

High resolution absorption spectrum of the molecular eigenstates of pyrazine

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A method is demonstrated to measure high resolution absorption spectra, in the near ultraviolet region, with a bolometer in a molecular beam. The high resolution absorption spectrum of the *P*, *Q*, and *R* branches of the $^1B_{3u}$ (0-0) electronic transition of pyrazine was recorded. The observed residual Doppler linewidth is reduced to 50 MHz in the near ultraviolet region. Simultaneously with the absorption spectrum, the laser induced fluorescence spectrum was observed. A comparison is made between excitation and absorption intensities of the molecular eigenstate spectrum. It is concluded that substantial differences exist between both spectra. The intensities are not proportional, which is most clearly visible in the *Q* branch. This confirms earlier time resolved measurements and low resolution absorption spectra. However, the quantum yield of various, closely spaced molecular eigenstates is in the same order of magnitude. This observation justifies the approximation of absorption intensities by excitation intensities in some work.

I. INTRODUCTION

Together with pyrimidine the pyrazine molecule serves as a prototype of an intermediate case molecule in the theory of intramolecular radiationless transitions.¹ This molecule has received much attention and a large amount of theoretical and experimental data has become available over the years. The development of narrow band lasers, in frequency as well as in time domain, opened the possibility to obtain extensive time-resolved and energy-resolved information. For a recent review see Ref. 2 and references therein. The main attention is focused on the fluorescence decay of the first excited S_1 ($^1B_{3u}$) singlet electronic state of pyrazine. It was shown that this decay is rotationally dependent³ and quantum beats were reported,^{4,5} which proved to be magnetic field dependent.^{6,7} The temporal decay is biexponential, i.e., it is characterized by a short- and a long-time component, as was first demonstrated by Frad *et al.*^{1,8} This biexponential decay was also shown to depend on the rotational J' quantum number.⁹ The described properties of the excited singlet state are attributed to the fact that the intramolecular dynamics in pyrazine are considered a limiting case of intermediate level structure (ILS).⁸ The experimental data are interpreted in terms of an excited singlet (S_1) state, connected via interstate coupling to a number of nearly isoenergetic triplet (T) levels. This results in a manifold of mixed states, containing singlet and triplet character. The molecular eigenstate (ME) spectrum was first directly observed by van der Meer *et al.*¹⁰ It was found that the $S_1 \leftarrow S_0$ 0_0^0 electronic band displays a near symmetric top rotational structure with well resolved $P(J'')$ and $R(J'')$ branches. These branches consist of groups of lines, characterized by a single J quantum number, well separated by empty regions in between. The K rotational structure is hidden due to the distribution over different molecular eigenstates. The splittings caused by the $S_1 - T$ coupling are thus of the same order of magnitude as the K structure. The $P(1)$ transition, terminating in

the ($J' = 0, K' = 0$) level of the S_1 state, appeared to exist of about 36 lines in a 7.5 GHz region¹¹ instead of the single line which would be expected in the absence of the state mixing. Attempts have been made to reconstruct the unperturbed, so-called zero-order, singlet and triplet states and their coupling matrix elements V_{sr} ,^{12,13} in order to obtain more detailed information about the coupling mechanisms involved in the radiationless decay of the MEs. This is only possible in case one "doorway state" is present, i.e., a state with an allowed transition dipole moment to the ground state, connected to a number of "dark" states. For this so-called deconvolution procedure the energies and relative absorption intensities of the ME manifold are needed. Such a single doorway state is obviously present in the $P(1)$ and $R(0)$ spectra, where a unique S_1 singlet level is excited: ($J' = 0, K' = 0$) and ($J' = 1, K' = 0$) respectively. That is the main reason that such deconvolution has first only been reported for the $P(1)$ spectrum. Recently, Siebrand *et al.* have extended the deconvolution to $J' = 1-4$ states.¹⁴ It was shown¹¹ that it is not correct to approximate the absorption intensities of the MEs by their excitation intensities as was previously assumed. The latter intensities are relatively easy to obtain from high resolution laser induced fluorescence spectra. The ME-absorption spectrum is much harder to obtain. It may be derived from the excitation spectrum if the lifetime of the individual MEs is known.¹¹ These lifetimes (typically 400 ns) can be obtained by modulation of a cw narrow band laser excitation of the MEs in a collimated molecular beam and monitoring the temporal decay. This was achieved for the strongest lines in the $P(1)$ spectrum.

In recent work, more attention was given to the nature of the coupling mechanisms involved in the decay. The absolute quantum yield under medium resolution of 1 cm^{-1} was determined for the J' levels.¹⁵ The presence of Coriolis coupling was demonstrated¹⁶ with an assumed K scrambling at higher J' levels. The existence of "grass" was predicted¹⁷: a broad background in the ME spectra of weak lines with a 1.5

GHz linewidth. To test these models, additional data on the ME spectra is needed. More information is required on the (J', K') dependence of the quantum yield, coupling strength and lifetimes of higher energy MEs. For deconvolution of other $P(J'')$ or $R(J'')$ manifolds it is necessary to assign the K' quantum numbers to selective individual doorway states.¹⁴ This may, e.g., be achieved by double resonance techniques. Another problem to be solved is the conversion of excitation intensities into absorption intensities. In other words, the quantum yield of individual MEs is needed.

We will here approach the latter problem. It will be demonstrated that it is possible to obtain high resolution absorption spectra of the ME structure of pyrazine. Due to the complexity of the spectrum at room temperature it is not possible to use conventional Lamb dip spectroscopy. Therefore, excitation has to be performed on molecules in a cold molecular beam by narrow band laser radiation. The LIF spectrum is determined in the usual way. The molecular beam has to be strongly collimated to resolve the ME structure. Therefore, the direct absorption of radiation from the crossing laser is extremely weak. However, instead of determining the decrease of energy in the laser beam, we will show that it is possible to determine the increase in energy contained in the molecular beam. Since the quantum yield of the pyrazine rovibronic states is low (on the order of a few percent) it is a good approximation to state that nearly all the absorbed energy stays in the molecular beam and only a tiny fraction is lost via fluorescence. In the present work such an increase in energy was determined by the use of a bolometer detector to monitor the internal energy of the molecules in the beam.

II. EXPERIMENTAL

The molecular beam apparatus used in this experiment has been described in detail elsewhere.¹⁸ Hence, only the features relevant for the present work will be discussed. The apparatus is schematically depicted in Fig. 1. The supersonic beam is formed from a continuous expansion of pyrazine seeded with helium through a 75 μm diameter nozzle. The sample of pyrazine (Janssen Chimica) with a 99 + % purity was kept at room temperature. The backing pressure of helium was in the range 0.25–0.5 bar. Normally, argon seeding results in a much better rotational and vibrational cooling under comparable expansion conditions. However, in the present experiments argon could not be used because it condenses on the cold surface of the bolometer element. The molecular beam is strongly collimated by two conical skimmers of 1.5 mm diameter, in a differential pumping system.

Molecules were excited at 30 cm from the nozzle, by a cw tunable radiation field from a frequency doubled ring dye laser (a modified Spectra Physics 380D). Intracavity frequency doubling was performed with an angle tuned LiIO_3 crystal.¹⁹ About 1 mW of single frequency radiation was obtained around 324 nm with a 3 MHz bandwidth. Frequency calibration was performed with a temperature stabilized

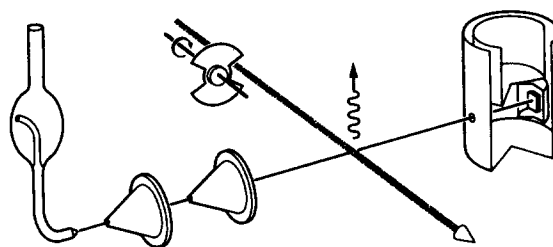


FIG. 1. Outline of the spectrometer. The molecular beam, formed from an expansion, is crossed by the laser and detected by a bolometer.

sealed Fabry–Perot interferometer at the fundamental wave. Part of the output of the laser was sent to this interferometer and frequency markers were recorded simultaneously with a spectrum. The laser beam is mechanically chopped at 90 Hz. The total undispersed laser induced fluorescence (LIF) is collected by two spherical mirrors and imaged at the photocathode of a photomultiplier (EMI 9863QA).

Approximately 30 cm downstream of the crossing of the laser, the molecular beam reaches the bolometer. The doped germanium detector with a size of 1 \times 1 mm (Infrared Laboratories) is mounted on a diamond substrate of 2 \times 5 mm. The element is operated in the region 2.2–4.2 K by pumping a helium bath cryostat. At 4.2 K the noise equivalent power of the bolometer is 4.8×10^{-13} W/Hz^{1/2} and the responsivity R is $R = 5 \times 10^4$ V/W. The initial response time is 2.5 ms but during the measurements this value slowly increases due to the so-called cryofrost. This effect is caused by the fact that molecules tend to condense on the cold detector surface. Therefore the source was not heated and a diluted mixture of pyrazine vapor was used. The pressure in the bolometer compartment of the apparatus was kept at 10^{-7} mbar. Nevertheless, cryofrost imposes a limit on the operational time of the bolometer of about 4 h. External sources of heat radiation were shielded by two screens at 4.2 and 77 K. Stray laser light does not significantly reach the detector due to spatial filtering and the large distance between the laser excitation area and the bolometer.

The total beam signal is given by

$$S_B = RNE, \quad (1)$$

where N is the number of particles per second and E is the energy of the beam. Apart from the continuous translational and internal energy of the molecules, E contains contributions from the absorption energy. Only the latter one is detected by a phase sensitive detection method. A 1 s time constant was used. The noise in the absorption spectra is mainly due to the molecular beam.

III. DETECTION OF ABSORPTION SIGNALS WITH A BOLOMETER

Since a bolometer detector essentially detects the heat of the molecules in the beam we have to be careful in interpreta-

tion of the recorded signals. It will be shown that the signals detected by a bolometer, inserted in the molecular beam, are essentially proportional to the high resolution absorption spectrum in the case of molecules with a low quantum yield. We consider a molecule, in our case pyrazine, with a ground state $|g\rangle$ and an excited molecular eigenstate $|u\rangle$. It is assumed that $|u\rangle$ can be reached, starting from $|g\rangle$ with a narrow band laser. The number of molecules in $|g\rangle$ and $|u\rangle$ is denoted as N_1 and N_2 , respectively. The laser radiation density per unit volume and frequency interval is given by ρ_L . The excited state exhibits a decay rate Γ consisting of a radiative part Γ_r and a nonradiative contribution Γ_{nr} due to coupling with dark states:

$$\Gamma = \Gamma_r + \Gamma_{nr}. \quad (2)$$

Other decay channels like predissociation and ionization are neglected. The rate Γ_r results from the various Einstein coefficients A_{2i} for spontaneous emission to ground state levels $|i\rangle$. The number of molecules in the excited state $|u\rangle$ is given by

$$N_2 = N_1 \frac{B_{12} \rho_L}{\Gamma} \quad (3)$$

with B_{12} the Einstein coefficient for induced absorption. The molecules are excited in a continuous molecular beam by an on-off modulated laser radiation field. The bolometer signal S_B is detected by a phase sensitive method. We will now consider the various contributions to this demodulated signal. In the case that some molecules disappear from the beam after excitation to $|u\rangle$, a negative signal is detected by the bolometer. Since in pyrazine, after excitation to the S_1 state, the effects of predissociation and ionization may be neglected, we can assume that all the molecules excited by the laser stay in the beam and reach the bolometer. The lifetime of the excited state is much shorter than the time of flight between the excitation area and the bolometer (of the order of 300 ns and 300 μ s, respectively, for pyrazine). Therefore, a number of molecules have decayed to vibrational levels ($|i\rangle$) of the electronic ground state with energy E_i before they are detected. The distribution over states $|i\rangle$ is determined by the Franck-Condon overlap of $|u\rangle$ and $|i\rangle$. The signal on the bolometer increases due to this radiative decay from $|u\rangle$ with

$$S_r = \beta R N_2 \sum_i \frac{A_{2i}}{\Gamma} E_i, \quad (4)$$

where R indicates the responsivity of the detector element and β the detection efficiency due to geometrical factors. The remaining molecules, with absorbed energy E_a , reach the detector. The probability for this process is Γ_{nr}/Γ . Due to this nonradiative process the bolometer signal increases as

$$S_{nr} = \beta R N_2 \frac{\Gamma_{nr}}{\Gamma} E_a. \quad (5)$$

Here we have to make the assumption that the energy transfer from the excited state molecule to the bolometer is

state independent. For vibrational energies as in Eq. (4) the sticking probability and energy transfer will be very nearly state independent but for electronic energies as in Eq. (5) this is less evident. If the nonradiative process involves coupling with the triplet state, the molecules condensed on the bolometer may lose part of their absorbed energy through phosphorescence, i.e., visible or UV radiation which is not detected by our bolometer. Such phosphorescence processes have been demonstrated in other molecules.^{21,22} In order to include the effects due to phosphorescence, Eq. (5) has to be multiplied by a factor α describing the energy transfer efficiency, where α may be state dependent. In case of pyrazine in its gas phase the phosphorescence yield is low.⁸ We may therefore safely assume that $\alpha \approx 1$ and state independent. The state dependence of α is experimentally accessible by detection of the eventual phosphorescence emerging from the detector surface. Such experiments are currently being undertaken in our laboratory. Preliminary results indicate that indeed no, or very little, phosphorescence emerges from the detector surface.

Combining Eqs. (4) and (5) we find

$$S_B = \beta R \frac{N_2}{\Gamma} \left[\sum_i A_{2i} E_i + \Gamma_{nr} E_a \right]. \quad (6)$$

The first term in this expression is of order $\Gamma_r \langle E_i \rangle$, where $\langle E_i \rangle$ is the average energy in the ground electronic state of vibrations that contain a significant Franck-Condon overlap with the excited state. Since, in the case of pyrazine, $\Gamma_r \ll \Gamma_{nr}$ and $\langle E_i \rangle \ll E_a$, Eq. (6) is simplified to

$$S_B = \beta R N_2 \frac{\Gamma_{nr}}{\Gamma} E_a. \quad (7)$$

The number of excited state molecules N_2 is related to the laser induced fluorescence signal by

$$S_{LIF} \propto \frac{\Gamma_r}{\Gamma} N_2. \quad (8)$$

Here the proportionality constant is determined by geometrical factors like the collection efficiency. The quantum yield Y_{me} of the molecular eigenstate $|u\rangle$ is defined as

$$Y_{me} = \frac{\Gamma_r}{\Gamma}. \quad (9)$$

Combination of Eqs. (7) and (8) yields

$$\frac{S_B}{S_{LIF}} \propto \left(\frac{1}{Y_{me}} - 1 \right) E_a; \quad (10)$$

and since $Y_{me} \ll 1$,

$$\frac{S_{LIF}}{S_B} \propto Y_{me}. \quad (11)$$

In this expression S_{LIF} gives the excitation spectrum of the excited state and Y_{me} the relative quantum yield for the ME spectrum. It follows that S_B is proportional to the absorption spectrum.

IV. RESULTS

With the experimental setup described we recorded simultaneously laser induced fluorescence spectra (FS) and the bolometer spectra (BS). The first one displays the exci-

tation, while the latter basically the absorption of the O_0^0 transition in pyrazine. At different backing pressures (0.25–0.5 bar) high resolution spectra were obtained of the $J' = 0-5$ states. As was shown before,¹⁰ the LIF data display bunches of lines in a confined spectral area where one or few transitions to a given (J', K') state would be expected. The regions between these groups of lines appear empty. Figures 2(a)–2(f) display the $P(3)$ – $R(3)$ transitions. The $R(0)$ transition has not been shown due to the low signal-to-noise ratio. The Q branch was also recorded, depicted in Figs. 3(a)

and 3(b). The obtained signal-to-noise ratio in the BS amounts $S/N \approx 10$. This is more than two orders of magnitude below the value for the FS. Combined with the fact that the quantum yield of pyrazine is low (ultimately a few percent) this demonstrates the enormous sensitivity of LIF detection. The S/N value obtained for the BS varies due to the changing sensitivity of the detector element caused by cryofrost. The operational temperature was also somewhat different in various measurements. The indicated intensity scale in Figs. 2 and 3 is therefore in arbitrary units.

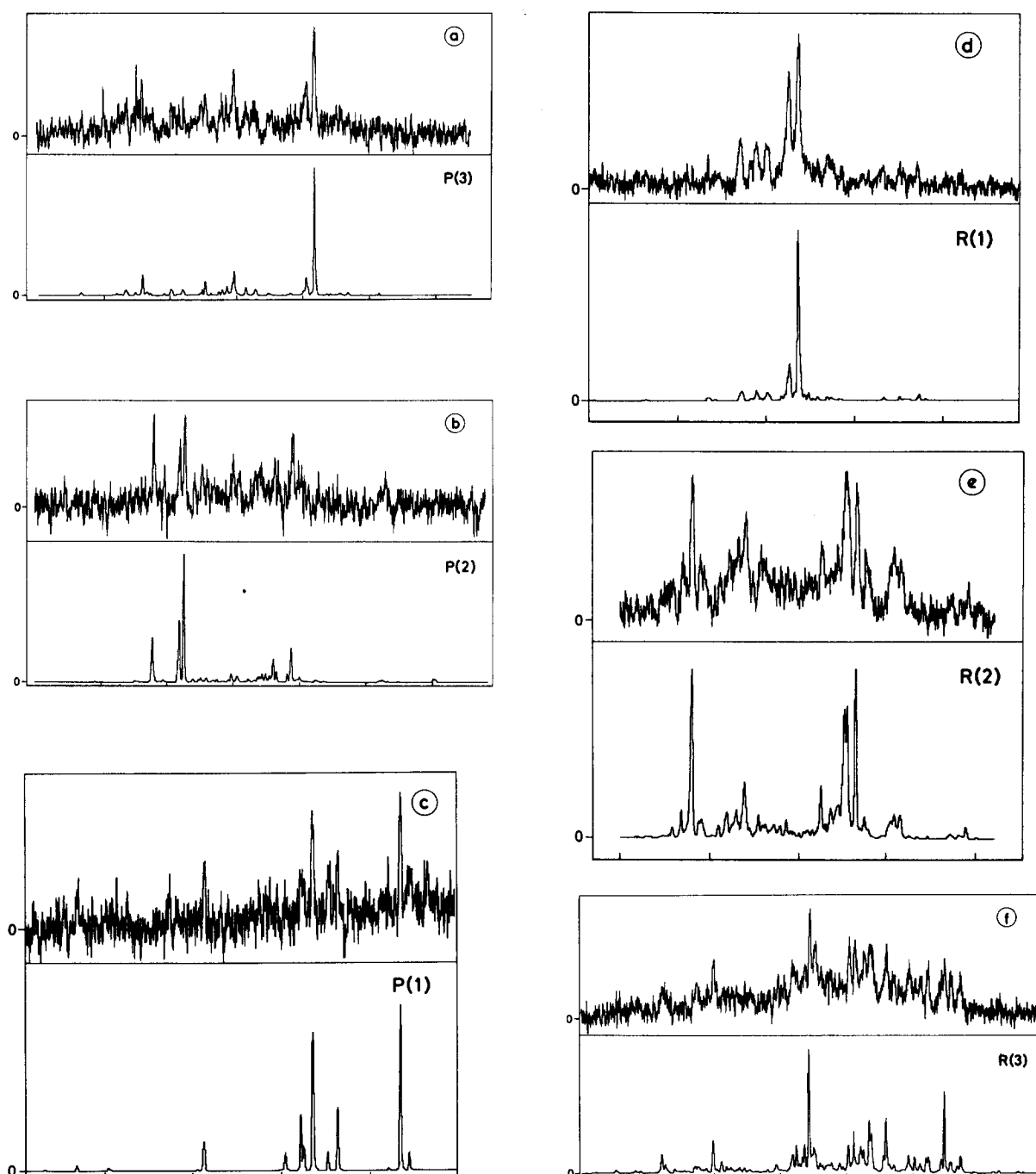


FIG. 2. (a)–(f) High resolution spectra of the P and R branches of the $0-0$ electronic transition of pyrazine. The top traces display the bolometer spectra and the bottom traces the laser induced fluorescence spectra. The intensity axis is in arbitrary units and only the zero level is indicated. The frequency is increasing from left to right and marked every GHz.

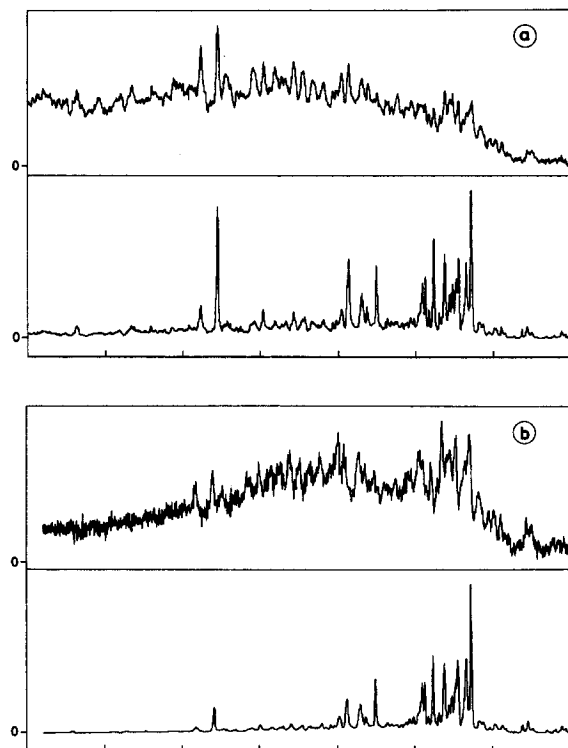


FIG. 3. (a) and (b) The Q branch of the 0-0 transition of pyrazine, measured with backing pressures of 0.25 (a) and 0.5 bar (b). The top traces display the bolometer spectra and the bottom traces the laser induced fluorescence spectra. The intensity axis is in arbitrary units and only the zero level is indicated. The frequency is increasing from left to right and marked every GHz.

The observed linewidth in the LIF spectra amounts to 25 MHz. This value is dominated by the residual Doppler broadening, due to the divergence of the molecular beam. The spatial sensitivity of the collection optics somewhat narrows the detected area of the molecular beam. Therefore, the Doppler linewidth is smaller in the FS compared to the BS, where the entire opening angle of the molecular beam is detected. The BS displays a linewidth of 50 MHz.

V. INTERPRETATION AND CONCLUSIONS

Although the signal-to-noise ratio obtained in the experiment described is limited, a number of qualitative conclusions can be drawn. A more quantitative analysis needs higher quality data. For example, the absorption signal may be increased by a multipass laser excitation or by an increased laser power. As shown in Sec. III, the bolometer signal essentially displays the ME-absorption spectrum of pyrazine, since this molecule satisfies the main limitations; (i) the quantum yield is low^{8,20} and (ii) a state independent detection on the bolometer is guaranteed since also the phosphorescence yield is low.⁸ The ratio of the line intensities of the FS and BS is equal to the ratio of relative excitation and absorption intensities and therefore denotes the relative quantum yield Y_{me} of a given ME state.

As can easily be seen from Figs. 2 and 3, the spectral intensities in the FS and BS are not proportional, which indicates that the absorption and excitation intensities of individual transitions are not proportional. This confirms our

time-resolved data¹¹ of $P(1)$ ME transitions, for which a similar observation was made for $J' = 0$ coupled states. The main result of these experiments was that the decay rates of the zero-order singlet $^1B_{3u}$ and triplet $^3B_{3u}$ states are of comparable magnitude. Both decay rates are ascribed as mainly due to a coupling to the high density of highly vibrationally excited states of the S_0 ground electronic state. The present data show that this conclusion is not limited to $P(1)$ states but, as could obviously be expected, is applicable to all J', K' states. In other words, even with the present S/N ratio it is clear that the quantum yield is not constant for various ME states. Since no complete K' assignment has been made for pyrazine, it is not possible to distinguish a (J', K') selective dependence of Y_{me} . For a given J' group of lines all Y_{me} 's are of the same order of magnitude. No lines are observed to be strong in absorption and weak in fluorescence, or vice versa, and it is concluded that Y_{me} is a gradually varying function of excited state energy. Recently, Siebrand *et al.*¹⁴ proposed a K' assignment for the $J' = 0-4$ states from a careful comparison of $P(J'')$ and $R(J'' - 2)$ LIF spectra. Rotational constants were derived for the $^1B_{3u}$ electronic state. This analysis rests heavily on the determination of the center of gravity of groups of lines belonging to a certain K' state. The assumption was made [with the exception of the $P(1)$ transition] that the observed excitation intensities closely resemble the absorption intensities within a $P(J'')$ or $R(J'')$ spectrum. It is concluded from the present work, that both spectra indeed show a similar intensity distribution for low J' states, although deviations do exist. This justifies the deconvolution process as performed in Ref. 14.

Special attention should be paid to the observed Q branch. In Figs. 3(a) and 3(b) this spectrum is depicted for a 0.25 and 0.5 bar helium backing pressure. The differences are striking. It is clear that the intensity distribution in the FS and BS is quite different. For the FS the maximum intensity is reached near the origin of the Q branch at the high energy side, whereas the BS is much broader, mainly extending to the low frequency side. The FS exhibits sharp ME structure, while the BS has a similar sharp structure but on top of a broad band. The relative intensities in this structure are quite different between both spectra, as was already concluded from $P(J'')$ and $R(J'')$ transitions. Although there is no complete rotational assignment for the pyrazine molecule, we estimate from comparison with other molecules under similar expansion conditions, that the rotational temperature is about 5 K for a 0.5 bar helium pressure. If this pressure is reduced by a factor of 2, the rotational temperature increases and more (J'', K'') ground state levels are populated. The intensity distribution in the Q branch consequently changes and transitions from high J'' levels appear. From Fig. 3(a) it is clear that the low pressure Q branch is much more extended to the low frequency side and so at this side most spectral lines belong to high J levels. It is concluded that high J' levels appear much weaker in fluorescence than in absorption. An experimental determination of the absolute quantum yield¹⁵ with a resolution of 1 cm^{-1} , showed a dependence of $Y = 0.124/(2J' + 1)$ for $J' = 5-22$. Since the quantum yield decreases with J' , the FS decreases faster than the BS. Although we cannot comment on the

quantitative dependence of Y , present high resolution data confirm the decrease of Y with increasing J' .

Recently, Amirav²⁰ showed from direct absorption measurements in a jet expansion that the absorption signal stretches out, between the various $P(J'')$ and $R(J'')$ transitions, into areas where no LIF signal is detected. The spectral resolution in this experiment was limited to 2 GHz and therefore no ME structure was resolved. Amirav attributed¹⁷ this absorption to the existence of "grass": a broad continuous background underneath the sharp ME structure. This does not show up in our spectra, neither in absorption, nor in excitation. We performed scans over large frequency regions and did not find evidence for the existence of grass in the excitation spectra of pyrazine. The quantum yield decreases with increasing J' , as was concluded from the BS, and therefore the highest sensitivity in the FS is reached between low J' -state transitions. The S/N ratio in the FS amounts to 5×10^3 in the region of the $P(2)$ transition, where grass was predicted. The computer collection of data allows us to exploit this dynamic range fully. No background underneath the ME structure was observed in the BS either. One might argue that the S/N ratio in the BS is somewhat too low to draw this conclusion. However, although the grass was predicted to be very weak in the excitation spectra due to the low quantum yield, it was claimed by Amirav that it would be tremendously enhanced in absorption spectra. We conclude that no experimental evidence was found for the grass in high resolution spectra.

Finally, we have shown that it is possible to obtain high resolution spectra of pyrazine, both in excitation and in absorption.

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