

$^1B_{3u}$ Pyrazine. Experimental Tests of the Theory of Radiationless Transitions†

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Pyrazine (1,4-diazabenzene) has played a central role in the development of the theory of radiationless transitions. In this paper, we will describe studies of the decay behavior and fluorescence quantum yield of the isolated molecule and several of its isotopically labelled derivatives following pulsed dye laser excitation of “single” rotational levels of the $^1B_{3u}$ ($n\pi^*$) state in a seeded supersonic jet, both in the presence and absence of an external magnetic field. We shall demonstrate that pyrazine can be transformed from a “small” molecule to a “large” molecule by very small perturbations; e.g., by climbing up the rotational ladder of the first excited singlet state, by isotopic labeling, and/or by applying dc magnetic fields of the order of 100 G. Thus, the experiments provide important tests of the predictions of the theory for the first time. Specifically, we will show that, under “intermediate-case” conditions, (1) the fast component of the decay is indeed coherent in nature, (2) the coupled state is triplet in character (and, thus, that the process we are monitoring is intersystem crossing (ISC)), (3) nuclear spin is conserved in ISC, (4) rotations and small magnetic fields play an important role because of the angular momentum selection rules for ISC, and (5) the levels mixed by the magnetic field are most likely the fine-structure components of the different angular momentum levels of the mixed, singlet–triplet state. The relationship of these results to those of other workers in the field will also be discussed.

INTRODUCTION

The azabenzenes, particularly pyrazine (1,4-diazabenzene), have played a major role in the development of the theory of radiationless transitions.¹ This is because they typically exhibit, unlike small molecules and large, statistical ones, a fluorescence quantum yield

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which is pressure dependent and a fluorescence decay which is non-exponential. These properties, which place most azabenzenes in the "intermediate-case" category of the theory, are believed to derive from relatively small singlet-triplet energy gaps and relatively large intramolecular couplings between these zero-order states. Thus, it is imagined that the states in the vicinity of the singlet origin are mixed states which possess both singlet and triplet character, and that the decay properties of the "prepared" state depend not only on the characteristics of the molecule, but also on those of the exciting light; i.e., on its spectral distribution and its temporal behavior.

In an early, and elegant, treatment of this problem, Tramer and co-workers² suggested that the fluorescence decay of pyrazine could, under most conditions, be described as a sum of two exponential components. It was argued that the rapidly decaying component represents the evolution in time of a coherent superposition of molecular states having only singlet character into a set of *quasi-stationary* mixed singlet-triplet states, and that the slowly decaying component represents the subsequent evolution of an incoherent superposition of the independent decays of each of these *quasi-stationary* states. These slow decays may be either radiative or non-radiative, depending on the nature of the coupled state. This model, and its refined versions, accounts for most of the observed dynamic properties of the azabenzenes and many other intermediate-case molecules.³

Our entry into this field was prompted by the recognition that most previous experimental tests of the predictions of the theory have been carried out under conditions where either the spectral width or the coherence width of the excitation source was large compared to the reciprocal level densities (ρ^{-1}) typical of the "intermediate-case" molecule. Pyrazine has, for example, a background density of states of the order of $100/\text{cm}^{-1}$ in the vicinity of the singlet origin.⁴ This means that very little in the way of detailed information about the nature of these mixed states (the molecular eigenstates) can be obtained from experiments performed with light sources having large (e.g., 1 cm^{-1}) spectral widths or subnanosecond pulse durations. Instead, one should move in the other direction if one wishes to provide further, and more stringent, tests of the theory. Towards this end, we have been performing, in the past few months, a number of experiments on pyrazine using our new supersonic jet apparatus and

a 5 ns pulse duration dye laser with a spectral width of 0.06 cm^{-1} ($\sim 2\text{ GHz}$). We are particularly interested in the dependence of level densities on angular momentum quantum numbers, and on small magnetic fields. Presented herein are the results of some of these experiments which, although incomplete, already demonstrate the validity of our approach.

SPECTROSCOPY

Figure 1 shows a portion of the fluorescence excitation spectrum of ${}^1B_{3u}(n\pi^*)$ pyrazine expanded in a pulsed supersonic jet of helium ($P_0 \sim 1\text{ atm}$, $x/D \sim 40\text{--}100$). Here, the (doubled) wavelength of our Quanta-Ray Nd^{+3} :YAG pumped dye laser is scanned over the region $3250\text{--}3100\text{ \AA}$ with an autotracking system, and the total fluorescence is detected by an EMI 9813QB photomultiplier tube, PAR162/165 boxcar integrator, and recorder. Immediately apparent are the high resolution capabilities of this technique, well known to workers in the field. In spite of the low quantum yield ($\sim 10^{-3}$), we have also found that dispersed fluorescence spectra of pyrazine are relatively easy to obtain. Figure 2 shows a typical spectrum, recorded while

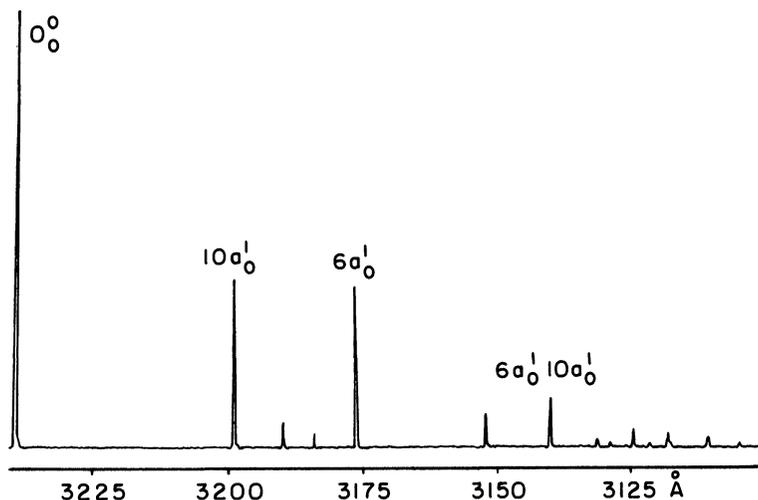


FIGURE 1 Fluorescence excitation spectrum of ${}^1B_{3u}(n\pi^*)$ pyrazine expanded in a seeded supersonic jet of helium.

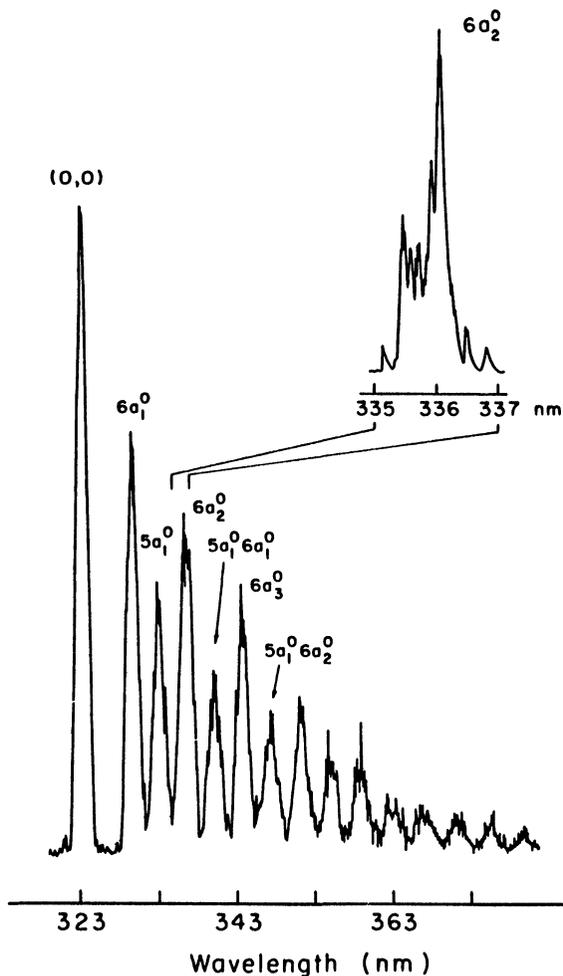


FIGURE 2 Dispersed fluorescence spectrum of ${}^1B_{3u}$ pyrazine observed on excitation of the 0_0^0 band in Figure 1.

exciting the 0_0^0 band and scanning the wavelength of an 0.25 m detection monochromator using 1 mm slits. Since the transition is electronically allowed, the strongest band in the spectrum is the resonance line which serves as an origin for a progression in the ground state in-plane stretching mode, ν_5 , of symmetry b_{2g} . This band

also serves as an origin for a progression in ν_{6a} . At higher resolution, using 150μ slits, additional structure is resolved in some of the bands. Resonance emission is also observed in the dispersed fluorescence spectra recorded while exciting the $6a_0^1$ and 5_0^1 vibronic bands. This indicates that intramolecular vibrational relaxation in the excited state is incomplete on the time scale of the emission process. Detailed studies of this effect, both in the presence and absence of collisions, are in progress.

Our main interest in the present work is in the rotationally resolved fluorescence excitation spectrum shown in Figure 3. Here, we again collect all of the emission, and pressure scan the dye laser across the 0_0^0 band with an etalon in the evacuable laser cavity. As pyrazine is a near oblate symmetric top with the transition moment parallel to the top axis, the band exhibits well-developed *P*-, *Q*-, and *R*-branch structure, in accord with the selection rules $\Delta J = 0, \pm 1$. Lines in the *P* and *R* branches, each of which is a superposition of all possible $\Delta K = 0$ transitions, are spaced by approximately $2\bar{B} \sim 0.4 \text{ cm}^{-1}$. Fits of the relative intensities of these lines, taking nuclear spin statistical weights into account, show that the rotational temperature of the ground state following expansion in the jet is about 2 K. Clearly, one can excite, depending on the choice of wavelength, a few rotational levels of the first singlet by positioning the laser on the *Q* branch, or "individual" rotational levels by positioning the laser on one of the lines in the *P* or *R* branch.

MAGNETIC FIELD EFFECTS ON FLUORESCENCE INTENSITY

Small d.c. magnetic fields have a remarkable effect on the properties of S_1 pyrazine. To illustrate this in a simple way, we show in Figure 4 a plot of the fluorescence intensity as a function of field from 0–150 G. Here, we excite in the *Q* branch of the 0_0^0 band, and detect the total emission with a $\sim 1 \mu\text{s}$ aperture duration on the boxcar integrator. Strong magnetic field quenching is observed; the fluorescence intensity is reduced to $\sim \frac{1}{3}$ of its zero-field value at fields in excess of 120 G, and the half-width of the Lorentzian-type curve is about 25 G. From these facts we can conclude that the coupled state is triplet in origin since large *g* values are necessary to account for such strong mixing effects at low fields.

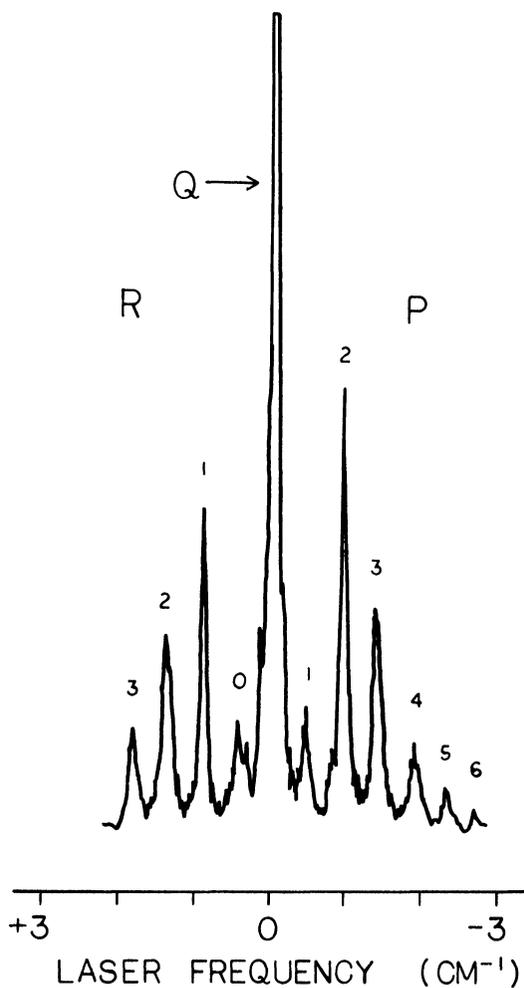


FIGURE 3 Rotationally resolved fluorescence excitation spectrum of the 0_0^0 band in Figure 1. Numbers denote the J'' values of the lower state.

DYNAMICS

What is the nature of this coupling, and how does it influence the dynamic behavior of the prepared state? What is the nature of the prepared state? Does it depend on the rotational level initially

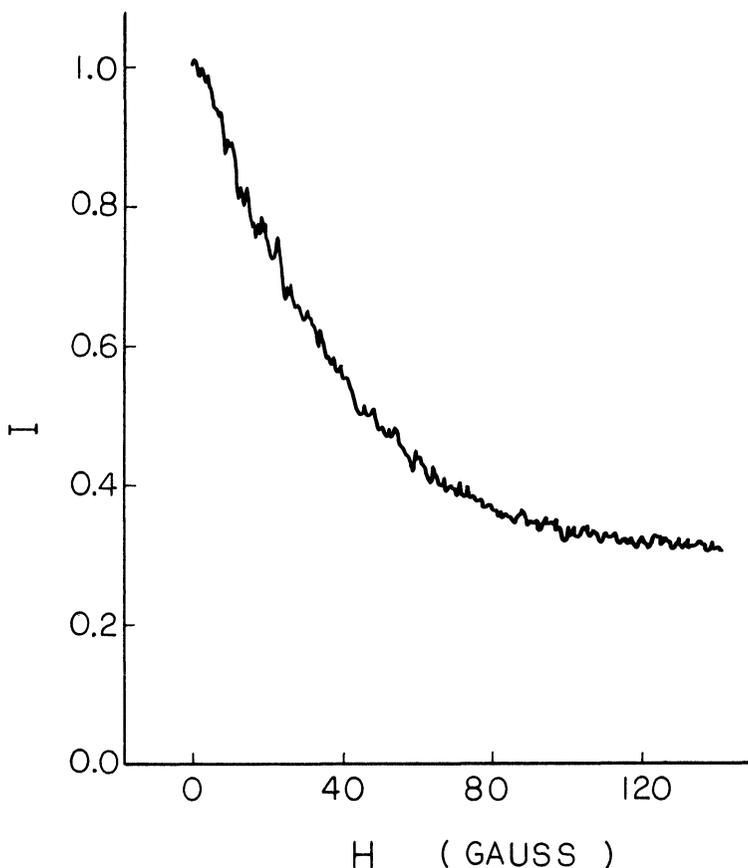


FIGURE 4 Fluorescence intensity of $^1B_{3u}$ pyrazine is a function of magnetic field. Excitation is in the Q branch of the 0_0^0 band, and detection is of the total fluorescence intensity with a $1 \mu\text{s}$ aperture duration on the boxcar integrator at zero delay.

excited? Is nuclear spin, as well as electron spin, important? And what role is played by small magnetic fields? To answer these questions, we probe the decay behavior of the excited state directly under a variety of conditions. Typically, this decay is biexponential in nature, as shown in Figure 5. Here, we excite in the Q branch of pyrazine- h_4 , and detect the emission as a function of time by scanning, slowly, the gate of the boxcar integrator with an aperture duration of 2 ns. A fit

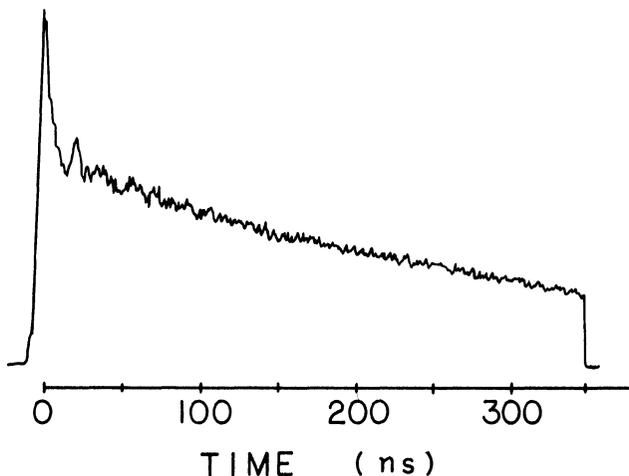


FIGURE 5 Decay of the fluorescence intensity of pyrazine- h_4 following excitation in the Q branch of the 0_0^0 band.

of this curve to a function of the form

$$I(t) = A^+ e^{-t/\tau^+} + A^- e^{-t/\tau^-} \quad (1)$$

gives lifetimes of ~ 5 and ~ 200 ns and a preexponential factor ratio, A^+/A^- , of ~ 1 . Nascent quantum beats are also observed under these conditions.

In the theory of the intermediate case, the time dependence of the fluorescence intensity is usually represented as a sum of coherent and incoherent terms, *viz.*

$$I(t) = 2 \sum_n \sum_m (C_n^s)^2 (C_m^s)^2 \exp[-1/2(\gamma_n + \gamma_m)t] \cos(E_n - E_m)t \\ + \sum_n (C_n^s)^4 \exp(-\gamma_n t) \quad (2)$$

Here, n and m denote *quasi*-stationary molecular eigenstates with energies E_n and E_m , widths γ_n and γ_m , and singlet amplitudes C_n^s and C_m^s . If the number of coupled states (N) is large (strong-coupling limit), then the “coherent” contribution to the decay (the $\sum_n \sum_m$ terms) should decay roughly exponentially on a time scale Δ^{-1} , where $\Delta = 2\pi v^2 \rho / t$ and v is the coupling matrix element; this is the “dephasing”

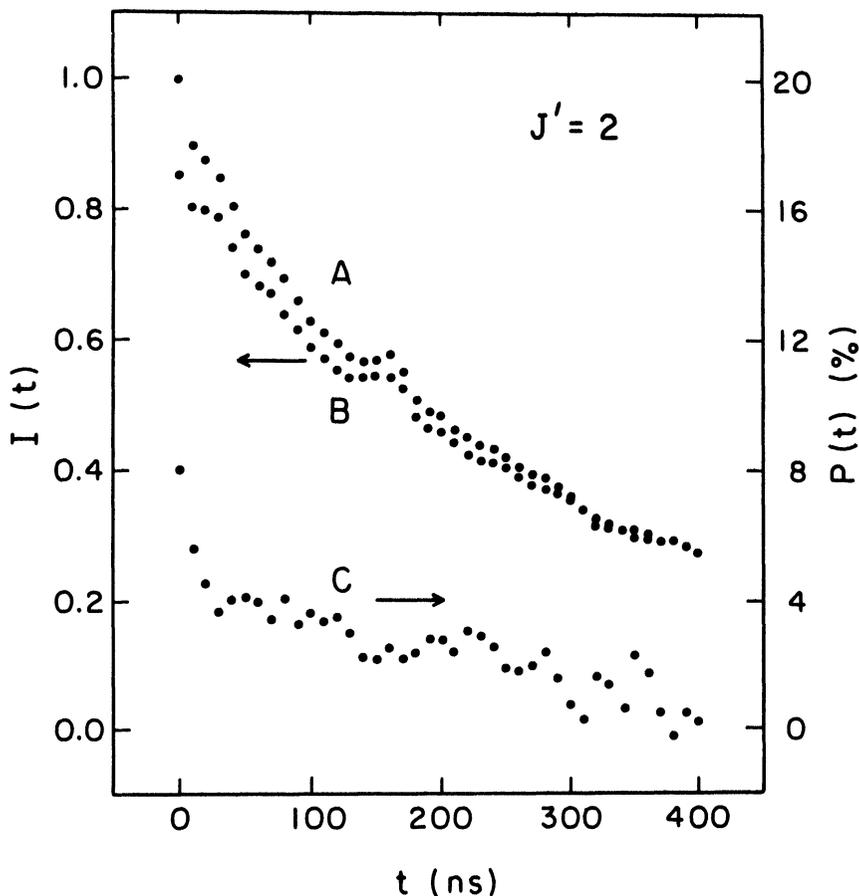


FIGURE 6 Time-resolved fluorescence decay of the $J' = 2$, zero-point vibrational level of $^1B_{3u}$ pyrazine following excitation with a ~ 5 ns linearly polarized light pulse. Curve A was obtained with the detection analyzer oriented to transmit parallel-polarized light (I_{\parallel}), curve B was obtained with the analyzer oriented to transmit perpendicularly-polarized light (I_{\perp}), and curve C is the degree of polarization, $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$.

time for the interfering $|n\rangle$ states which are spread out over an energy range Δ . At longer times $t \gg \Delta^{-1}$, the decay, with amplitude proportional to $1/N$, is governed by the incoherent terms $\exp(-\gamma_n t)$ characterized by the slower rates γ_n .

Polarization experiments

From what has been said so far, it would appear that pyrazine is, indeed, a classic example of the intermediate-case molecule. But, can we find other evidence to support this view? In particular, can we demonstrate that the fast component is, in fact, coherent? The answer is, yes, by measurements of the decay characteristics with simultaneous analysis of the polarization of the emitted light. In these experiments, we tuned the laser to a particular line in the P-or R-branch and used a Biomation 8100 transient recorder to improve the signal-to-noise, thus sacrificing the higher time resolution available from the boxcar integrator. Figure 6 illustrates the behavior observed during the first 400 nsec of the decay following excitation of the R1 line ($J' = 2$) with the linearly polarized laser pulse. Curve A was obtained with a polarization analyzer oriented to transmit parallel-polarized light (I_{\parallel}) and curve B was obtained with the analyzer oriented to transmit perpendicularly-polarized light (I_{\perp}). Each curve is a sum of 1000 scans, has been corrected for the small contribution (<1%) of scattered light, and is, as before, biexponential in character. The derived values of τ_+ and τ_- are the same in both curves. However, the contribution of the fast component, as measured by the A^+/A^- ratios, is significantly different. This is shown more clearly by curve C, a curve computed from A and B, which represents the time dependence of the degree of polarization,

$$P(t) = [I_{\parallel}(t) - I_{\perp}(t)]/[I_{\parallel}(t) + I_{\perp}(t)] \quad (3)$$

This curve demonstrates that the fluorescence is polarized, although the degree of polarization is small, and that the time profile of the depolarization curve is nonexponential in nature.

We believe the situation in Figure 6 is very reminiscent of a zero-field "level-crossing," previously observed in many atoms and small molecules⁵ but not, heretofore, in molecules the size of pyrazine. There, one prepares a coherent superposition of the magnetic sub-levels of that group of states which lies within the spectral width of the radiation field. This superposition corresponds to an orientation of molecules in the excited state which results, in the case of linearly-polarized excitation, in an alignment of the excited state magnetic moment along a fixed axis. The subsequent emission is then polarized along this axis. Although additional experiments are necessary to

completely specify the molecular eigenstates of pyrazine, J (representing the total angular momentum, including electron spin), and M (the projection of J onto a space-fixed axis) are both good quantum numbers. Thus, just as in the traditional level crossing experiment, two states, $|n, J', M + 1\rangle$ and $|m, J', M - 1\rangle$, can be excited coherently from the $|0, J'', M\rangle$ state due to the selection rule $\Delta M = \pm 1$. The resulting emissions from these states are left (σ^-) and right circularly polarized (σ^+) waves whose superposition will be linearly polarized.

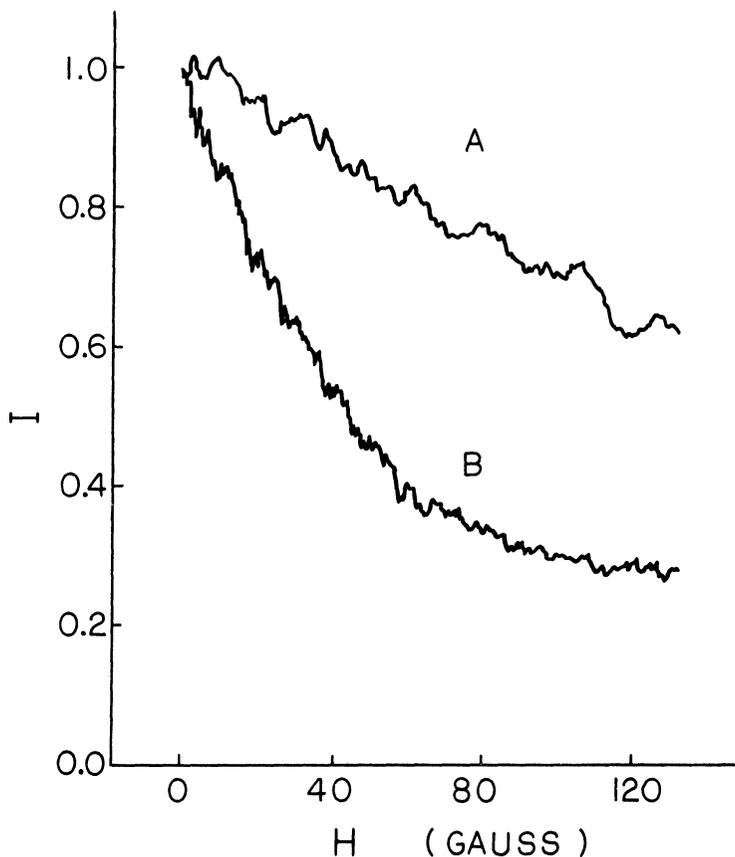


FIGURE 7 Fluorescence intensity of $^1B_{3u}$ pyrazine as a function of magnetic field. Excitation is in the Q branch of the 0_0^0 band. Curve A was obtained with a 2 ns aperture duration on the boxcar integrator at zero delay, and curve B was obtained with a $1 \mu\text{s}$ aperture at a delay of 100 ns.

The degrees of polarization expected from lines originating in $J' = 2$ and terminating in $J'' = 3, 2,$ and 1 are 14, $-64,$ and 45%, respectively.⁶ However, in our experiment we collect all of the emission from $J' = 2$, in accord with the selection rule $\Delta J = 0, \pm 1$, so it is not surprising that the residual polarization observed at $t = 0$ is small.

The interesting question is; what is the mechanism responsible for the depolarization in time? Molecular collisions can depolarize the emission, but we think the effect of collisions under our experimental conditions is negligible, especially at short times. We believe, instead, that the depolarization is caused by a dephasing of the molecular eigenstates. Recall that the application of an external magnetic field in a level-crossing situation introduces a frequency difference $\Delta\omega = 2g\beta H_z/\hbar$ between the $|J', M + 1\rangle$ and $|J', M - 1\rangle$ states. This frequency shift produces a phase shift of $\Delta\phi = 2g\beta H_z/\hbar$ between the σ^+ and σ^- components of the emitted light which, in turn, causes the plane of polarization to be rotated by an angle of $\theta = \Delta\phi/2 = g\beta H_z/\hbar$, so that the emission is depolarized. The most commonly known example of this effect is the magnetic depolarization of atomic resonance fluorescence, the so-called Hanle effect.⁷ However, similar effects might be expected even in zero-field if *nondegenerate* levels are excited coherently. This is clearly the case in pyrazine. Here, there exists a finite frequency difference $\Delta\omega_{nm} = (E_n - E_m)/\hbar$ between $|n, J', M\rangle$ and $|m, J', M\rangle$ states in the *absence* of a field, and the dephasing of these states, occurring at a frequency of the order of $\Delta\omega_{nm}$ (which, in turn, is directly related to the coherence width of the excitation source), causes a very fast depolarization of the fluorescence. A slower depolarization, associated with the dephasing of coherently prepared M states, might also be expected at longer times, yielding an overall decay which is nonexponential in nature.

Magnetic quenching. Coherent or incoherent?

Having demonstrated that the decay of S_1 pyrazine is at least partly coherent in nature, we next ask whether the magnetic quenching of the fluorescence is associated mainly with the coherent or the incoherent component. Again, this question can be answered simply; Figure 7 compares plots of the intensity vs. magnetic field obtained by monitoring, respectively, the fast and slow component by suitable positioning of the boxcar gate. Curve A was obtained sitting on the

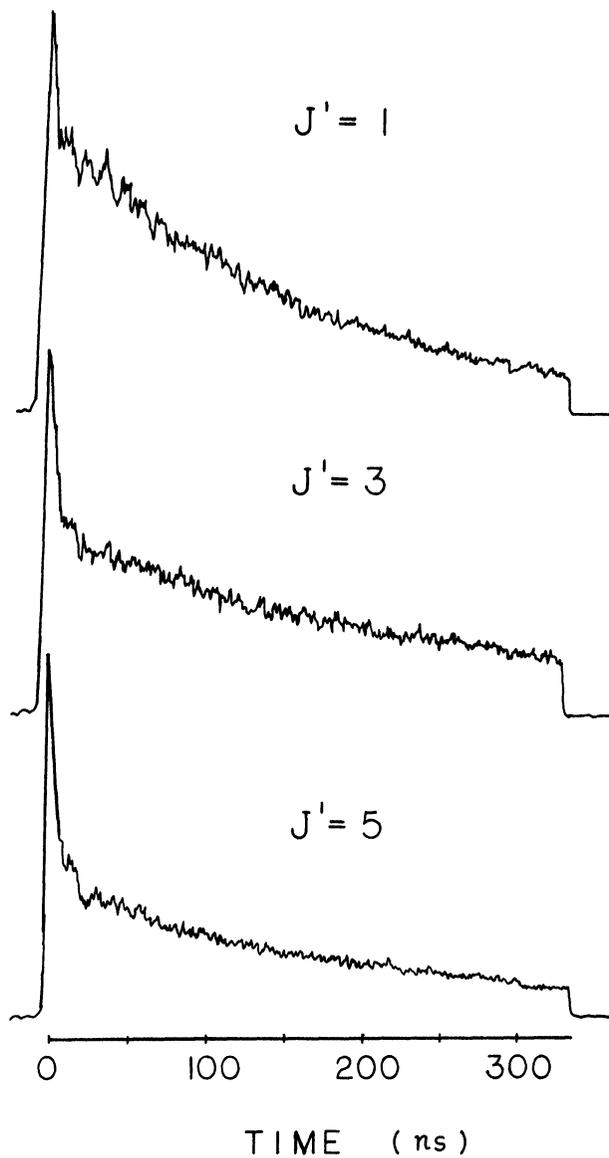


FIGURE 8 Rotational state dependence of the decay of ${}^1B_{3u}$ pyrazine. J' denotes the total angular momentum quantum number of the upper state.

peak of the decay curve, with an aperture duration of 2 ns; whereas curve B was obtained with a delay of 100 ns with respect to the peak, with a 1 μ s aperture duration. Clearly, it is the incoherent component which is more strongly quenched; theory would suggest, then, that the number of strongly coupled levels is markedly increased by the field.

J' -dependence

ter Horst, Pratt, and Kommandeur⁸ were the first to observe that the decay behavior of S_1 pyrazine is strongly dependent on the rotational quantum number of the upper state. Because of certain ambiguities in that work, we have repeated the experiments with some care, and show in Figure 8 some of our own results. We observe, as did ter Horst, *et al.*,⁸ a growing in of a short component as a function of J' . By fitting well over 150 curves of this type to Eq. (1), we have found, as shown in Figure 9, that the ratio of preexponential factors, A^+/A^- , increases approximately linearly with $2J'+1$ for $J'=1-7$. Similar results have been obtained by ter Horst, in more recent work,⁹ and by Saigusa and Lim,¹⁰ albeit under rather different conditions. We also find that a particular J' , whether prepared by excitation *via* R -branch transition from the level $J''=J'-1$ or by excitation *via* a P -branch transition from the level $J''=J'+1$, has the *same* A^+/A^- value. Finally, we note that neither τ_+ , nor τ_- , are J' -dependent within experimental error. These three results, taken together, give us some important clues about the origins of these effects.

First, theory suggests, in the strong coupling limit, that the slow component should decay with a rate which is given by

$$(\tau^-)^{-1} = \gamma_s/N + \gamma_t \quad (4)$$

Since N clearly increases with J' , whereas τ^- does not, we must have $\gamma_t \gg \gamma_s/N$; i.e., the incoherent decay rate is primarily determined by the triplet character of the prepared state. A triplet decay rate of $3.4 \times 10^6 \text{ s}^{-1}$ for pyrazine excited at the $S_1 \leftarrow S_0$ origin has been measured by Dietz, *et al.*,¹¹ in agreement with this conclusion. Second, from the fact that τ^+ is also independent of J' , it follows from the relations $(\tau^+)^{-1} \sim 2\pi c \Delta$ and $\Delta \sim 2\pi v^2 \rho$ that $v^2 \rho$ is not influenced by rotational excitation, assuming that we excite, in any given experiment, all of the singlet character associated with a particular J' . So

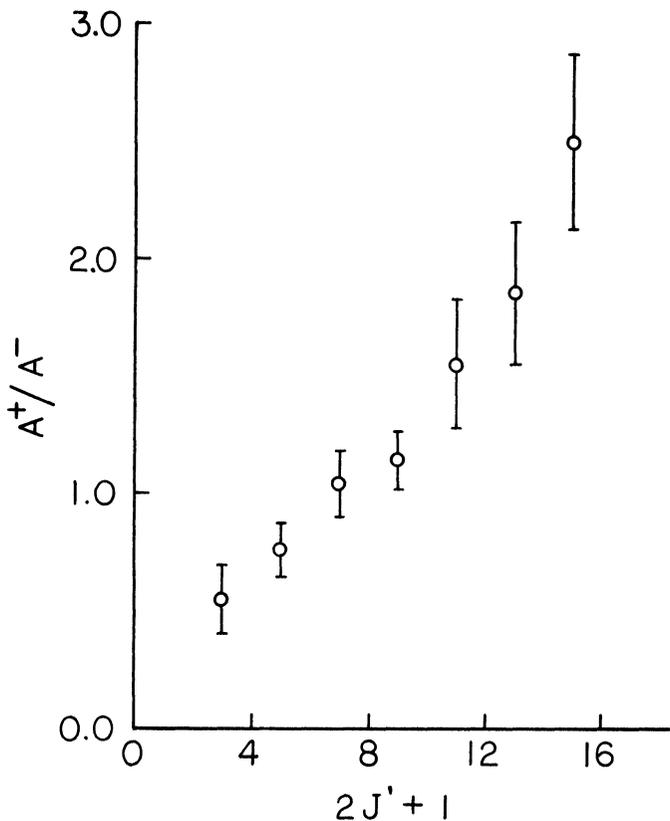


FIGURE 9 Plot of A^+/A^- as a function of $2J'+1$, as determined by computer fits of the rotationally resolved biexponential decay curves.

how can we explain the results in Figure 9? Very simply, or so it would seem. Recall that ρ is a measure of the vibronic level density in the triplet manifold, and takes no account of angular momentum selection rules. But for intersystem crossing, the total angular momentum J must be conserved, as well as its projection P on the top axis.¹² If we populate, in the zero-order description, a given singlet level having the quantum number $J_S (=N_S)$, then the *rotational* selection rule for ISC is $\Delta N = N_T - N_S = 0, \pm 1$. There are also selection rules on K , derived from the requirement that $\Delta P = 0$, but the fact that P - and R -branch excitations terminating in the same J' have the same

A^+/A^- values strongly suggests that K is not a good quantum number in ISC. Several factors may be responsible for this, including deviations from symmetric top behavior in the singlet state and a variety of non-rigid body couplings in the triplet state. Thus, all “ K ” states for a given N'_S of the singlet state can couple to all “ K ” states of a given $N'_T + 1$, N'_T , or $N'_T - 1$ state of the triplet. As the number of possible “ K ” states increases as $2J' + 1$, the number of coupled states also increases as $2J' + 1$, as observed. Positive proof that rotational angular momentum selection rules are involved in the ISC process has been provided by other experiments on isotopically labeled pyrazines,¹³ which show that the number of coupled states is proportional to $(2J' + 1)\rho/\sigma$, where σ is the number of irreducible representations to which the nuclear spin functions belong (the so-called symmetry number). Symmetry plays an important role in this problem because it restricts the number of states with which the initially prepared state can interact.

Magnetic field effects on the decay

Figure 10 shows a representative example of the effect of small magnetic fields on the decay behavior of “individual” rotational levels of S_1 pyrazine. Here, we excite a single line in the P or R branch and detect the transient response with a boxcar whose gate, of duration 2 ns, is swept slowly across the decay curve at different fields. We find that, just as with increasing J' (cf. Figure 8), there is an increase in the contribution of the fast component with increasing field but that neither τ_+ , nor τ_- , are influenced by the field. Plots of A^+/A^- vs. H for four selected J' values are shown in Figure 11. Clearly, the number of coupled states increases in a sigmoidal fashion with the field, reaching a plateau at fields on the order of 100 G. Similar effects have been observed by Felker, *et al.*¹⁴ using pulses of ~ 15 ps duration.

The data in Figure 11 provide rather convincing evidence for a quantum-mechanical mixing process. But what is the detailed nature of this process? It is known that triplet pyrazine, examined in a low temperature crystal by ODMR techniques, has fine-structure splittings of the order of 1 GHz.¹⁵ If this were also true of triplet pyrazine near the singlet origin, then we might anticipate that the effect of the field is to mix the three fine-structure components of each triplet rotational level *via* the electron Zeeman interaction, thereby increas-

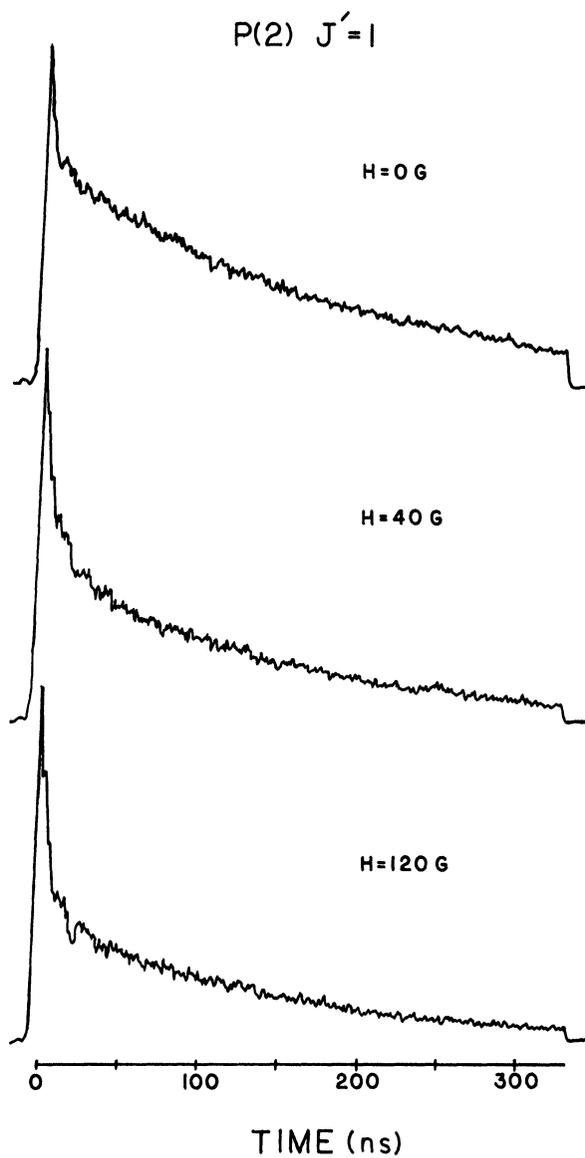


FIGURE 10 Magnetic field dependence of the decay of "single" rotational levels of $^1B_{3u}$ pyrazine.

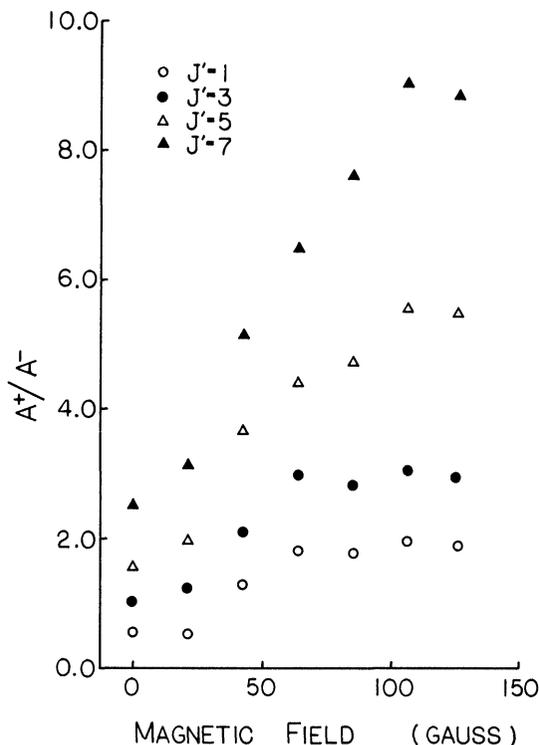


FIGURE 11 Plots of A^+/A^- as a function of magnetic field for selected rotational levels.

ing the number of coupled states by three, as only one of the components obeys the $\Delta J = 0$ selection rule in zero field. Some support for this idea comes from an examination of Figure 11 which shows that, for each J' , the ratio of the A^+/A^- value in "high" field to that in zero field is approximately three. Felker, *et al.*¹⁴ observed the same behavior and also interpreted their results as being due to fine-structure mixing.

One problem remains. This is that the fields required for mixing two states separated by 1 GHz should be much larger than those employed here, even for states with large (i.e., triplet) g values. One way to reduce these energy denominators would be to invoke the hyperfine interaction which, although second order in zero field, is

strong enough to couple the nuclear spins to the electron spins at low fields. Nuclear spin would then be decoupled from rotation, and the symmetry restrictions noted above could be relaxed, leading to an increase in the A^+/A^- values. A simple test of this idea was performed by preparing specifically deuterated pyrazines and examining their decay properties. Fortunately, the deuterium shifts in the excitation spectra are fairly large, as shown in Figure 12. Therefore, it is not necessary to prepare isotopically pure samples but only to excite, separately, the Q branches of the d_0 , d_1 , d_2 , d_3 , and d_4 species. Figure 13 shows the results obtained for the d_3 molecule at fields of 0 and 120 G. Comparison of the zero field curve with that in Figure 5 shows

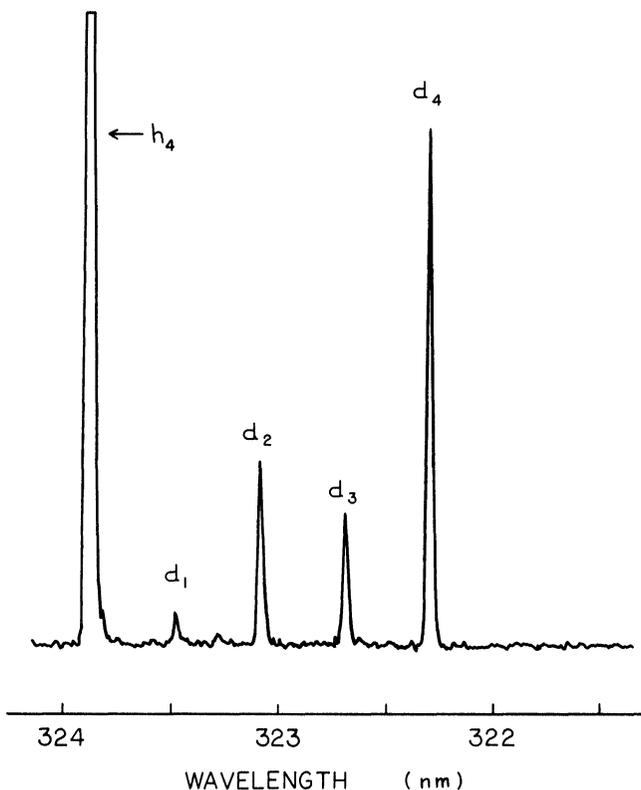


FIGURE 12 Fluorescence excitation spectrum of $^1B_{3u}$ pyrazine- h_4 , $-dh_3$, $-d_2h_2$, $-d_3h$, and $-d_4$ in the vicinity of the 0_0^0 band.

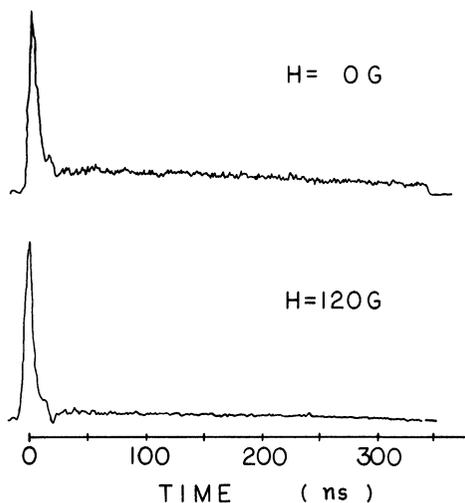


FIGURE 13 Magnetic field dependence of the decay of pyrazine- d_3h . Excitation is in the Q branch of the 0_0^0 band.

that deuterium substitution produces the expected increase in the number of coupled states. But the d_3 molecule also shows a marked magnetic field effect; A^+/A^- is again increased by about three on going from 0 to 120 G. This would not be the case if rotational levels of different symmetry in zero field were being mixed, because the d_3 molecule has a symmetry number of one. All isotopically labeled molecules behave in much the same fashion.

We are left with only one alternative. This is that, in fact, the fine-structure components *are* separated by much less than 1 GHz in the vicinity of the singlet origin, and are, indeed, strongly mixed by fields of the order of 100 G, as originally suggested by Zewail and co-workers.¹⁴ An average separation of the order of 100 MHz in zero field would be required to explain the observations. Is this reasonable? The answer is, gratifyingly, yes. Evidence supporting this view comes from three different sources. First, as already noted, more refined density of state calculations, taking rotations and nuclear spin into account, suggest that $(2J'+1)\rho/\sigma \sim 100/\text{cm}^{-1}$ near the singlet origin.^{4,16} Second, as discussed elsewhere in these Proceedings, Kommandeur and co-workers¹⁶ have recently obtained ultra high-

resolution excitation spectra which reveal, for the first time, that each of the *P*- and *R*-branch lines in Figure 3 in fact consists of a number of components. The average spacing of these presumed molecular eigenstates is about 100 MHz. But it remains to show that turning on a small field increases the number of these states by a factor of three; i.e., that it *is* the fine-structure components which are mixed by the field. Since we do not have access to a narrow-band cw laser, we have taken a different approach. Recall from Herzberg that the $J=0$ angular momentum state of a Hund's case (b) molecule with $S \neq 0$ is not split by the fine-structure interaction.¹⁷ An analogous

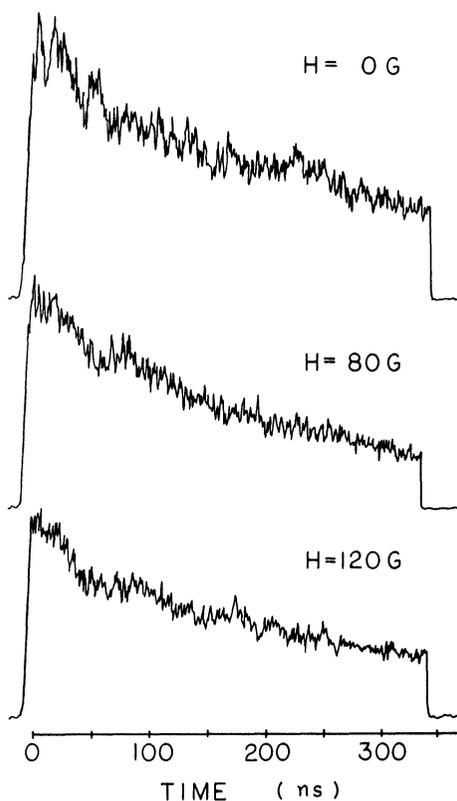


FIGURE 14 Magnetic field dependence of the decay of the $J'=0$ level of $^1B_{3u}$ pyrazine- h_4 .

situation should exist for the molecular eigenstates of pyrazine even though N and S may not be well defined. That is, there is only one way that “ N ” and “ S ” can be combined to produced $J = 0$, whereas there are three ways for all other J . Therefore, if we excite the $P1$ line of pyrazine (i.e., $J' = 0$), we expect no magnetic field effect if the role of the field is to mix the equivalent of the fine-structure components of the true molecular eigenstates. This is exactly what is observed, as shown in Figure 14. Not only does the $J' = 0$ decay not have a fast component in zero field, but also there is no growing in of a fast component at higher fields, unlike all other J' . We therefore conclude that the levels mixed by the field in the latter cases are the three fine-structure components of each J' ($J' \neq 0$), components whose average separation is much less than that of the “pure” triplet. We thus have an explanation for the remarkable influence of small magnetic fields on the static and dynamic properties of “ S_1 ” pyrazine. The fact that the level spacing in the vicinity of the singlet origin is very much less than that predicted by the zero order picture may also have profound implications for other types of radiationless processes.

SUMMARY

By performing time-resolved measurements of the fluorescence intensity of “ S_1 ” pyrazine under collision-free conditions, we have shown that the decay of the initially prepared state is both coherent and incoherent in nature, placing the molecule solidly in the category of the intermediate case of the theory of radiationless transitions. Indeed, most of the predictions of the theory are verified experimentally, provided the underlying assumptions are carefully stated and proper account is taken of the appropriate angular momentum selection rules. Our experiments in the presence of small magnetic fields have shown that the coupled state is triplet in origin, and thus that the nonradiative process we are monitoring is intersystem crossing. For such a process, $\Delta J = 0$; thus, the number of coupled states is strongly dependent on the rotational state which is initially excited. At low J' , we approach the weak-coupling limit whereas at high J' , we approach the strong-coupling limit, especially for deuterated molecules. The triplet character of the prepared state plays the dominant role in determining the decay rate of the slow, or incoherent,

component. Because of symmetry selection rules, nuclear spin is conserved in intersystem crossing.

Magnetic field experiments have also shown that the levels mixed by the field are the fine-structure components associated with each J' , except for $J' = 0$. However, because the fields required to mix these levels are much smaller than the frequency separations in the coupled but *separate* manifolds of the singlet and triplet states, we are led inescapably to the conclusion that the true molecular eigenstates in the vicinity of the S_1 origin of pyrazine are mixed "ST" states with very small (e.g., 100 MHz) energy differences. Supporting evidence for this conclusion has recently been provided by the experiments of Kommandeur, *et al.*¹⁶

To paraphrase G. N. Lewis,¹⁸ it is no longer necessary to assume, as did Tramer and co-workers,² the existence of these mixed states. Molecular eigenstates are real, and their properties can be measured. But, in order to obtain the maximum possible information about these states, it is necessary to use light sources with very small coherence widths. Narrow band, single frequency, doubled dye lasers with high UV outputs are one possibility, but so also are coherent microwave and radiofrequency sources for which the Doppler broadening problems in the gas phase will be much less severe. We hope, in the next few months, to be addressing some of these problems in our laboratories. If we can succeed in preparing a single, or a small group of these states, then we can test a number of other features of the theory, such as the assumption that there is only one off-diagonal matrix element, and that there is a uniform density of triplet levels. We can also determine whether a single molecular eigenstate shows any dynamic behavior at all, and, at the other end of the scale, probe the origins of chaos in quantum mechanical systems. Thus, a number of challenges remain for the experimentalist who seeks a "grand unified theory" of the radiationless process.

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