The Spectrum of the Molecular Eigenstates of Pyrazine and the Reconstruction of Decays of Rotational States of the $^1B_{3u}$ (0–0) Transition of Pyrazine

BAREND J. VAN DER MEER, HARRY Th. JONKMAN and
JAN KOMMANDEUR

*Laboratory for Physical Chemistry, University of Groningen, Nijenborgh 16, 9747
AG Groningen, The Netherlands*

The spectrum of the molecular eigenstates (ME) belonging to the various rotational members of the $^1B_{3u}$ (0–0) transition of pyrazine was measured with a very narrow band laser in a molecular beam with a Doppler width of 30 MHz.

It is shown that, when the ME's belonging to a single rotational state are Fourier-transformed, the beating decays of these states are obtained. A problem is constituted by the lack of a fast component in these reconstructions, while it is observed in experiments on higher J -states.

INTRODUCTION

The theory of radiationless transitions from electronic states of molecules appears to be well understood.¹ When molecules are large, the state excited by light is coupled to such a dense manifold of vibronic states of a lower lying electronic state that one can apply Fermi's Golden Rule and short (compared to the radiative rate) exponential decay together with a low quantum yield is observed. When, on the other hand, a small molecule is excited, the total density of states at the frequency of the light is so small, that in general only one state is excited within the bandwidth of the exciting light, and pure, but lengthened, exponential decay is observed. The radiative

strength of the "light" state is diluted by the interaction over the background states.

The case of "intermediate level structure" is perhaps most interesting, because depending on the coherent width of the exciting light source, either one or more states can be excited, and the dependence of the radiationless transition on the preparation of the state can be demonstrated.

This paper reports on a study of these effects for the radiationless transition of the $^1B_{3u}$ state of pyrazine. By observing spectra and decays in a supersonic nozzle the effect of rotations and nuclear spin could be observed as well.⁸ A measurement of the Intermediate Level Structure allowed a quantitative determination of the matrix elements responsible for Intersystem Crossing.

EXPERIMENTAL

The high resolution spectra were obtained at the University of Nijmegen using a modified Spectra Physics ring laser (bandwidth 200 kHz), intracavity doubled by a lithium iodate crystal. We were able to scan more than 100 GHz at the time.²

The molecular beam in this case was produced in a supersonic expansion of a mixture of argon and pyrazine through a 100 μm nozzle at a total backing pressure of 7 atm. In order to reduce the Doppler width the molecular beam was collimated by two skimmers placed at 2.5 and 15 cm from the nozzle using differential pumping. The laser crossed the molecular beam 30 cm from the source. The residual Doppler width is 30 MHz.

The decays were measured in a different apparatus, a pulsed supersonic nozzle ($d = 1$ mm), excited at 4 cm downstream with a Molelectron DL14 P dye laser, doubled in frequency.

The molecular eigenstates

Calculations of the density of vibronic triplet states at the energy of the first excited singlet states yield a value of about 75 cm^{-1} .^{1,3,6} Their average separation is therefore in the order of ten times the Doppler width in the molecular beam. One therefore may hope to observe these separate states in absorption. One should realize that most of

this so-called molecular eigenstate spectrum will be "empty," i.e., transitions will only occur in regions, where a singlet transition would take place in the absence of coupling between singlets and triplets. Since we are working in a beam these singlet transitions will be the rotational states, and since the beam is cold to the lowest rotational states. Of particular interest are the $P(1)$ and $R(0)$ regions since here only one rotational transition occurs ($J'=0, K'=0 \leftarrow J''=1, K''=0$ and $J'=1, K'=0 \leftarrow J''=0, K''=0$, respectively), while for higher members of the P and R branches transitions from various K -states will occur in the same region. In Figures 1a and 1b we display the spectra of the molecular eigenstates belonging to $P(1)$, $P(2)$ and $R(0)$ and $R(1)$, respectively. Note that they are widely separated in frequency. The first moments $\int I(E)E dE$ of the intensities of the band gives the position of the "original" singlet, and these positions have been indicated by S . The frequencies of these "original" transitions with respect to the center of the rotational spectrum have been given as well. In Table I we have collected the energies and the intensities of the $P(1)$ and $R(0)$ members of the eigenstate spectrum.

The molecular eigenstates are mixtures of singlet and triplet states, coupled by some magnetically active matrix element. It will be clear therefore, that molecules do not "know" of singlet and triplet states. But spectroscopists do! It seemed therefore worthwhile to interpret the $P(1)$ and $R(0)$ branches in terms of one singlet state interacting with $(N-1)$ mutually orthogonal triplet states, where N is the number of transitions occurring in the relevant region. Since the transitions are widely separated this appears to be a perfectly permissible exercise.

We then have a rather unusual problem: Given a set of eigenvalues (the energies of the transitions) and a set of amplitudes of one (singlet) state (the square roots of the intensities of the transitions) de-diagonalize the matrix to the form representing the interaction of one state with $(N-1)$ mutually orthogonal others.

This matrix has N diagonal elements and $N-1$ different non-diagonal elements. For the solution we have $(N-1)$ energy differences and N amplitudes. Together with the requirement of ortho-normality for the states we thus get $2N-1$ non-linear equations, which should be solved numerically. With a little luck such solutions were found by standard computational procedures for the $P(1)$ and $R(0)$ members. The results for $P(1)$ are given in Figure 2, where we display the

FIGURE 1a The molecular eigenstate spectrum of the $P(1)$ and the $P(2)$ rotational members of the ${}^1B_{3u}$ (0-0) transition of pyrazine.

basis set of singlets and triplets, as well as the molecular eigenstates with their singlet amplitudes. In Figure 3 we give the matrix representing the singlet triplet interaction for the $P(1)$ region. Figure 4 finally gives the matrix of the squares of the coefficients, showing how the various singlet and triplet states are mixed.

FIGURE 1b The molecular eigenstate spectra of the $R(0)$ and $R(1)$ members.

It should be noted that this is the simplest treatment one can give to this problem. It only separates the radiative state from the non-radiative ones. The singlet is certainly the $J=0, K=0$ ($P(1)$) or the $J=1, K=0$ ($R(0)$) rotational state of the $^1B_{3u}$ (0-0) electronic state, but about the nature of the triplets no information is gathered.

TABLE I
Energies^a and intensities of the molecular eigenstate spectrum belonging to the $P(1)$ and $R(0)$ members of the ${}^1B_{3u}$ (0-0) transition of pyrazine- h_4

$P(1)$		$R(0)$	
Energy (MHz)	Intensity (rel)	Energy (MHz)	Intensity (rel)
		2164	0.01
831	0.22	2136	0.01
738	1.00	1179	0.00
608	0.07	926	0.10
51	0.52	884	0.06
-56	0.17	796	0.23
$S = -12\ 192$		$S = +12\ 192$	
-227	1.00	331	0.06
-325	0.15	304	0.12
-367	0.49	-10	0.16
-538	0.17	-309	0.05
-1439	0.16	-369	0.04
-2516	0.03	-475	0.10
-2855	0.05	-550	0.09
		-664	0.04
		-1299	1.00

^a The energy of the center of gravity (S) is referred to the center of the whole rotational spectrum of the ${}^1B_{3u}$ (0-0) transition. The ME energies are referred to S . From $E_S(R(0)) - E_S(P(1))$ the rotational constant $\frac{1}{2}(A' + B')$ can be obtained. Its value from this spectrum is $0.203 \pm 0.003\text{ cm}^{-1}$, to be compared with an earlier value obtained by Innes¹⁰ of 0.2052 cm^{-1} . The agreement appears to be satisfactory.

Assigning vibrational quantum numbers to the triplet states appears to be a hopeless and meaningless task. Suffice it to state that their density appears to be in agreement with fairly simple calculations. A similar position should be taken with respect to the matrix elements for the coupling. There is no sign of a "democratic distribution" as has sometimes been suggested. Each and every triplet state is coupled differently to the singlet. In any case, the vibrational components are not thoroughly mixed at some 4000 cm^{-1} above the triplet ground state, otherwise the matrix elements would vary in a more continuous manner. Finally, in view of their magnitude (from $100\text{--}300\text{ MHz} \approx 0.03\text{--}0.1\text{ cm}^{-1}$) it would seem rather hopeless to calculate these numbers as has been endeavored by some.

FIGURE 2 The zero order states and the ME's of the $P(1)$ member compared. The heavily drawn parts in the ME's indicate the amplitude of the singlet.

Reconstitution of decays from the ME-spectrum

Since the ME-spectrum basically contains the (square of) amplitudes in ω -space, using linear response theory one should in principle be able to reconstruct decays by Fourier-transforming the (square root of the) spectrum to find the equations of motion of these amplitudes in t -space. Since we are dealing with a quadratic process (the light emitted is proportional to the square of the singlet amplitude), we should square the Fourier transform to obtain the actual decay, which can then be compared with experiment. In general, however, this decay will consist of various beats and small changes in frequency

INTERACTION MATRIX

823			56								
	626		83								
		441	422								
56	83	422	0	126	131	77	54	86	287	236	283
			126	-3							
			131		-86						
			77			-300					
			54				-336				
			86					-515			
			287						-1375		
			236							-2490	
			283								-2818

(ENERGY IN MHZ)

FIGURE 3 The interaction matrix representing the singlet-triplet interaction for the $P(1)$ member.

.88	.12	0	0	0	0	0	0	0	0	0	0
0.01	.12	.86	0	0	0	0	0	0	0	0	0
.060	.43	.12	.15	.03	.10	.01	.03	.01	0	0	0
.05	.25	.02	.13	.04	.04	.25	.04	.04	.04	.01	.01
0	.01	0	.59	.30	.08	.01	.01	0	0	0	0
0	.01	0	.11	.61	.23	.01	.03	0	0	0	0
0	0	0	.01	.01	.24	.55	.19	0	0	0	0
0	0	0	0	0	.06	.38	.56	0	0	0	0
0	0	0	0	0	.02	.01	.04	.93	0	0	0
0	0	0	.01	0	.01	0	.01	.01	.94	0	0
0	0	0	0	0	0	0	0	0	0	.98	.01
0	0	0	0	0	0	0	0	0	0	.01	.98

FIGURE 4 The matrix of the squares of the amplitudes of the zero-basis states in one another, showing how the various zero-order states are mixed.

lead to completely different patterns. Therefore, for comparison of experiment and reconstruction it is better to Fourier-transform once more the decays, thus obtaining the frequencies they contain, which then are the difference frequencies in the part of the ME spectrum that was excited by the laser.⁴

To this purpose we should realize that the ME spectrum is a convolution of the lifetime and the residual Doppler broadening. Since the decay we want to reconstruct is an intramolecular property, the Doppler width can for the moment be ignored. The lifetimes of the ME's, as far as we know, are *not* determined by the diluted singlet amplitude, but they seem to have a constant lifetime of about 450 ns⁵ as shown by the long-time decay. This time is considerably shorter than what one would estimate for the diluted lifetime, which works out as 200 ns multiplied by 10 (the radiative lifetime of the $^1B_{3u}$ state as determined from the integrated absorption multiplied by the number of participating states). A similar observation can tentatively be made for the $^1B_{3u}$ ($6a^1$)-transition, where the ME's appear to have lifetimes of about 250 ns. This then means there is yet another radiationless process converting triplet states into vibronic components of the ground singlet state. (In its turn this would mean that we *still* don't measure real molecular eigenstates, but in reality states very close to that elevated status.) Solution of this problem awaits lifetime measurements of the individual ME's, which have not yet been carried out.

This all being so, it appears best to assign a constant lifetime to the ME's, which in the reconstruction means convoluting the stick spectrum of amplitudes, obtained after taking the square roots of the stick spectrum obtained after removal of the Doppler widths, with a complex Lorentzian of a width of 1 MHz: $A(\omega_i) \otimes L(\omega - \omega_i)$. To obtain the part of these amplitudes that is excited we should multiply with a (Gaussian) function of the laser amplitude $G(\omega - \omega_0)$, centered at ω_0 : $E(\omega) = \{A(\omega_i) \otimes L(\omega_i - \omega)\} \cdot G(\omega - \omega_0)$. To obtain the decay we should then calculate $|FT(E(\omega))|^2$ and finally Fourier transform this quantity to obtain a spectrum of the beats in the decay: $FT|FT(E(\omega))|^2$. This result can then be compared to the Fourier transform of the experimentally determined decays, and if linear response theory holds, they should be the same!

Such a comparison for the decays of the $P(1)$ ME's is made in Figure 5 for a decay of an excitation with our 300 MHz (fwhm) laser

somewhere in the center of the ME-spectrum, where we think our laser is positioned. Apart from amplitudes (but they depend strongly on position) the agreement is excellent. The larger the coherent width of the laser, the more frequencies will turn up in the decay. In Figure 6 we therefore compare a reconstruction of a decay with the Fourier transform of a beat pattern obtained by the chairman of this conference and his co-workers,⁶ using a picosecond laser with a width of about 60 GHz, well exceeding the whole width of the ME spectrum. Again, the agreement is very satisfactory. All the frequencies that we obtain (up to about 1000 MHz, the limit of their time-detection) are also contained in their "spectrum". They do have some extra peaks, probably because their laser is so broad they also excite part of the Q or $P(2)$ members, leading to some frequencies arising from those ME-spectra.

FIGURE 5 Comparison of the fourier transforms of a reconstructed and an experimental decay with a laser of 300 MHz coherence width.

FIGURE 6 Comparison of the Fourier transforms of a reconstructed and an experimental decay with a laser of 60 GHz coherence width.

The conclusion of this section can be, that at least for the $P(1)$ member linear response theory appears to work, reconstructions from spectra in ω -space leading to decays that can be observed in time.

The fast component

It is well-known⁷ that the theory of Intermediate Level Structure at higher densities leads to bi-exponential decay. The ratio of the amplitudes of the fast and slow components (A^+/A^-) is then usually taken to indicate the number of levels involved in the interaction of the “doorway” state. It is, of course, a very approximate theory, assuming a “democratic distribution” of the interaction elements and thus a Lorentzian distribution of singlet amplitudes over a fairly homogeneous triplet manifold. Clearly, from our results this is not the case, and therefore one has to use the Fourier-transform technique to compare reconstructed and actual decays. But, as strong a fast component as usually appears to be obtained^{5,9} is never evident from the Fourier transforms of our spectra.

Saigusa and Lim⁹ for instance, in their study of the magnitude of the fast component as a function of rotational quantum number reach values for $A^+/A^- = 5$ at $J = 4$ in the P -branch. They take this to mean that the number of states involved in the interaction of a rotational state goes up linearly with J . Our ME spectra, however, appear to indicate otherwise. In Table II we give the number of states (N) "counted" in the ME-spectra, going from $P(4)$ to $R(3)$. Although this number *appears* to go up, one should realize that these spectra are incoherent super positions of $(2J + 1)$ K -transitions in the P -branch and $(2J - 1)$ K -transitions in the R -branch. Dividing by $2J + 1$ and $2J - 1$ respectively yields a fairly constant value around 6–15, which would mean that the number of states involved in the interaction is essentially independent of J . Nevertheless, Lim's experiment stands, we find similar effects ourselves. Rayleigh scattering may at first sight be held responsible, since in particular non-resonant states would contribute to it. But the Fourier transform technique takes Rayleigh scattering into account, it belongs to the linear phenomena. It may also be that we have under- or overestimated the lifetimes of the various ME's. If they were broader (but 50 MHz is the maximum our spectra allow) other results would be obtained, among which one might find a fast component. In any case, the question is not settled; it seems incorrect, however, to assume that A^+/A^- counts the number of states, when excitation is not by a very wide coherent laser pulse.

We can conclude, however, that linear response theory works for the $P(1)$ and $R(0)$ members of the $^1B_{3u}$ (0–0) transition of pyrazine, and in these regions the decays for any position or width of a laser can be reconstructed from the ME spectrum.

TABLE II
Number of triplets per rotational singlet level

	N	$2J \pm 1$	$N/2J \pm 1$
$P(4)$	43	7	7
$P(3)$	35	5	7
$P(2)$	31	3	10
$P(1)$	12	1	12
$R(0)$	15	1	15
$R(1)$	24	3	8
$R(2)$	38	5	8
$R(3)$	50	7	7

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