K. F. Freed and Y. B. Band, *Excited States*, **3**, in press.

(3) G. W. Robinson, *Excited States*, **1**, 1 (1974).

(4) We employ the familiar clamped-nucleus (adiabatic) version, in which the electronic wave functions depend parametrically on the nuclear positions, rather than the so-called crude Born-Oppenheimer approximation where the electronic wave functions are obtained at a single configuration.¹ The latter would, for instance, yield predicted force constants which differ from measured values by an order of magnitude⁵ and which poorly describe the optically excited states.

(5) O. Atabek, A. Hardisson, and R. Lefebvre, *Chem. Phys. Lett.*, **20**, 40 (1973).

(6) K. F. Freed, *J. Chem. Phys.*, **45**, 4214, 1714 (1966).

(7) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **38**, 1187 (1963).

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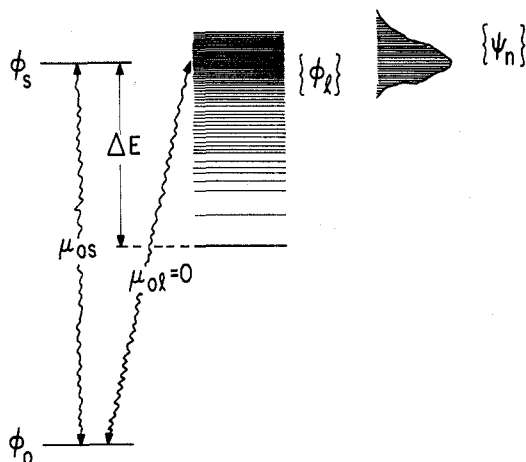


Figure 1. The molecular energy level model used to discuss radiationless decay processes in polyatomic molecules. For electronic relaxation the states ϕ_0 , ϕ_s , and $\{\phi_l\}$ are Born-Oppenheimer zeroth order molecular levels. They respectively correspond to one of the thermally populated ground electronic state vibrational sublevels, a vibronic component of an excited electronic state, and a dense manifold of lower electronic levels associated with an origin below that of the electronic state of ϕ_s . The transition dipole μ_{0s} is nonzero for transitions between ϕ_0 and ϕ_s , while μ_{0l} is assumed to vanish ($\{\phi_l\}$ may emit to higher lying levels of the ground electronic state, ϕ_0^v).

number of levels, a molecule in $\{\phi_l\}$ will eventually “resonate” back to ϕ_s , whereupon it can either fluoresce or “cross back” to $\{\phi_l\}$. Continuing this process, it is clear that $\Phi_f = 1$ in an isolated molecule like the one depicted in Figure 1. This is in marked contrast to the case of condensed media where vibrational relaxation of the initially formed $\{\phi_l\}$ levels rapidly carries the molecule to lower $\{\phi_l\}$ levels from which it can no longer “cross back” to ϕ_s because of insufficient energy.

Electronic relaxation experiments at very low pressures were first performed by Kistiakowsky and Parmenter and their co-workers⁸ for the benzene molecule. Here ϕ_0 is the ground singlet S_0 , ϕ_s is the first excited singlet state S_1 , while $\{\phi_l\}$ can contain high-lying levels of S_0 and triplet levels, T. The experiments conclusively showed that Φ_f for benzene is not unity (≈ 0.3) in the limit of low pressures. Kistiakowsky and Parmenter astutely noted that those results were hard to reconcile with the principles of quantum mechanics—those principles which, as argued above, predict $\Phi_f = 1$.

Douglas⁹ found τ^{rad} in SO_2 and NO_2 to be much longer than that deduced from the integrated absorption intensity, and subsequent experiments yield $\Phi_f = 1$ at very low pressures.¹⁰ Douglas explained this lifetime lengthening (and the presence of many additional spectral lines) with the theoretical energy level diagram in Figure 1. When the couplings between ϕ_s and $\{\phi_l\}$ are diagonalized, the resultant molecular eigenstates, $\{\psi_n\}$, each contain a piece of ϕ_s and, consequently, only a fraction of the original oscillator strength. Hence, the $\{\psi_n\}$ are characterized by longer lifetimes than that deduced from the integrated absorption intensity. The distribution of the ϕ_0 - ϕ_s oscillator strength among a large number of $\{\psi_n\}$ also

explains the presence of additional spectral lines.

At this juncture both the large molecule benzene and the small molecules SO_2 and NO_2 experiments are rationalized using the same energy level scheme (Figure 1). In order to explain the observed $\Phi_f < 1$ in benzene, radiationless transition theory was then formulated in terms of the molecular eigenstates basis that so simply explains the small-molecule situation.¹¹ If the molecule begins in ϕ_s , this initial nonstationary state can be represented as a superposition of the molecular eigenstates

$$\phi_s = \sum_n C_{ns} \psi_n \quad (3)$$

In the absence of matter-radiation interaction, each ψ_n with energy E_n evolves separately in time. Hence, the nonstationary state at time t is

$$\Psi(t) = \sum_n C_{ns} \exp(-iE_n t/\hbar) \psi_n \quad (4)$$

The probability of finding the system in ϕ_s at time t decays exponentially for short enough times with the decay rate

$$k_{nr}(s \rightarrow l) \doteq \frac{2\pi}{\hbar} \sum_l |v_{ls}|^2 \rho_l(E_s) \quad (5)$$

where v_{ls} is the ϕ_s - $\{\phi_l\}$ effective coupling and ρ_l is the $\{\phi_l\}$ density of states. However, for long times, we again obtain the result that $\Phi_f = 1$ at zero pressure since the zeroth order state ϕ_s can reoccur at subsequent times.

This leaves the puzzling question of explaining why experiments yield $\Phi_f < 1$ for molecules like benzene, in contrast to the above rigorous quantum mechanical arguments for Figure 1. Furthermore, it is necessary to understand what physical features are responsible for the difference between C_6H_6 and SO_2 and NO_2 .

This irreversibility paradox also arose about a hundred years ago in a different context. Boltzmann used plausible physical assumptions to develop an equation describing the nonequilibrium behavior of a dilute classical fluid. The equation predicts that an initial nonequilibrium state decays to the appropriate equilibrium Maxwell-Boltzmann distribution in accord with our experience that isolated systems tend to equilibrium. However, for finite systems the Poincaré recurrence theorem states that, if we wait long enough, the system will ultimately return arbitrarily close to its initial state. For instance, consider a system with all the molecules in one half of the container. After the removal of the partition, the system tends toward an equilibrium distribution with particles uniformly distributed throughout the container. The recurrence theorem implies that, if we waited sufficiently long, the system would spontaneously return to its initial state with all the particles in the original half of the container. Boltzmann's equation was severely criticized because it did not exhibit these recurrences which are a direct consequence of the laws of classical mechanics. Boltzmann's reply was basically, “You wait for the recurrences!” Any reasonable estimate yields recurrence times many orders of magnitude longer than the age of the universe.

In a discussion of irreversibility and radiationless transitions we note that any real experiment is per-

(8) G. B. Kistiakowsky and C. S. Parmenter, *J. Chem. Phys.*, **42**, 2942 (1965); E. M. Anderson and G. B. Kistiakowsky, *ibid.*, **48**, 4787 (1968); C. S. Parmenter and A. H. White, *ibid.*, **50**, 1631 (1969)

(9) A. E. Douglas, *J. Chem. Phys.*, **45**, 1007 (1967).

(10) M. H. Hui and S. A. Rice, *Chem. Phys. Lett.*, **17**, 474 (1972); L. E. Brus and J. R. McDonald, *J. Chem. Phys.*, **61**, 97 (1974).

(11) M. Bixon and J. Jortner, *J. Chem. Phys.*, **48**, 715 (1968); **50**, 3284, 4061 (1969); D. Chock, S. A. Rice, and J. Jortner, *ibid.*, **49**, 610 (1968).

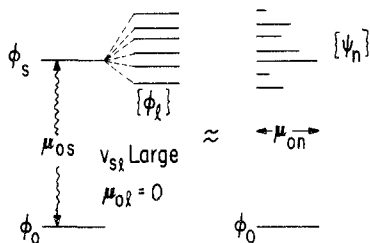


Figure 2. A schematic representation of the small molecule limit. The Born–Oppenheimer levels on the left are the same as those presented in Figure 1. The molecular eigenstates, $\{\psi_n\}$, diagonalize the molecular Hamiltonian, \mathcal{H}_{mol} , and, in the absence of accidental degeneracies, they differ negligibly from the eigenfunctions of the effective Hamiltonian (eq 7) incorporating the effects of all decay processes of this set of closely coupled levels.

formed over a finite amount of time, so it is only necessary to pose questions of practical irreversibility on real finite timescales.^{1,12} If the model in Figure 1 were a complete description of the system, ϕ_s is found to decay irreversibly into $\{\phi_i\}$ for times

$$t \lesssim \hbar \rho_i \quad (6)$$

less than or comparable to quantum mechanical Poincaré recurrence times.¹³ Thus, if the molecule crosses over from ϕ_s to $\{\phi_i\}$, it cannot return to ϕ_s for times satisfying (6). In general, Figure 1 is incomplete under real experimental conditions.^{1,12} Molecules in $\{\phi_i\}$ may collide with one another (even in interstellar space) or with the walls of the vessel, thereby removing energy to prevent recurrences. They may also emit radiation in the optical or infrared region (rates $\approx 10^3$ – 10^4 s⁻¹) to remove recurrences. When these additional decay processes are appended to Figure 1, irreversible decay occurs for $t \gtrsim \Gamma_i^{-1}$, where Γ_i are typical decay (collisional plus radiative, etc.) rates for $\{\phi_i\}$.

For a particular system it is necessary to consider the full quantum mechanical description of the radiative, nonradiative, collisional, etc. decay of a number of closely coupled levels on timescales of interest, and it is important to determine the true nature of the initially prepared state—it is often *impossible* to excite the zeroth-order state ϕ_s . An essential feature of the theoretical description of these problems emerges in the form of the effective Hamiltonian^{1,12}

$$\mathcal{H}_{\text{eff}} = \mathcal{H}_{\text{mol}} - i\hbar\Gamma/2 \quad (7)$$

where \mathcal{H}_{mol} is the molecular Hamiltonian for the excited levels ϕ_s and $\{\phi_i\}$ (with vibronic couplings to other states incorporated), and Γ is a diagonal matrix of ϕ_s and $\{\phi_i\}$ decay rates in the simplest situations. The nature of the initially prepared levels and their decay processes are governed by the eigenfunctions of (7) along with the characteristics of the excitation source.¹⁵

There is a continuous gradation of properties from those characteristic of small-molecule behavior to those appropriate to the statistical limit as the parameter¹

$$m = \hbar \rho_i \Gamma_i \quad (8)$$

(12) K. F. Freed, *J. Chem. Phys.*, **52**, 1345 (1970).

(13) More precise computations imply actual recurrence times orders of magnitude longer than the simple estimate (eq 6).¹⁴

(14) W. M. Gelbart, D. F. Heller, and M. L. Elert, *Chem. Phys.*, **7**, 116 (1975).

(15) W. Rhodes, *J. Chem. Phys.*, **50**, 2885 (1969); *Chem. Phys. Lett.*, **11**, 179 (1971).

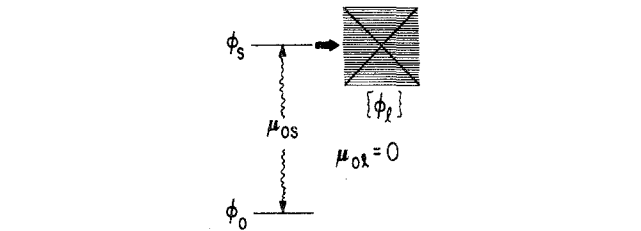


Figure 3. A pictorial description of the large molecule statistical limit. The zeroth-order levels are as in Figure 1. The $\{\phi_i\}$ form a dense set of states acting as a decay sink on the timescales of real experiments.

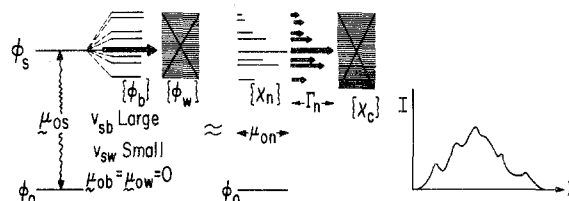


Figure 4. A particular example of the intermediate case is represented¹⁷ showing the strongly and weakly coupled levels, $\{\phi_b\}$ and $\{\phi_w\}$, respectively. The states $\{\chi_n\}$ diagonalize the effective Hamiltonian (eq 7) in the $\{\phi_s, \phi_b\}$ basis, representing a small-molecule-like situation as in Figure 2. However, the $\{\phi_w\}$ provide a decay sink for nonradiative transitions, so the resonant states $\{\chi_n\}$ carry a portion of the $\phi_0 \rightarrow \phi_s$ oscillator strength and have nonradiative decay rates $\{\Gamma_n\}$ characteristic of a composite of the decays of the zeroth order ϕ_s and $\{\phi_b\}$. A schematic view of the spectrum for this intermediate case is also depicted. The lifetime and quantum yield can vary across the spectrum. (The decay is, in general, nonexponential.) A similar variation can also emerge under higher resolution from a zeroth order level ϕ_s which had been assigned as being in the statistical limit from low-resolution experiments.

varies from $m \ll 1$ (small molecule) through $m \gg 1$ (statistical limit). For $m \ll 1$ and sparse level distributions, the $i\hbar\Gamma/2$ term in (7) can be treated as a perturbation. The eigenfunctions of (7) are then the molecular eigenstates, $\{\psi_n\}$, the eigenfunctions of \mathcal{H}_{mol} alone. The decay rates of individual ψ_n are the diagonal matrix elements of Γ in the $\{\psi_n\}$ basis—the original $\phi_0 \leftrightarrow \phi_s$ oscillator strength is distributed among a number of $\{\psi_n\}$, leading to longer fluorescence lifetimes and many additional spectral lines. This situation is depicted schematically in Figure 2. Conventional (even picosecond laser) optical excitation cannot initially excite the nonstationary level ϕ_s for v_{si} large; it excites individual $\{\psi_n\}$ or coherent linear combinations thereof. The small-molecule ($m \ll 1$) limit, therefore, corresponds directly to the spectroscopist's views of perturbations in molecular spectra.

At the opposite extreme, $m \gg 1$, the eigenfunctions of (7) correspond to the kineticist's view of a zeroth-order "resonance", ϕ_s , with two decay mechanisms, radiative to ϕ_0^v and nonradiative to $\{\phi_i\}$. Now conventional excitation can initially prepare the molecule in ϕ_s . After crossing from ϕ_s to $\{\phi_i\}$, the experiment is over or the $\{\phi_i\}$ have decayed to lower levels, so the decay is practically irreversible, as summarized in Figure 3.

Interesting intermediate cases^{12,16,17} can arise for $m \approx 1$ or when symmetry constraints decompose the $\{\phi_i\}$ into a sparse set of levels, $\{\phi_b\}$, strongly coupled to ϕ_s , and a denser set of weakly coupled $\{\phi_w\}$ for which the

(16) A. Nitzan, J. Jortner, and P. Rentzepis, *Proc. R. Soc. London, Ser. A*, **327**, 367 (1972).

(17) K. F. Freed, *Top. Curr. Chem.*, **31**, 105 (1972).

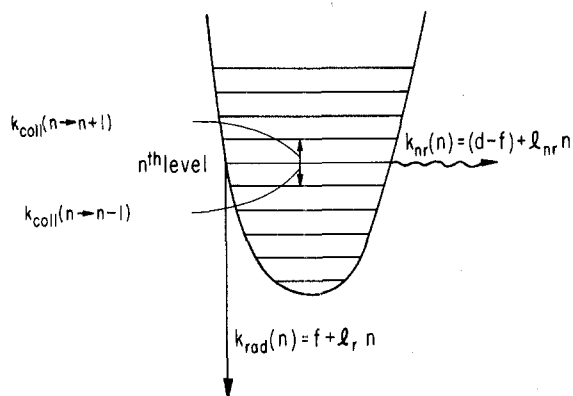


Figure 5. The effective oscillator used to represent the vibronic levels of a polyatomic molecule. The energy levels are $\Delta E_{\text{ex}} = (n + 1/2)\hbar\omega_{\text{eff}}$ and collisions may change the energy by one quantum $\hbar\omega_{\text{eff}}$ (a "stepladder" collisional model). The radiative and nonradiative decay rates are taken as linear functions of ΔE_{ex} .

conditions $m_b \ll 1$ and $m_w \gg 1$ ensue. The molecule then acquires properties characteristic of both the small- and large-molecule limits as described in Figure 4. Here conventional optical excitation from ϕ_0 results in a coherent linear superposition of the eigenfunctions, χ_r , of (7) within the $\{\phi_s, \phi_b\}$ basis (decays into $\{\phi_w\}$ are included in the rates Γ_r). The subsequent decay of this initial state could, in principle, exhibit quantum mechanical interference effects, but to date the decay is generally a double exponential. Examples in which $\phi_s, \{\phi_b\}$ correspond to S_2, S_1 are naphthalene and 3,4-benzopyrene, while for benzophenone they are S_1, T_1 .¹⁶ The initial rapid decay arises because¹⁸ the ϕ_s components of the different χ_r become out of phase with each other with time because of the differing energies of the "resonances". This dephasing rate is given by (5) since for short enough times it appears as if ϕ_s is decaying exponentially into the $\{\phi_b\}$. The longer time decay is just that characteristic of the decays of individual χ_r .

Collisional Effects on Electronic Relaxation

The collisional effects in the small, large, etc., molecule limits differ markedly. In the statistical limit collisions may alter the vibrational energy content, ΔE_{ex} , of the molecule, a feature which is qualitatively represented by the stepladder model in Figure 5.¹⁹ The vibrational manifold of an electronic state is depicted there as a D -fold degenerate oscillator with $D > 1$ reflecting the increasing density of states with higher ΔE_{ex} . Collisions enable changes of ΔE_{ex} of $\pm\hbar\omega_{\text{eff}}$ with a $0 \rightarrow 1$ collision rate of ν . The $k_{\text{nr}}(\Delta E_{\text{ex}})$ are taken to increase linearly with ΔE_{ex} , in general accord with observations for $S_1 \rightarrow T_1$ transitions in aromatic hydrocarbons.²⁰ The infinite coupled kinetic equations of this model can be analytically solved in closed form.^{19,21} Amusingly, this infinite level kinetic scheme exhibits a double-exponential decay of the total radiative emission after the excitation of a single vibrational level,¹⁹ in accord with the frequent experimental observations of double-exponential decay at finite pressures. These are often empirically explained in terms

of a two-level scheme for the excited state. However, the full model predicts a rather complicated pressure and wavelength dependence of these two decay rates and their relative intensities which would be impossible to reconcile with a simple two-level model. Experiments by Beddard et al.²⁰ and by Brown et al.²² on a number of aromatic hydrocarbons demonstrate how the model of Figure 5 provides a good representation of the observed pressure and wavelength dependences. The model has also been generalized to the case of two degenerate oscillator manifolds to represent, say, the S_1 and T_1 electronic states.²¹ Again the model is amenable to exact analytic solution, and it is hoped that it will stimulate further experiments on triplet yields to enable the separation of $S_1 \rightarrow T_1$ from $S_1 \rightarrow S_0$ quantum yields as well as the vibrational energy dependences of the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ decay rates.

Whereas the pressure dependence of electronic relaxation in statistical limit molecules is simply understood on the basis of collisional transitions between levels of differing vibrational energy content and radiative and nonradiative decay rates, the behavior of small and intermediate case molecules is more interesting. Molecules like methylene, glyoxal,²³ and pyrimidine²⁴ do not exhibit $S_1 \rightarrow T_1$ decay in the isolated molecule. Internal conversion is observed only to be collisionally induced. The process of collision-induced intersystem crossing would appear to conjure up the picture of the perturber's spin-orbit or exchange interaction inducing the $S_1 \rightarrow T_1$ transition during the collision. In the well-studied case of glyoxal, Beyer and Lineberger²³ find $S_1 \rightarrow T_1$ cross sections of 1.3 and 2 Å², respectively, for He and H₂ as perturbers, providing rates of the order of 4–5% of gas kinetic values—enormous in view of the miniscule spin-orbit and exchange interactions for He and H₂. For a wide series of collision partners the $S_1 \rightarrow T_1$ rates are observed to correlate well with expected total collision rates²⁵ arising from the long-range interactions involving the perturber's permanent electric dipole moment and dipole polarizability. Parmenter²⁴ has introduced an alternative correlation with well depths of the perturbing molecule's Lennard-Jones interactions, again properties having nothing whatsoever to do with spin multiplicity changes in the collision partner. These facts along with other observations make it patently clear that some other mechanism is operative.

At very low pressures ($\sim m$ Torr) the depletion of the S_1 state obeys Stern–Volmer kinetics, so the theory can initially be confined to the very low pressure limit. Here, the isolated molecule eigenstates, discussed above, should be adequate for a zeroth-order description. Recall that the molecular eigenstates of Figures 1 and 2 do not undergo irreversible intramolecular relaxation because of the insufficient final density of vibronic levels. But these molecular eigenstates cannot be represented as pure singlets or triplets. There are levels, designated $S + t$, with primary singlet parentage and a little triplet admixture; others, $T + s$, involving a little singlet mixing into a pure triplet level; and, perhaps,

(18) F. Lahmani, A. Tramer, and C. Tric, *J. Chem. Phys.*, **60**, 4431 (1974).

(19) K. F. Freed and D. F. Heller, *J. Chem. Phys.*, **61**, 3942 (1974).

(20) G. S. Beddard, G. R. Fleming, O. L. J. Gijzeman, and G. Porter, *Proc. R. Soc. London, Ser. A*, **340**, 519 (1974).

(21) K. H. Fung and K. F. Freed, *Chem. Phys.*, **14**, 13 (1976).

(22) R. G. Brown, M. G. Rockley, and D. Phillips, *Chem. Phys.*, **7**, 41 (1975).

(23) R. A. Beyer and W. C. Lineberger, *J. Chem. Phys.*, **62**, 4024 (1975).

(24) A. E. W. Knight and C. S. Parmenter, *Chem. Phys.*, **15**, 102 (1976); C. S. Parmenter, private communication.

(25) C. A. Thayer and J. T. Yardley, *J. Chem. Phys.*, **57**, 3992 (1972).

some pure triplet levels, T. Collision-induced transitions between perturbed levels, $S + t \leftrightarrow T + s$ or T, are fundamentally different from those between hypothetical pure $S \leftrightarrow T$ states in the same molecule.²⁶ The former *do not* require the assistance of spin-orbit or exchange interactions of the collision partner, while the latter do. While the detailed theory can be given²⁶ for low enough pressures and low enough triplet densities of states, the essential features emerge from a consideration of the golden-rule approximation²⁷ which shows how the $S + t \leftrightarrow T + s$ collision rate "borrows" some collision rate from the hypothetical pure state $S \leftrightarrow s$ and $t \leftrightarrow T$ collisions. The latter naturally explains the observed perturber dependence of the collision-induced intersystem crossing rates. For large molecules detailed calculations would be rather tedious, so average behaviors should be qualitatively correct. These predict the collision-induced intersystem crossing rates to vary as²⁸ $x^2 n_T (n + 1) \sigma$, with x^2 a measure of the average population of singlet in $T + s$ levels, n the number of nearby triplet vibronic levels, n_T the number of available final triplet vibronic levels, and σ an average total *rotationally inelastic* collision rate for the hypothetical pure S level which is taken to be comparable to the $T \leftrightarrow T'$ vibrationally inelastic collision rate between nearly degenerate triplet vibrational levels. The observed values of the quenching rates and of σ are consistent^{26b} with x^2 being small enough to have a negligible influence on the $S + t$ state optical absorption spectrum, so this spectrum would appear to be of pure S-type character (apart possibly from some very weak perturbations).

The above mechanism applies also to collisional processes between mixed states of the same multiplicity, a situation which becomes more likely to be observed with quite small molecules. In small molecules the density of zeroth-order final levels is sufficiently small that both the forward and reverse $S + t \leftrightarrow T + s$ (or $S + s' \leftrightarrow s + S'$) transitions may be observable. Furthermore, the above arguments concerning average behavior are probably not of quantitative accuracy for individual state-to-state collision rates, and a detailed quantum mechanical evaluation of these transition rates becomes feasible. At high pressures in intermediate sized molecules, the theory²⁶ predicts quenching behavior that deviates sharply from Stern-Volmer kinetics because rapid $T \leftrightarrow T'$ vibrational relaxation converts the {T} manifold into an effective quasicontinuum, enabling the occurrence of statistical limit-like decay.

Evaluation of Nonradiative Decay Rates

It is of importance to rationalize the properties of observed nonradiative decay rates. Consider the large molecule statistical limit either in the isolated molecule gas phase or in inert media at low temperatures. The latter situation corresponds to the one initially investigated in greater detail.

Employing a Condon-like approximation Robinson and Frosch^{3,7} rewrote the rate expression for molecules in inert condensed media as

$$k_{nr}(s \rightarrow l) = \frac{2\pi}{\hbar} \beta_e^2 F \rho_{\text{eff}}(l) \quad (9)$$

with β_e the electronic matrix element, F the Franck-Condon factor at the appropriate energy (E_s), and $\rho_{\text{eff}}(l)$ the $\{\phi_l\}$ -state "effective" density of states necessary for (9) to reproduce the correct (5). Despite the ambiguity of the choice of ρ_{eff} , they⁷ noted that $\ln F \propto -\Delta E_{sl}$, where ΔE_{sl} , the energy gap, is the separation of the potential minima for states s and l . This behavior has been observed for $T_1 \rightarrow S_0$ intersystem crossing rates for aromatic hydrocarbons,²⁹ where a very sizable deuterium isotope effect appears, for the $S_2 \rightarrow S_1$ internal conversion in substituted azulenes,³⁰ and for relaxation between different electronic states of rare earth ions in crystals.³¹

The energy gap law was derived theoretically by Engleman and Jortner³² using the simplest model containing the dominant accepting vibration, the mode taking up most of the electronic energy, ΔE_{sl} . Although a general theory including all the molecular vibrations has been given,^{1,33} it is instructive to consider a model of intermediate degree of sophistication.¹ Let us assume that the potential surfaces in s and l are harmonic in zeroth order and differ only in the energies of their minima and in the bond lengths. The normal modes, j , in the two states are parallel, and only the equilibrium positions suffer a displacement, δq_j . For low enough temperatures the molecules in s are in the vibrationless level. After the decay, they are characterized by the vibrational quantum numbers $\{n_j\}$ in l . The individual Franck-Condon factors, F_i , are equal to $\exp(-X_i) \cdot X_i^{n_i}/(n_i)!$ where $X_i = \frac{1}{2}(m_i \omega_i / \hbar)(\delta q_i)^2$ with ω_i the i th-mode frequency. The full rate expression (5) is then proportional to

$$k_{nr}(s0 \rightarrow l) \propto \left[\prod_j \sum_{n_j=0}^{\infty} X_j^{n_j}/(n_j)! \right] \delta[\Delta E_{sl} - \sum_j n_j \hbar \omega_j] \quad (10)$$

where the delta function applies the constraint of energy conservation that the electronic energy, ΔE_{sl} , be converted into vibrational energy. Expressions like (10) were studied long ago by Boltzmann in his treatments of equilibrium statistical mechanics where he considered Boltzmann weight factors $X_i^{n_i}/(n_i)!$ for placing n_i particles in states i with degeneracy X_i . For large ΔE_{sl} he evaluates the maximum term in the summation over $\{n_i\}$ subject to the energy conservation requirement treated by the method of Lagrange multipliers. (The total number of vibrational quanta produced, $\sum_j n_j$, is, of course, not fixed.) The algebra is presented in all elementary texts on physical chemistry, and it is found^{1,33} that (10) results in the energy gap law

$$k_{nr}(s0 \rightarrow l) \propto \exp(-\gamma \Delta E_{sl} / \hbar \omega_M) \quad (11)$$

with ω_M the maximum vibrational frequency and γ a quantity expressible in terms of the molecular parameters. (The general theory includes the dependence of γ on frequency changes in the vibrations.^{1,33,34}) γ is

(29) W. Siebrand in "The Triplet State," A. B. Zahlan, Ed., Cambridge University Press, London, 1967, p 31.

(30) S. Murata, C. Iwanaga, T. Toda, and H. Kokubun, *Chem. Phys. Lett.*, **13**, 101; **15**, 152 (1972).

(31) F. K. Fong, S. L. Naberhuis, and M. M. Miller, *J. Chem. Phys.*, **56**, 4020 (1972).

(32) R. Engleman and J. Jortner, *Mol. Phys.*, **18**, 145 (1970).

(33) K. F. Freed and J. Jortner, *J. Chem. Phys.*, **52**, 6272 (1970).

(26) (a) K. F. Freed, *J. Chem. Phys.*, **64**, 1604 (1976); (b) *Chem. Phys. Lett.*, **37**, 47 (1976).

(27) W. M. Gelbart and K. F. Freed, *Chem. Phys. Lett.*, **18**, 470 (1973).

(28) The extra n_T follows from eq 20 of ref 26a and was omitted in eq 2 and 3 of ref 26b. (Also S-T couplings require only that the total angular momentum (and its space-fixed projection) be conserved; consequently rotational and hyperfine sublevels may be coupled.)

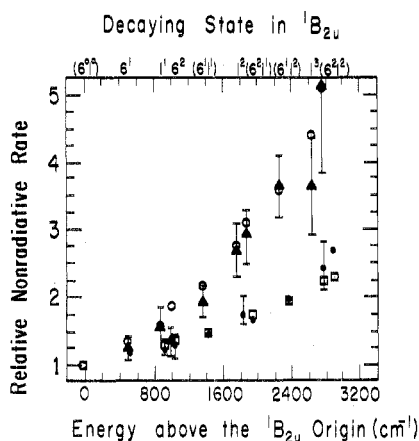


Figure 6. Vibronic level dependence of relative $S_1 \rightarrow T_1$ decay rates in C_6H_6 and C_6D_6 . Experimental values (\bullet , C_6H_6 ; \blacktriangle , C_6D_6) are taken from ref 35. Calculated values³⁴ (\square , C_6H_6 ; \circ , C_6D_6) employ spectroscopically determined³⁸ CC and CH bond-length changes and fitted values of the T_1 frequencies for ν_1 and ν_6 (independent of isotopic substitution). The symbol $1^m 6^n$ refers to levels of S_1 with m quanta in ν_1 and n in ν_6 . Similar agreement is obtained³⁸ when ν_{16} excitations are also present.

fairly insensitive to deuteration in aromatic hydrocarbons, but the shift of ω_M from $\sim 3100 \text{ cm}^{-1}$ (CH stretch) to $\sim 2300 \text{ cm}^{-1}$ (CD stretch) explains the observed large isotope effect in the $T_1 \rightarrow S_0$ decay rates.

A stringent test of our understanding of nonradiative decay rates is provided by examining the rates, $k_{nr}(s_i \rightarrow l)$, from individual single vibronic levels (SVL) in molecules under collision-free conditions. In particular, it is necessary to explain how the k_{nr} vary with excitation in particular vibrations in s . An extensive series of experimental studies on SVL decay rates of individual levels of benzene and its deuterated analogues has been performed by Rice and co-workers.³⁵ These experiments can observe the nonradiative decay rates of the S_1 levels with progressions in the ν_1 , ν_6 , and ν_{16} vibrations of a_{1g} , e_{2g} , and e_{2u} symmetry respectively. The evaluation of the absolute rates (eq 5) requires the evaluation of accurate S_1 and T_1 electronic wave functions (better than SCF quality) to provide the electronic matrix element as well as the calculation of Franck-Condon factors for all 30 benzene vibrations.^{1,34} Little is known about the T_1 vibrational frequencies, and with these 30 adjustable parameters it would be possible to fit almost anything! The approach taken theoretically^{1,34,36} is to consider only relative nonradiative decay rates, so the nasty electronic matrix elements cancel as an overall factor as do contributions to the Franck-Condon factors from the poor accepting vibrations (other than the optical modes ν_1 , ν_6 , ν_{16}). Contributions from anharmonicities have been included with no qualitative changes.³⁷ Spectroscopically determined C-C and C-H bond lengths are employed.³⁸ The observed SVL k_{nr} are employed with the theory to determine the three T_1 vibrational frequencies for ν_1 , ν_6 , ν_{16} from the $S_1 \rightarrow T_1$ decay rates (27 of them). Figure

6 displays the comparison of theory³⁴ and experiment for states having only ν_1 and ν_6 excitations. $S_1 \rightarrow T_1$ frequency shifts for these three vibrations are found to be independent of deuteration in conformity with their primarily carbon atom motions. The predicted frequency changes are in general accord (sign and order of magnitude) with values deduced by other indirect methods. In partially deuterated benzenes a local mode approximation³⁵ gives a reasonable fit to relative experimental decay rates with the same parameters which were obtained in the calculations on C_6H_6 and C_6D_6 . Two photon excitation techniques now enable the consideration of states with excitation in different vibrations. Observed SVL k_{nr} are qualitatively similar in their dependence on excess vibrational energy ΔE_{ex} to the ν_1 , ν_6 , and ν_{16} modes,³⁹ but the experiments (ν_{14} mode) have also verified the theoretical prediction³⁶ of the possibility of having k_{nr} decrease with vibrational excitation.

Benzene is, perhaps, an ideal system for study because the CC and CH bond length changes are available from independent spectroscopic studies and because the absorption spectra are relatively free from sequence congestion. The presence of the rapid "channel three" decay at $\Delta E_{ex} \approx 3000 \text{ cm}^{-1}$ is a complicating factor here,⁴⁰ but the theoretical predictions of SVL k_{nr} have been helpful in suggesting a rationale for this behavior and its absence in higher homologues.^{1,34} The availability of very narrow frequency-width dye lasers now enables the observation of structure in the density of states weighted Franck-Condon factor,⁴¹ a situation to be anticipated by the hierarchy of structure seen in the analogous nuclear nonradiative decay processes. Supersonic beam spectroscopy⁴² will provide the means for further investigation of this structure and of any rotational dependences of k_{nr} .

Vibrational Relaxation

Unimolecular reaction theories are generally presented as being predicated on the assumption of very rapid intramolecular vibrational relaxation between the large number of nearly degenerate levels at a given ΔE_{ex} . It is not widely appreciated that a kinetically equivalent theory invokes the *opposite* extreme by assuming the intramolecular relaxation rates to be slow compared to reaction rates.⁴³ In this approach it is the random nature of thermal collisions which leads to a statistical distribution of energized molecules. Observed partial nonrandomizations in chemical activation experiments can be explained with such an analysis. It is clear that reality lies somewhere between these two opposite extremes and that it is of fundamental importance to consider experiments probing intramolecular vibrational relaxation in systems with well-defined initial vibrational states. An ideal system for study involves that of photodissociation phenomena² where it is possible to investigate the product quantum state distribution and its dependence on the initially prepared vibronic level. Theoretical and experimental work in this area

(34) M. G. Prais, D. F. Heller, and K. F. Freed, *Chem. Phys.*, **6**, 331 (1974).

(35) K. G. Spears and S. A. Rice, *J. Chem. Phys.*, **55**, 5561 (1971); A. S. Abramson, K. G. Spears, and S. A. Rice, *ibid.*, **56**, 2291 (1972); C. Gutman and S. A. Rice, *ibid.*, **61**, 651 (1974).

(36) D. F. Heller, K. F. Freed, and W. M. Gelbart, *J. Chem. Phys.*, **56**, 2309 (1972).

(37) I. H. Kuhn, D. F. Heller, and W. M. Gelbart, *Chem. Phys.*, in press.

(38) D. M. Burland and G. W. Robinson, *J. Chem. Phys.*, **51**, 4548 (1969).

(39) L. Wunsch, H. J. Neusser, and E. W. Schlag, *Chem. Phys. Lett.*, **32**, 210 (1975).

(40) J. H. Callomon, J. E. Parkin, and R. Lopez-Delgado, *Chem. Phys. Lett.*, **13**, 125 (1972).

(41) W. E. Howard and E. W. Schlag, *Chem. Phys.*, **17**, 123 (1976).

(42) R. E. Smalley, B. L. Ramakrishna, D. H. Levy, and L. Wharton, *J. Chem. Phys.*, **61**, 4363 (1974).

(43) K. F. Freed, *Chem. Phys. Lett.*, **42**, 600 (1976).

is beginning to appear. It is a field of greater interest to photochemistry, atmospheric chemistry, chemistry, chemical lasers, and chemical dynamics, and a separate article would be necessary to cover this field. Another system for studying intramolecular vibrational relaxation has been provided by Lim and co-workers⁴⁴ and involves the investigation of combined electronic and vibrational relaxation. Before briefly discussing some of these developments, it is important to clarify our understanding of the phenomenon of intramolecular vibrational relaxation.⁴³

Chemists naturally picture molecular vibrations in terms of normal modes or some more realistic (anharmonic) local modes. High vibrational excitation implies that one such basis function, ϕ_s , is coupled to a large number of nearly isoenergetic zeroth-order vibrational states $\{\phi_j\}$ by residual anharmonic interactions. The situation can be represented schematically in Figure 1, *identical with the case of electronic relaxation*, where the $\{\psi_n\}$ are now vibrational eigenstates.⁴³ All theoretical results on electronic relaxation can immediately be employed apart from changes imposed by differences in molecular parameters between the two phenomena. Hence, depending on the value of the parameter in (8), we may anticipate small, intermediate, and large molecule limits for intramolecular vibrational relaxation. The small molecule case is described in terms of vibrational eigenstates, $\{\psi_n\}$, the spectroscopic view of anharmonic mixing of levels, while true intramolecular relaxation can occur in the statistical limit where the high density of $\{\phi_j\}$ levels prohibits recurrences to ϕ_s on the time scales of real experiments. In the interesting intermediate case the zeroth-order ϕ_s can undergo a dephasing process¹⁸ (purely reversible, in principle) which resembles an intramolecular decay.

The experiments of Lim and co-workers⁴⁴ consider the dependence of k_{nr} on ΔE_{ex} for high levels of excitation for a number of interesting situations. Excitation of aromatic hydrocarbons just below and above the S_2 threshold leads (after rapid internal conversion in the latter case) to differently prepared initial distributions in S_1 vibronic levels at the same energy. Below the

threshold, optical methods select levels with primarily CC vibrational excitation, while above it the $S_2 \rightarrow S_1$ internal conversion preferentially excites CH stretches. If intramolecular vibrational relaxation were rapid, both situations should yield identical k_{nr} . In naphthalene, β -naphthol, β -naphthalamine, anthracene, 9,10-dimethylanthracene, phenanthrene, and fluorene the experimental k_{nr} exhibit memory of the preparation of the initial state, thereby demonstrating the absence of intramolecular vibrational relaxation on the nanosecond timescale. The experiments of Okajimi and Lim⁴⁵ on tetracene and pentacene can be interpreted⁴³ as displaying the transition from small molecule behavior at low ΔE_{ex} to the intermediate, or large, case at higher ΔE_{ex} .

Prospectus

Nonradiative decay processes are of importance in a wide variety of chemical phenomena and systems, yielding a rich diversity of problems and applications. The area has witnessed great activity and advancement in recent years, with a strong interaction between experiment and theory. New methods in both domains promise to provide a wealth of new information and understanding in the near future, both to the areas discussed herein and to others, such as photodissociation,² photoisomerizations,⁴⁶ laser-induced chemistry,⁴⁷ and relaxation processes in condensed media,⁴⁸⁻⁵⁰ which space limitations have prevented us from discussing.

This work has benefitted from active interaction and collaboration with experimentalists and theoreticians in the area as well as with my students and research associates. The article is adapted from the talk presented at the Centennial Meeting of the American Chemical Society in April 1976 and the one given as the 1976 Denkwalter Lecture at Loyola University of Chicago. The research was supported, in part, by NSF Grant CHE75-01549. I am grateful to the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant. Figures 1-4 and 6 have been reprinted with permission from ref 1 (copyright 1976, Springer-Verlag).

(44) C. S. Huang, J. C. Hsieh, and E. C. Lim, *Chem. Phys. Lett.*, **28**, 130 (1974); **37**, 349 (1976); J. C. Hsieh, C. S. Huang, and E. C. Lim, *J. Chem. Phys.*, **60**, 4345 (1974); J. C. Hsieh and E. C. Lim, *ibid.*, **61**, 737 (1974).

(45) S. Okajimi and E. C. Lim, *Chem. Phys. Lett.*, **37**, 403 (1976).
(46) W. M. Gelbart, K. F. Freed, and S. A. Rice, *J. Chem. Phys.*, **52**, 2460 (1970).
(47) S. Mukamel and J. Jortner, *J. Chem. Phys.*, **65**, 5204 (1976).
(48) D. J. Diestler, *Top. Appl. Phys.*, **15**, 169 (1976).
(49) H. Metiu, D. W. Oxtoby, and K. F. Freed, *Phys. Rev. [Sect.] A*, **15**, 361 (1977).
(50) K. F. Freed and H. Metiu, *Chem. Phys. Lett.*, in press.