Rotational state dependence of pyrazine fluorescence: Initial decays for the vibrationless $^1B_{3u}$ state

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We report new measurements of the rotational state dependence of the initial fluorescence decay of the vibrationless $^1B_{3u}$ state of pyrazine. Through examination of excited state dynamics from a Green's function point of view the apparently inconsistent data from several sources are reconciled.

I. INTRODUCTION

The spontaneous emission from an excited state of a polyatomic molecule with intermediate-case level structure does not decay exponentially, as does an isolated nonstationary state embedded in a smooth continuum of other states.[1-3] The observed nonexponential temporal decay is interpreted as arising from rapid evolution of the initially formed singlet wave packet to generate mixed singlet–triplet levels, followed by slow depopulation via radiation from the singlet components of the mixed levels. The evolution of the wave packet is, in the absence of the coupling to the radiation field, a coherent process, so the mixed levels have well defined phase relations and can generate a beat spectrum. Of course, depopulation via photon emission from the mixed levels is an incoherent process.

Pyrazine has long been considered to be a molecule with intermediate case level structure; it has been extensively studied for the purpose of testing aspects of the theoretical interpretation of evolution of a prepared state sketched in the preceding paragraph.[4-8] In this paper we report the results of direct time domain studies of wave packet evolution in isolated pyrazine molecules, in particular the rotational state dependence of the initial decay rate. Our new data, which replace those in a preliminary report,[9] complement the data obtained by other investigators,[6,7] and the full data set permits construction of a rather complete description of the dynamics of wave packet evolution in the isolated pyrazine molecule. That evolution is found to be coherent except for the small coupling to the radiation field which leads to photon emission. In the accompanying paper this conclusion will be used to clarify the role, or lack of role, of chaos in the description of the dynamics of quantum mechanical systems which have discrete energy level spectra, and to distinguish between apparent decay of amplitude and real decay of amplitude in wave packet evolution.

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II. EXPERIMENTAL DETAILS

A block diagram of the apparatus used is shown in Fig. 1. Pyrazine, seeded in a free supersonic jet of He, was excited by a mode locked Ar^+ laser-synchronously pumped dye laser system (DCM dye). To obtain pulses with the desired spectral and temporal resolution a custom designed low finesse ($R = 0.32$) 0.25 μm solid etalon was inserted in the dye laser cavity and a 12% output coupler was employed. The output pulses were characterized by temporal autocorrelation function measurements and spectral content measurements. The product of the full widths at half maximum (FWHM) of these measurements yielded $\Delta\nu_{1/2}\Delta t_{1/2} = 0.441$, and for the ratio of full width at quarter maximum and FWHM we found 1.55, which implies that the pulses were nearly transform limited.

The output of the dye laser, about 100 mW of 646.8 nm light, was doubled using a 2 mm thick $LiIO_3$ crystal. Given the properties of the incident pulses, we expect the UV pulses to be 22 ps in duration and have a FWHM of 0.7 cm^{-1}. This resolution is just sufficient to resonantly excite, in a clean fashion, one of the rotational transitions of pyrazine, if the exact position of that transition is known. The convolution of the 22 ps pulse duration and the 80 ps system response function resulted in an overall response function with a width of 85 ps.

To carry out photoexcitation measurements the dye laser cavity was shortened by 200 μm; this configuration generates pulses of 100 ps duration and 0.15 cm^{-1} FWHM. For Rayleigh scattering measurements the etalon was removed from the dye laser cavity and the 12% output coupler replaced with a 55% output coupler; this configuration generates UV pulses of 3 ps duration and with spectral width sufficient to span almost all of the rotational contour of pyrazine.

Emission from pyrazine was collected using $f/2$ optics. Field stops in the image plane of the collector discriminate against scattered light very effectively ($I_{\text{signal}}/I_{\text{scattered light}} = 500$ for the outermost parts of the rotational contour) so no spectral filtering of the emission was required. To carry out Rayleigh scattering measurements a 0.3 m McPherson monochromator was used as a narrow band filter (0.7 nm) to discriminate against red shifted emission and to exclude uncertainty arising from possible wavelength dependence of the detector sensitivity.

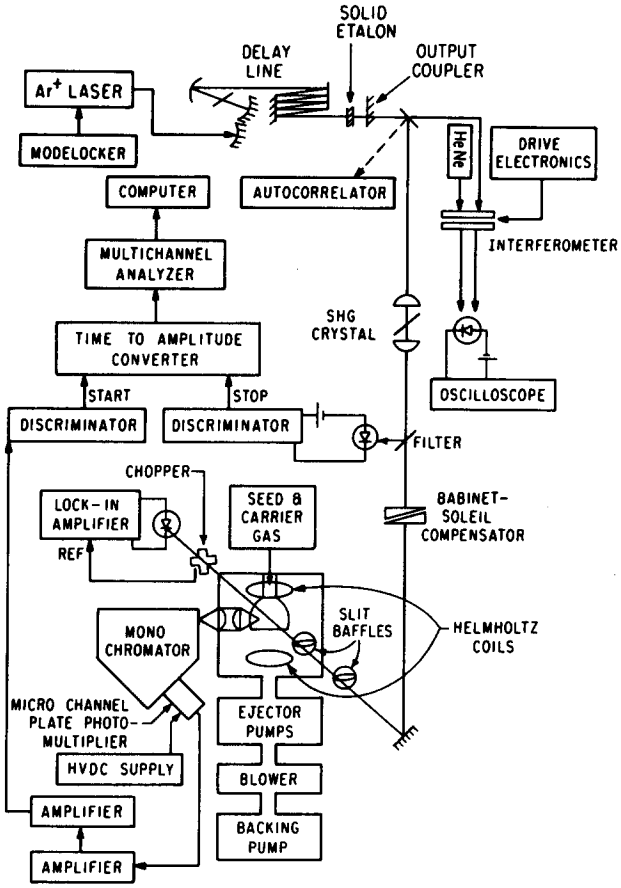

FIG. 1. Block diagram of the apparatus.

The experimental chamber was evacuated through a custom designed 120° internal angle chevron baffle by three nonfractioning Edwards 9B3 ejector pumps, backed by a roughing pump–Roots blower combination. The system throughput is greater than 45 Torr l/s. The stagnation pressure used was 2 atm, leading to a chamber pressure of 1–3 mTorr. We have used both a 27 × 270 μm slit nozzle and a 100 μm diameter pinhole nozzle.

The system response was measured by Rayleigh scattering from Ar clusters in a free jet expansion of pure Ar with 20 atm backing pressure. Light was detected with a Hammamatsu R1645V-01 channel–plate photomultiplier. The system response was 100 ps for the Rayleigh scattering measurements and 85 ps otherwise. The channel–plate photomultiplier was connected to two cascaded Hewlett Packard 8447E amplifiers of 1.5 GHz effective bandwidth. The amplified signal was then sent to an Ortec 934 four channel constant-fraction discriminator which produced start pulses for an Ortec 457 time-to-amplitude converter. The output of a fast photodiode illuminated by the laser light (see Fig. 1) was sent to another input of the same discriminator to be shaped and then was fed into the time-to-amplitude converter as stop pulses. This arrangement uses the full repetition rate of the laser, and requires a slight modification of the time-to-amplitude converter (replacing an internal delay line by a 2.7 Ω shunt resistor; suggested by Paulus of Ortec). The output of the time-to-amplitude converter was digitized and stored in a Camberra Series 30 multichannel analyzer.

The gas handling system was constructed of stainless steel; all surfaces in contact with the seed gas were teflon coated. 99.99% pure helium or argon gases were passed through a Matheson 0.02 μm filter and then sent to a 2.0 μm Nupro filter loaded with pyrazine. The seeded helium passes to the nozzle, which was heated to prevent crystallization of pyrazine on the orifice. Pyrazine was purchased from Aldrich Chemical Co. and purified by sublimation.

The excitation wavelength of the dye laser was monitored continuously, and adjusted as necessary, by using a Burleigh RC110 planar Fabry–Perot etalon referenced to a He–Ne laser standard.

III. EXPERIMENTAL RESULTS

A. Reality of the initial decay component

As mentioned earlier, the temporal decay of pyrazine fluorescence is nonexponential. In the intermediate level structure model of pyrazine the fluorescence decay is approximated by two exponential terms with widely different time constants. Kommandeur has reported[10] that the ratio of the amplitudes of the fast to slow components in that two term representation of the decay is a very sensitive function of excitation wavelength. He finds, using a laser with ~200 MHz bandwidth, that excitation at the peak of a rotational transition gives an order of magnitude larger value for the ratio A_{fast}/A_{slow} than does excitation in the trough between the centers of two rotational transitions. It is then argued that no variation in coupling constants over an energy range of ~0.2 cm^{-1} could be so large as to account for the observations. Kommandeur suggests that the observations are consistent with interpreting the fast initial decay in the fluorescence as arising from Rayleigh–Raman scattering, and that pyrazine does not conform to the intermediate case of radiationless transition theory.

We have carried out a careful comparison of Rayleigh scattering from Ar clusters in a free jet expansion of pure Ar and Rayleigh scattering from pyrazine seeded in a free jet expansion of He. The excitation laser was adjusted to provide UV pulses of 3 ps FWHM. Raman scattering from these samples, and any possible ambiguity associated with a wavelength dependence of the detection system response function, were excluded by use of a monochromator with a 0.7 nm spectral window centered at the excitation wavelength used. For this experiment the excitation chosen corresponds to the 0_0^0 transition of pyrazine.

The signal generated by Rayleigh scattering from Ar clusters at the wavelength of the 0_0^0 transition of pyrazine is shown in Fig. 2. The circles displayed on the same figure show the signal observed when pyrazine seeded in He is excited and detected using the same conditions. The line in the figure is the result of convoluting the system response function with a double exponential decay, the long lived component of which has a lifetime fixed at 100 ns. On the time scale defined by the short lived

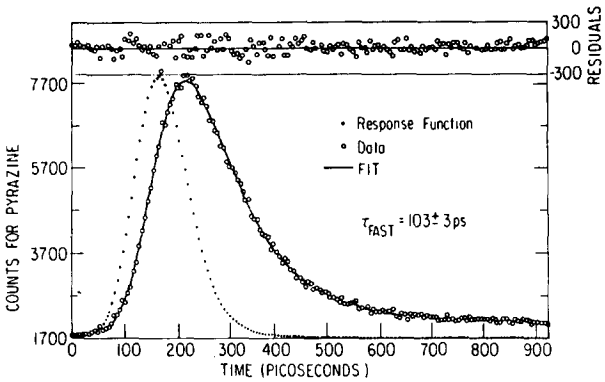

FIG. 2. Signals generated from Rayleigh scattering from argon clusters and from a pyrazine seeded He jet.

component of the fluorescence, the precise value of the lifetime of the long lived component has little influence on the quality of the fit. The residuals resulting from this convolute–compare routine are also shown in Fig. 2. It is clear that the time evolution of detected signal is different for Rayleigh scattering from Ar clusters and fluorescence emission from pyrazine. The latter has a lifetime of 103 ps in this experiment. We conclude, in opposition to Kommandeur's suggestion, that the short time decay of fluorescence of pyrazine is real in the sense of being characteristic of intermediate level structure dynamics and not of incidental Rayleigh scattering.

Our experimental results, described in the preceding paragraph, are not in conflict with Kommandeur's observation that there is a drastic change in the value of A_{fast}/A_{slow} when the excitation wavelength is detuned from resonance with a rovibronic transition. To see this we note that the time resolution in Kommandeur's experiments is such that discrimination between Rayleigh scattering and the short lived component of the fluorescence decay is not possible. There are, then, two points to be made. First, the conventional interpretation of A_{fast}/A_{slow} as equal to the number of coupled levels is only valid if all those levels are resonantly, coherently, excited. If this is not the case, as it cannot be when the excitation bandwidth does not span all of the coupled levels, the evolution of the prepared wave packet is usually not describable as a simple superposition of fast and slow decay components.

Second, accepting that the value of A_{fast} measured by Kommandeur contains contributions from Rayleigh scattering and from the initial fluorescence decay of pyrazine, the observed variation of A_{fast}/A_{slow} can be explained as follows. If the excitation wavelength falls between those of two transitions, and the excitation bandpass is small compared to the separation of the transitions, said transitions, and others, are coherently but nonresonantly pumped. If the excitation wavelength falls on a transition of course that transition is pumped resonantly, but other transitions are also pumped nonresonantly. The fluorescence emission from a resonantly pumped transition is so much more intense than the scattering resulting from nonresonant pumping of all other transitions that the former dominates the latter. Clearly, however, as the ratio of resonant to nonresonant excitation is changed, so also will be the ratio of fluorescence to scattered light. The nonresonant excitation we have just discussed is the basis for generating Rayleigh scattering.[11] This explanation is the same as that given by Kommandeur except for his further suggestion concerning the intrinsic properties of pyrazine.

B. Rotational state dependence of the decay of fluorescence

To generate excitation pulses with adequate resolution to study the rotational state dependence of the fluorescence decay of pyrazine we shortened the dye laser cavity by 200 μm. The pulses obtained using this configuration are 70 ps long and have a spectral width of 0.25 cm^{-1} (FWHM) in the UV. The UV intensity could be maintained constant to ±3%. The spectrum shown in Fig. 3 was obtained by tilting the intracavity etalon at constant speed. Note that there appear to be differences in the spacings of adjacent rotational transitions. These small changes in the apparent spacings of the transitions arise from the nonlinear dependence of the wavelength of the dye laser on the tilt of the intracavity etalon. A spectral scan of the same region using an extracavity monitoring Fabry–Perot interferometer shows the expected equidistant spacings of the rotational transitions.

The photoexcitation spectrum of Fig. 3 was used as a reference for lifetime measurements in the following fashion. A particular transition, corresponding to a selected value of J in the excited state, was pumped using the shortened dye laser cavity configuration described above. The dye laser cavity length was then adjusted to provide proper mode locking. The excitation wavelength was continuously monitored, relative to the wavelength of a He–Ne laser taken as a standard, by analyzing the outputs of both the dye laser and He–Ne laser with a planar Fabry–Perot interferometer. The period of time used for any one set of measurements was usually restricted to less than 10 min to minimize any possible effects of long

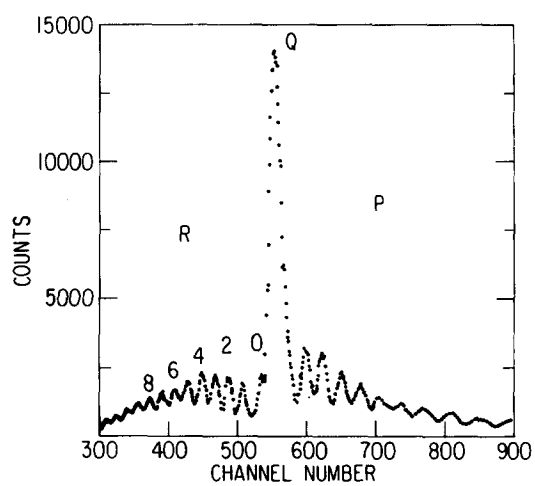

FIG. 3. Photoexcitation spectrum displaying rotational resolution of $^1B_{3u}$ pyrazine.

term drifts in the system electronics, slow changes in room temperature and the like. Under these conditions the scattered light level was negligibly small. An independent verification of the unimportance of scattered light was carried out by making measurements with some scattered light present and correcting for that scattered light. The analyses of the two kinds of measurements yielded the same results.

The results of our measurements of the rotational state dependence of the fast component of the fluorescence decay of pyrazine are shown in Table I. Clearly, these data show that the decay of the short lived component, which is of single exponential form to within experimental error, is independent of J. It appears that our preliminary data[9] were flawed by incipient mode locker failure and collection optics inefficiencies; we withdraw those data which appeared to show J dependence of the fast decay component of the pyrazine fluorescence. We shall see that our new data nicely complete the dynamical description of pyrazine and are in agreement with the high resolution (200 kHz) spectrum of pyrazine reported by Meerts, Majewski, and Kommandeur.[6]

It is appropriate to comment on the precision and accuracy of the data displayed in Table I. First, the precision of the measurements of relative lifetimes is ±3 ps, whereas the accuracy is somewhat poorer, namely ±5 ps. The inaccuracies in our measurements arise from the wavelength dependence of the response of the channel plate photomultiplier and from the interpretation of the response function of the system. The wavelength dependence of the channel plate photomultiplier is known to be very small relative to that of ordinary photo tubes, and in our lifetime experiments the total emission from pyrazine was detected, so this source of error is likely small. On the other hand, our excitation pulses were 22 ps long and the interaction of the pulses, the molecules of the sample and the detector is not described properly as a simple double convolution. Rather, to adequately describe the overall system behavior it is necessary to use a convolution of the excitation pulse shape and the molecular decay in the quantum mechanical amplitude space, and then convolute the absolute square of that function with the instrumental response function.[12] In our case the instrumental response function was broadened by 5 ps as a consequence of using 22 ps pulses in place of delta function pulses. Rather than displaying complicated calculations we take this broadening as a measure of the inaccuracy of our data.

Support for our error estimate can be obtained from the computed value of the degeneracy weighted average of the lifetimes of all the rotational states excited when a particular pump pulse is employed. We have carried out this computation for the case of 3 ps excitation, corresponding to a spectral bandwidth of about 4 cm^{-1}, and find 107 ps, which can be compared with the value measured, reported in Sec. III A, of 103 ± 3 ps.

IV. DISCUSSION

We now examine the dynamics of evolution of the state generated when $^1B_{3u}$ pyrazine is excited. Our experimental results are consistently interpreted under the assumption that the evolution of that state is coherent (except for photon emission). We shall see that other data for the fluorescence decay of $^1B_{3u}$ pyrazine are consistent with the same assumption.

A. Qualitative properties of rovibronic molecular eigenstates

In order to understand the emission signals from intermediate case molecules such as pyrazine we must take note of the complexity of the level structure. This is particularly the case for spectroscopic experiments carried out with rotational resolution in supersonic jets. It is also important to recognize that mechanistic interpretations of experiments are often futile. By this we mean that it is very difficult to say that the result of an experiment is uniquely the consequence of, e.g., Coriolis or spin-rotation coupling.

To be more concrete, consider Fig. 4, which shows a schematic representation of the zeroth order triplet Born–Oppenheimer states close in energy to a singlet Born–Oppenheimer rovibronic state. Only Hund's case b triplet states which can couple to the singlet state are drawn, and the role of nuclear spin is implicit in the selection of states shown. Many more states exist, but conservation of angular momentum prohibits us from seeing them.

Imagine, now, that the intramanifold couplings are "turned on." Since there is relatively little vibrational excitation in the singlet state of interest we expect that rotation-vibration coupling has only a small effect in this manifold. Such is not the case for the triplet manifold. Here we expect the rotation vibration interaction will destroy the "goodness" of the K quantum number, and that Coriolis coupling will help remove the degeneracy of states with quantum numbers K and $-K$. Note that since the triplet rotational states of interest need to be close in energy to the singlet rovibronic state they must be built upon different vibrations. This makes it extremely difficult to isolate a coupling mechanism which dominates in the description of the level structure unless only a very few

TABLE I. Rotational state dependence of the initial decay of fluorescence of pyrazine (accuracy and precision ± 5 ps).

Branch	P						Q	R						
J	7	6	5	4	3	2		1	2	3	4	5	6	7
Lifetime (ps)	108	110	108	107	102	100	110	94	96	108	114	109	104	104

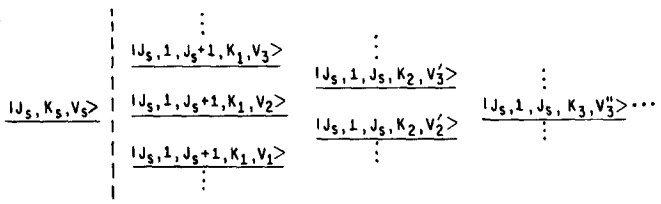

FIG. 4. Schematic representation of the underlying triplet structure. Note the vibrational complexity which arises from the conservation of angular momentum. The states having quantum numbers $\pm K$ are degenerate or very nearly so.

states dominate the mixed state wave function. The only concrete statement that can be made is that the number of levels which need to be considered in the relaxation process increases with J and is roughly proportional to $(2J_S + 1)$.[4,6]

Given the prediagonalized triplet manifold of states the spin-orbit interaction will mix in the singlet state, generating molecular rovibronic eigenstates. We have so far not considered the magnetic substates. In experiments carried out in magnetic fields one, of course, needs to consider them; their influence on the dynamics will be discussed below.

B. Qualitative characteristics of the fluorescence decay kinetics

To understand the dependence of $A_{\text{fast}}/A_{\text{slow}}$ on J_S and on magnetic field strength we must examine some of the formal properties of the fluorescence decay kinetics of intermediate case molecules. Recall that for such molecules the fluorescence decay is, to a good approximation, the sum of two exponential decays.[3] The faster (initial) decay is interpreted as arising from the unphasing of the prepared singlet wave packet into mixed singlet–triplet states. In the intermediate case limit the density of these mixed states is too small to generate a continuum. Nevertheless, the initial decay rate can be calculated from the "Golden Rule" expression valid for evolution of a zero order state coupled to a zero order continuum. To see that this is so consider a situation where one prepares a zeroth order singlet state $|i\rangle$ by using a sufficiently short duration pulse of light. One may demonstrate[3] that in this case the frequency integrated photon counting rate is

$$\dot{P}(t) = K|\langle i|e^{-iHt}|i\rangle|^2, \tag{1}$$

where K is a constant depending upon Hönl–London factors, Franck–Condon factors, and geometry of detection. The Hamiltonian in Eq. (1) is taken to include the radiation field and the radiation–matter interaction. Using standard resolvent operator or Green's function techniques we may write[12]

$$\langle i|e^{-iHt}|i\rangle = 1/(2\pi i)\int_{-\infty}^{\infty} e^{-i\omega t}G_{ii}(\omega)d\omega \quad t \geq 0, \tag{2}$$

where

$$G_{ii}(\omega) = \langle i|1/(\omega + i\eta - H)|\, i\rangle. \tag{3}$$

For the situation where the zeroth order singlet $|i\rangle$ is coupled to a set of triplets, and also to the radiation field, it is a simple exercise[12] to show that

$$G_{ii}(\omega) = \left[\omega + i\eta - \omega_i + \frac{1}{2}i\gamma + \sum_j \frac{|V_{ij}|^2}{\omega + i\eta - \omega_j}\right]^{-1}, \tag{4}$$

where $\{j\}$ labels the triplet states, γ is the radiative width of $|i\rangle$ and V can be taken as the spin-orbit interaction. Equation (4) is exact and, as one may see, leads to a rational fraction with poles in the lower half plane.

The dynamics of the molecular relaxation is governed by the "self-energy" term

$$\Sigma_\eta(\omega) = \sum_j \frac{|V_{ij}|^2}{\omega + i\eta - \omega_j}. \tag{5}$$

The case of initial exponential decay corresponds to having $\Sigma_\eta(\omega) \approx$ constant $= \Sigma_\eta(\omega^*)$, where ω^* is a high frequency, since short times are of interest. If we take $\omega^* = \omega_i$ (the same assumptions give γ = constant) we see that the Green's function contains a pole with an imaginary part given by the sum of the radiative width and a width determined from the Golden Rule. This argument is not intended to be a derivation, but rather to make the point that our ability to make the approximation cited depends on the details of the structure of $\Sigma_\eta(\omega)$. If $\Sigma_\eta(\omega)$ is very smooth, given an η much smaller than the radiative width, then the initial decay dominates the signal.

Armed with these notions we can understand the features of the pyrazine emission signals. The lack of an initial fast exponential decay of the $J = 0$ state time evolution, as reported by Kommandeur,[8] means that $\Sigma_\eta(\omega)$ is not sufficiently smooth to be approximated in the manner described.[7] The lack of a J dependence of the fast components, reported in this paper, follows from the Golden Rule as discussed by Novak and Rice.[13] The increasing dominance of the initial decay, measured as the ratio $A_{\text{fast}}/A_{\text{slow}}$,[10] comes about because $\Sigma_\eta(\omega)$ becomes smoother as J increases. Table II shows our measurements of $A_{\text{fast}}/(2J + 1)A_{\text{slow}}$. The fact that these ratios are not too strongly varying is in accord with the predictions of

TABLE II. $A_{\text{fast}}/A_{\text{slow}}$ as a function of quantum number (error ± 10%).

	P branch						
J	2	3	4	5	6	7	
$\frac{A_{\text{fast}}}{(2J+1)A_{\text{slow}}}$	0.17	0.17	0.20	0.23	0.28	0.36	
	R branch						
J	1	2	3	4	5	6	7
$\frac{A_{\text{fast}}}{(2J+1)A_{\text{slow}}}$	0.5	0.32	0.32	0.34	0.37	0.39	0.41

Freed and Nitzan,[3] who suggest an egalitarian model of level coupling.

We now consider the results of magnetic field experiments.[14,15] The dependence of A_{fast}/A_{slow} on magnetic field strength is sigmoidal, i.e., it first increases then saturates as the magnetic field increases. Zewail[5] and Pratt and co-workers[14,15] suggest that this behavior is the result of coupling an increasing number of triplet states to the singlet as the magnetic field strength increases. We suggest, instead, that the observed behavior of A_{fast}/A_{slow} is a manifestation of temporal coherent evolution of the state of the molecule. Level substructure can be seen only if level splittings are large enough for destructive interference to develop within the time window defined by the experimental conditions. With increasing magnetic field strength the unphasing of these sublevels shows up within the experimental time window, and the saturation region is reached if unphasing is complete within that time window. Put another way, features of the coherent evolution of the state are pulled within the time window of the experiment by the magnetic field. Finally, in terms of the formal Green's function analysis sketched above, the dependence of A_{fast}/A_{slow} on magnetic field strength can be viewed as arising from a smoothing of $\Sigma_\eta(\omega)$ due to lifting of degeneracies in the energy level spectrum. Note that to use this analysis consistently we must include the Zeeman interaction in the intramanifold triplet prediagonalization.

ACKNOWLEDGMENTS

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