# Rotational effects on pyrazine S 1(1 B 3u ) dynamics and the problem of the missing states

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## COMMUNICATIONS

# Rotational effects on pyrazine $S_1({}^1B_{3u})$ dynamics and the problem of the missing states

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The $S_1({}^1B_{3u})$ state of pyrazine serves as a touchstone for the theory of radiationless transitions. This theory is confronted with the wealth of experimental results. A full account on the "story of pyrazine" is given elsewhere.[1] One of the major problems, known as the "problem of the missing states," emerges from the number of spectrally observed, mixed singlet–triplet states [molecular eigenstates (MEs)] in each rotational transition. This number is too low and is rotational independent[2-5] and thus is in conflict with the emission quantum yield[6,7] and time resolved[8,9] data which require a much larger number of MEs and its rotational dependence. This problem also pertains to the origin of the short component in the time resolved emission after incoherent nanosecond laser excitation.[1-4] A multitude of weak Coriolis coupled MEs denoted as "grass" were introduced[10,11] to account for for this short component within the intermediate level structure limit.

Coriolis coupling was shown to be the dominant intrastate vibronic coupling leading to vibrational energy redistribution (IVR) in benzene,[12,13] 9-cyanoanthracene,[14] anthracene,[15] and pyrimidine.[16]

It was predicted by the author[1] that the absorption contour of a single rotational transition should be broader in absorption than in excitation, and a low quantum yield absorption should extend to the valley between adjacent rotational transitions where no MEs were observed in the high resolution excitation spectra.[1] The debated grass[10,11] is real, but in the form of a continuous absorption having a low quantum yield. Here I address the question of the existence and nature of this predicted grass.

Our experimental apparatus[6,17] was extended to include an eximer pumped dye laser (Lambda Physik EMG 53 MSC + FL2002E) having a 2 GMz spectral resolution using an étalon and pressure tuning. Pulsed planar jets were generated by expansion of seeded argon through a nozzle slit.[18]

Direct absorption and fluorescence excitation spectra were simultaneously measured on each laser pulse and then averaged. The laser repetition rate was doubled as compared with the pulsed nozzle repetition rate and a second differentiation was performed between the timed (with the gas pulses) and untimed laser light pulses. This procedure resulted in a flat, zero wavelength independent absorption base line.

Figure 1 shows the absorption and excitation spectra of pyrazine $S_1({}^1B_{3u})$ origin. It is clearly observed that the
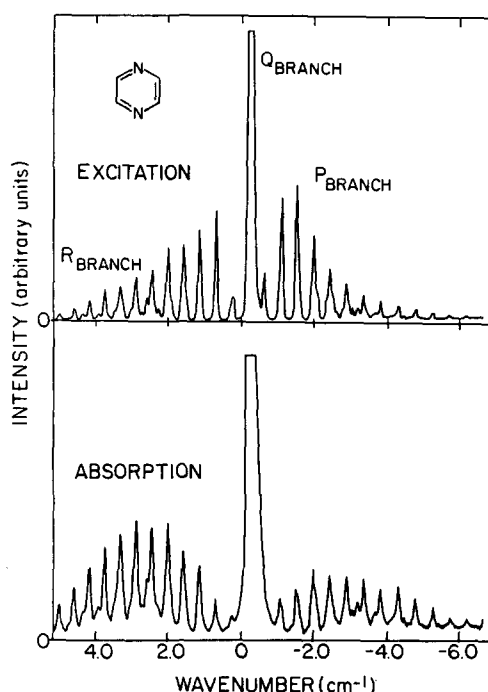


FIG. 1. Absorption and fluorescence excitation spectra of pyrazine $S_1({}^1B_{3u})$ electronic origin. Spectral resolution is 2 GHz. The two spectra were simultaneously measured using an étalon and pressure turning. Nozzle temperature was 24 °C, argon backing pressure was 60 Torr, and the laser crossed the pulsed planar jet 16 mm from the nozzle.
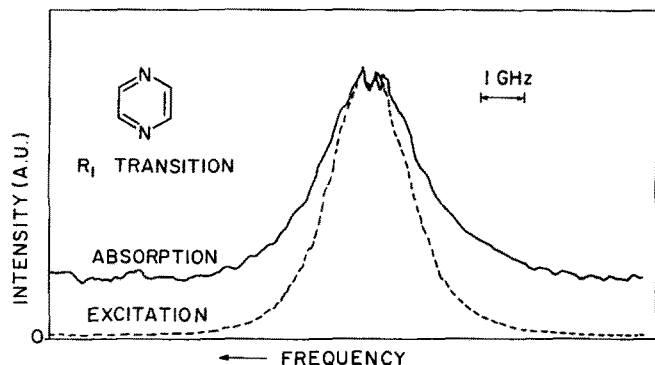
FIG. 2. Absorption (full line) and fluorescence excitation (dashed line) spectra of the $R_1$ rotational transition of pyrazine $S_1$ ($^1B_{3u}$) electronic origin. Experimental conditions are as in Fig. 1.

Finally we note that these experimental results are in contrast to predictions based on the existence of a high quantum yield near resonance Raman light scattering (NRLS) in the valleys.[2–4,19] NRLS has 100% quantum yield, much higher than that of the $S_1$ origin of pyrazine.[6] NRLS imply a higher excitation spectrum in the valley compared with the absorption spectrum. The experimental results are inconsistent with that prediction.

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emission quantum yield reduces with the rotational quantum number both in $P$ and $R$ branches.[6] A closer inspection reveals that the absorption signal between rotational transitions is much larger than the corresponding excitation signal.

In Fig. 2, the $R_1$ transition is magnified. Figure 2 nicely demonstrates that the absorption contour is broader than the excitation contour and a low quantum yield absorption extends to the two sides of this transition. These experimental results constitute and demonstrate two important findings: (a) the dynamics of pyrazine $S_1$ ($^1B_{3u}$) electronic origin is governed by many more MEs than is deducted from ultrahigh resolution *excitation* spectra;[2–5] (b) there is a dramatic large variation in the observed emission quantum yield which is much smaller (by a numerical factor of 20!) in the valleys between adjacent rotational transitions.

We are now in the position to state that the problem of the missing states is solved. The missing states are grass, namely a low quantum yield, short time emission, inhomogeneous superposition of homogeneously broadened MEs($J''$,$K'\neq0$).[1] They are characterized by a fast intratriplet IVR. In the excitation spectra they are missing because they are broad and have low ($6\times10^{-4}$) emission quantum yield; thus, they are below the detection sensitivity limit of Kommandeur and co-workers,[2–5] as they are predicted to be $\sim10^{-3}$–$10^{-4}$ of the peak height of MEs($J''$,$K''=0$) in the ultrahigh resolution spectra.[2–5]

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# Photoinitiated H+CO₂→OH+CO reactions: OH distributions and three-body interactions in CO₂H₂S complexes[a]

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In previous publications, we reported using weakly bonded complexes as precursors in studies involving oriented and aligned reactants.[1–5] This method provides a unique environment wherein the V, R wave functions and equilibrium geometry determine the initial positions and momenta of the nuclei in the reaction which follows photoexcitation, thereby allowing geometrically constrained entrance channels to be explored. In these studies of precursor geometry