

HIGH-RESOLUTION QUANTUM BEAT SPECTROSCOPY OF THE PERTURBED $J' = 1$ LEVEL OF THE ${}^1B_{3u}$ STATE OF PYRAZINE

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Received 26 January 1988

An external modulated cw narrow band laser and a collimated molecular beam was used to apply high-resolution quantum beat spectroscopy to the molecular eigenstate spectrum of pyrazine. A resolution of 1 MHz was achieved in the near ultraviolet region. A beat pattern was observed from the temporal decay following excitation of a molecular eigenstate in the $J' = 1, K' = 0$ manifold. From the inhomogeneity of the molecular eigenstate spectrum it is concluded that it is difficult to deconvolute the molecular eigenstates into unperturbed zero-order states of pyrazine.

1. Introduction

The electronic decay of the first excited singlet ${}^1B_{3u}$ state of pyrazine has been the subject of extensive studies in recent years. The intramolecular dynamics of this molecule are attributed to the limiting case of intermediate level structure (ILS) [1]. Quantum beats were observed, which proved to depend on the rotational state [2,3] and on an applied magnetic field [4]. The temporal decay is double exponential as was first demonstrated by Frad et al. [5]. The data are interpreted in terms of an excited singlet (S_1) state $|S\rangle$, connected via interstate coupling to a number of nearly isoenergetic triplet (T) states $\{|T\rangle\}$. This results in a manifold of mixed states $|n\rangle$, the molecular eigenstates (ME):

$$|n\rangle = C_S |S\rangle + \sum_T C_T |T\rangle, \quad (1)$$

where the coefficients C_S and $\{C_T\}$ denote the singlet and triplet contents of the ME state. The states $|S\rangle$ and $|T\rangle$ are usually called zero-order states. The resolved ME spectrum of pyrazine was first observed by van der Meer et al. [6]. The 0_0^0 parallel rovibronic band of this near-symmetric top molecule

contains P(J'') and R(J'') branches with groups of lines belonging to specific J values, separated by empty spectral regions. The K -rotational structure is perturbed due to the S_1 -T coupling and a number of ME states are observed within each P(J'') or R(J'') group of lines. For example the P(1) or R(0) spectra terminate in a single excited state level; ($J' = 0, K' = 0$) or ($J' = 1, K' = 0$) respectively, and would normally consist of a single spectral line. However, it appeared that the P(1) transition contains at least 36 lines in a 7.5 GHz region [7]. Also the R(0) transition is perturbed, as depicted in fig. 1, and it does not consist of a single spectral line. This spectrum contains a series of about 100 spectral lines [8] in a 4.7 GHz region.

It is possible to derive the zero-order singlet and triplet state basis and the coupling matrix elements V_{ST} from the ME spectrum of the $J' = 0$ levels [9]. Lawrance and Knight [10] presented a mathematical approach with a Green's function method, to derive the unique solution of this deconvolution procedure. The method is limited by the condition that a spectrum can only be deconvoluted if it involves a single excited singlet state, with an allowed transition dipole moment to the ground electronic state, which is coupled to a number of dark states (T). Such a unique "doorway state" is found in the P(1) and R(0) spectrum. As input for the deconvolution procedure, the frequencies and relative ab-

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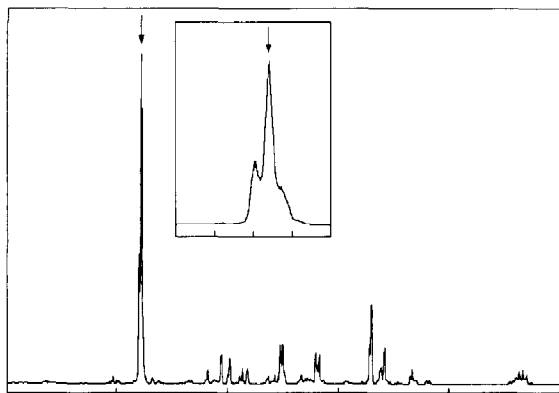


Fig. 1. Molecular eigenstate spectrum of the ($J' = 1, K' = 0$) coupled states of pyrazine. The frequency scale is marked in GHz. The line indicated was used in the quantum beat experiments. The insert shows an exploded view of a 200 MHz region containing this transition.

sorption intensities of the ME spectrum are needed. In a recent experiment we showed that it is incorrect to replace the absorption intensities by the experimentally observed excitation intensities from laser-induced fluorescence spectra [7]. From the lifetimes of the ME states it was deduced that absorption and excitation intensities are not proportional for the P(1) spectrum. Since zero-order triplet states undergo a significant non-radiative decay into unknown dark states (T' or S_0 levels).

Recently several attempts have been made to obtain more specific information about the various coupling mechanisms that play a role in the radiationless decay of pyrazine [11,12]. It would be very helpful if more detailed information were available about the (J', K') dependence of the coupling strength and quantum yield for higher-energy ME states of pyrazine. Therefore a deconvolution of several (J', K') levels would be worthwhile. In the present paper we show that a careful interpretation of the spectra is needed. It will be shown for one of the R(0) ME states that spectral lines may still be inhomogeneous despite the high resolution achieved. In that case there is no straightforward interpretation of the line intensity and care is needed in the deconvolution into the zero-order basis.

2. Experimental

The experimental apparatus was the same as used in a previous time-resolved experiment on the $J' = 0$ levels of pyrazine [7]. A collimated molecular beam was crossed at right angles with a cw single-frequency tunable laser. The beam was formed from an expansion of pyrazine vapour, at room temperature, and argon through a 100 μm diameter nozzle at a total backing pressure of 0.5 bar. The rotational temperature is estimated to be about 3 K. Narrow-band radiation was obtained from an intracavity frequency-doubled ring laser with a 0.5 MHz bandwidth and a typical cw output power of 2 mW [13]. The laser was modulated with an electro-optic modulator in conjunction with a polarizer. This resulted in pulses of single-frequency laser radiation with a light on-off ratio of about 150. The repetition rate was 12 kHz and the typical pulsewidth 40 ns. The total undispersed laser-induced fluorescence was collected and imaged into a photomultiplier (EMI 9863 QA). A time-resolved single-photon counting technique was used and pile-up was carefully avoided. By accumulating measuring cycles a histogram is obtained of counted photons versus time.

3. Results and interpretation

As already pointed out, a single-doorway state is needed in an ME manifold to apply deconvolution into zero-order states and to derive the coupling matrix elements [10]. Therefore one has to make a (J', K') assignment of the ME states. In general this may be achieved by labelling specific states in a double-resonance experiment. In case of the R(0) manifold of ME states such assignment is obvious. These transitions start from the ($J'' = 0, K'' = 0$) ground state level and with the selection rules $\Delta J = 1, \Delta K = 0$ it follows that the unique ($J' = 1, K' = 0$) level of the S_1 state is reached. It is therefore valid to apply the deconvolution procedure. However, a more practical problem is encountered in the form of spectral congestion. In fig. 1 the R(0) spectrum is shown. The experimental linewidth is 12 MHz, due to the residual Doppler effect. Even at such high resolution the ME spectrum is not completely resolved. This is demonstrated for the strongest line of R(0), marked

in fig. 1. As the insert shows, this line consists of at least three transitions. They are partly resolved and their frequencies and intensities may be deduced. The two satellite lines are separated about 19 and 15 MHz from the main strongest transition.

The laser was held on top of the middle transition and its radiation was modulated with 40 ns pulses. The detected fluorescence as function of time is shown in fig. 2. A clear beat pattern is observed. The laser pulse is not Fourier limited, but from its width in the time domain we estimate that its width in the frequency domain is 30 MHz. This means that states within typically 15 MHz of the centre frequency are coherently excited by the laser. The two lines next to the main peak are therefore under weak excitation conditions. If only a single state was excited, the temporal decay would be of single exponential form, as observed for all states in P(1) [7]. If more than one state is coherently excited a quantum beat pattern is observed as in fig. 2. From such a beat pattern it is possible to derive the energy splitting of the involved coherently excited levels, as is customary in quantum beat spectroscopy, by Fourier transformation. The Fourier transform of the decay curve of fig. 2 yielded only a single splitting. Thus the beat pattern merely results from two coherently excited levels. In that case the decay is described by

$$I(t) = I_0 \exp[-(t-t_0)/\tau] \times \{1 + B \cos[2\pi\nu_{12}(t-t_0)]\}, \quad (2)$$

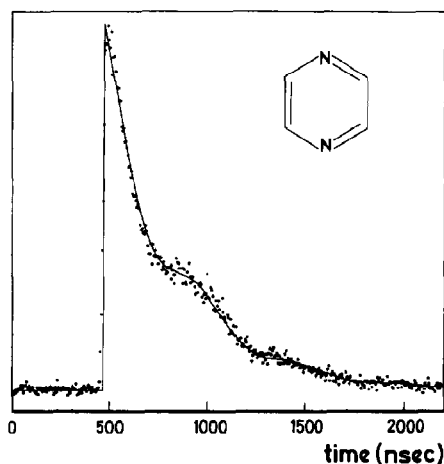


Fig. 2. Decay of the strongest line of the R(0) transition. The dots represent the experimental points, while the curve drawn indicates the theoretical path.

where ν_{12} indicates the frequency splitting between the two excited levels. The shape of the laser pulse is taken as a δ pulse at $t=t_0$. This is a valid approximation if the lifetime of the excited state is much longer than the pulsewidth. We now adopt the constraint that indeed only two levels are involved in the observed decay and fit eq. (2) to the experimental data. The resulting curve is shown in fig. 2. It can be seen that the agreement between experimental and calculated data is good. The parameters in eq. (2) have the values: $\nu_{12}=1.9(1)$ MHz, $B=0.16(2)$ and $\tau=395(10)$ ns. The observed frequency splitting is of course in agreement with the direct Fourier transform, only its accuracy is somewhat higher because of the extra constraint. We conclude that the frequency components are not due to the partially resolved lines in fig. 1, since their splitting is much larger (≈ 50 MHz). Therefore the main peak of the considered transition is still not completely resolved. At least two spectral lines are present with considerable excitation intensity. The origin of the two lines is unclear. They may simply result from two accidentally isoenergetic triplet levels or from hyperfine structure. Another possibility is a splitting of a state due to the earth's magnetic field. As will be shown elsewhere, the ME spectrum of pyrazine, the R(0) band included, is affected by magnetic fields.

In summary there are three main conclusions from this work: (i) The obtainable resolution of a cw narrow band laser in combination with a collimated molecular beam can be further improved into the range of 1 MHz. (ii) At least one and probably more lines in the high-resolution ME spectrum of pyrazine are not completely resolved. (iii) Due to this effect a deconvolution into zero-order states and the derivation of coupling strengths as a function of (J , K') becomes more difficult, even at low J values. A careful analysis is therefore needed if one wishes to derive more detailed information on the coupling mechanisms involved in the radiationless decay of pyrazine.

Acknowledgement

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Mate-

rie (FOM) and has been made possible by financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO).

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