

PYRAZINE: An "Exact" Solution to the Problem of Radiationless Transitions

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Probably the most worthwhile experiment of all would be to choose a molecule tailor-made for the purpose of studying the intermediate case, . . . *pyrazine* would be a good choice.

G. Wilsce Robinson, 1967

Thus with considerable prescience did Robinson (1) conclude his 1967 paper in which the terms "small-molecule limit," "large-molecule limit," and the "intermediate case" were first introduced. Pyrazine (1,4-diaz-

abenzene) is a relatively simple molecule with 10 atoms and 24 vibrational degrees of freedom. The molecule does not appear to be particularly unique. But to a select few chemists and physicists, those who have been fortunate enough to participate in the discoveries described here, pyrazine is very special. To appreciate why, it is necessary to set the stage for these developments, and for this we must go back to the theory of radiationless transitions.

A radiationless transition is a change in the electronic state of a molecule that occurs without the absorption or emission of radiation. In bound states there are two processes of this type, internal conversion (IC) and intersystem crossing (ISC). The first, IC, is a transition between states of the same multiplicity, whereas the second, ISC, is a transition between states of different multiplicity. The concept of a molecular radiationless transition was developed to account for certain key observations in early experiments on the luminescence of organic molecules in the condensed phase. Following the absorption of light, many aromatic molecules were found to have emission quantum yields less than unity. Observed radiative lifetimes are often considerably shorter than values calculated from the integrated absorption coefficients. And most molecules excited to a higher electronic state emit light only from a lower electronic state. But initially the radiationless transition was a *theoretical* construct that attempted to reconcile these observations without any direct *experimental* evidence for its existence. For example, an atomic or molecular system in a stationary state cannot be induced to make transitions to other states in the absence of a radiation field. Nonradiative transitions therefore require the existence of compound or mixed states, consisting of a superposition of eigenstates of the total Hamiltonian. Only then can a relaxation process take place. By demonstrating for the first time that such states do in fact exist, and showing that it is possible to transform back and forth between the observed frequency spectrum and the time evolution of the prepared state, the pyrazine molecule provided an "exact" solution to the radiationless transition problem.

Much has already been written about radiationless transitions. The concept dates back to the discovery of predissociation by Henri (2) in 1923. Early work in the field has been reviewed by Henry & Kasha (3), who note especially the contributions of Zener, Sponer, Teller, Gouterman, Coulson and Zalewskii, Robinson and Frosch, Ross and co-workers, Lin, and Siebrand to both continuum- and bound-state problems. Robinson in his historical review (4) also stresses the contributions of Wentzel, O. K. Rice, Lewis, Franck, and Livingston to the basic conceptual framework. The spectroscopist Douglas (5) played a key role in convincing workers in the field that radiationless transitions were possible in isolated molecules.

More recent reviews [e.g. Jortner et al (6), Freed (7), and Avouris et al (8)] rely heavily on the analytical treatment of the problem developed by Bixon & Jortner (9a,b), whereas Tramer & Voltz (10) and Rhodes (11) give the essential features of the model in more physical terms, emphasizing the particular importance of the nature of the excitation source.

In a broader sense, radiationless transitions in a polyatomic molecule are related to the transfer of energy from one part of a multidimensional potential energy surface to another. The concept is therefore relevant to all types of chemical transformations, from "simple" unimolecular reactions induced by light (e.g. photodissociation) to more complex ones, like photosynthesis. Since energy must be conserved in a nonradiative process, other degrees of freedom play a role, thereby establishing a connection between radiationless transitions and intramolecular dynamics. Franck-Condon factors and the vibrational degrees of freedom [e.g. promoting modes and accepting modes (12)] were a primary focus of early work in the field. But it was also anticipated by some that other "lower forms of energy" (4), i.e. rotations, translations, and the spin degrees of freedom, might also participate. Perhaps the most significant result of all the work on pyrazine to date is not the "solution" to the radiationless transition problem but the experimental demonstration that the rotational degrees of freedom are intimately involved in radiationless decay. We even think we know why, and believe that this knowledge may help in achieving true laser-specific chemistry and in addressing other issues, such as the possible existence of chaos in quantum mechanical systems. But that is getting ahead of the story.

Theory

We begin conventionally. Radiationless transition theory is usually presented in terms of an initial level $|0\rangle$ before excitation, a zero-order level $|s\rangle$ that is prepared by the excitation, and a dense manifold of final levels $\{|k\rangle\}$ into which the level $|s\rangle$ can decay. Figure 1 depicts schematically the energy level scheme of a polyatomic molecule in the region of the initially prepared level, $|s\rangle$, with a "natural" energy uncertainty γ_s . Under isolated molecule conditions, γ_s corresponds to the radiative decay width of the level $|s\rangle$. Isoenergetic with $|s\rangle$ is a manifold of rovibrational levels of a lower excited state or the ground state, $\{|k\rangle\}$, each with an energy uncertainty γ_k . The zero-order levels $\{|k\rangle\}$ have an average spacing of ϵ_k and interact with the level $|s\rangle$ *via* off-diagonal terms in the molecular Hamiltonian of magnitudes v_{sk} . We imagine that $|s\rangle$ is prepared in a time that is short compared with all decay times of interest. Ignoring a number of subtleties in the theoretical treatment, the behavior of a molecule following excitation depends primarily on the energy level density ρ_k , the decay

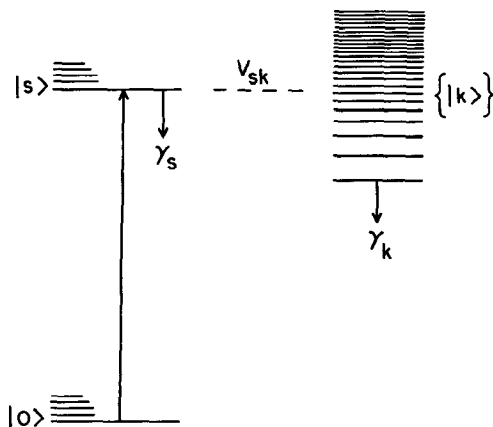


Figure 1 Energy level diagram of a "large" molecule.

widths γ_k , and the $|s\rangle - \{|k\rangle\}$ couplings v_{sk} . The important parameter characterizing the different molecular "limits" is $x_k = \rho_k \gamma_k$. If the average level spacing ϵ_k is small compared to the radiative decay width γ_k , then $x_k \gg 1$. Under these conditions, there is apparently irreversible non-radiative relaxation to the levels $\{|k\rangle\}$ with the Golden-Rule rate $k_{nr} = (2\pi/\hbar)v_{sk}^2\rho_k$. If, further, $(v_{sk}^2/\epsilon_k) \gg \gamma_s$, then the initial level decays exponentially with a rate that is faster than the radiative rate and the emission quantum yield is low. This is the large-molecule, or statistical, limit. Alternatively, if the average level spacing ϵ_k is large compared to γ_k , then $x_k \ll 1$. Under these conditions there is no radiationless transition in the limit of zero pressure even if v_{sk} is large. Instead, the oscillator strength associated with $|s\rangle$ is spread out over a number of levels, most of which lie outside the excitation bandwidth, and "extra" lines appear in both the absorption and emission spectra. If only a few of the coupled levels lie within the excitation bandwidth, then the initial state decays exponentially with a rate that is slower than the radiative rate and the emission quantum yield is high. Quantum beats may also be observed. This is the small-molecule limit. Of course, as Robinson (1) realized, the most interesting examples are those that lie between the two extremes, the so-called intermediate-case molecules ($x_k \sim 1$). In such cases, radiationless transitions occur but are "reversible," and the decays are frequently nonexponential (and strongly pressure dependent). And many species exhibit small-, intermediate-, or large-molecule behavior, depending on the magnitude of the excitation energy and the temporal nature of the excitation source.

In pyrazine, the level $|s\rangle$ has its origin in the lowest $n\pi^*$ singlet state, ${}^1B_{3u}$, whose zero-point vibrational level lies at $30,876 \text{ cm}^{-1}$ above the

corresponding level $|0\rangle$ of the 1A_g ground electronic state (13). An allowed optical transition connects the levels $|0\rangle$ and $|s\rangle$ (14). The dark levels $\{|k\rangle\}$ have their origin in the lowest $n\pi^*$ triplet state, ${}^3B_{3u}$, whose zero-point vibrational level lies at $26,820\text{ cm}^{-1}$ above the ground state (15a,b). The zero-point energy gap is thus 4056 cm^{-1} , leading to a density of zero-order ${}^3B_{3u}$ levels at the singlet origin of order $100/\text{cm}^{-1}$ as estimated from the Haarrhoff formula (16). Additional levels contributing to the dynamics at this energy could have their parentage in a second triplet state lying below ${}^1B_{3u}$ (14, 17) or in highly excited levels of the ground state. In any event, optical excitation of the 0_0^0 band of the ${}^1B_{3u} \leftarrow {}^1A_g$ transition with a few nanosecond pulsed light source leads, under collision-free conditions, to a nonexponential decay, as was first shown in the low pressure bulb experiments of Frad et al (18). A typical result from our own supersonic jet work is shown in Figure 2, for both pyrazine- h_4 and pyrazine- d_4 (19). Note the strong dependence of the decay on level density. The fluorescence quantum yield (2.8×10^{-3} at 300 K) is also strongly pressure dependent (18). These

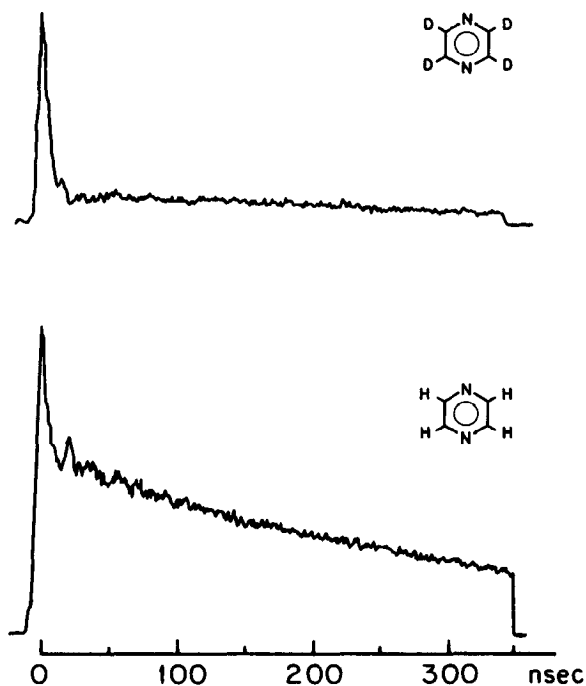


Figure 2 Decay of the fluorescence intensity of pyrazine- d_4 and pyrazine- h_4 , following nanosecond excitation of the Q branch of 0_0^0 band of the ${}^1B_{3u} \leftarrow {}^1A_g$ transition in a He supersonic jet. From Ref. 19.

properties place pyrazine firmly into the intermediate-case category of the theory, at least under these excitation conditions.

Considerable insight into the behavior of the intermediate case can be gained from the following simple model (20). We take as our effective Hamiltonian the expression

$$\mathcal{H} = \mathcal{H}_0 + \sum_{\mathbf{k}} v_{s\mathbf{k}} + \mathbf{u} \cdot \mathbf{E}. \quad 1.$$

Here, \mathcal{H}_0 generates the zero-order levels $|0\rangle$, $|s\rangle$, and $\{|k\rangle\}$, the terms $v_{s\mathbf{k}}$ connect $|s\rangle$ with the levels $\{|k\rangle\}$, and the transition moment $\mathbf{u} \cdot \mathbf{E}$ connects $|s\rangle$ with $|0\rangle$. The time-dependent wavefunction in the presence of the (weak) radiation field may be written as a superposition state

$$\Psi(t) = c_0(t)|0\rangle + c_s(t)|s\rangle + \sum_{\mathbf{k}} c_{\mathbf{k}}(t)|k\rangle. \quad 2.$$

Since only the level $|s\rangle$ carries oscillator strength ($\gamma_{\mathbf{k}} = 0$), we are interested only in the coefficient $c_s(t)$, which determines the behavior of the fluorescence in time, or its Fourier transform, $c_s(\omega)$, which determines the absorption spectrum. Both $c_s(t)$ and $c_s(\omega)$ are strongly dependent on the scheme of zero-order energies (ϵ_s , $\{\epsilon_{\mathbf{k}}\}$) and the matrix elements $v_{s\mathbf{k}}$. If the level $|s\rangle$ is not coupled to any others, with the exception of the states of the radiation field (of strength C), then the fluorescence decays exponentially with its radiative width

$$I_f(t) \sim |c_s(t)|^2 = C^2 \exp(-\gamma_s t). \quad 3.$$

In this case the frequency spectrum consists of a single Lorentzian line, of width γ_s . But if the level $|s\rangle$ is coupled to one other level, $|k\rangle$, by $v_{s\mathbf{k}} = v$, then the oscillator strength will be shared by the two levels, and the fluorescence decay properties will depend on how the two levels are excited. If both are excited coherently by the same photon, then the decay will contain both coherent and incoherent components. Suppose the two levels are initially degenerate. In that event, it is easy to show that

$$I_f(t) \sim |c_s(t)|^2 = \frac{C^2}{2} (1 + \cos 2vt) \exp(-\gamma_s t/2). \quad 4.$$

Each of the coupled levels decays incoherently with a radiative width of $\gamma_s/2$. But the decay also exhibits a coherent part, a superimposed quantum beat (or recurrence) of frequency $2v$, reflecting the fact that the frequency spectrum exhibits two lines separated by $2v$ with widths $\gamma_s/2$. This is the temporal analog of the two-slit (spatial) interference experiment. The amplitude of the beat, indeed, whether it is observed at all, will depend on how the levels are excited. For example, if the coherence width of the source is small compared to the level spacing, only one level can be excited

at a time and it will decay exponentially, with a width $\gamma_s/2$. No coherence effects will be observed. This nicely illustrates the sensitivity of the decay to the excitation conditions.

All of this is not new physics but it does help one to understand the intermediate case. Here there are many slits, or levels $\{|k\rangle\}$, different matrix elements v_{sk} , and perhaps more than one $|s\rangle$. Clearly, $|c_s(t)|^2$ may now exhibit superimposed quantum beats, of many different frequencies, as well as many incoherent decays with different widths. How, then, is it possible for a molecule like pyrazine to exhibit the apparently simple decay behavior shown in Figure 2? The answer to this intriguing question was first provided by Lahmani et al (21), who developed a simple but historically important model for the intermediate case (see also 22). In this model, the scheme of zero-order energies, matrix elements, and linewidths is the same as in Figure 1, but the authors chose instead to use this scheme to define an effective (non-Hermitian) Hamiltonian \mathcal{H}_{eff} with complex eigenvalues, in order to account for spontaneous decay:

$$E_n = \varepsilon_n - i\hbar\gamma_n. \quad 5.$$

This allows one to write the time-dependent wavefunction as a linear combination of the *quasi-stationary* states $|n\rangle$, the *molecular eigenstate* (ME) basis, as

$$\Psi(t) = \sum_n c_n |n\rangle \exp(-i\varepsilon_n t/\hbar) (-\gamma_n t). \quad 6.$$

The time evolution of the fluorescence intensity may then be determined by projecting out of this wavefunction the singlet character $|s\rangle$

$$I_f(t) = C^2 |\langle s | \Psi(t) \rangle|^2 \quad 7.$$

yielding, since

$$|n\rangle = c_{ns} |s\rangle + \sum_k c_{nk} |k\rangle \quad 8.$$

the result:

$$\begin{aligned} I_f(t) &= C^2 \left| \sum_n |c_{ns}|^2 \exp(-iE_n t/\hbar) \right|^2 \\ &= C^2 \sum_{n=m} |c_{ns}|^4 \exp(-2\gamma_n t) \\ &\quad + 2C^2 \sum_{n \neq m} |c_{ns}|^2 |c_{ms}|^2 \exp[-i(\varepsilon_n - \varepsilon_m)t/\hbar] \exp-(\gamma_n + \gamma_m)t. \end{aligned} \quad 9.$$

Here it has been assumed that the coherence width of the exciting photon is at least as large as the energy width $\Delta [= 2\pi v_{sk}^2 \rho_k]$ (9) over which the $|s\rangle$

character is distributed. Under these conditions, the fluorescence decay is clearly a sum of two parts, an incoherent contribution ($n = m$) arising from the independent decays of the *quasi*-stationary states and a coherent contribution ($n \neq m$) arising from the cross terms. Furthermore, in the case of a single level $|s\rangle$, equally spaced and equally coupled $\{|k\rangle\}$ levels, and strong coupling ($v\rho \gg 1$), Lahmani et al (21) showed that excitation by an infinitely short light pulse leads to a fluorescence decay of biexponential form

$$I_f(t) = A^+ \exp(-t/\tau^+) + A^- \exp(-t/\tau^-) \quad 10.$$

with $A^+/A^- = N (= 2\pi^2 v^2 \rho^2)$, the number of coupled levels $\{|k\rangle\}$, $\tau^+ = (2\pi v^2 \rho)^{-1}$, and $\tau^- = (\gamma_s/N + \gamma_k)^{-1}$. In this case the corresponding frequency spectrum would consist of a Lorentzian distribution of intensity over equally spaced ME's, with a width Δ . But the general features of the model remain essentially valid in the case of randomly spaced and randomly coupled $\{|k\rangle\}$ levels (21).

The short decay in Eq. 10 is produced by an interference effect between the *quasi*-stationary states excited at $t = 0$. Coherent excitation of two of these states would, of course, produce a single quantum beat. But here many states having different energies are imagined to be excited coherently, generating many quantum beats of different frequencies. All such states start out in phase so that the beats interfere constructively at $t = 0$. But since the states evolve differently in time, the superimposed beats interfere destructively at some later time. This is the source of the fast component. Thus, one can say that the evolution of the initially prepared nonstationary state into mixed singlet-triplet levels causes a loss of singlet character and, therefore, a fluorescence decay. The time required for this process is clearly Δ^{-1} or, if the coherence width $\Delta\omega$ is less than this, $\Delta\omega^{-1}$. Once dephased, the states comprising the initial nonstationary state acquire a new identity, $\{|n\rangle\}$. The long decay is an incoherent average of the individual decays of each of these ME's. Thus, the biexponential expression describes the evolution in time of a phase-coherent nonstationary state into a set of phase-incoherent individual *quasi*-stationary states. If these states contain both singlet and triplet electronic character, and the triplet character dominates, then the dephasing process converts a zero-order singlet into a zero-order triplet. This is ISC in the isolated molecule.

Time-Domain Experiments

Despite its approximate nature, Eq. 10 has been used to characterize the decay properties of many intermediate-case molecules, especially pyrazine [early time domain work on pyrazine is summarized in (23)]. What follows is a brief review of this time-domain work, organized partly historically

and partly according to the apparent coherence width of the exciting light. Short-time duration (larger width) experiments are considered first, followed by longer-time duration (smaller width) experiments. The subsequent review of previous frequency-domain work is similarly organized, proceeding from low resolution to increasingly higher resolution experiments, and thus also from larger to smaller widths.

Frad et al (18) found $A^+/A^- \sim 10^3$ in their single vibronic level (SVL) experiments on the 0_0^0 band of the ${}^1B_{3u} \leftarrow {}^1A_g$ transition. They also found that A^+/A^- increases with increasing vibrational energy in the singlet manifold but that $\tau^- \sim 200$ nsec does not, suggesting that the increase in ρ_k is compensated for by decreases in the v_{sk} values. McDonald et al (24), using a synchronously pumped mode-locked picosecond laser of unspecified coherence width, found biexponential decays for the isolated molecule with $\tau^+ \sim 125$ psec and $\tau^- \sim 130$ nsec for the 0_0^0 band. Only small variations in τ^+ were found with excess energies up to ~ 1400 cm^{-1} . Values of A^+/A^- vary from 560 to 2300 up to 585 cm^{-1} above the singlet origin, larger by factors of 25–30 than the calculated densities of states. McDonald et al (24) argued that at the excitation energies achieved in the triplet manifold, there is extensive scrambling of rotational states but that conservation of nuclear spin (σ , the symmetry number, is four for pyrazine- h_4) restricts the coupling of a single rovibronic level of the singlet to $(2J+1)/4$ of the $2J+1$ triplet rovibronic levels, thereby explaining some of the discrepancy between the experimental and theoretical values of N .

Using an ~ 8 psec light pulse, Jameson et al (25) found $\tau^+ \sim 100$ psec for pyrazine excited to the $6a^1$ vibrational level of S_1 . A^+/A^- was found to decrease significantly on rotational cooling in a supersonic jet. Quantum beats were observed on excitation of the 0_0^0 band under similar conditions (26). Saigusa & Lim (27) also observed that $A^+/A^- \propto J'$ and suggested that this effect has its origin in a rotational-state dependence of the number of effectively coupled triplet levels. Zewail and co-workers (28) introduced an external magnetic field into the experiment and showed that under ~ 15 psec excitation conditions, the decay of the 0_0^0 band is also biexponential, that the slow component exhibits quantum beats, and that A^+/A^- increases on application of fields up to 150 G. Fourier transforms of these decays showed monotonic shifts in the beat frequencies with field.

The focus of more recent picosecond time domain experiments on pyrazine has shifted to the origin of the fast component. Despite previous evidence for the molecular nature of the decay process, demonstrated by its sensitivity to the nature of the species being excited, there remained the interesting possibility that the fast component has its origin in a non-resonant light scattering (NRLS) process (29, 30). This possibility was suggested by the observation (31) that A^+/A^- apparently increases on

(nanosecond) excitation of the isolated molecule *between* lines in the P or R branch. But Lorincz et al (32) and Knee et al (33) both showed, using 10–100 psec fluorescence and pump-probe MPI detection techniques, respectively, that the decay time constant of the fast component is significantly longer (100–120 psec) than that of the exciting light (monitored by Rayleigh scattering in the first instance) when “individual” rotational levels of the 0_0^0 band are resonantly excited (Figure 3). In contrast, the fast decay would be expected to exactly follow the light source if NRLS contributes to the decay for off-resonant excitation. Lorincz et al (32) also showed that the decay time of the fast component is independent of J' under picosecond excitation conditions. Pyrazine- d_4 exhibits a significantly shorter fast component, but even under 80-psec excitation conditions both molecules show a weak but nonzero slow component intensity (34).

Very recently, Terazima & Lim (35) have observed in picosecond time-resolved fluorescence polarization experiments on pyrazine- h_4 that the 0_0^0 band polarization decreases from the regular-rotor limit value (36) to a constant value substantially smaller than that, on a time scale slower than the decay rate of the fast component but faster than the decay rate of the slow component. The decay rate of this polarization also was found to increase with increasing density of triplet rovibronic levels coupled to the initially prepared S_1 state.

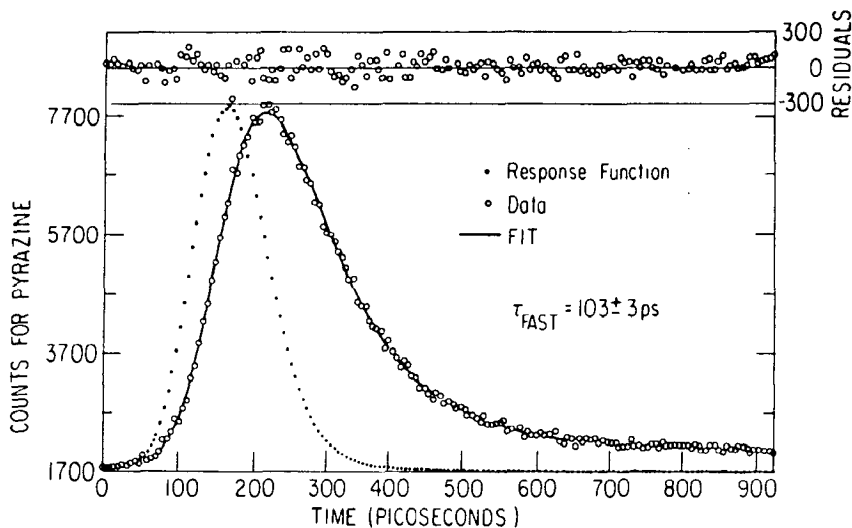


Figure 3 Decay of the fluorescence intensity of pyrazine- h_4 following picosecond excitation of the 0_0^0 band of the ${}^1B_{3u} \leftarrow {}^1A_g$ transition in a He supersonic jet (\circ), compared to the time-resolved Rayleigh scattering from Ar clusters under the same excitation conditions (\bullet). From Ref. 32.

Turning now to nanosecond experiments, ter Horst et al (37) found, in the first rotationally resolved studies of pyrazine, that the decay behavior of the isolated molecule is strongly dependent on rotational state. The light source in these single rovibronic level (SRVL) experiments was a nitrogen-pumped dye laser with a pulse duration of ~ 10 nsec. Decays in this case are also biexponential; τ^+ is approximately 10 nsec, τ^- approximately 400 nsec, and A^+/A^- (much smaller than in the case of picosecond excitation) increases roughly linearly with J' . Similar results were reported by Mikami et al (38). Quantum beats were observed upon exciting the $6a_0^1$ band with a nanosecond laser (39). In addition, by comparing the fluorescence decays of differently deuterated molecules, van der Meer et al (39) showed that the $\sigma(A^+/A^-)$ values of the 0_0^0 band scale monotonically with the number of deuteriums, thereby establishing unequivocally that rotations play a role in the radiationless decay.

Matsumoto et al (40) introduced polarization analysis into the experiment and showed that the fluorescence decay of the $J' = 2$ zero-point rovibrational level is depolarized nonexponentially in time. They argued that this effect is a manifestation of a zero-field "level crossing" of the nondegenerate ME's coherently excited by the few-nanosecond laser pulse. The same group (41) also reexamined the J' -dependence of the fluorescence decay of the 0_0^0 band under nanosecond excitation conditions and showed conclusively that this dependence is *quasi*-linear, as shown in Figure 4. Introducing the concept of a singlet-character weighted rotational factor, and relating the spin-orbit properties of the gas phase molecule to those of the molecule in the condensed phase, Matsumoto et al (41) suggested that the strong rotational state dependence has its origin in a breakdown of the $\Delta K = \pm 1$ selection rule for ISC. It was also found, in subsequent work (42), that applying a small magnetic field of up to 150 G to the rotationally selected fluorescence decays increases the A^+/A^- values of all $J' \neq 0$ levels in a sigmoidal fashion by a factor of approximately three (Figure 5). In contrast, both τ^+ (~ 7 nsec) and τ^- (~ 200 nsec) are independent of the field under nanosecond excitation conditions. This work also showed that the $J' = 0$ level decays *exponentially* in time and shows no magnetic field effect, a fact that figured prominently in the development of a model (42) to account for the observed rotational-state dependence of the decay.

Terazima & Lim (43) have recently studied the rotational contour dependence of the A^+/A^- ratio for the $10a^1$ level of pyrazine under nanosecond excitation conditions. As in the case of fluorescence from the zero-point vibrational level, the preexponential ratio for the $10a^1$ fluorescence approximately mimics the rotational structure of $\langle J \rangle$.

Summarizing the above results, we see that the isolated molecule exhibits

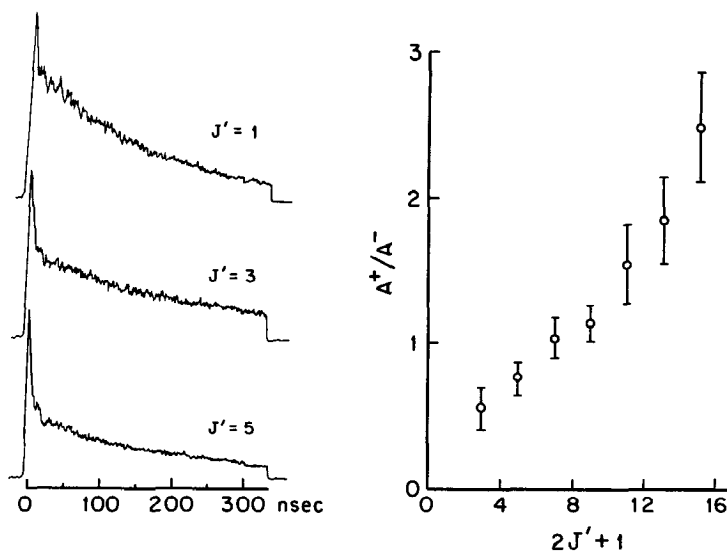


Figure 4 Rotational state dependence of the zero-point vibrational level fluorescence decay of $^1B_{3u}$ pyrazine, under nanosecond excitation conditions in a He supersonic jet. Also shown is a plot of the A^+/A^- values as a function of $2J'+1$, for $J' = 1$ to $J' = 7$. From Ref. 41.

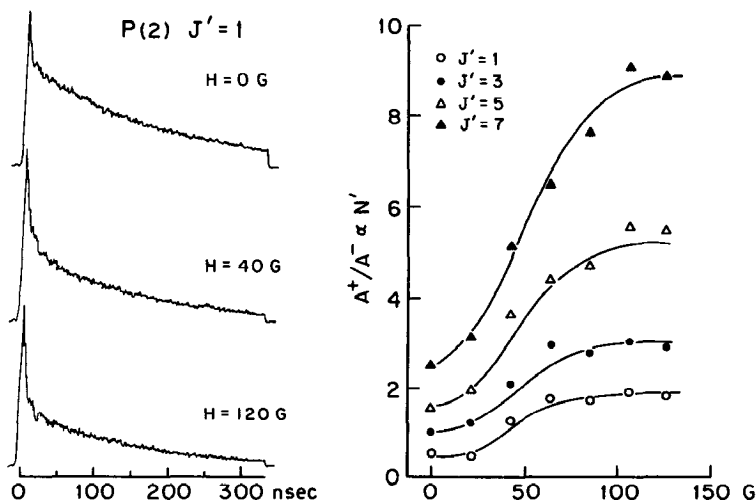


Figure 5 Magnetic field dependence of the fluorescence decay of the $J' = 1$ zero-point rovibronic level of $^1B_{3u}$ pyrazine, under nanosecond excitation conditions in a He supersonic jet. Also shown is a plot of A^+/A^- as a function of field for selected J' values. From Ref. 42.

a biexponential decay under both nanosecond (SRVL) and picosecond (SVL) excitation conditions with superimposed quantum beats appearing either on picosecond excitation of the origin or nanosecond excitation of higher vibronic bands. The decay is strongly magnetic field dependent, confirming triplet state involvement in the radiationless transition. A^+/A^- decreases with decreasing coherence width (cf Figures 2–4) and is also rotationally sensitive, increasing approximately linearly with J' . The fast decay follows the light source under nanosecond excitation conditions but approaches a constant value of ~ 100 psec for pulse durations significantly less than that. From this we conclude that $\Delta \sim 2$ GHz for all J' and that coherent excitation of the entire group of mixed states is not possible with nanosecond excitation. The A^+/A^- values in nanosecond experiments are therefore meaningful only in a relative sense. By this we mean that since $\Delta\omega < \Delta$, the dependences of A^+/A^- on excess energy, rotational state, and magnetic field are significant, but the absolute values of A^+/A^- are not. Considerable ambiguity exists concerning the actual density of states and whether ρ_k itself is rotationally dependent. But if $\rho_k \sim 10^3$ with pulse durations of ~ 100 psec or less, then the average values of v_{sk} and ϵ_k are ~ 25 MHz and 2 MHz, respectively. Finally, since τ^- approaches a constant value of ~ 100 nsec with pulse durations of ~ 1 nsec or less, we conclude either that N approaches a constant value, or that γ_k , rather than being zero, is on the order of 2 MHz. Thus, $x_k \sim 1$ and $v_{sk}\rho_k > 1$, confirming pyrazine's assignment as an intermediate-case molecule in the strong coupling limit.

Two caveats are necessary here. One is that, despite recent advances in pulsed laser technology, the coherence widths in most of the time-domain experiments on pyrazine to date were only very poorly defined. Only in the picosecond work of Lorincz et al (32) is it known that the pulses were nearly transform limited. Further, full knowledge of the spatial coherence in the interaction region is necessary to accurately define a coherence width $\Delta\omega$ that is appropriate for the ensemble excited in any real experiment. A second caveat, somewhat more obvious, is that the parameters deduced above are also model dependent, since the theory of Lahmani et al (21) is only approximate and is strictly valid only for a Lorentzian distribution of interacting states. Nonetheless, the model is conceptually useful, and a comparison of its predictions with experiment does give order of magnitude estimates for the parameters governing the radiationless decay of the isolated molecule.

Single molecular eigenstates (SME) would, of course, be expected to exhibit single exponential decays, rather than the biexponential decay characteristic of the intermediate case. Very recently, such a SME measurement has become possible using the tunable single-frequency laser

described in the next section. van Herpen et al (44) found, for eight of the perturbed $J' = 0$ levels of the ${}^1B_{3u}$ state, single exponential decays with lifetimes ranging from 200 to 560 ± 50 nsec. The decay behavior of $J' = 0$ levels is more complex, with some apparently single levels exhibiting quantum beats. More importantly, the observed lifetimes of the measured $J' \neq 0$ levels do *not* scale with the excitation intensities in the *ultra* high-resolution spectrum. The authors suggest that this deviation is caused by a non-radiative decay of the zero-order ${}^3B_{3u}$ levels with $\gamma_k \sim 2$ MHz, in apparent agreement with the earlier time-domain work.

Frequency-Domain Experiments

Pyrazine is a good example of the well-known physical fact that the decay behavior of a molecule is determined by its energy distribution function, or frequency spectrum, and its interaction with the light source. This is because the time dependence of the *quasi*-stationary states in the Schrödinger representation depends only on the energies of the states and possible interference effects between them. By applying this principle to pyrazine, and examining its decay properties using light sources with different coherence widths, we have deduced some approximate characteristics of this distribution: its width, the number of states comprising this distribution, and their average separation. But these parameters are clearly model dependent. An unambiguous, *model-independent* solution to this problem requires measuring the actual spectrum, resolving the postulated mixed states that are apparently responsible for the radiationless transition, and showing that Fourier transformation of these states into the time domain produces a decay that agrees with experiment, under any well-defined excitation conditions.

This is a formidable task. To put the problem in perspective, we show in Figure 6 the vibrationally resolved fluorescence excitation spectrum of pyrazine in a supersonic jet (19). The resolution in this experiment is ~ 1 cm^{-1} , sufficient to observe the Franck-Condon active vibrational modes in the ${}^1B_{3u}$ state. Under these SVL conditions, the 0_0^0 band of the isolated molecule exhibits a fluorescence quantum yield that is magnetic field dependent, decreasing to roughly one third of its zero field value at a field of 150 G (19). In early pioneering work, Baba and co-workers (45a-e) scanned across the rotational contour of the 0_0^0 band and showed that the quantum yield exhibits a very sharp peak near the band origin, suggesting that S_1 - T_1 coupling is enhanced with increasing rotational motion. More recently, Amirav & Jortner (46) have reexamined this problem using supersonic jet techniques. The quantum yield from the S_1 origin rotational contour exhibits a marked J' dependence, which can be fit by the empirical relation $Y = 0.124/(2J' + 1)$ for $J' = 5$ -22. The vibrational state dependence of Y

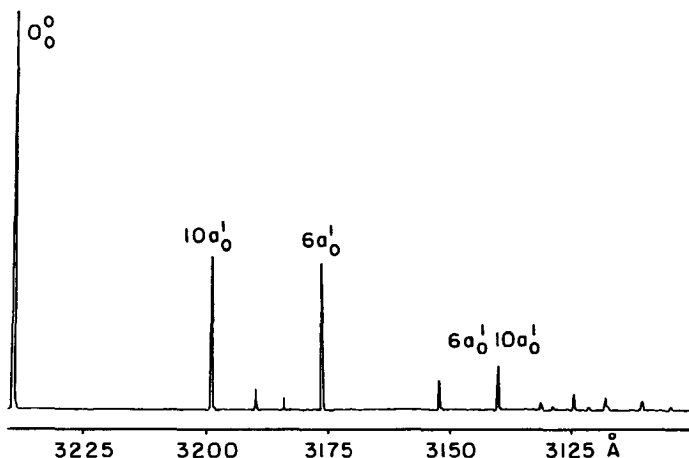


Figure 6 Vibrationally resolved fluorescence excitation spectrum of pyrazine in a He supersonic jet. From Ref. 19.

on the excess vibrational energy E_V exhibits an approximate exponential decrease with increasing E_V in the range $E_V = 0-1300 \text{ cm}^{-1}$, with possible saturation at $E_V = 1300-1800 \text{ cm}^{-1}$. de Lange et al (47) have also examined the relative quantum yield of the 0_0^0 band under somewhat higher resolution conditions and have isolated only the slow component using a nanosecond laser and a boxcar integrator. They also find a strong rotational state dependence, decreasing from a relative value of 0.43 at the Q branch to ~ 0.01 on the wings of the P and R branches.

Increasing the frequency resolution by a factor of ~ 20 permits observation of this rotational structure, as shown for the 0_0^0 band in Figure 7 (19). A parallel-type band, this spectrum consists of a strong Q branch (with $\Delta J = 0$) flanked by P- and R-branch transitions (with $\Delta J = \mp 1$), separated by $\sim 2\bar{B} \sim 0.4 \text{ cm}^{-1}$. As pyrazine is a near oblate symmetric top in both electronic states (48), each P- and R-branch transition is a superposition of all possible $\Delta K = 0$ transitions, although K is not a rigorously good quantum number. The peak of the Q branch is at $30,876 \text{ cm}^{-1}$, in the ultraviolet region of the electromagnetic spectrum. Further, the time scale of the dynamics, as measured by the average inverse separation of the ME's deduced from the time-domain experiments, is much longer than the reciprocal spectral resolution in either Figures 6 or 7 ($\sim 5 \text{ psec}$ and $\sim 100 \text{ psec}$, respectively). Thus, if we want to resolve the individual mixed states that together comprise these observed distribution functions, and that, when excited coherently, are responsible for the decay behavior of the isolated molecule, we have to perform the ultraviolet experiment with a CW laser having a spectral width of less than 10 MHz!

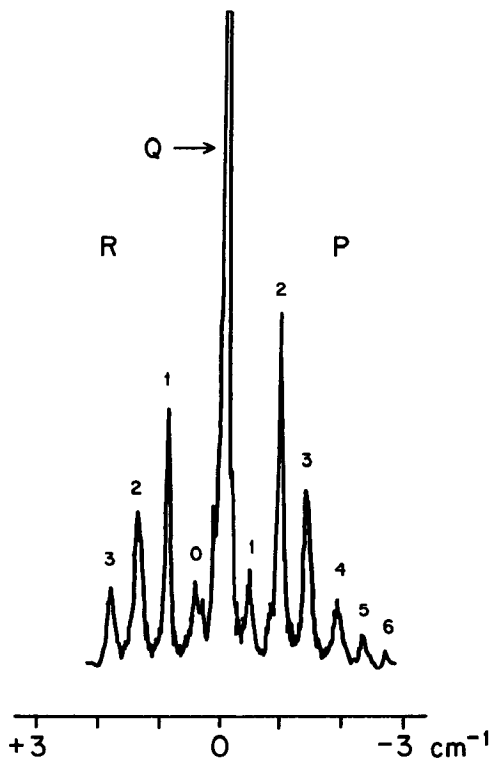


Figure 7 Rotationally resolved 0_0^0 band of the fluorescence excitation spectrum of pyrazine in a He supersonic jet. From Ref. 19.

As is often the case in science, such a device already existed elsewhere, in the form of a tunable, intracavity-doubled, single-frequency dye laser developed at Nijmegen by Majewski (49). Further, Majewski & Meerts (50) had already shown that the combination of this light source with a well-collimated molecular beam and a sensitive fluorescence detection system yielded electronic spectra with rovibronic resolution for several large molecules and their van der Waals complexes. The resolution in these early experiments was limited by the Doppler width to ~ 35 MHz, but as this is ~ 50 times higher than the resolution in Figure 7, it was clearly sufficient to observe something new in pyrazine. What brought the different research groups together and made these experiments possible was a chance meeting at the May 1982 thesis defense of Kommandeur's student ter Horst who, with Pratt, had discovered the rotational sensitivity of the biexponential decay (37). The first results of the *ultra* high-resolution

experiment on pyrazine were published in November 1982 by van der Meer et al (51). These spectra have since been reexamined several times; what is presented here is a sampling of the most recent results, largely unpublished as of this writing.

Each of the *ultra* high-resolution spectra of pyrazine has its parentage in a different J' rotational member of the spectrum in Figure 7, and thus each is separated, one from another, by ~ 12 GHz. Shown in Figure 8 is a scan of the P1 member accessing, in the ${}^1B_{3u}$ state, all $J' = 0, K' = 0$ levels. Of course, if the ${}^1B_{3u} \leftarrow {}^1A_g$ transition were an electronic transition between two ordinary singlet states, this spectrum would consist of only a single line. But ${}^1B_{3u}$ pyrazine is not ordinary, and as a result the spectrum (Figure 8) exhibits many lines. This is the first resolved intermediate level structure of a polyatomic molecule. Thus, molecular eigenstates are "real,"

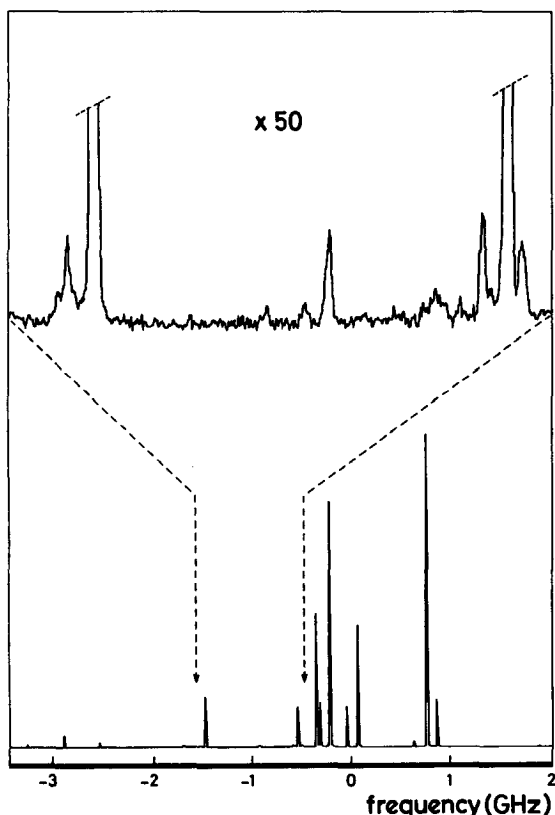


Figure 8 The P1 molecular eigenstate spectrum of pyrazine. Inset shows some of the weaker lines observed at higher gain. From Ref. 44.

and their properties can be measured. Spread over a width of approximately 7.5 GHz (only the strong central portion is shown in Figure 8), the P1 spectrum consists of many randomly spaced lines of widely varying intensity (different $|c_{ns}|^2$), each of approximately 10 MHz (Doppler-limited) width. The resolution in this experiment is $\sim 1:10^9$! The original spectrum (51) showed 12 lines; recent improvements in dynamic range have revealed at least 36 lines in the P1 spectrum. These lines are identified as the (at least approximate) ME's that derive from the mixing of one zero-order singlet level (the $J' = 0$ zero-point rovibrational level of the ${}^1B_{3u}$ state) with many nearly isoenergetic zero-order triplet levels, $J' = 0$ rovibronic levels lying ~ 4000 cm^{-1} above the origin of the ${}^3B_{3u}$ state. Although the density of these levels is high (by *actual* count, $\geq 36/7.5$ GHz $\sim 150/\text{cm}^{-1}$), it is still sufficiently sparse that only a limited number of ME's are contained within the coherence width of a pulsed light source. The observed decay will then depend on the time duration of the source, which accounts for the widely varying decay behavior reported in the literature.

van der Meer et al also showed in their original report (51) that the square of the Fourier transform of the amplitude spectrum in Figure 8 yields the quantum beats observed in the fluorescence decay of the isolated molecule, as shown in Figure 9. To construct these transforms, the authors represented Figure 8 as a stick spectrum in frequency space, $A_s(\omega)$, using only the 12 strongest lines. They associated with each line a Lorentzian lineshape of unspecified width to give the homogeneously broadened amplitude spectrum, $A_l(\omega)$. This was multiplied by a "laser" function $\chi(\omega)$, centered at the peak S of $A_s(\omega)$, and Fourier transformed to obtain $c_s(t)$ and the decay, $|c_s(t)|^2$. Transforming $|c_s(t)|^2$ again gave the power spectra shown in Figure 9. The comparison between these reconstructed decays and experiment is satisfactory, under two different excitation conditions, demonstrating for the first time an "exact" solution to the problem of radiationless transitions. More recently, de Lange et al (52) have shown that Fourier transforms of "blocks" of singlet amplitudes with widths varying randomly between 2 and 5.5 GHz gave decays of ~ 100 psec, also in good agreement with experiment.

A second way of demonstrating that the *ultra* high-resolution spectra of pyrazine represent a solution to the radiationless transition problem is to show that it is possible to relate the observed spectra to the properties of the unperturbed primary and secondary zero-order states (6). Such a calculation was first performed by van der Meer et al (53) by a trial-and-error method and later by Lawrance & Knight (54) using a more elegant deconvolution procedure. The latter approach, based on earlier work by Berg (55) and Ziv & Rhodes (56a,b), requires the calculation of the real and

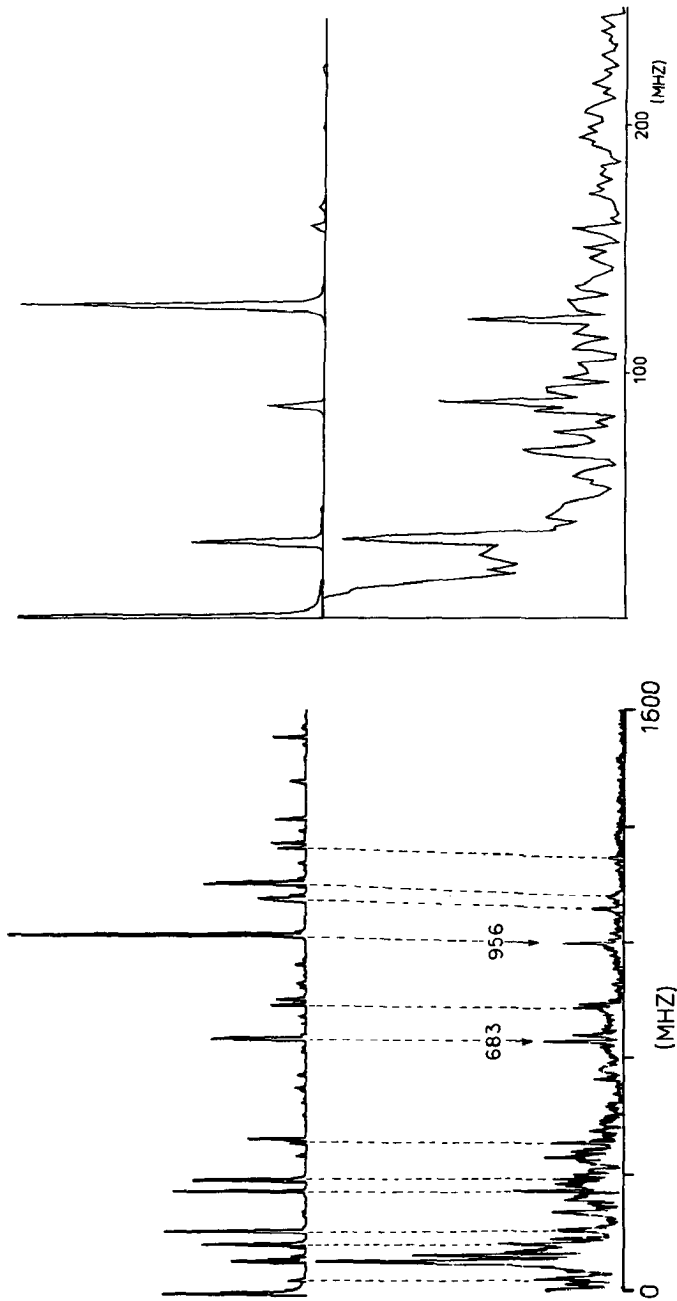


Figure 9 Reconstructed decays. On the left is the Fourier transform of the decay of the PI ME spectrum excited with a 60 GHz wide laser, centered at S (*top*), compared with the $H = 0$ experimental result of Felker et al (28). On the right is the Fourier transform of the decay of the PI ME spectrum excited with a 300 MHz wide laser, centered at S (*top*), compared with the experimental result of van der Meer et al (51). From Ref. 51.

imaginary parts of a Green's function derived from the energies, widths, and intensities in the experimental spectrum. This procedure is valid when only one of the zero-order levels carries oscillator strength and the interaction occurs between this level and a number of other levels that do not interact among themselves. Assuming these conditions are satisfied in the case of the P1 spectrum of pyrazine, Lawrance & Knight (54) used the original data of van der Meer et al (51) and obtained the results given in Table 1. Here, the ϵ_n are the relative energies of the ME's from Figure 8, referred to the energy of the zero-order singlet (determined by the center-of-gravity method), the $|c_{ns}|^2$ are the normalized intensities from Figure 8, and the ϵ_t and v_{st} are the relative energies and coupling matrix elements of the zero-order triplet levels interacting with $|s\rangle$. A constant linewidth of ~ 1 MHz was used in this calculation. By re-diagonalizing the problem, Lawrance & Knight (54) recovered the ME spectrum of van der Meer et al (51). The former authors also showed that their deconvolution procedure gives the unique set of zero-order levels and v_{st} values, although it should be noted that these are only approximate since it was assumed that Figure 8 is an absorption, rather than an excitation, spectrum.

Examination of Table 1 shows that a common assumption in the theory of radiationless transitions, that the coupling matrix elements are relatively constant, is incorrect. The values of v_{st} span nearly an order of magnitude,

Table 1 Energies, intensities, and lifetimes of the P1 molecular eigenstates of the zero-point vibrational level of the ${}^1B_{3u}$ state, together with the relative energies and coupling matrix elements of the interacting zero-order ${}^3B_{3u}$ levels^a

ϵ_n , MHz	$ c_{ns} ^2$	τ , nsec	ϵ_t , MHz	v_{st} , MHz
-2856	0.012	—	-2823	290
-2517	0.007	—	-2497	228
-1440	0.040	200	-1381	287
-537	0.042	512	-519	84
-366	0.122	443	-341	54
-324	0.037	—	-304	76
-228	0.248	342	-91	130
-57	0.042	437	-9	128
51	0.129	560	437	423
609	0.017	—	620	79
738	0.248	280	817	56
831	0.055	529		

^a Refs. 44, 51, 54.

from ~ 50 to ~ 500 MHz. Further, the matrix elements (typically larger than the estimate $\bar{v}_{sk} \sim 25$ MHz obtained from the time-domain work) vary in a seemingly random fashion with respect to the corresponding zero-order triplets (whose average separation also exceeds $\bar{\epsilon}_k$). Examination of the mixing coefficients (54) also shows that in most cases only one or a few triplet levels contribute significantly to the character of each eigenstate, this trend being most evident for those eigenstates furthest removed from the zero-order singlet, and that the singlet character of the eigenstate closest in energy to a particular triplet does not correlate with the corresponding v_{st} value. We can attribute these fluctuations to widely varying Franck-Condon factors for the radiationless transition, which suggests that the $J' = 0$ levels of the zero-order triplet state are vibrationally unique (i.e. nonergodic) at an energy of ~ 4000 cm^{-1} above the ${}^3\text{B}_{3u}$ origin (57). Application of this procedure to other vibronic bands should help to quantify the notion of promoting modes and accepting modes.

Also listed in Table 1 are the SME lifetimes of van Herpen et al (44) for comparison purposes. As already noted, there is little or no correlation between the intensities of the lines and their lifetimes, leading to the conclusion that the zero-order triplets have some finite nonradiative width. Including these widths then allows one to derive the absorption spectrum from the excitation spectrum and again reconstruct the zero-order situation. By doing this in an approximate way, and including all 36 states, van Herpen et al (44) showed that qualitatively the situation remains the same. Some slight redistribution of singlet amplitudes occurs, but there remain large fluctuations in the values of v_{st} , the zero-order energies, and the compositions of the molecular eigenstates.

We have also obtained the *ultra* high-resolution spectra of several other J' members of the spectrum in Figure 7. Shown in Figure 10 is a comparison of two of these spectra, R0 and P2. Again, each consists of many more lines than expected, and most of these exhibit incompletely resolved structure, making an actual count of the level densities accessed by $J' = 1$ excitation impossible, at this time. We also cannot deperturb these spectra, both because of their inhomogeneity [recall the quantum beat results of van Herpen et al (44)] and because the method of Lawrance & Knight (54) and other existing deconvolution procedures require that there be only one zero-order state possessing oscillator strength. Clearly this is the case only for R0 and P1. But there is one approach that might be tried, as suggested by the format of Figure 10. This is to take advantage of the fact that the two spectra "line up"; that there are some lines, or groups of lines, that are common to the two spectra when plotted on the same relative frequency scale. (Many more coincidences occur than are explicitly shown in Figure

10.) This might be expected if K is a good, or nearly good, quantum number, since the R0 line accesses $J' = 1, K' = 0$ levels, and the P2 line accesses $J' = 1, K' = 0, \pm 1$ levels. With higher quality data, it may be possible to deperturb R0 and compare the resulting ϵ_t and v_{st} values of the $J' = 1, K' = 0$ levels with those of the $J' = 0, K' = 0$ levels, to determine the source of the J' -dependent effects. We may also be able to subtract the R0 spectrum from P2 and produce a "spectrum" of the $J' = 1, K' = \pm 1$ levels that might also be deperturbed, providing one can find a way to estimate the asymmetry splitting, perhaps by double resonance experiments. A similar procedure might then be used for other pairs of spectra (e.g. R1, P3; R2, P4; etc). But if we compare R1 with P3, which should have additional $K' = \pm 2$ levels, the regularity seems to disappear. The

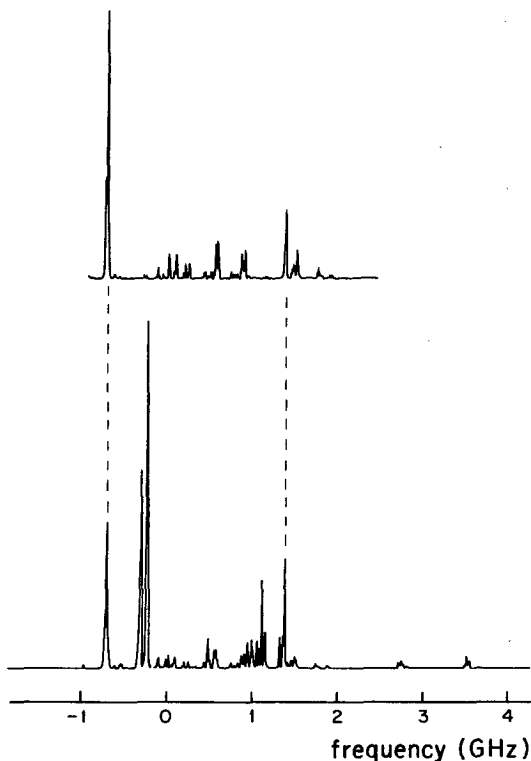


Figure 10 A comparison of the R0 (*top*) and P2 (*bottom*) molecular eigenstate spectra of pyrazine.

same holds when we compare R2 with P4. It is difficult to know, at this juncture, what is responsible for these effects; the small but different asymmetry splittings in the spectra, possible hyperfine coupling, and/or the destruction of the K quantum number (see below). There is the additional complication that, whereas the ME's of pyrazine behave like a singlet state with respect to their intensity distribution, these hybrid or compound states may behave more like a triplet state with respect to their (sub)rotational structure. It should be clear from the data presented here that the ME's at the singlet origin of the ${}^1B_{3u}$ state are, on average, much more triplet than singlet in character. For example, only one singlet level contributes to P1, and there are at least 36 lines in this spectrum. And singlet-triplet electronic transitions, it will be recalled (58), exhibit significantly less stringent rotational selection rules (59)!

de Lange et al (47) have also studied the 0_0^0 band ME spectra of some deuterated pyrazines. In the case of pyrazine- dh_3 , they observed P1, P2, and the Q branch, all of which have reasonable intensity. However, the R0 member is unusually weak, and R1 is difficult to observe. Even more unusual is pyrazine- d_3h , where P1 has reasonable intensity, Q and P2 are weak, and no members of the R branch could be observed.

Finally, we report here briefly on studies of the magnetic field dependence of the *ultra* high-resolution spectrum of pyrazine. These results have also not been fully analyzed as of this writing. But even a quick perusal of the data in Figure 11 shows that the quantum yield of each ME depends on its triplet character and/or on the character of other levels coupled to the triplet. The P1 spectrum shows only a weak field dependence for fields up to 60 G, as would be expected for $J' = 0$ levels. But all $J' \neq 0$ spectra are strongly perturbed by the application of very small fields. For example, Figure 11 shows the P3 spectrum at zero (applied) field and a field of 30 G. Both spectra were recorded at the same absolute intensity level and, as will be seen, even this small field produces a significant quenching of the fluorescence intensity. Moreover, although there is little change in the relative positions of the lines, their relative intensities are also affected dramatically. Further studies of these striking effects are in progress.

Intramolecular Dynamics

Having demonstrated that pyrazine has, indeed, provided an "exact" solution to the problem of radiationless transitions, we turn our attention briefly to another issue, namely what this remarkable molecule has taught us (and is likely to teach us in the future) about intramolecular dynamics. It is not sufficient, in our view, to simply demonstrate that the time- and frequency-domain experiments are mutually consistent. That is, after all,

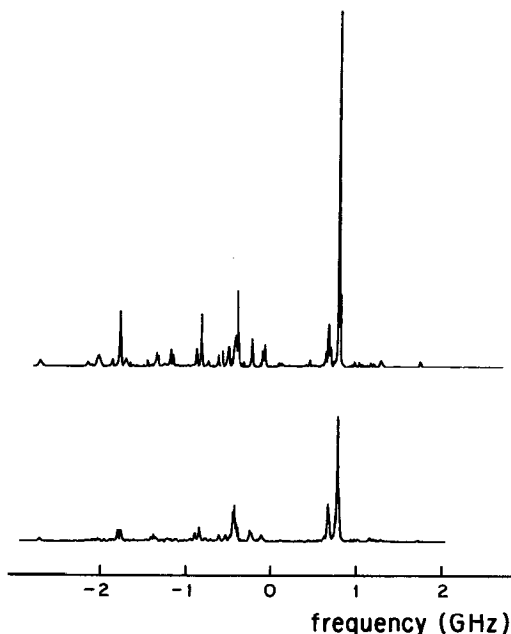


Figure 11 Magnetic field dependence of the P3 molecular eigenstate spectrum of pyrazine. (Top) zero field; (bottom) 30 G.

only an exercise in linear response theory and the mechanics (albeit elegant) of the Fourier transform relationship. A central issue, so far not addressed here, is why rotations are important in the radiationless decay of the isolated molecule. We cannot answer this question unambiguously, but we can offer a model that consistently explains all existing experiments and helps to suggest new ones, experiments that we believe will considerably enhance our understanding of energy flow in large molecules.

To motivate this discussion, we cite several unexplained observations, many of which have already been mentioned. These include the findings that (a) the number of levels observed in both the time- and (*ultra* high-resolution) frequency-domain experiments exceed the Haarhoff estimate of $100/\text{cm}^{-1}$ [a reliable experimental estimate is available only from the P1 ME spectrum, which gives, for $J' = 0$, σ times ($\geq 150/\text{cm}^{-1}$) equals ($\geq 600/\text{cm}^{-1}$)]; (b) the magnetic fields required for saturation of the A^+/A^- values, and quenching the ME spectra, are much smaller than the expected fine-structure splittings of the zero-order triplet levels; (c) the values of $\bar{\nu}_{3k}$ and $\bar{\epsilon}_k$ deduced from an analysis of the decay experiments are much smaller

than those obtained from the deconvolution of the P1 ME spectrum; (d) a nonzero value of $\gamma_k \sim 2$ MHz, much larger than expected for zero-order triplet levels, is required to fit the decay behavior of both superposition states and $J' = 0$ SME's; and (e) many $J' \neq 0$ levels in the *ultra* high-resolution experiment are still inhomogeneously broadened, even at a resolution of 10 MHz. The fluorescence quantum yield also requires that the dilution factor N [or N_{eff} (46)] be much higher than the Haarhoff estimate of the number of ${}^3\text{B}_{3u}$ levels available at the origin of the ${}^1\text{B}_{3u}$ state. All of these findings may be explained if we assume that other states contribute to the dynamics at this energy. While there is some evidence for a second triplet state below ${}^1\text{B}_{3u}$ (14, 17), the presently available data (60) suggest that this gap is small, ≤ 1000 cm^{-1} , too small to support a high density of additional zero-order triplet levels. Thus, the only logical conclusion to be derived from these observations is that ground state levels may also be involved.

Figure 12 illustrates the kind of model we have in mind (10, 42, 47, 57, 61, 62). We imagine that there are two types of zero-order triplet levels,

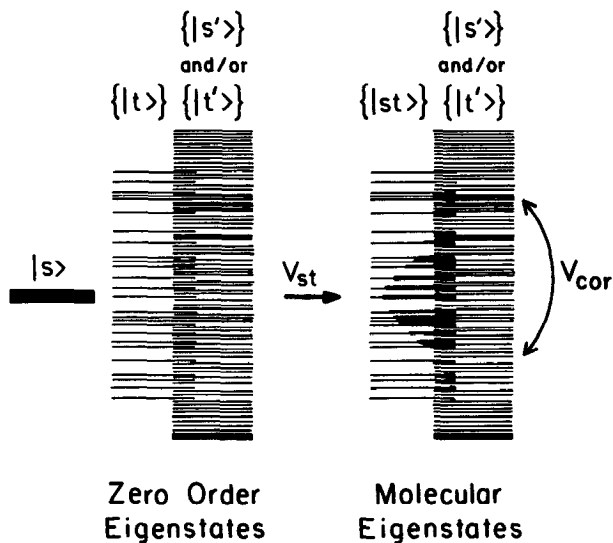


Figure 12 Schematic model for intraelectronic state coupling near the S_1 origin of pyrazine. $|s\rangle$ represents the zero-order optical state, $|t\rangle$ the zero-order triplet states with which it has significant coupling (v_{st}) in the isolated molecule, and $|s'\rangle$ and $|t'\rangle$ the zero-order ground state and triplet levels that have relatively small coupling (v_{cor}) with $|st\rangle$. After Knight et al (Ref. 61).

$\{|t\rangle\}$ and $\{|t'\rangle\}$, as well as a high density of nearly isoenergetic ground state levels $\{|s'\rangle\}$. The set $\{|t\rangle\}$ is strongly coupled to $|s\rangle$ because the levels contained therein have the correct symmetry and obey the ISC selection rules, yielding mixed levels $\{|st\rangle\}$ that carry most of the oscillator strength to $|0\rangle$. These are the levels responsible for the strong lines detected in the *ultra* high-resolution spectra. The sets $\{|t'\rangle\}$ and/or $\{|s'\rangle\}$ are only weakly coupled to $\{|st\rangle\}$, but their densities are much greater than the density of $\{|st\rangle\}$ levels, giving rise to weaker lines and/or a continuous background in the *ultra* high-resolution spectra. (These weaker lines, if they exist, may be very difficult to detect owing to their long lifetimes.) Coriolis interactions, either between $\{|t\rangle\}$ and $\{|t'\rangle\}$ or between $|s\rangle$ and $\{|s'\rangle\}$, are imagined to be responsible for these weak couplings. (The possible existence of these couplings accounts for our referring to the *ultra* high-resolution data as "approximate" ME spectra, and to our solution of the radiationless transition problem as "exact.") Nonvanishing matrix elements of the Coriolis interaction in nearly oblate symmetric molecules take the form $|v_{\text{cor}}^c| \propto K$, which is diagonal with respect to K , and $|v_{\text{cor}}^{a,b}| \propto [(J \mp K)(J \pm K + 1)]^{1/2}$, which is off-diagonal with respect to K (63). The relative values of $|v_{\text{cor}}^c|$ and $|v_{\text{cor}}^{a,b}|$ depend on the Coriolis interaction parameters and the rotation axis relevant to the particular coupling. Coriolis coupling for any $|st\rangle$ level is therefore not precluded. But it would be expected to be smallest for $J' = K' = 0$ states. Thus, the main predictions of the model are that $J' = 0, K' = 0$ ME's will behave like the states of a small molecule, exhibiting a single exponential decay with coherent preparation and a sharp, sparse *ultra* high-resolution spectrum, whereas $J' \neq 0, K' \neq 0$ ME's will behave quite differently, exhibiting biexponential decays and much more complex *ultra* high-resolution spectra. The presently available data, from both the time- and frequency-domain experiments, are consistent with these predictions. Thus, it appears that rotationally induced vibrational state mixing, in the $\{|t'\rangle\}$ and/or $\{|s'\rangle\}$ manifolds, plays a key role in the ISC process in the isolated molecule.

Other data may be offered to support this view: (a) the approximately linear dependence of A^+/A^- on J' ; (b) the intermediate decay rate of the fluorescence polarization, suggesting K' scrambling (via off-diagonal Coriolis coupling), at least at higher J' ; (c) the inverse J' dependence of the quantum yield; (d) the wide range and apparently random nature of the v_{st} values obtained from the deconvolution of the P1 spectrum; and (e) the apparent breakup of the ME spectra for higher J' values. The J' -resolved quantum yield results for pyrazine-*h*₄ and the "anomalous" *ultra* high-resolution data for pyrazine-*dh*₃ and pyrazine-*d*₃*h* may also be satisfactorily interpreted by invoking Coriolis coupling. In addition, rotationally sensitive, K -state dependent, singlet-triplet perturbations have recently

been detected in the *ultra* high-resolution ${}^1B_1 \leftarrow {}^1A_1$ fluorescence excitation spectrum of pyrimidine (64). The singlet-triplet gap in this molecule, the 1,3-diazabenzene analog of pyrazine, is much smaller ($\sim 2000\text{ cm}^{-1}$) than in pyrazine. As a result, pyrimidine exhibits far fewer avoided crossings between zero-order $J' \neq 0$ $|s\rangle$ and $|t\rangle$ levels, making possible an exact analysis (65) and, we hope, important clues for the ultimate solution of the pyrazine problem.

Irrespective of its origin, it is clear from the data presented here that the radiationless decay of the isolated pyrazine molecule is strongly dependent on its rotational state. The rotation-dependent vibrational state mixing effects observed in ISC indicate the importance of rotational motion in intramolecular dynamics, a message that is communicated as well by recent studies of several other highly excited molecules (66–72). This means that it should be possible, at least in principle, to control the vibrational motion of the eigenstates excited by a narrow band laser by properly selecting the rotational angular momentum content of the prepared state, thereby providing a route to true level-specific chemistry. But before we can apply this technique to control chemical bond forming or breaking processes in an isolated molecule, we have to learn how to control its vibrational motion by identifying the levels, determining the matrix elements, and assessing the role of other degrees of freedom in promoting energy flow. We may also seek to determine the spectroscopic signatures of dynamically chaotic systems (73–75). Whatever the bias of the experimentalist, the single-frequency ultraviolet laser, in combination with a molecular beam, will be an indispensable tool for those who seek to accomplish one or more of these objectives.

Conclusions

A model-independent solution to the problem of radiationless transitions in a polyatomic molecule has been provided by demonstrating the existence of previously postulated but heretofore undetected mixed states in the *ultra* high-resolution fluorescence excitation spectrum of pyrazine in a molecular beam. Excited coherently by a pulsed light source, these states form a nonstationary superposition state that evolves smoothly into a phase-incoherent mixture of molecular eigenstates. Magnetic field experiments have shown that these states have significant triplet character, thereby demonstrating that the relaxation process we are monitoring is intersystem crossing (ISC), from single rovibronic levels of the S_1 state to nearly isoenergetic levels of a triplet state. Several spectra of these mixed singlet-triplet eigenstates are presented, some for the first time. We show that Fourier transforming these data yields quantum beats in the fluorescence decay whose frequencies agree with those measured in time-domain experi-

ments. The sensitivity of the decay to the coherence width of the exciting light source is also demonstrated. We also establish a connection between radiationless transitions and intramolecular dynamics by demonstrating that the ISC process is rotationally sensitive, perhaps *via* Coriolis-induced mixing of the zero-order vibrational levels. The existence of this sensitivity, if it can be controlled, may provide a route to true laser-specific chemistry in other polyatomic molecules.

In retrospect, pyrazine is a special molecule because it represents the ideal combination of system and light source to study electronic relaxation, at least near the S_1 origin. The dynamics at this energy is sufficiently slow to make possible the frequency resolution of its (at least approximate) molecular eigenstates, the truly unique property of an intermediate case. Many other molecules would be equally useful probes of intramolecular dynamics at the appropriate excitation energy, and we plan future *ultra* high-resolution experiments on a number of them. But, despite all of the effort to date, even pyrazine is not completely understood. We do not agree as to the relative importance of $|t'\rangle$ and $|s'\rangle$ states in intramolecular decay. We have not established an accurate measure of the density of states, particularly for $J' \neq 0$, and therefore do not know whether this density is dependent on rotational state. The possible J' , K' dependence of the coupling matrix elements also needs to be determined. We have yet to demonstrate the existence of a biexponential decay in simulated nanosecond transforms of the $J' \neq 0$ spectra.¹ We have not demonstrated, unequivocally, that Coriolis coupling is important. Nor have we assessed the possible importance of axis switching, nonplanar distortions, and/or hyperfine coupling in the triplet state on level densities. We still do not know absolute values of the quantum yield for the $J' = 0$, $K' = 0$ levels. The dependence of the dynamics on vibrational state remains to be explored. And, finally, we need to develop additional methods, both theoretical and experimental, for assessing the degree of vibrational state mixing in the zero-order triplet and/or ground state manifolds. Nonetheless, we have made great progress in our understanding of radiationless transitions in the past few years, chiefly because of the experiments on pyrazine, and there is the hope that many of the above problems will be resolved in our continuing studies of this marvelous molecule.

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Our collaborators on this project, P. J. de Lange, K. E. Drabe, K. W. Holtzclaw, H. Th. Jonkman, J. Konings, Y. Matsumoto, L. H. Spangler,

¹ In this connection, it is interesting to note that a simulation of the biexponential decay of the 4^1 level of butynal has been successfully performed, where $N = 12$, randomly distributed ϵ_k within $\Delta\omega \sim 200$ MHz, $\bar{\nu}_{sk} = 16$ MHz, $\gamma_s = 5.5 \times 10^5$ s⁻¹, and $\gamma_k = 4 \times 10^4$ s⁻¹ (76).

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