

SPECTRUM OF THE MOLECULAR EIGENSTATES OF PYRAZINE

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The molecular eigenstate spectrum belonging to the P and R branches of the ${}^1B_{3u}(0-0)$ electronic transition of pyrazine- h_4 was recorded with a 200 kHz wide laser in a supersonic nozzle at a temperature of ≈ 1 K. The square of the Fourier transform of the amplitude spectrum yields the quantum beats in the fluorescence decay that have been reported before.

1. Introduction

Recently considerable interest has arisen in the fluorescence decay of the ${}^1B_{3u}$ electronic state of pyrazine. Shortly after our initial report [1] of the variation of the decay with rotational quantum number, Okajima et al. [2] and our group [3] simultaneously reported quantum beats. We also showed the effect of nuclear spin [3]. More recently Saigusa and Lim [4] reported the dependence of bi-exponential decay on the rotational quantum number, and Felker et al. [5] published a first exploration of the magnetic-field dependence of the beat frequencies.

All these properties derive from the fact that pyrazine is an intermediate levels structure (ILS) molecule [6], where the density of states of the manifold into which the excited state is decaying, is so sparse that a limited number of molecular eigenstates (MEs) is contained within the coherence width of the exciting source. The observed decay then depends on this width and that accounts for the greatly varying reports on decay behaviour [1,7] and beat patterns [2,3,5].

If the coherence width is sufficiently narrow, however, it will at most contain one state and by scanning

with this width one obtains the spectrum of the molecular eigenstates, i.e. a spectrum of the mixed singlet-triplet states [6], mixed by the matrix elements that were responsible for the observed beats and fast decays in experiments with lasers of larger width (i.e. smaller temporal coherence).

In this paper we report the spectrum of the molecular eigenstates of pyrazine, which can be related to the beat spectrum in the decay.

2. Experimental

The spectra were obtained with a modified Spectra Physics ring laser (bandwidth 200 kHz), intracavity frequency doubled by a lithium iodate crystal. We were able to scan continuously more than 100 GHz at the time [8].

The molecular beam 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 beat experiment was carried out with a supersonic

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nozzle, at 4 cm distance from the nozzle using a Molecron DL2 dye laser, doubled in frequency.

3. Results

Figs. 1a, 1b, 2a and 2b show the ME spectrum belonging to the P and R branches of the ${}^1B_{3u}(0-0)$ excitation (the temperature is estimated to be ≈ 1 K; note the extended "empty" regions between the various rotational members). Since we can safely assume that all intensity derives from the zero-order rotational singlet states, the intensities in any one band are a measure of the singlet amplitude in the MEs, and the positions of the zero-order singlets (S) are given by the "centers of gravity" of the spectra given by $E_S = \int I(E)E dE$. They are indicated in figs. 1 and 2. For

the P(1) member we give energies and intensities in table 1.

From the positions of the centers of gravity of R(0) and P(1) one can, independent of the approximation symmetrical or asymmetrical top, derive the rotational constant $\frac{1}{2}(A' + B') = 0.201 \pm 0.003 \text{ cm}^{-1}$, in good agreement with the value 0.2052 cm^{-1} reported by Innes [9]. Our uncertainty derives from the uncertainties in determining the positions of the centers of gravity.

It is generally agreed [5,6,10] that calculations yield a background density of states of ≈ 100 per cm^{-1} , not counting spin degeneracy and neglecting nuclear spin effects. Taking these into account one has to multiply by 3 ($S = 1$) and to divide by 4 (σ), yielding $\rho_T \approx 75 \text{ cm}$. To the P(1) member appear to belong ≈ 12 states, of which one was a singlet. We therefore have

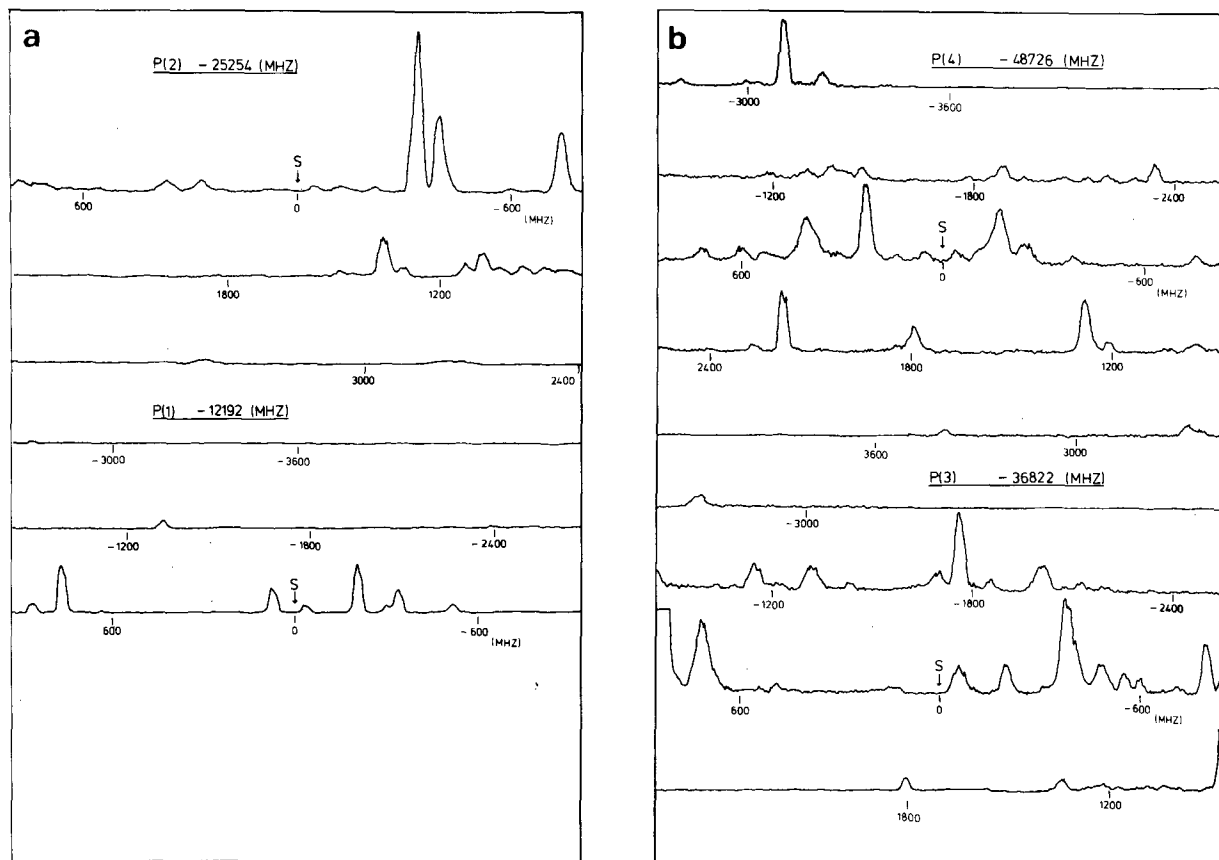


Fig. 1. The molecular eigenstate spectrum in the P branch of the ${}^1B_{3u}(0-0)$ transition of pyrazine. The derived positions of the zero-order singlet rotational states are indicated by the letter S. Their energies, referred to the center of the total spectrum, are indicated.

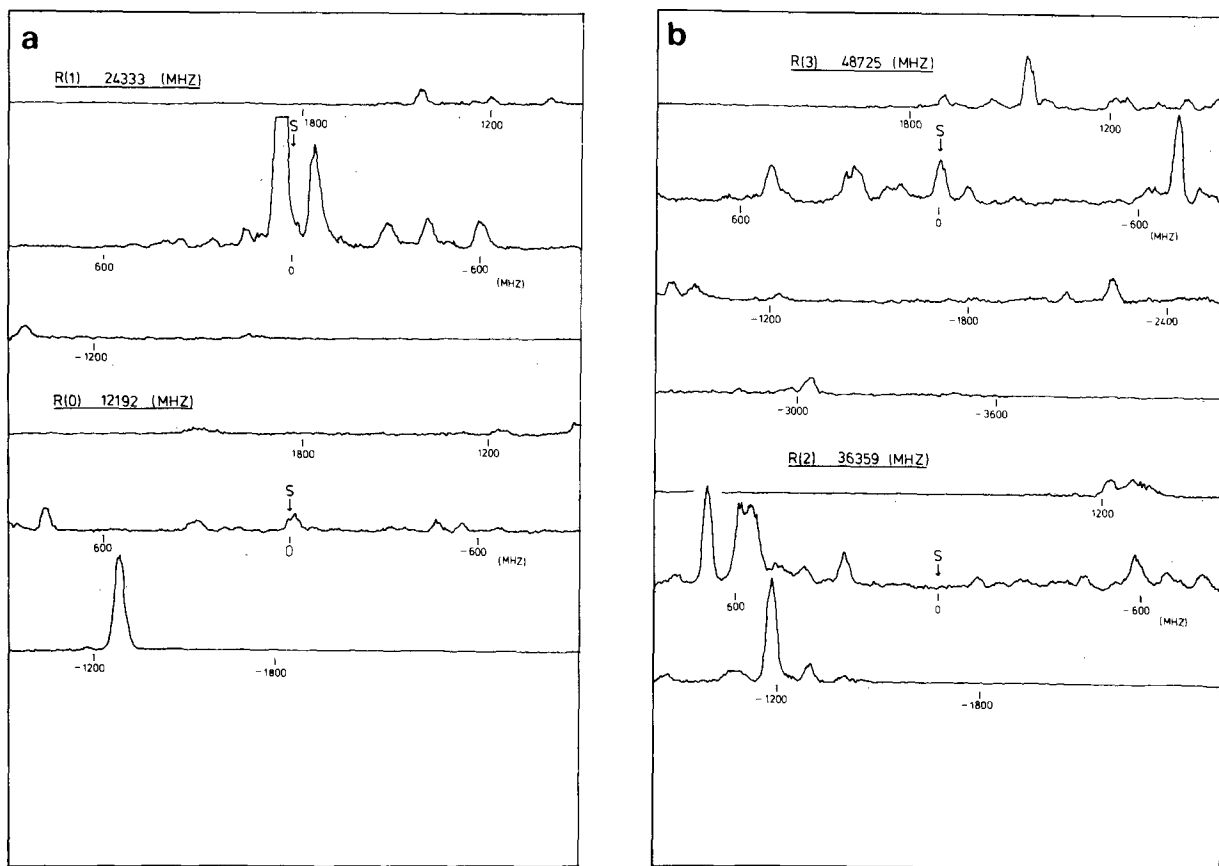


Fig. 2. As fig. 1 but now for the R branch.

Table 1

Energies ^{a)} and intensities of the molecular eigenstate spectrum belonging to the P(1) member of the ${}^1B_{3u}(0-0)$ transition of pyrazine- h_4 . $\nu_S = -12192$ MHz

Energy (MHz)	Relative intensity
831	0.22
738	1.00
608	0.07
51	0.52
-56	0.17
-227	1.00
-325	0.15
-367	0.49
-538	0.17
-1439	0.16
-2516	0.03
-2855	0.05

^{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.

11 triplet states over ≈ 4000 MHz, which yields an average density of ≈ 80 per cm^{-1} , a surprisingly good agreement.

4. Reconstruction of the decay from the ME spectrum

The lines in the region of the P(1) and R(0) members are due to MEs deriving their intensities from single rotational singlet states ($J' = 0, K' = 0$ and $J' = 1, K' = 0$, respectively). The other parts of the spectrum are superpositions of ME lines deriving intensities from states with one J' , but with all K values up to $J' - 1$ (P branch) or J' (R branch). It should be possible to reconstruct the beating decays of P(1) and R(0) from their energy spectra.

The energy spectrum $|A(\omega)|^2$ of figs. 1 and 2 is a convolution of the lifetime and 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 MEs are *not* determined by the diluted singlet amplitudes, but there appears to be another non-radiative process operative (probably triplet-ground-state intersystem crossing), which gives a constant lifetime to the MEs (450 ns for the 0-0 band [5] and 250 ns for the $6a_0^1$ transition [1]). The amplitude stick spectrum $A^s(\omega_i)$ should therefore be convoluted with a complex Lorentz function to give the lifetime-broadened amplitude spectrum $A^l(\omega) = A^s(\omega_i) \otimes L(\omega_i - \omega)$. To obtain the excitation amplitude spectrum $E(\omega)$ this function must be multiplied by the laser function $f(\omega - \omega_0)$: $E(\omega) = \{A^s(\omega_i) \otimes L(\omega_i - \omega)\} f(\omega - \omega_0)$, where ω_0 denotes the center of the laser width. Because we are considering emission, a quadratic process, the decay is then given by the square of the Fourier transform of $E(\omega)$: $|\text{FTE}(\omega)|^2$. It appears to be customary in this field [3,5] to Fourier transform the decay to display better the beat frequencies. It should be noted that these are the difference frequencies occurring in the energy spectrum. Fig. 3 therefore compares not the decay, but its Fourier transform as observed experimentally by Felker et al. [5] with the

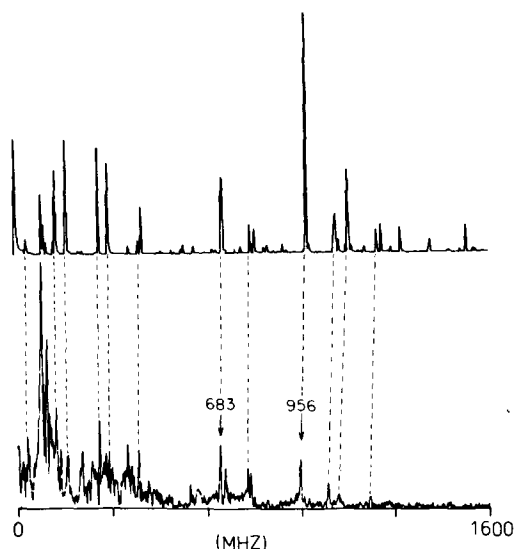


Fig. 3. The Fourier transform of the decay of the P(1) member as calculated from the ME spectrum (given in table 1) excited with a 60 GHz wide laser, centered at S (top), compared with the $H = 0$ experimental result of Felker et al. [5] (bottom).

Fourier transform of the decay as calculated from the ME spectrum of P(1) with a laser width of $(15 \text{ ps})^{-1} \approx 60 \text{ GHz}$, well exceeding the total width of a component of the ME spectrum.

It is clear that almost all frequency components of Felker et al.'s decay are reproduced. There are some extra features in their Fourier transform, since their laser was spectrally much wider and they undoubtedly included beats originating from the Q branch, R(0) are P(2). This also holds for the fast component which they observe experimentally, but which does not occur in the decay calculated from the ME spectrum.

At this point it appears worthwhile to point out that for the complete understanding of the spectroscopy and the dynamic processes our direct method of measuring the ME spectrum is superior to the indirect method of measuring quantum beats. The frequencies of the latter are difference frequencies in the ME spectrum and there is no way the spectrum can be reconstructed from them. The reverse, however, is possible and apart from problems with the Doppler width, it is gratifying to see how well the method works.

To illustrate how the laser width affects the time evolution, we measured a decay of the P(1) member

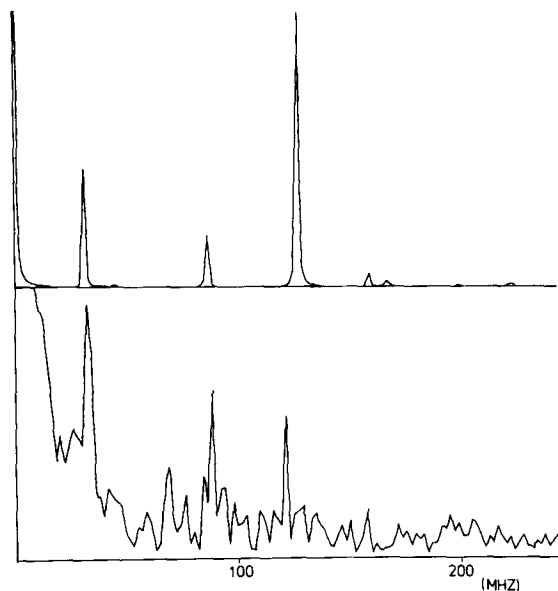


Fig. 4. The Fourier transform of the decay of the P(1) member as calculated from the ME spectrum (given in table 1) excited with a 300 MHz (fwhm) wide laser, centered at -380 MHz with respect to S (top), compared with our own experimental result (bottom).

of ${}^1B_{3u}(0-0)$ transform with a 300 MHz broad dye laser. The 300 MHz (fwhm) was obtained from a line-width of 0.01 cm^{-1} , as determined with an interferometer. Fig. 4 compares the Fourier transform of this decay with one calculated from the ME spectrum, also using a 300 MHz width and positioning the center of the laser at -380 MHz with respect to S, the position at which to the best of our knowledge it is in the actual experiment. The agreement is very good, except for one aspect. The 300 MHz wide laser has at least three modes and shows some frequency drift. Allowing for mode hopping over 600 MHz, averaging the decays and Fourier transforming that result yields the same spectrum, but produces in addition a frequency at 175 MHz, which – possibly due to our detection – we do not observe in transforms of the experimental decays. Apart from this feature, however, the agreement is excellent.

5. Conclusion

The spectrum of the molecular eigenstates of pyrazine, together with their decay times contain all information necessary to obtain decays at any laser width and position. Efforts to obtain these spectra for the deuterated pyrazines and pyrimidine are presently being undertaken.

Acknowledgement

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