

PYRIMIDINE, AN INTERMEDIATE STATE MOLECULE?

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The $S_1(^1B_1) \leftarrow S_0(^1A_1)$ transition in pyrazine has been investigated. High resolution laser induced fluorescence spectra were obtained by crossing a well collimated molecular beam with UV radiation of an intra-cavity frequency doubled ring laser. The extreme resolution enabled us to observe the molecular eigenstates of the electronically excited state. Most of the spectral features of the S_1 state could be interpreted in terms of a slightly perturbed axis switched rotor spectrum. The perturbations show up both in the energy levels of the S_1 and in the intensities of the observed transitions.

1. INTRODUCTION

In the past few years considerable experimental and theoretical progress has been made towards the understanding of the electronic, vibrational and rotational spectra of polyatomic molecules. This progress was powered by high resolution lasers operating in either the ultraviolet, visible, or infrared region of the electromagnetic spectrum. In the present work we will describe the applications of laser

studies of the structural and dynamic properties of the electronically excited state of the medium size molecule pyrimidine. We will demonstrate that structural parameters of near microwave accuracy can be derived from data obtained for electronically excited states. The experimental set-up consists of a single frequency near UV laser combined with laser induced fluorescence (LIF) spectroscopy in a well collimated molecular beam. This set-up has been used to obtain spectra with rovibronic resolution.

The present work discusses the results on pyrimidine (1,3 diabenzene). The O_0^0 band of the $S_1 \leftarrow S_0$ spectrum was fully resolved under ultra high resolution conditions. Most of the features of this spectrum could be explained using an asymmetric rotor Hamiltonian. This characterizes pyrimidine as a "small" molecule. Several clear disagreements point to the presence of local perturbation. The positions and the intensities of some lines deviate significantly from their "best fit" values. The same lines show a dependence in a weak magnetic field (< 60 G). Extra lines are also observed in the vicinity of the perturbed lines, which are broadened and/or split in the presence of a field. The latter observations will be ascribed to an isolated intersystem crossing (ISC) between the S_1 and a nearly isoenergetic rovibronic level of a lower triplet state (T_1).

2. EXPERIMENTAL

The experimental set-up has been described in detail elsewhere¹; only the most relevant features will be discussed here. The narrow band ultraviolet (UV) radiation has been obtained by the method of second harmonic generation (SHG)².

Briefly the SHG is obtained by placing a LiIO_3 angle tuned single crystal of 1 mm thickness in a modified Spectra Physics ring dye laser. Stabilized scans over 4 cm^{-1} with a linewidth of less than 0.5 MHz could easily be made. About 1 mW of continuous wave (CW) power has been applied at the interaction zone with the molecular beam. The absolute frequency calibration has been performed on the calibration absorption spectrum of iodine³. Relative frequencies have been measured by a sealed off temperature stabilized Fabry-Perot interferometer.

The molecular beam was formed by expanding a mixture of pyrimidine in argon through a 100 μm nozzle. The total back- ing pressure was 1 bar and the source was kept at room temperature, in order to achieve rotational resolution the molecular beam was strongly collimated by a dual skimmer and differential pumping arrangement. The interaction zone where the laser beam crosses the molecular beam was placed 30 cm from the orifice. This set-up reduced the Doppler width to 15 MHz. Fluorescence excitation spectra were obtained by collecting the undispersed total fluorescence, detected by a EMI 9864/950 QA photomultiplier and measured by a standard photon counting system.

3. ENERGY LEVELS OF THE S_1 STATE

The 0_0^0 band of the $^1S_1(^1B_2) \leftarrow S_0(^1A_1)$ electronic transition has its origin at 322 nm. We have investigated this transition under high resolution. A very well resolved spectrum was obtained with no overlapping lines, with the exception of some accidental overlaps. The spectrum consists of a large concentration of transitions (Q-branch) near the band

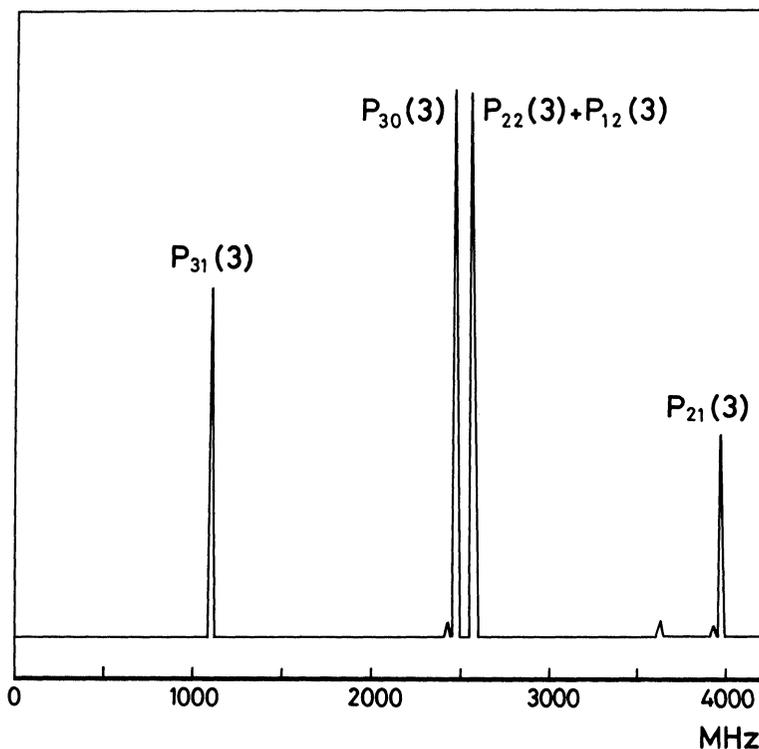


FIGURE 1 High resolution spectrum of pyrimidine near the P(3) rotational transition. The rotational assignments are indicated as $P_{K''_-, K''_+}(J'')$

origin and clusters of lines separated by about 12 GHz going up (R-branch) and down (P-branch) in frequency from the central part of the spectrum. This is in accord with the assignment of a c-type transition for the 0_0^0 band⁴. Because of the strong cooling in the adiabatic expansion during the formation of the molecular beam only the lower rotational states were populated, and we were only able to observe up to P(4) and R(2) in the P and R-branch, respectively. If weak features were neglected each cluster of lines contained the expected

number and intensities for the corresponding R(J'') and P(J'') transition. The P(2) transition is shown in fig. 1. The spectrum shown in this figure is typical for the spectra observed.

In the next step assignments were made of the individual rotational transitions. We started with the P and R branch transitions. It was very soon recognized that in order to explain the rotational lines, axis switching in the excited electronic state had to be adopted. This is a quite acceptable situation, since the rotational constants A and B in the ground electronic state are very close⁵ and a small deformation of the molecule upon electronic excitation can easily interchange the role of the short and long axis in the plane of the molecule. The axis switching modifies the selection rules of the rotational transition. If we characterize a rotational level of the ground state by $(J'', K''_{-1}, K''_{+1})$ and that of the excited electronic state by (J', K'_{-1}, K'_{+1}) then the selection rules in the axis switched case for a c-type transition are (e=even, o=odd): $(K''_{-1}, K''_{+1}) \leftrightarrow (K'_{-1}, K'_{+1}) = (ee) \leftrightarrow (oe), (eo) \leftrightarrow (eo), (oo) \leftrightarrow (oo),$ and $(oe) \leftrightarrow (ee)$. A complete discussion of this problem is given by Smalley et al.⁶.

Using the selection rules for the axis switched case all strong transitions in the P and R-branches could be assigned as well as most of the low $J(J'' < 4)$ Q-branch lines. A fit to an asymmetric rotor Hamiltonian was made. In this fit we included the assigned optical transitions from the current work and microwave (MW) transitions originating in the ground electronic state⁵. The accuracies of the rotational constants in the ground electronic state are completely determined by the latter lines, because of the much higher accuracy of the MW spectrum. Although the overall agreement between the

TABLE I Observed and calculated rovibronic frequencies of the $S_1 + S_0$ transition of pyrimidine. Frequencies are in MHz relative to the band origin ν_0 . The lines marked with an asterisk are omitted from the least square fit (see text).

Type	K''_{-1}	K''_{+1}	K'_{-1}	K'_{+1}	J'	observed value	observed error	obs.-calc.
P(4)	4	0	3	0	3	-50126.	50.	-64.
	3	1	3	1	3	-47677.	40.	-55.
	4	1	2	1	3	-52788.	40.	-67.
	2	2	1	2	3	-50284.	40.	-38.
	3	2	2	2	3	-50126.	50.	-20.
	1	3	1	3	3	-49996.	40.	-20.
	2	3	0	3	3			
P(3)	3	0	2	0	2	-37417.	40.	21.
	2	1	2	1	2	-35924.*	40.	123.
	3	1	1	1	2	-38794.	40.	9.
	2	2	1	2	2	-37322.	40.	25.
	1	2	0	2	2			
P(2)	2	0	1	0	1	-24776.	40.	60.
	1	1	1	1	1	-24137.*	40.	97.
	2	1	0	1	1	-25367.	40.	-4.
P(1)	1	0	0	0	0	-12231.*	40.	112.
R(0)	0	0	1	0	1	12286.	40.	80.
R(1)	1	0	2	0	2	24366.	40.	31.
	0	1	2	1	2	25290.*	40.	135.
	1	1	1	1	2	23462.	40.	16.
R(2)	2	0	3	0	3	36501.	40.	9.
	1	1	3	1	3	38103.	40.	22.
	2	1	2	1	3	34446.	40.	-11.
	1	2	2	2	3	36362.	40.	51.
	0	2	1	2	3	36047.	40.	25.
Q	0	1	0	1	1	-223.	20.	34.
	1	1	1	1	1	122.*	20.	88.
	2	1	2	1	2	165.*	20.	117.
	1	1	1	1	2	-821.	20.	1.
	3	1	3	1	3	40.	20.	-60.
	0	2	1	2	2	-280.	20.	17.
	1	2	0	2	2	-350.	20.	18.
	1	2	2	2	3	-692.	20.	24.
	2	2	1	2	3	-1021.	20.	-1.
	2	2	3	2	4	-1071.	20.	5.

Table I continued

3	2	2	2	4	-2096.	20.	-2.
1	3	1	3	3}	-647.	20.	-26.
0	3	0	3	3}			
2	3	1	3	4	-1305.	20.	-14.
1	3	2	3	4	-1256.	20.	1.
3	3	3	3	5	-2084.	20.	-4.
2	3	2	3	5	-2209.	20.	-11.
0	4	1	4	4}	-999.	20.	-4.
1	4	0	4	4}			
2	4	3	4	6}	-2822.	20.	-24.
3	4	2	4	6}			
1	5	1	5	5}	-1465.	20.	-11.
0	5	0	5	5}			
2	5	2	5	6}	-2379.	20.	30.
1	5	1	5	6}			
0	6	1	6	6}	-2002.	20.	-3.
1	6	0	6	6}			

TABLE II Molecular constants of pyrimidine in the S_0 and S_1 states. $\Delta I = I_c - I_b - I_a$, the inertial defect.

constant	value
A'' (MHz)	6276.80(4)
B'' (MHz)	6067.12(4)
C'' (MHz)	3084.47(4)
$A' - A''$ (MHz)	76(3)
$B' - B''$ (MHz)	-214(3)
$C' - C''$ (MHz)	-42.5(5)
$\Delta I''$ (amu \AA^2)	0.0328
$\Delta I'$ (amu \AA^2)	0.240
ν_0 (cm^{-1})	31072.658(5)

observed and calculated frequencies from the optical spectrum was quite acceptable, there were a number of transition for which the observed and predicted lines were as large as 135 MHz.

A closer look at which of the optical transitions did not fit well learned that two and three lines shared in the electronically excited state the $J'_{K'_1 K'_2} = 1_{11}$ and 2_{21} , respectively. In addition a large disagreement was found for the transition to the 0_{00} state. These transitions are marked with an asterisk in table I. Omitting the marked lines from the least squares fit considerably improved the quality of the fit. The parameters determined from the latter fit are given in table II. The differences between observed and predicted frequencies are presented in table I. From this frequency fit we conclude that of the low J' levels the 0_{00} , 1_{11} and 2_{21} of the S_1 -state are perturbed. These levels are pushed down in energy by about 100 MHz. Although this is a rather small shift even in the light of the high resolution of the present experiment, two additional experimental observations which will be discussed below strongly support this conclusion.

4. INTERSYSTEM CROSSING IN PYRAZINE

The planar pyrimidine molecule can be characterized by the C_{2v} molecular symmetry group. The molecule has two pairs of equivalent atoms: two hydrogen atoms are in equivalent positions as well as the two nitrogen atoms. As a consequence of the Pauli exclusion principle the rotational sublevels yield different spin statistical weights (g_n). The values for g_n in the S_0 state are: 15 for $(K''_{-1}, K''_{+1}) = (ee)$ or (oo) and

21 for (eo) or (oe)^{7,8}. If there are no perturbations in the spectrum the relative intensities of the transitions are determined by the rotational temperature (T_{rot}) in the molecular beam, the Hönl-London factors ($A_{J''K''_1K''_+1}$) and the rotational energy in the S_0 state:

$$I = I_0(2J''+1)g_n A_{J''K''_1K''_+1} \exp(-E(J'',K''_1,K''_+1)/kT_{\text{rot}})$$

Since pyrimidine is a near oblate symmetric top it can easily be shown that for example the intensity ratio of the $P_{21}(3)$ and $P_{31}(3)$ transitions must be 21 to 15. As can be seen from fig. 1 this is clearly not observed. The $P_{21}(3)$ transition ending in the 2_{21} state of S is too weak. A positive correlation between deviations in the intensities and frequencies was found for all other transitions. It should further be noted that the $P_{21}(3)$ transition is accompanied by a few small satellites. It is felt that all three phenomena are caused by a weak intersystem crossing.

A very convincing proof of the presence of this ISC and its nature is demonstrated in fig. 2. Here we see the $P(3)$ transition in a weak magnetic field of 60 G. In comparing fig. 2 with fig. 1 it is clear that only the $P_{21}(3)$ transition is strongly affected. The line splits and its intensity is distributed. From the magnetic field dependence it follows that the nature of the ISC must be a coupling of the S_1 state with a nearly isoenergetic rovibronic level of a lower triplet state. Although the $P_{21}(3)$ transition is used here as an example, the results are characteristic for the behaviour of the other perturbed transitions. A more complete discussion will be given in a forthcoming paper.

The marking difference between ISC in pyrimidine and pyrazine⁹, where the $P(1)$ transition is already split into 12

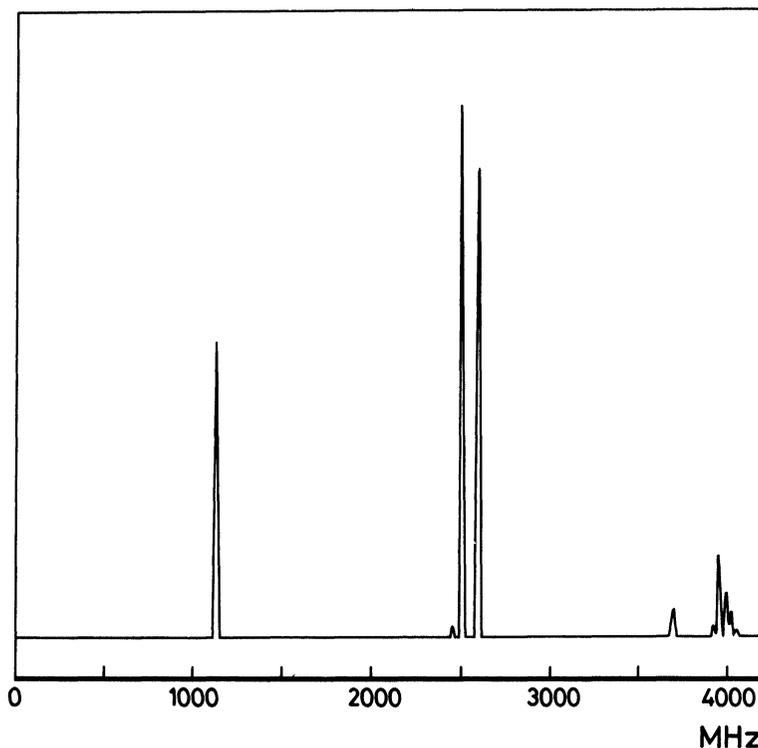


FIGURE 2 The P(3) rotational transition in pyrimidine in an external magnetic field of 60 G.

lines originates in the different density of triplet levels near the S_1 origin. In pyrimidine the S_1-T_1 gap is small ($\sim 2000 \text{ cm}^{-1}$); hence the density of T_1 levels near the S_1 origin is also small, resulting in "isolated" singlet-triplet avoided crossings. These are the source of the perturbations of the high resolution spectrum. Pyrazine, on the other hand, has a much larger S_1-T_1 gap ($\sim 4000 \text{ cm}^{-1}$) and a higher density of T_1 levels near the S_1 origin. We would propose here as a definition of an intermediate state molecule, a molecule in which the ISC couples the S_1 state to a limited

say between 5 and 100, background states. The strength of this coupling must further be such that it yields an observable mixing between the S_1 and the background state. Mixing can be induced by spin-orbit in the S_1 - T_1 coupling, and/or of vibrational or Coriolis origin. This definition of intermediate states is not equivalent to the one introduced by Tramer et al.^{10,11}, based on the presence of biexponential decays in the S_1 states. It has however been shown¹² that the observed biexponential decay in pyrazine, i.e. fast component, is of a different origin as the mechanism proposed by Tramer et al. Within the new definition proposed above pyrimidine behaves as a "small" molecule, while pyrazine must be characterized as an intermediate state molecule.

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