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PYRAZINE REVISITED

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ABSTRACT : Pyrazine is shown by its Molecular Eigenstate Spectra and by its quantum beats to be a small molecule. The effect of Coriolis coupling and non-resonant light scattering are discussed. This paper further treats the so-called "fast component". Its existence with a decay time of about 100 psec has by now been firmly established. It finds its cause in the "bunching" of the molecular eigenstates in frequency space. For broad (i.e. psec) lasers it is therefore still useful to speak of pyrazine as an ILS-molecule. The characterization depends on the laser one uses in the experiment.

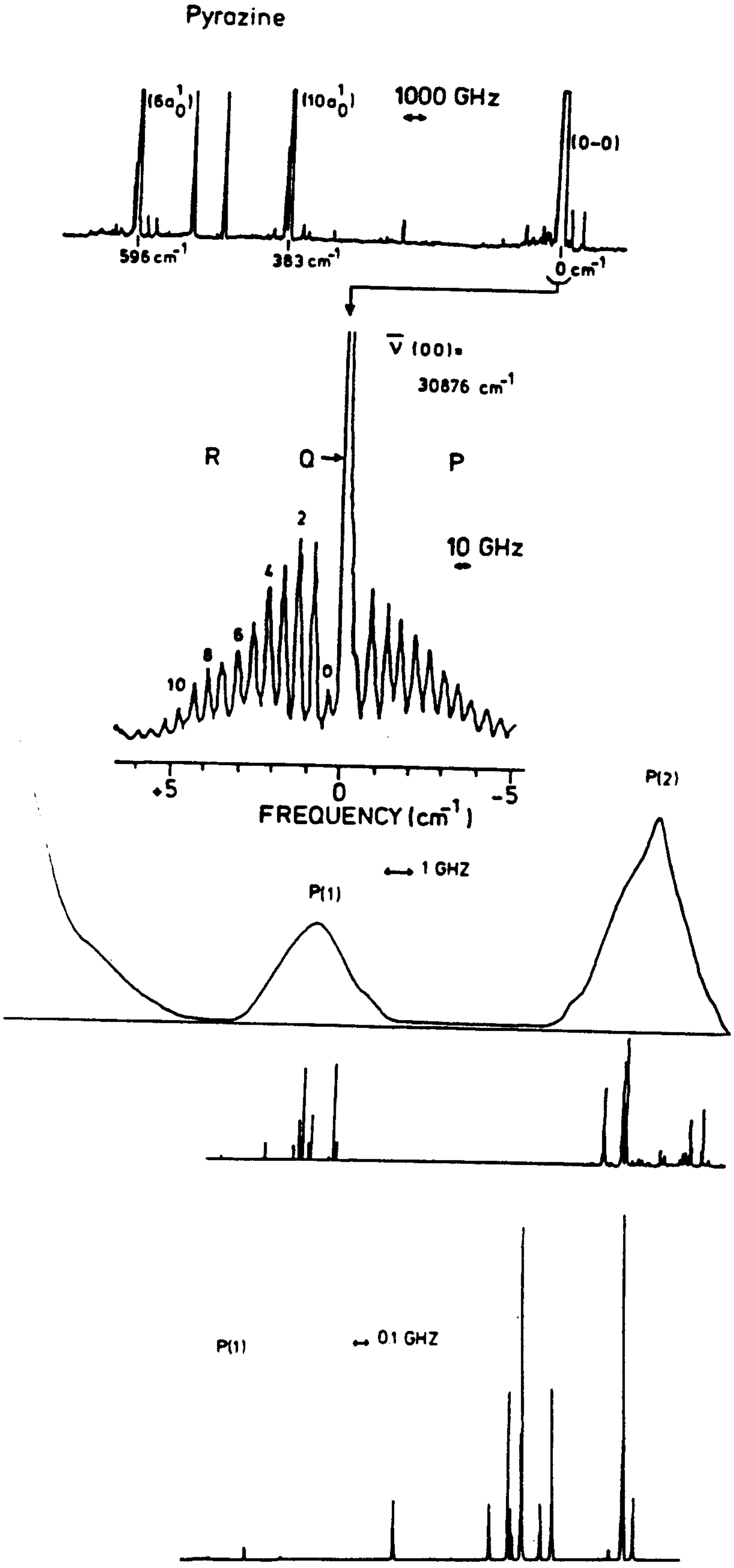
I INTRODUCTION

The ten atom molecule pyrazine ($C_4N_2H_4$) has for a long time been taken as the prime example of Intermediate Level Structure (ILS). The original concept came from Tramer et al. (1, 2), who convincingly showed that an intermediately dense manifold of triplet vibronic states that a singlet excited state was coupled to, would lead to so-called bi-exponential decay, where the ratio of the amplitudes of the fast and the slow component (A^+/A^-) yielded a measure of the number of dark states coupled to the "doorway" state. Pyrazine was considered to be a prime example and the theory was successfully applied to other molecules as well (3).

With the advance of high resolution lasers and with the use of supersonic nozzles and molecular beams, the situation changed. In particular through the work of van der Meer et al. (4), who showed with a 200 kHz wide laser in a 5 MHz Doppler broadened molecular beam, that the single rotational singlet transitions in reality were split into many isolated lines (see fig. 1). From their work they could show that these lines were due to transitions from a ground rotational state to the molecular eigenstates formed from a ro-vibronic singlet state and some 12 to 14 background triplet states (4). This observation put pyrazine in one class with molecules such SO_2 and NO_2, which have been traditionally classified as "small molecules" for the purposes of radiationless transitions. In agreement with this classification, exciting one ME with a very narrow laser yielded single exponential decay (5) and exciting a limited number of ME's (6,7,8) yielded quantum beats.

But what then was the cause of the fast component obsesrved? Tramer's original calculation (1) appeared to exclude its occurrence for a limited number of coupled levels (≈ 13) such as in pyrazine, and moreover the A^+/A^- ratio never had the values derived from the spectroscopic experiments. Nevertheless the existence of the fast component was recently most firmly established by the work of Rice (9) and Zewail (10).

Also, there was a problem with the quantum yield. For a really small molecule one might expect it to be one, while it was measured to be in the order of 10^{-2} (11). Moreover, it was measured to inversely depend on the



a) The vibronic spectrum of pyrazine in a supersonic jet

b) The $^1B_{3u}$-(0-0) transition blown up so as to yield the rotational spectrum

c) The rotational components P(1) and P(2) and the underlying ME's.

d) The ME-spectrum of P(1)

Figure 1

rotational quantum number J (11,12) similar to the J-dependence of the A^+/A^- ratio (9,13).

A suggestion was made (14) that at least the fast component might be due to non-resonant light scattering (NRLS), which, of course, should have a quantum yield of one and might show up very preponderantly in an electronic decay, but it would appear that the experiments of Rice (9) and Zewail (10) have shown the contribution of NRLS to be at most a minor effect.

This paper therefore addresses three major questions.

1) What is the reason for the low quantum yield?
2) What is the fast component due to?
3) Where does the J^{-1} dependence of quantum yield and A^+/A^- derive from?

II THE QUANTUM YIELD

Pyrazine may behave as a small molecule with respect to the triplet manifold, but not with respect to the singlet ground state manifold S_0. It is very dense, and a very small interaction v has a considerable effect on the quantity $2\pi v^2\rho$, which would describe the coupling to the dense manifold S_0. Of course, the triplet state T will also be coupled to S_0, but _ceterus_ _paribus_ this coupling will be one or two orders of magnitude less because it is spin-forbidden. The low quantum yield in this view must be due to the S - S_0 coupling. This can be studied by looking at the relative (integrated) intensities of the rotational excitation spectra. These spectra are the result of a product of absorption intensities and quantum yields. The absorption part can be readily calculated using a Boltzmann distribution and the Hoehnle-London factors for the intensities of rotational transitions. In fact it was found (15) that most states _are_ in Boltzmann equilibrium, except for the A_g ground J = 0, K = 0 state, which can only be reached by a $\Delta J = 2$ transition, which apparently is impeded in the low density part of a supersonic nozzle. Careful comparison of calculated and experimental values yielded (15) for the z and x,y components of the Coriolis constants the values listed in table I. By also taking the hyperfine interaction in the triplet-state into account, the value of the quantum yield and the average life-time of the ME transitions can be as satisfactorily explained as can be hoped for in such a complicated molecule as pyrazine.

TABLE 1 Coriolis Constants for the $^1B_{3u}$(0-0) of pyrazine

$K \quad K+1 : \Gamma_+^{xy} = B_+(J-K)(J+K+1) \qquad B_+ = 0{,}30\ \Gamma$

$K \quad K-1 : \Gamma_-^{xy} = B_-(J+K)(J-K+1) \qquad B_- = 0{,}00\ \Gamma$

$K \quad K \quad : \Gamma^z = A_z\ K^2 \qquad A_z = 0{,}20\ \Gamma$

Γ is a measure for the J,K independent radiationless rate ($\Gamma \approx 3 \times 10^8$ sec^{-1})

Also, by considering K-scrambling to occur at higher J an explanation could be found for the J^{-1} dependence of the quantum yield as found for higher J's (11,12). K-scrambling leads to averaging of the Coriolis parameters to a J, K independent constant. As J goes up, the number of states a K-scrambled state can interact with is increased by 2J+1, without the normally concomitant reduction of the matrix element v. Therefore, the value of $2\pi v^2\rho$ goes as (2J+1), and this yields the observed $(2J+1)^{-1}$ dependence of the quantum yield.

III THE FAST COMPONENT

The experimental evidence for the fast component has by now been firmly established. Originally measured by Tramer et al (2), its occurrence has essentially been verified by every worker in the field. In particular the recent experiments by Rice (9) and Zewail (10) have shown most clearly that a decay of about 100 psec is present in the decay of pyrazine, visible of course only when the laser time is considerably shorter than this value. The A^+/A^- ratio was given to vary between 0,3 (Zewail) and from (1 to 5) (Rice), linearly dependent on J (see also (13)) and this of course is in flagrant contradiction to the number of states measured spectroscopically (≈ 13). The explanation, however, is quite simple. In their original theory Tramer et al. (1) assumed the singlet amplitudes of the molecular eigenstates to have a Lorentzian distribution, due to the fact that they assumed the matrix element to be invariant over the background manifold, and the manifold to be more or less uniformly spaced.

Nothing could be further from reality. As the de-diagonalisation of the ME-spectra showed (4,16) the matrix elements of the S-T coupling are observed to vary between 50 and 2000 MHz and the spacings of the triplet manifold are quite irregular. Also, the absortion spectrum of one set of ME's belonging to a particular rotational transition really cuts off, no absorption can be discerned (S/N $\approx$ 1000) beyond the range ($\approx$ 2000 MHz), where the ME's occur.

This means then that the ME-spectra occur in bunches (blocks) over about 2000 MHz, after which frequency space is empty for 10.000 MHz, where the next block of ME's occurs. Taking a laser with a frequency width $\Delta\omega >> 2000$ MHz therefore excites basically a relatively narrow block of absorption, with some internal structure, which, however, after Fourier transformation only manifests itself at longer times. The actual block yields upon Fourier transformation a function like $\sin(\Delta\omega t)/t$, which after squaring (since the radiation will follow $|c_s(t)|^2$, the square of the singlet amplitude in the ME's!) may for a while deceptively look like an exponential.

Performing on a computer the Fourier Transform of a broad laser multiplied into the actual P(1) and P(2) ME-spectra yielded at 180 psec decay (17) (see fig. 2), not too far from the value of about 100 ps as

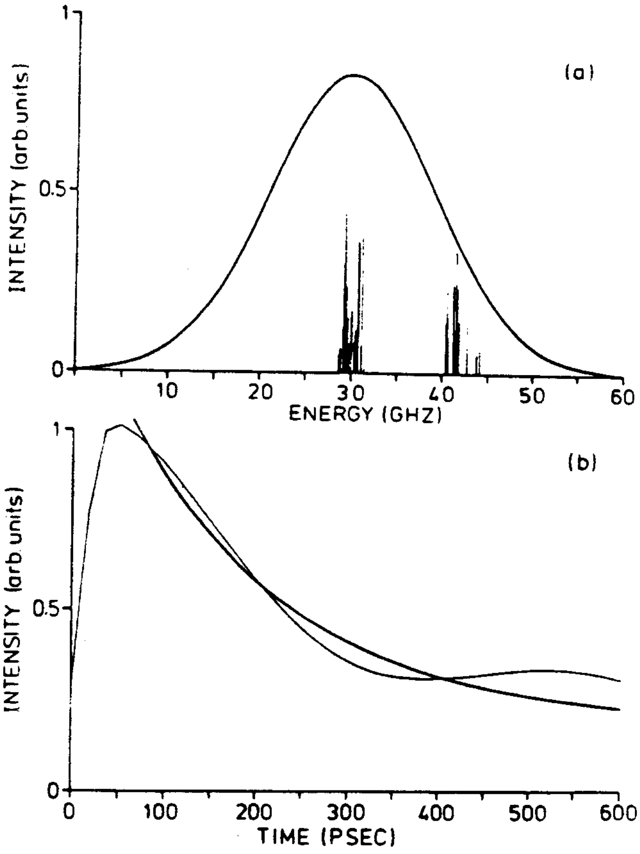


Fig.2. a) The laser and the P(1), P(2) ME spectra. Note the "bunching".
b) Decay obtained from the square of the Fourier transtorm of a).

observed by Rice (9) and Zewail (10). The fast component then is still due to the original dephasing as described by Tramer (1). It differs mainly in the fact that the singlet amplitude is not at all distributed like a Lorentzian, and therefore the quantitative conclusions drawn from the A^+/A^--ratio are unreliable.

Why then does the A^+/A^- ratio depend so strongly on J? The following explanation has been put forward (17). The dephasing is a fast process, it takes about 100 psec. The Coriolis interaction of S_1 with S_0 happens on a time-scale of about 3000 psec. This follows from our Coriolis constants, but also from the quantum yield of 1% and a radiative lifetime of 300 nsec. It seems then, that the dephasing process is over before the S_1-S_0 interaction has run any significant part of its course. Conventionally one mesures A^+ at very short times (<100 psec) and A^- at much longer times (≈ 100.000 psec). If the decay would be exponential one could easily calculate back from a measurement at any time window, but since the decay is at least biexponential (if the quantum beats are averaged out!) the "initial" quantum yield appears to be much higher than the "delayed" quantum yield. Since the "delayed" quantum yield depends on $(2J+1)^{-1}$, the A^+ (initial) and A^-(delayed) ratio depends on (2J+1).

CONCLUSIONS

It would seem that the decay of the $^1B_{3u}$ electronic state of pyrazine can be largely understood. For narrow lasers ($\Delta\omega$ < 1GHz) it behaves like a small molecule, for broader lasers ($\Delta\omega$ > 10 GHz) it shows ILS behavior. The classification of pyrazine depends as much on the molecular structure as on the laser used in the experiment! After all, it is quantum mechanics. The answer one gets depends on the experiment one performs!

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