

Rotational assignments in the S_1 (${}^1B_{3u}$) state of pyrazine by UV-UV pump-probe laser spectroscopy

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We have applied an UV-UV pump-probe experiment to the $0_0^0 S_1({}^1B_{3u}) \leftarrow S_0({}^1A_g)$ vibronic transition in pyrazine. The use of two single-frequency lasers and a molecular-beam apparatus made it possible to verify experimentally the rotational assignments for the strongest lines in the high-resolution spectrum of the S_1 state in pyrazine. The experimental results confirm the previously made identifications.

1. Introduction

It is nowadays well established that the first excited singlet state in pyrazine ($p\text{-C}_4\text{H}_4\text{N}_2$) is coupled with nearly iso-energetic vibrationally excited triplet states [1]. Due to this coupling, mixed singlet-triplet states result, the molecular eigenstates. As a result, each single rovibronic transition of the $S_1({}^1B_{3u}) \leftarrow S_0({}^1A_g)$ electronic transition in pyrazine consists of a cluster of lines: the molecular-eigenstate spectrum. The analysis of such a molecular eigenstate spectrum is usually performed with the deconvolution procedure developed by Lawrance and Knight [2]. In this procedure, the zeroth-order singlet state and the zeroth-order triplet states are reconstructed with the use of the line positions and the absorption intensities of the molecular-eigenstate spectrum. However, this deconvolution procedure is only valid in the case of a single bright state coupled to a set of dark states. Therefore, the procedure was in first instance only applied to the P(1)-branch of the $0_0^0 S_1 \leftarrow S_0$ transition in pyrazine [3].

Recently, the analysis of the molecular-eigenstate spectrum of the $0_0^0 S_1 \leftarrow S_0$ electronic transition in pyrazine (a parallel c-type band) was extended to excited states with rotational quantum number $J' \leq 3$ [4]. This was accomplished by a careful comparison of the transitions in the P-branch and the R-branch to the same excited rovibronic state. In this way, the

complex spectrum could be disentangled into clusters of lines belonging to the same rovibronic transition. However, transitions to the excited rovibronic state with rotational quantum number $K'_{+1} = J'$ are not present in the R-branch. In principle, a comparison of the Q-branch and the P-branch can be used for the assignment of the lines to the excited states with $K'_{+1} = J'$. However, due to the strong accumulation of the lines in the Q-branch, this method is not practically applicable. Therefore, the positions in the P-branch of the transitions to the excited states with $K'_{+1} = J'$ were calculated with the deduced rotational constants. The extra lines in the P-branch with respect to the correspondent R-branch were then attributed to the transitions to the $K'_{+1} = J'$ states in such a manner that the centers of gravity of the assigned lines correspond to the calculated positions. However, as the frequency spread of the lines in the spectrum is comparable to the rotational splittings, part of the identifications is somewhat arbitrary.

We have, therefore, decided to verify experimentally some of the assignments of the lines in the $0_0^0 S_1 \leftarrow S_0$ vibronic transition in pyrazine. The method used is a pump-probe experiment. The pyrazine molecule has no permanent electric dipole moment as it belongs to the molecular symmetry group D_{2h} . Hence, it is not possible to use microwave radiation

as the pumping source. Therefore, an UV-UV pump-probe experiment is chosen.

2. Experimental

The experimental set-up is shown in fig. 1. A molecular beam is formed by a continuous expansion of pyrazine vapor seeded in argon through a nozzle with a diameter of 100 μm . The pyrazine sample (Janssen Chimica, purity 99+%) was kept at room temperature. The molecular beam is skimmed twice in a differentially pumped system.

As a distance of 30 cm from the nozzle orifice, the molecules are excited by the continuous wave radiation field of a single-frequency ring dye laser (a modified Spectra Physics 380D). By intracavity frequency doubling with a Brewster cut LiIO_3 crystal, about 8 mW UV radiation was obtained. The bandwidth of the laser is 3 MHz as a result of the frequency jitter of the laser. This pump is tuned to a strong line belonging to the rovibronic $(J', K'_{-1}, K'_{+1}) \leftarrow (J'', K''_{-1}, K''_{+1})$ cluster of lines of the $0_0^0 S_1 \leftarrow S_0$ transition in pyrazine. In this way, a hole is pumped in the population distribution in the electronic ground state at the state with rotational quantum numbers $(J'', K''_{-1}, K''_{+1})$. In order to keep the pump laser tuned on the molecular transition, the laser-induced fluorescence signal is monitored continuously. The linewidth of the molecular transition is Doppler limited and amounts to 12 MHz. The pump laser is modulated with a mechanical

chopper. This allows the use of standard lock-in techniques and the possibility to measure against zero background.

After excitation of the molecules with rotational quantum numbers $(J'', K''_{-1}, K''_{+1})$ by the pump laser, the molecules travel for another 30 cm. The lifetime of the molecules in the excited state is about 200–600 ns [3]. This is much shorter than the estimated travel time of 0.5 ms. However, the hole burnt in the population distribution remains almost completely due to the low quantum yield of pyrazine [5,6] and due to the distribution over the different rovibronic states in the electronic ground state after fluorescence relaxation. This hole in the population distribution at the rotational ground state $(J'', K''_{-1}, K''_{+1})$ is probed with a second cw single-frequency ring dye laser (also a modified Spectra Physics 380D). The UV output power of the probe laser was 3 mW and the bandwidth of the laser was 0.5 MHz due to frequency jitter. In the experiment, the probe laser is scanned across the P-branch containing the pumped line and the laser-induced fluorescence is detected. As the pump laser is modulated, the intensities of the lines with the same rotational ground state as the pumped line are also modulated. In this way, a rotational identification can be made for the lines in the molecular-eigenstate spectrum of the $0_0^0 S_1 \leftarrow S_0$ transition in pyrazine.

3. Results and discussion

Some severe experimental difficulties are encountered in such a molecular-beam UV-UV pump-probe experiment. The lifetime of the excited molecular eigenstates are known to be in the 200–600 ns range [3]. Hence, the homogeneous linewidth $\Delta\nu_L$ of the transitions due to the lifetime broadening is 0.8–0.3 MHz. This is small compared to the inhomogeneous Doppler linewidth in our molecular beam of 12 MHz. The frequency jitter of the pump laser amounts to 3 MHz, i.e. about five times the homogeneous linewidth $\Delta\nu_L$ whereas the frequency jitter of the probe laser is comparable to the homogeneous linewidth $\Delta\nu_L$. As a consequence, the pump laser and the probe laser interact to a large extent with different velocity groups of molecules in our molecular beam, even if the center frequencies of the lasers are equal.

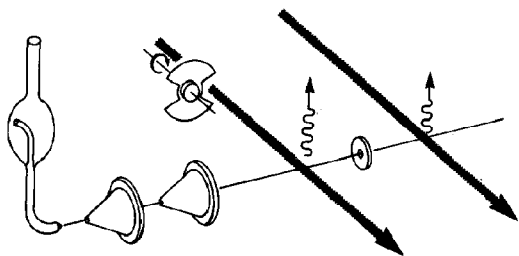


Fig. 1. Outline of the experimental set-up. The molecular beam is crossed with an UV pump laser at a distance of 30 cm from the nozzle. The pump laser is modulated by a chopper. The hole in the population distribution of the molecules in the beam produced by the pump laser is probed with a second UV laser 60 cm away from the nozzle.

We have, therefore, focused the lasers to an estimated spot size of 70 μm in the molecular beam. In this way, the lines are homogeneously broadened due to the small interaction time of the molecules with the laser beams. In the case of a Gaussian laser-beam shape, the time-of-flight-broadened linewidth $\Delta\nu_T$ (fwhm) is given by [7]

$$\Delta\nu_T = \frac{2}{\pi} \sqrt{2 \ln 2} \frac{v_B}{d}$$

In this equation, v_B represents the beam velocity and d equals the laser-beam diameter between the points where the intensity drops to e^{-2} . With the values appropriate to our experimental conditions, a homogeneous time-of-flight linewidth $\Delta\nu_T = 3$ MHz is obtained.

In this way, the pump laser and the probe laser interact with the same group of molecules despite the frequency jitter of the lasers. However, the disadvantage of the strong focusing of the two lasers is obvious. In order to interact with the same molecules, the interaction point of the probe laser and the molecular beam has to be on the line connecting the nozzle and the interaction point of the pump laser and the molecular beam. Therefore, the probe laser and the pump laser have to be aligned within a few tens of micrometers. As a result, small vibrations of the building and/or the beam machine affect the pump-probe signal strongly.

Despite the experimental difficulties, we were able to obtain an UV-UV pump-probe signal on the strongest lines of the $0_0^0 S_1 \leftarrow S_0$ transition in pyrazine. In fig. 2 the laser-induced fluorescence spectrum of the P(2)-branch of the $0_0^0 S_1 \leftarrow S_0$ transition in pyrazine is shown. The insert shows the pump-probe spectrum recorded with the pump laser tuned to the line marked with an asterisk. Although the signal-to-noise ratio in the pump-probe spectrum is low, it is clearly established that the two strong lines lying closely together are members of the same rotational transition, whereas the strong line on the low-frequency side of the P(2)-branch is part of a different rotational transition. In the rotational assignments based on a comparison of the P(2)-branch and the R(0)-branch, the strong line on the lower-frequency side of the P(2)-branch is identified as a $(J', K'_{-1}, K'_{+1}) \leftarrow (J'', K''_{-1}, K''_{+1}) = (1, 1, 0) \leftarrow (2, 2, 0)$

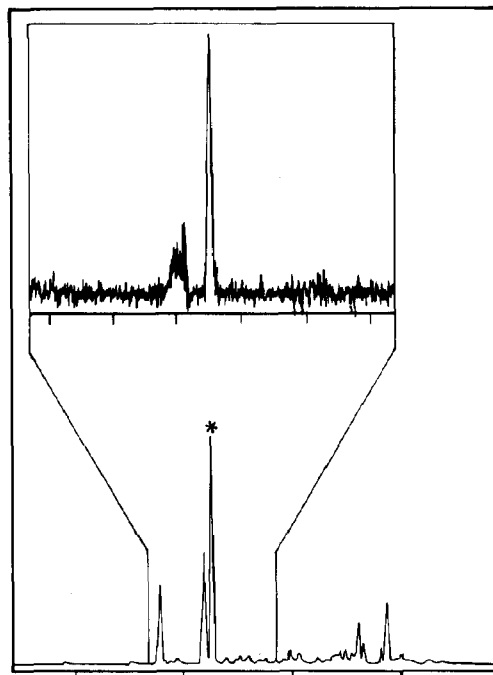


Fig. 2. The laser-induced fluorescence spectrum of the P(2)-branch of the $0_0^0 S_1 \leftarrow S_0$ transition in pyrazine. The frequency is marked every GHz and increases from left to right. The insert shows the pump-probe spectrum with the pump laser tuned to the line marked with an asterisk. Here, the frequency is marked every 200 MHz.

transition, whereas the two strong lines lying closely together were identified as $(J', K'_{-1}, K'_{+1}) \leftarrow (J'', K''_{-1}, K''_{+1}) = (1, 1, 1) \leftarrow (2, 2, 1)$ transitions [4]. The result of the pump-probe experiment, therefore, affirms conclusively these assignments based on the comparison of the different branches and based on the calculation of the center of gravity of the rotational transition. It is clear, however, that we can hardly comment on the small lines in the laser-induced fluorescence spectrum of the P(2)-branch due to the low-signal-to-noise ratio in the pump-probe experiment.

In the P(3)-branch, there is only one relatively strong line. In order to determine the rotational quantum numbers of this line, we have also measured the pump-probe signal in the Q-branch, with the pump laser tuned to the same strong line in the P(2)-branch (marked with an asterisk in fig. 2). In

this way, we probe the lines of the rovibronic transition $(J', K'_{-1}, K'_{+1}) \leftarrow (J'', K''_{-1}, K''_{+1}) = (2, 1, 1) \leftarrow (2, 2, 1)$. It appears that there is a strong line in the Q-branch exhibiting a detectable pump-probe signal. This result proves that the transition to the $(J', K'_{-1}, K'_{+1}) = (2, 1, 1)$ rovibronic state is a relatively strong line in the P(3)-branch and the R(1)-branch. This result justifies the assignment made previously [4], where the strongest line in the P(3)-branch is assigned as the transition to the $(J', K'_{-1}, K'_{+1}) = (2, 1, 1)$ rovibronic state.

We conclude that it is possible to obtain the rotational assignments for the strongest lines in the high-resolution spectrum of the $0_0^0 S_1 \leftarrow S_0$ transition in pyrazine despite the experimental problems. The assignments made previously [4] were confirmed for some lines with this experimental method.

Acknowledgement

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