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Rotational and vibrational state dependence on intramolecular coupling and dynamics in the S_1 state of pyrazine

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In this paper we report on the absolute fluorescence quantum yields, Y , from photoselected rotational and vibrational states within the S_1 manifold of pyrazine cooled in planar, pulsed, supersonic expansions of Ar. The Y data from the S_1 origin exhibit 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 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 a possible saturation at $E_v = 1300-1800 \text{ cm}^{-1}$. The low absolute Y values can be attributed to intramolecular nonradiative decay of S_1-T molecular eigenstates. The marked rotational state dependence of Y from the S_1 origin can be interpreted in terms of the intermediate level structure (ILS) provided that the dilution factor is $N_{\text{eff}} = 16(2J' + 1)$ for $J' = 5-22$. This N_{eff} exhibits a qualitatively different J' dependence than the number of effectively coupled states originating from a single $J'K'$ doorway state $N(\text{spectroscopic}) = 12-15$ for $J' = 0-3$, which was inferred by Kommandeur *et al.* [Chem. Phys. Lett. **92**, 565 (1980)] from high resolution spectroscopic studies. In order to reconcile our Y data, together with the available psec time-resolved data and the spectroscopic information in terms of the ILS model, one has to assert that the range $J' = 3-5$ marks a crossover from J' independent to J' dependent N_{eff} .

I. PROLOGUE

The theory of intramolecular, interstate, radiationless transitions¹⁻⁴ provides a general framework for the elucidation of the diverse features of the decay of electronically vibrationally excited states of large molecules. The $S_1(^1B_{3u})$ state of the pyrazine molecule,⁵ for which extensive time-resolved and energy-resolved information became available recently,⁶⁻²⁴ serves as a touchstone for a critical scrutiny of the theory of radiationless transitions. Following the pioneering work of Tramer *et al.*^{5,25} conventional wisdom has attributed intramolecular dynamics in this system to the intermediate level structure (ILS)^{3,25-27} on the basis of the following evidence.

(1) Spectroscopic resolution of the molecular eigenstates (MEs). The high-resolution spectra of Kommandeur and colleagues⁷⁻¹⁰ have provided central information on interstate S_1-T coupling by resolving bunches of MEs, each having a parentage in a J' rotational member of the $S_1(0-0)$ origin. The total number, $N(\text{expt})$, of spectroscopically observed MEs was attributed to incoherently superimposed distinct K' transitions for each J' . The number $N(\text{spectroscopic})$ of effectively coupled states originating from a single $J'K'$ doorway state is then^{9,10} $N(\text{spectroscopic}) = N(\text{expt})/(2J' \pm 1)$, which assumes the values

$$N(\text{spectroscopic}) = 12-15 \quad \text{for } J' = 0-3. \quad (1.1)$$

The energetic spread of the MEs ($\delta = 3-4 \text{ GHz}$) and their number, Eq. (1.1), was found to be approximately independent of J' in the range $0-3$. For $J' = 0, K' = 0$, the value of N/δ is consistent with the vibrational density of states.^{9,10}

(2) The dependence of the time-resolved pattern from $^1B_{3u}(v' = 0, J' = 0, K' = 0)$ on the optical excitation mode.⁸⁻¹³ The time-resolved decay from the bunch of MEs originating from the vibrationless $J' = 0, K' = 0$ state ex-

hibits a long decay component ($\tau_- \simeq 400 \text{ ns}$) with quantum beats.^{11,13} The temporal quantum beat pattern reveals a marked dependence on the (ns or ps) excitation mode, which is in quantitative agreement with the corresponding energy-resolved MEs spectrum.⁹

(3) Biexponential time-resolved decay for $J' > 0$ members of the $^1B_{3u}$ origin.^{5,6,8,12,15-17,20-24} A bimodel temporal decay of the $^1B_{3u}(v' = 0, J' > 0)$ bunches coherently excited by a ps laser is characterized by a short lifetime of $\tau_+ = 100-120 \text{ ps}$ ²⁰⁻²⁴ and by a long time $\tau_- \simeq 400 \text{ ns}$,^{8-10,12,13,15-17,20} both of which are independent of J' in the range $J' = 1-10$. The amplitude ratio, A_+/A_- for the short and long components under ps excitation exhibits a linear J' dependence, i.e.,

$$A_+/A_- = \alpha(2J' + 1) \quad (1.2)$$

with $\alpha \simeq 0.3-1.3$.^{12,20,22,24} Similar behavior was recorded for the decay pattern of $v' = 0, J' > 0$ states under ns laser excitation with lower values of $\alpha \simeq 0.15-0.3$.^{6,8,15-17}

Are these observations compatible with the standard theory^{3,25-27} for ILS? Observations (1) and (2) provide overwhelming evidence for the assignment of the MEs, which originate from the $S_1(v' = 0, J' = 0, K' = 0)$ state to the small molecule limit or rather the "few-level" case of the ILS, i.e., a sparse "diluted" manifold of MEs, whose energetic spread is lower than or comparable to the coherence width of the available ps or ns lasers, but the total number of MEs is too low to warrant dephasing under coherent excitation conditions. On the other hand, the wealth of experimental information on bunches of MEs originating from $J' > 0$ states is internally inconsistent. While energy-resolved spectroscopic data [observation (1)] indicate that the bunches of MEs originating from each of the $J' > 0$ states correspond to the small molecule limit, the time-resolved information [obser-

vation (3)] indicates that these MEs correspond to the ILS. To be more specific, we raise the following issues:

(A) The mystery of the “missing states.” Provided that observation (3) is taken as evidence for the temporal decay of a coherently excited ILS under ps excitation conditions, the dilution factor N for $S_1(v' = 0, J' > 0, K')$ - T mixing extracted from the A_+/A_- data^{12,22} is proportional to $(2J' + 1)$, which is in accord with Rice's notion of the breakdown of K selection rules for S_1 - T mixing.²⁰ This result seems to be incompatible with relation (1) for the energy-resolved data.

(B) The origin of the short-decay component under ps excitation conditions. The observation of the $\tau_+ = 120$ ps short-decay component for $J' > 0$ MEs induced by ps excitation is incompatible with the low value of N (spectroscopic), Eq. (1.1), which would imply the exclusive appearance of a long-decay component with superimposed quantum beats.²⁸

(C) The “hidden” energetic distribution. The short-decay lifetime $\tau_+ = 120$ ps implies the existence of an energetic distribution with a width of $\Delta \approx 3$ GHz, which seems to be absent in Kommandeur's MEs spectra,^{9,10,28} although the value of Δ is close to the spread of the bunches of the MEs for $J' = 0-3$.^{9,10}

(D) The nature of the short-decay component under ns excitation conditions. The existence of a short time-resolved decay component under ns excitation conditions is incompatible with the level structure, in view of the 3.5 GHz energetic spread of the MEs. Thus, a coherent excitation of the level structure cannot be accomplished by ns excitation, so that the A_+/A_- ratio obtained under these conditions cannot be attributed to dephasing of the entire S_1 - T mixed MEs manifold and cannot infer the total number of the diluted MEs.

(E) The surprisingly low fluorescence quantum yields. The fluorescence quantum yield $Y \approx 2.8 \times 10^{-3}$ for the electronic origin of S_1 at 300 K⁵ implies a very high value of the dilution factor, N , within the framework of the conventional ILS scheme.^{3,25,26} The pure radiative lifetime of the S_1 state, as inferred from the integrated oscillator strength, is $(\gamma_s^{\text{rad}})^{-1} = 200$ ns.^{10,28} This value together with the experimental (J' independent) decay lifetime of the MEs $(\gamma_{\text{ME}})^{-1} = 400$ ns^{8,9,12,15,16} results in the quantum yield $\gamma_s^{\text{rad}}/N\gamma_{\text{ME}}$, so that $N \approx 10^3$ at 300 K. This value of N exceeds N (spectroscopic), Eq. (1.1), by about two orders of magnitude.

An important energy-resolved observable, which may elucidate the nature of interstate coupling and dynamics involves quantum yield data. In this context, Tramer *et al.*⁵ obtained absolute fluorescence quantum yields from the electronic origin and from excited vibronic levels of S_1 , while Baba *et al.*¹⁸ measured relative fluorescence quantum yields from the S_1 origin at room temperature. We wish to report absolute fluorescence quantum yields, Y , from the photoselected rotational and vibrational levels within the S_1 electronic manifold of jet-cooled pyrazine. We were able to establish the rotational state dependence of Y within the S_1 electronic origin and the vibrational state dependence of Y for excess vibrational energies $E_v = 0-1800$ cm⁻¹ above the origin. The absolute quantum yield data, which exhibit strong rotational state dependence, provide novel informa-

tion concerning rotational state dependence of the intramolecular interstate and intrastate coupling and dynamics. The information emerging from the energy-resolved quantum yield data is quite unique as it cannot be extracted from the time-resolved decay lifetimes, which are practically independent of the rotational state.^{8,12,15,16,20-22,28}

II. EXPERIMENTAL

Our experimental techniques²⁹⁻³¹ for the measurement of absolute fluorescence quantum yields were extended to allow for a better spectral resolution. Absorption spectra and fluorescence excitation spectra of pyrazine cooled in planar supersonic expansions were simultaneously determined using a pulsed xenon lamp and a monochromator. Pulsed planar jets were generated by expansion of seeded Ar through a nozzle slit. Two nozzle slits were used in these experiments having the dimensions of 0.22×33 and 0.27×90 mm. The repetition rates of both nozzles were 6 Hz and the width of gas pulses was 300 μ s. Pyrazine was heated in the nozzle chamber to 40 °C and mixed with Ar at the stagnation pressure of $p = 30-100$ Torr. Light from a pulsed simmered Xe flashbulb (pulse duration 24 μ s) was passed through a 0.75 m Spex monochromator equipped with a 2400 lines/mm grating. The spectral resolution was 0.11 Å for 15 μ slits. The light emerging from the monochromator focused onto the jet parallel to the slit at a distance of $x = 10$ mm from it. The light beam was split by a sapphire window and monitored by two vacuum photodiodes. The attenuation ΔI of the light beam due to absorption was determined from the difference in the light intensity before and after crossing the planar jet. The lamp-induced fluorescence (LMIF) intensity I_F was monitored by a photomultiplier. The absorption signal $\Delta I/I_0$ and the LMIF signal I_F/I_0 were normalized to the incident light intensity I_0 . The relative quantum yield, q , is given by $q = I_F/\Delta I$. The q values across the ${}^1B_{3u}(0-0)$ rotational contour were obtained from the simultaneous scans of fluorescence and absorption and normalized relative to the peak of the Q rotational band. q values from different vibronic levels and measured at the Q rotational bands were determined, as previously described,²⁹⁻³¹ and were normalized to the fluorescence quantum yield at the peak of the Q band of the ${}^1B_{3u}(0-0)$ origin. The role of collisions was studied by varying both the stagnation pressure of the Ar gas and the pyrazine concentration by changing the nozzle temperature. Absolute quantum yields³¹ for the peak of the ${}^1B_{3u}(0-0)$ Q band were obtained by measuring the q values from the S_1 origins of pyrazine and of 4-chloro-*trans*-stilbene in an expansion containing both molecules. The quantum yield from the S_1 origin of the reference molecule was taken to be 0.65.³¹ In this manner, the q scale of pyrazine was calibrated to give the absolute fluorescence quantum yields, Y , from photoselected rotational and vibrational states.

III. RESULTS

Figure 1 shows the LMIF spectrum together with the absorption spectrum of pyrazine in the region 3000–3252 Å. The most prominent spectral feature involves the S_1 origin at 3237 Å. The absorption spectrum and the LMIF spectrum for the rotational contour of the electronic origin, which

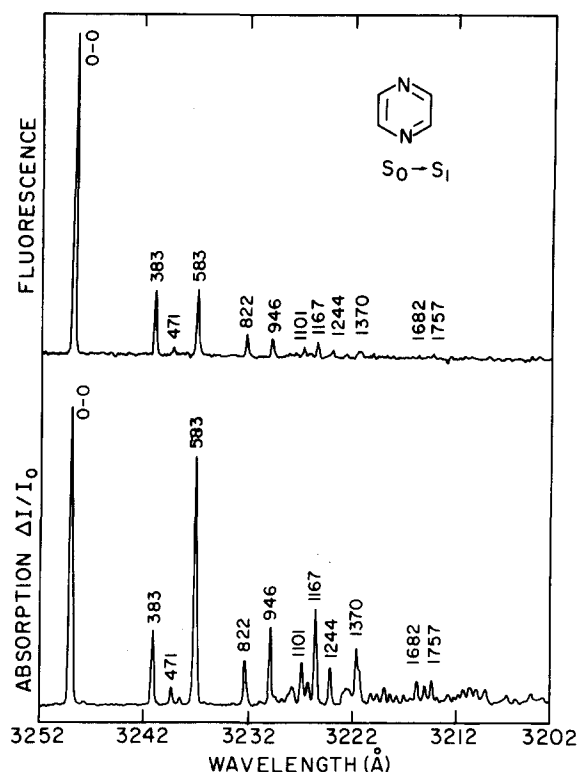


FIG. 1. Fluorescence excitation (upper spectrum) and absorption (lower spectrum) of pyrazine over the range 3252–3202 Å in pulsed planar jets of Ar. Pyrazine was heated in the nozzle chamber to 40 °C seeded into Ar at the stagnation pressure $p = 105$ Torr and expanded through a 0.27×90 mm nozzle slit. The light from the monochromator (spectral resolution 0.25 Å) crossed the planar jet at $x = 10$ mm from the nozzle.

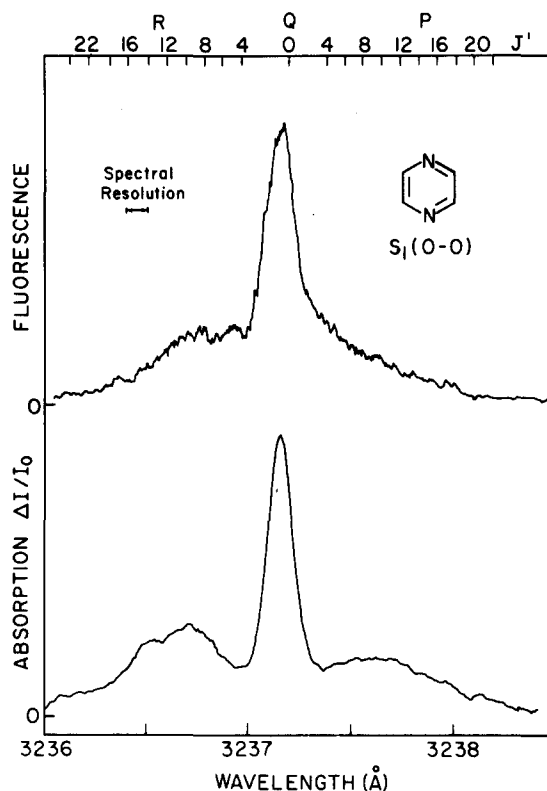


FIG. 2. Fluorescence excitation (upper spectrum) and absorption (lower spectrum) of the electronic origin of jet-cooled pyrazine (rotational temperature $T_R \sim 30$ K) in the range 3236–3238 Å. Experimental conditions as in Fig. 1. Spectral resolution is 0.11 Å.

were simultaneously obtained under medium spectral resolution (1 cm^{-1}), are portrayed in Fig. 2. The P branch of the rotational contour peaks at $J' \approx 8$ which, together with the rotational constants,³² results in the rotational temperature of $T_R = 30$ K for pyrazine in the planar jet. Similar rotational temperatures were obtained from the analysis of the rotational contours of aniline, anthracene, and tetracene under similar expansion conditions through the same nozzle slits.³³ A cursory examination of the LMIF and absorption data in Fig. 2 reveals a marked dependence of q on the rotational state. The relative quantum yields obtained were calibrated to the absolute value $Y \approx 7.3 \times 10^{-3}$, which was independently measured for the peak of the Q branch. The energy dependence of the Y values for the rotational contour of the electronic origin is presented in Fig. 3. The absolute accuracy of these quantum yield data is $\pm 25\%$, while the precision is $\pm 10\%$. We have devoted some attention to collisional effects on the quantum yields from the electronic origin. These quantum yields were found to be independent on the stagnation pressure of Ar in the range $p = 30$ –60 Torr, indicating that the role of Ar–pyrazine collisions is negligible. An effect of pyrazine (S_1) + pyrazine(S_0) collisions, somewhat diminishing the rotational state dependence of the quantum yield, was exhibited at a higher pressure of pyrazine, i.e., at nozzle temperatures exceeding 40 °C.

The Y values for the S_1 origin at $T_R = 30$ K (Fig. 4) exhibit a minimum in the vicinity of the peak of the Q

branch, in marked contrast to the sharp peak for the relative quantum yields at the same energy reported by Baba *et al.*¹⁸ for this molecule at 300 K. It is possible to reconcile this difference between the present results and Baba's data in terms of the different rotational temperatures employed in the two experiments.

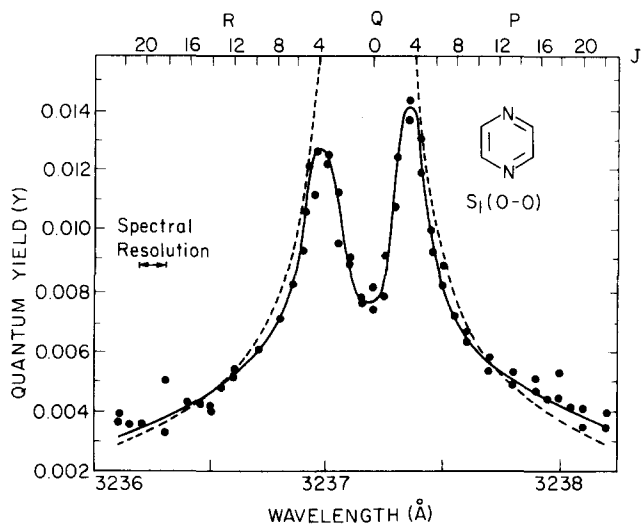


FIG. 3. Absolute fluorescence quantum yields (full dots) from the S_1 origin of jet-cooled pyrazine ($T_R \sim 30$ K) at a spectral resolution of 0.11 Å. The J' values for the P and R branches are marked on the top of the figure. The full curve was drawn for the sake of a visual representation of the data. The dashed curves correspond to the empirical relation $Y = 0.124/(2J' + 1)$.

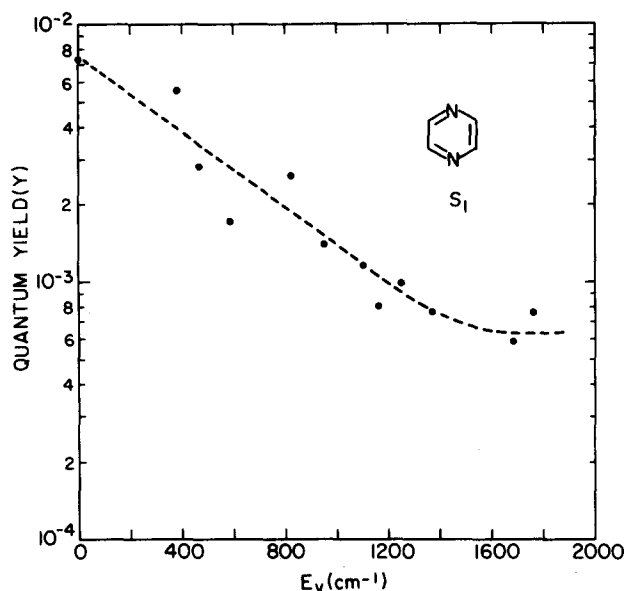


FIG. 4. Absolute fluorescence quantum yields from photoselected vibrational states of pyrazine in the range $E_v = 0$ –1800 cm^{-1} . Quantum yields were obtained at 2.5 cm^{-1} resolution at the Q bands of the vibronic transitions. The dashed curve was drawn for the sake of a visual presentation of the experimental data.

The absolute fluorescence quantum yield data from the rotational contour of the electronic origin (Fig. 3) reveal the following features:

- (1) Low Y values, which fall in the range $Y = 1.4 \times 10^{-2}$ for $J' = 4$ to $Y \simeq 2 \times 10^{-3}$ for $J' = 22$ were observed.
- (2) The Y values exhibit a marked J' dependence, decreasing monotonically with increasing J' .
- (3) The J' dependence of Y can be fitted quantitatively by the empirical relation

$$Y = 0.124 / (2J' + 1) \quad \text{for } J' = 5\text{--}22 \quad (3.1)$$

or, alternatively, by the relation $Y = 0.062/J'$ for $J' = 5\text{--}22$. These empirical relations are well obeyed for both the R and the P branches. We would also like to point out that the minimum in the Y curve in the vicinity of the peak of the Q branch at 30 K (Fig. 3) can be attributed to the thermal population of higher J states, which contribute to the reduction of the quantum yield. This dip in the Y values around the Q branch can quantitatively be accounted for³⁴ in terms of relation (3.1). Finally, we note that the J' dependence of the quantum yields at $J' > 5$ recorded by us is in agreement with Baba's analysis¹⁹ of his recent relative quantum yield data¹⁸ which, after a correction for an identified background absorption, reveal a qualitative rotational state dependence in accord with Eq. (3.1).

We now turn to the vibrational state dependence of the absolute fluorescence quantum yields from the S_1 manifold. Figure 4 portrays the dependence of Y on the excess vibrational energy E_v in the range $E_v = 0$ –1800 cm^{-1} . These quantum yields were measured at low resolution (2.5 cm^{-1}) at the Q bands of the corresponding vibronic transitions. Three features are revealed by these Y data.

- (4) Y exhibits an apparent exponential decrease with increasing E_v (Fig. 4) with a possible saturation at $E_v > 1300 \text{ cm}^{-1}$.

- (5) Our value of $Y = 7.3 \times 10^{-3}$ at the peak of the Q branch of the electronic origin at $T_R = 30 \text{ K}$ is higher than the room temperature quantum yield $Y = 2.8 \times 10^{-3}$ reported by Tramer *et al.*⁵

- (6) The discrepancy between the jet cooled and room temperature⁵ Y data is diminished at high E_v , e.g., at $E_v = 1757 \text{ cm}^{-1}$, $Y = 8.8 \times 10^{-4}$ at 30 K, while $Y = 10^{-3}$ at 300 K.⁵ These two values are identical within experimental uncertainty.

IV. ANALYSIS

The quantum yields from a sparse level structure, e.g., the small molecule limit, or the intermediate level structure is expected to depend on the excitation mode.³ When the molecule is excited by a "chaotic" light source, where the diffusion rate for phase fluctuations³⁴ exceeds the energetic span of the MEs, the quantum yield is identical to that obtained under coherent excitation conditions.³⁵ The Xe lamp employed in the present experiments can be described reasonably well in terms of such a "chaotic" light source, so that the quantum yields reported herein essentially correspond to those obtained under coherent excitation conditions.

The most striking features of our quantum yield data from the S_1 origin pertain to the low absolute Y values ($Y = 1.4 \times 10^{-2}$ – 2×10^{-3}) and their J' dependence. These low values of Y point towards the existence of an effective intramolecular decay channel, which can involve either $S_1 \rightarrow T$ intersystem crossing or, alternatively, internal conversion to the ground state. The energy gap between the electronic origins of S_1 and T is 4056 cm^{-1} ,²⁰ whereupon the vibrational density of triplet states in the vicinity of the electronic origin²⁰ is $\rho_v \simeq 100 \text{ cm}^{-1}$, which is in accord with Kommandeur's counting^{9,10,28} of MEs for $J' = 0$, $K' = 0$. It appears that in this energy range the triplet manifold is too sparse to provide an effective quasicontinuum for intramolecular relaxation. Accordingly, the low absolute quantum yields imply that the major photophysical decay channel for the S_1 origin, as well as for higher vibronic levels, involves intramolecular relaxation to S_0 . This interstate relaxation, which is described in terms of zero-order states, may involve either (i) direct $S_1 \rightarrow (S_0)$ internal conversion, or (ii) $S_1 \rightarrow T \rightarrow (S_0)$ relaxation mediated by the (sparse) triplet manifold. The J' dependence of Y implies the rotational state dependence of either the direct process (i) or the mediated process (ii). As the interstate relaxation occurs from $S_1 + T$ mixed MEs, the issue at hand is whether the nonradiative relaxation of an ME originates either from its singlet (S_1) or from the triplet (T) component. In view of the invariance of the experimental decay lifetimes $(\gamma_{ME})^{-1}$ for distinct MEs,^{9,10,28} and their magnetic field independence,¹⁷ it appears that $(\gamma_{ME})^{-1}$ is independent of the S_1 weight of the particular ME. Accordingly, the mediated mechanism (ii) should be preferred for the description of the nonradiative decay of the individual MEs.

A. Rotational state dependence

The description of the absolute quantum yields in terms of the intermediate level structure (ILS) model specifically implies that

- (1) MEs originate from S_1 - T coupling.
- (2) Interstate relaxation of S_1 to S_0 is mediated by $S_1 \leftrightarrow T$ coupling. The $(S_1 + T)$ MEs decay to S_0 .
- (3) The decay of the $(S_1 + T)$ MEs to S_0 is dominated by their triplet component.

The conventional theory for the intermediate level structure^{3,25-27} (ILS) predicts that the quantum yield under chaotic excitation conditions is given by

$$Y = Y_+ + Y_-, \quad (4.1)$$

where Y_- is the contribution of direct decay, which is

$$Y_- = \gamma_s^{\text{rad}} / \gamma_{\text{ME}} N_{\text{eff}} \quad (4.2)$$

and where γ_s^{rad} is the singlet pure radiative width. γ_{ME} is the decay width of each of the MEs which, on the basis of experimental lifetime data,^{6,8,12,13,15-17,20,22,28} is taken to be identical for all the MEs. Finally, N_{eff} is the effective dilution factor, which is discussed in Appendix A and given by Eq. (A13). The contribution from dephasing Y_+ is

$$Y_+ = \frac{\gamma_s^{\text{rad}}}{\Delta + \gamma_s^{\text{rad}}} \quad (4.3)$$

with $\Delta = 2\pi\langle v^2\rho\rangle$ which, on the basis of experimental evidence, is taken as $\Delta = (\tau_+)^{-1}$, being independent of J' . Taking $\Delta = (0.12 \text{ ns})^{-1}$, $\gamma_{\text{ME}} = (400 \text{ ns})^{-1}$, $\gamma_s^{\text{rad}}/\Delta = 6 \times 10^{-4}$, then Eq. (4.1) gives $Y_- = 2/N_{\text{eff}}$. The quantum yields now assume the explicit form

$$Y = 6 \times 10^{-4} + 2/N_{\text{eff}}. \quad (4.4)$$

The contribution of Y_+ is expected to be negligible for $N_{\text{eff}} < 10^2$, so that for the electronic origin of the jet-cooled molecule we can set

$$Y \simeq 2/N_{\text{eff}}. \quad (4.5)$$

The quantum yield data for the electronic origin are not expected to provide information on the dephasing component. Furthermore, from the analysis of the Y data, one cannot infer whether the short component exists for the time-resolved decay of photoselected J' states at the origin. The information emerging from the Y data solely pertains to the decay of the individual MEs. Equation (4.1) is consistent with the experimental rotational state dependence of Y [Eq. (3.1)], provided that

$$N_{\text{eff}} = N_0(2J' + 1) \quad \text{with} \quad N_0 = 16 \quad \text{for} \quad J' = 5-22. \quad (4.6)$$

Our experimental quantum yield data are applicable only for high values of J' ($= 5-22$). For low J' values deviations from relation (4.4) will presumably be exhibited. Utilizing the spectroscopic results for N_{eff} for $J' = 0$ obtained in Appendix A, we estimate $Y(J' = 0) = 0.22$. The reduction of the quantum yield from unity at $J' = 0$ originates from the $T \rightarrow S_0$ decay of the triplet component of each ME. For $J' = 0$ no mystery of "missing states" is expected to be encountered. The dramatic decrease of Y with increasing J' will be exhibited at higher values of J' . On the other hand, for higher values of J' the dilution factor N_{eff} , Eq. (4.6), (for $J' > 5$), exhibits a qualitatively different J' dependence than N (spectroscopic), Eq. (1.1). This brings back the mystery of missing states, as our quantum yield data and Kommandeur's spec-

troscopic data^{9,10,28} cannot easily be reconciled within the framework of the conventional theory of the ILS.

B. Vibrational state dependence

An attempt has been made to account for the vibrational state dependence of Y (Fig. 4) in terms of Eqs. (4.2), (4.4), and (4.6) with Δ , γ_{ME} , and N being dependent on E_V . On the basis of the experimental evidence Δ changes weakly, being practically invariant, with increasing E_V in the range $E_V = 0-1800 \text{ cm}^{-1}$,²³ so that the vibrational energy dependence of the quantum yield is

$$Y(E_V) = 6 \times 10^{-4} + \frac{\gamma_s^{\text{rad}}}{\gamma_{\text{ME}}(E_V) N_0(E_V) (2\langle J' \rangle + 1)}, \quad (4.7)$$

where $\gamma_{\text{ME}}(E_V)$ is the lifetime of the MEs at E_V , which on the basis of scarce experimental information exhibits a weak dependence on E_V ,²⁸ while $\langle J' \rangle$ is the thermally averaged value of the accessible J' . On the basis of general arguments concerning the increase of the vibrational density of states with increasing E_V , one expects that the $J' = 0$ dilution factor $N_0(E_V)$ increases exponentially with increasing E_V , reaching the asymptotic value of $\gamma_s^{\text{rad}}/\Delta(E_V) \sim 6 \times 10^{-4}$ at high E_V values. This pattern marks the gradual transition from the ILS to the statistical limit with increasing E_V . This expectation is borne out by the nearly exponential decrease of the experimental $Y(E_V)$ data in Fig. 4. We further note that the threefold difference between $Y(E_V = 0)$ at the Q branch of the electronic origin for the jet-cooled molecule at 30 K and Tramer's value at 300 K⁵ is in reasonable agreement with the ratio $\langle J \rangle(T_R = 300 \text{ K})/\langle J \rangle(T_R = 30 \text{ K}) \approx 3$, which determines the ratio of the average dilution factors at the two temperatures. Finally, the absence of the temperature dependence of $Y(E_V)$ at high E_V is in accord with the predictions of Eq. (4.7), which implies an asymptotic $\langle J \rangle$ -independent experimental value of 6×10^{-4} for the quantum yield. The temperature independent value of 8×10^{-4} at $E_V = 1876 \text{ cm}^{-1}$ inferred from the present results and from Tramer's data⁵ is in quantitative agreement with these expectations.

V. CONCLUDING REMARKS

The standard model for the intermediate level structure (ILS) attributes the rotational state dependence of the energy-resolved fluorescence quantum yield to the J' dependence of the effective dilution factor, Eq. (4.6), which causes the decrease of the (average) pure radiative lifetimes of the MEs $\langle \gamma_n^{\text{rad}} \rangle \simeq \gamma_s^{\text{rad}}/N_{\text{eff}}$ (Appendix A) with increasing J' . The J' dependence of N_{eff} implies the breakdown of K selection rules for S_1 - T coupling, leading to complete scrambling of all states with different values of K within the triplet manifold,^{17,20} which presumably originates from Coriolis interactions, as originally proposed by Rice *et al.*²⁰ and elaborated upon by Pratt *et al.*¹⁷ Accordingly, the rotational state dependence is then attributed to S_1 - T interstate coupling and mixing rather than to relaxation, as the genuine intramolecular decay channel in this model involves essentially the $T \rightarrow S_0$ intersystem crossing, which corresponds to the statistical limit and which is invariant with respect to the rotational state.

Does the same model account for the time-resolved data? The amplitude ratio A_+/A_- under perfect coherent excitations and perfect response of the photon-counting system should, according to Eq. (A14) and the value of N_{eff} inferred from our quantum yield, Eq. (4.6), be given in the form

$$A_+/A_- = 16(2J' + 1); \quad J' = 5-22. \quad (5.1)$$

For Lim's ps studies,¹² where coherent excitation conditions prevail, the detection time τ_D seems to be $\tau_D \simeq 1$ ns and the experimental amplitude ratio is expected to be given in terms of Eq. (1.2) with $\alpha = 16\tau_+/ \tau_D \simeq 2$ (for $J' = 5-22$), which is in accord with the experimental value $\alpha = 1.3$ observed by Lim *et al.*¹² for high values of J' ($= 10-20$). On the other hand, the recent (deconvoluted) ps time-resolved data of Rice *et al.*^{21,22} give $\alpha = 0.3$ for $J' = 2-10$, being about one order of magnitude too low than those expected on the basis of the quantum yield data. It will be imperative to settle the quantitative discrepancy between the results of Lim *et al.*¹¹ and of Rice *et al.*^{20,21} While Lim's results¹² are consistent with the notion of dephasing of a coherently excited wave packet of MEs, the low value of α reported by Rice *et al.*^{20,21} cannot be reconciled with this picture.

The description of our quantum yield data and Lim's time-resolved data¹² in terms of the conventional ILS scheme seems to be incompatible with Kommandeur's spectroscopic data.^{9,10,28} For $J' > 5$, the dilution factor, Eq. (4.6), emerging from the analysis of the Y data, exhibits a quantitatively different behavior than $N(\text{spectroscopic})$, Eq. (1.1) for $J' < 3$. Regarding the discrepancy between the dynamic and the spectroscopic data, it should be noted that the spectroscopic data monitor the level structure for $J' < 3$, while the Y data interrogate the dynamics for $J' > 5$. It is just possible that the range $J' = 3-5$ marks a crossover from J' independent N_{eff} to J' dependent N_{eff} , which will imply the setting in of efficient Coriolis mixing within the triplet manifold at higher values of J' . Obviously, spectroscopic data at higher values of J' will be of considerable interest in this context.

To reconcile the extensive physical information pertaining to the photophysics of the S_1 state of pyrazine, which is surveyed in Sec. I, together with our Y data in terms of the ILS model, two auxiliary assumptions have to be invoked:

(i) The breakdown of K selection rules for S_1-T coupling for $J' > 5$ but not for low values of J' (< 3).

(ii) The occurrence of an efficient intramolecular non-radiative decay of the S_1-T MEs to S_0 , which is due to the dominating triplet character of these MEs.

Assumption (i) is necessary to settle the discrepancy between spectroscopy and dynamics regarding the mystery of missing states [point (A), Sec. I], as well as the origin of the short-decay component under ps excitation conditions [points (B) and (C) of Sec. I]. Accordingly, assumption (i) will result in a sufficient number of MEs in the energy range of $\Delta \sim 3.5$ GHz for each J' (> 3) to warrant observable dephasing under coherent excitation conditions. The origin of the short time-resolved decay component under ns excitation conditions [point (D), Sec. I] is cause for concern as it is incompatible with the model at hand. To account for the

appearance of the short-decay component, Kommandeur proposed^{28,37} the occurrence of near-resonant Rayleigh and Raman scattering from a "small molecule" level structure. Some difficulties inherent in Kommandeur's model are: (1) The finite lifetime $\tau_+ = 120$ ps for the short-decay component, which can be reconciled with Kommandeur's scheme only provided that the short-decay component has a different physical origin under ns and under ps excitation. (2) The low absolute values of the quantum yields and their J' dependence. These can be made compatible with Kommandeur's model only provided that assumption (i) is invoked again. (3) The magnetic time-resolved data under ns excitation, which reveal a threefold increase of A_+/A_- in a weak magnetic field.^{16,17} Extensive model simulations are required to establish whether these results can be accounted for in terms of Kommandeur's model. (4) The absence of a short component under ns excitation of the $R(0)$ and $P(1)$ branches^{8,16,17} is intriguing, as it seems to be incompatible with this model. (5) An appreciable reduction in the short near-resonant light-scattering decay component is expected under realistic excitation conditions, which is induced by the phase fluctuations of the dye laser.³⁵ In order to establish the contribution of light scattering, a more careful characterization of the (ns) laser sources will be required.

A few years ago the reasonably self-consistent physical picture, which has emerged from the analysis of the Y data on the basis of Eqs. (4.1)–(4.6), would have been considered as strong evidence for the validity of the ILS model for the description of the dynamics of the mixed S_1-T MEs in the S_1 state of pyrazine. With the current sophistication of experimental techniques and of theoretical concepts, such an easy way out may be no longer acceptable. As is apparent from the foregoing discussion the standard model for the ILS has to be supplemented by three auxiliary, and as yet unverified, assumptions, i.e., assumptions (i) and (ii) together with Kommandeur's assumption of near-resonant light scattering,²⁸ in order to account for all the wealth of photophysical information available for this system. Alternative approaches should be considered. Regarding the nature of the short time-resolved decay component under ps excitation, it is in our view still an open question whether it originates from dephasing or, alternatively, from statistical decay into an additional intramolecular channel. In this context, we are even more concerned with the appearance of the short-decay component under ns excitation conditions, which may arise from statistical intramolecular decay, if such a channel is open. With the proviso that an additional intramolecular decay channel does exist, it should exhibit rotational state dependence,³⁶ which is required to account for the experimental J' dependence of the time-resolved (A_+/A_-) and energy-resolved (Y) observables. We are currently exploring K -selective models involving interstate (S_1-S_0) or intrastate (T_1) Coriolis coupling in order to obtain a self-consistent description for the wealth of experimental observables, bridging the gap between spectroscopy and dynamics in this interesting system.

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APPENDIX A: INTERSTATE S_1 - T COUPLING IN PYRAZINE

Consider a bunch of well separated molecular eigenstates (MEs), originating from the mixing of a single S_1 doorway state with the triplet (T) manifold, which are given by the traditional expression

$$|n\rangle = a_s^n |S_1\rangle + \sum_T \beta_T^n |T\rangle. \quad (\text{A1})$$

We now proceed to provide explicit expressions for the fluorescence quantum yields under various excitation conditions. For a spectrally narrow excitation source, which partially or entirely spans a single (Doppler broadened) ME, the quantum yield is³

$$Y_n = \int \sigma_n^F(E) dE \int \sigma_n^A(E) dE, \quad (\text{A2})$$

where $\sigma_n^A(E)$ and $\sigma_n^F(E)$ are the absorption cross section and the fluorescence cross section, respectively, for the n th ME. When the spectral distribution of the exciting source is broader, spanning a subset $\{n\}$ of the MEs, the quantum yield assumes the form³

$$Y_{\{n\}} = \sum_{\{n\}} \int \sigma_n^F(E) dE \sum_{\{n\}} \int \sigma_n^A(E) dE, \quad (\text{A3})$$

where the sums are taken over the subset n . We note in passing that $Y_{\{n\}} \neq \sum_{\{n\}} Y_n$. Finally, the fluorescence quantum yield for chaotic (or coherent) excitation of the entire bunch of MEs, and neglecting short-time dephasing, is given by³

$$Y_- = \sum_n \int \sigma_n^F(E) dE \sum_n \int \sigma_n^A(E) dE. \quad (\text{A4})$$

Making use of the general formalism of Nitzan and Jortner³⁸ for light scattering from intramolecular resonances, the integrated areas of the absorption and fluorescence cross sections for each ME, apart from irrelevant numerical factors, are given by

$$\begin{aligned} \int \sigma_n^A(E) dE &\propto \gamma_n^{\text{rad}(0)}, \\ \int \sigma_n^F(E) dE &\propto \gamma_n^{\text{rad}(0)} \gamma_n^{\text{rad}} / \gamma_n, \end{aligned} \quad (\text{A5})$$

where $\gamma_n^{\text{rad}(0)}$ is the partial radiative width of $|n\rangle$ due to its decay to the electronic origin of the ground state, γ_n^{rad} is the total radiative width of $|n\rangle$ due to its decay to all the vibronic components of the ground state, and γ_n is the total decay width of $|n\rangle$, which is given by $\gamma_n = (\gamma_n^{\text{rad}} + \gamma_n^{\text{nr}})$. Here, γ_n^{nr} corresponds to the nonradiative width of the n th ME due to $T \rightarrow S_0$ intersystem crossing. The quantum yield for spectral-

ly narrow excitation is given from Eqs. (A2) and (A5) by $Y_n = \gamma_n^{\text{rad}} / \gamma_n$, as is expected. For other excitation modes, the following general expressions emerging from Eqs. (A3)–(A5) require detailed information on the radiative and non-radiative widths of the individual MEs. Very simple expressions can, of course, be obtained for a democratic interstate mixing²⁶ which, unfortunately, is not applicable for a real life situation.^{9,10} A considerable simplification of the results is encountered under the following circumstances: (i) The decay of the MEs is dominated by the nonradiative $T \rightarrow S_0$ channel, i.e., $\gamma_n^{\text{rad}} \ll \gamma_n^{\text{nr}}$. (ii) The nonradiative widths of all the MEs are equal, i.e., $\gamma_n^{\text{nr}} = \gamma_{\text{ME}}$ for all n . These assumptions are borne out by the available lifetime data^{9,10,28} for the S_1 origin of pyrazine. We can now make use of relations (A2)–(A5) and obtain for the excitation of a single ME,

$$Y_n = |a_s^n|^2 \gamma_s^{\text{rad}} / \gamma_{\text{ME}} \quad (\text{A6})$$

and for a subset of MEs,

$$Y_{\{n\}} = \left(\sum_{\{n\}} |a_s^n|^4 \sum_{\{n\}} |a_s^n|^2 \right) (\gamma_s^{\text{rad}} / \gamma_{\text{ME}}). \quad (\text{A7})$$

Finally, for the case of chaotic (coherent) excitation we can invoke the normalization condition $\sum_n |a_s^n|^2 = 1$ to obtain

$$Y_- = \sum_n |a_s^n|^4 (\gamma_s^{\text{rad}} / \gamma_{\text{ME}}). \quad (\text{A8})$$

From these analyses the following interrelationships between energy-resolved and time-resolved data emerge:

(a) The peak absorption intensity, A_n , for each inhomogeneously broadened feature in the high-resolution spectrum, corresponding to a distinct n th ME, is $A_n \propto |a_s^n|^2$, provided that the inhomogeneous line broadening is independent of n .

(b) The peak intensity for excitation of each ME in the high-resolution LIF spectrum is $I_n \propto |a_s^n|^4$.

(c) From Kommandeur's high-resolution LIF spectra^{9,10,28} the fluorescence quantum yields can be estimated from the relations

$$Y_n = \frac{I_n^{1/2}}{\sum_n I_n^{1/2}} (\gamma_s^{\text{rad}} / \gamma_{\text{ME}}), \quad (\text{A9})$$

$$Y_{\{n\}} = \frac{\sum_{\{n\}} I_n}{\sum_{\{n\}} I_n^{1/2} \sum_{\{n\}} I_n^{1/2}} (\gamma_s^{\text{rad}} / \gamma_{\text{ME}}), \quad (\text{A10})$$

and

$$Y_- = \frac{\sum_n I_n}{\left| \sum_n I_n^{1/2} \right|^2} (\gamma_s^{\text{rad}} / \gamma_{\text{ME}}). \quad (\text{A11})$$

(d) Equations (A9)–(A11) exhibit the explicit dependence of the quantum yield on the excitation mode for a realistic model system.

(e) The relevant quantum yield, Eq. (A11), can be written in the form

$$Y_- = \frac{\gamma_s^{\text{rad}}}{\gamma_{\text{ME}} N_{\text{eff}}}, \quad (\text{A12})$$

where

$$N_{\text{eff}} = \sum_n |a_n^+|^4 = \left| \sum_n I_n^{1/2} \right|^2 \sum_n I_n \quad (\text{A13})$$

is the effective dilution factor for a nondemocratic distribution.

(f) The reciprocal value of N_{eff} , i.e.,

$$N_{\text{eff}}^{-1} = \sum_n |a_n^+|^2 / \sum_n |a_n^+|^4 \quad (\text{A14})$$

is known in the theory of ill-condensed matter as the "participation ratio",³⁹ which determines electron localization in disordered materials. This concept was invoked in intramolecular dynamics in the context of vibrational energy redistribution.^{40,41}

(g) The effective dilution factor, Eq. (A13), also determines the amplitude ratio A_+/A_- obtained under coherent excitation and ideal detection conditions. Following the detailed analysis of time-resolved decay^{3,5} one obtains

$$A_+/A_- = N_{\text{eff}}. \quad (\text{A15})$$

This relation is meaningful only provided that the number of coupled states and their density is sufficiently large to result in dephasing.

(h) The effective dilution factor, Eq. (A13), can be considerably lower than Kommandeur's number of states $N(\text{spectroscopic})$, Eq. (1.1). From the high-resolution LIF spectra,^{9,10,28} together with Eq. (A13), one can estimate

$$N_{\text{eff}} = 9.1 \quad \text{for } J' = 0, \quad K' = 0 \quad [P(1) \text{ branch}]$$

and

$$N_{\text{eff}} = 9.6 \quad \text{for } J' = 1, \quad K = 0 \quad [R(0) \text{ branch}].$$

Obviously, $N(\text{spect})$, Eq. (3.1), constitutes an upper limit for N_{eff} .

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