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Magnetic field dependence of rotationally resolved excitation spectra of the $^1\text{B}_{3u} 0_0^0$ transition of jet-cooled pyrazine

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We report rotationally resolved excitation spectra of the $^1\text{B}_{3u} 0_0^0$ transition of jet-cooled pyrazine in magnetic fields up to 50 kG. The emission intensity of every rotational line is found to decrease by a factor of three for magnetic fields larger than about 300 G. For still larger magnetic fields up to 50 kG the total emission intensity remains constant. The effect of collisions on the threefold quenching of the emission is studied separately, and found to be of minor importance. It is concluded that the reduction of the quantum yield due to the magnetic field originates from an intramolecular process. The threefold decrease of the quantum yield is interpreted in terms of a nonradiative decay rate constant of the zero-order triplet states. The decay rate constant consists of both a magnetic field dependent part (about 0.3 MHz at zero field) and a magnetic insensitive part (about 0.7 MHz).

1. Introduction

The spectroscopy of the lowest excited singlet state of pyrazine in a molecular beam has received considerable attention [1]. The experimental results and the interpretation were often rather conflicting [1] until an ultrahigh-resolution excitation spectrum was obtained [1,2] and it was realized that experimental results in the time domain will often depend on the coherence bandwidth of the excitation source. The high-resolution spectra of van der Meer et al. [2] and ref. [1] show that the $^1\text{B}_{3u} \nu' = 0$ state is coupled to a number of triplet states. Despite this very detailed information, the behaviour in time-resolved measurements on a rather long time scale (the so-called slow component in the emission decay) cannot always be understood solely in terms of the eigenstates. Of particular relevance in this context are the widths of the zero-order singlet and triplet states.

In this paper we focus attention on the width of the zero-order triplet states, and exploit the effect of a

magnetic field to get information on the width of these triplet states.

The first measurements of the magnetic field effect on the emission of the $^1\text{B}_{3u} 0_0^0$ transition of jet-cooled pyrazine were reported by Felker et al. [3]. These authors reported a threefold increase of the A_+/A_- ratio (where A_+ and A_- are the preexponential factors of the fast and slow component of the fluorescence decay, respectively). In addition they observed a change in the quantum beat frequencies as a function of the magnetic field H .

The results were confirmed by Matsumoto et al. [4,5], who also found that A_- decreases by a factor of three in a magnetic field. In addition they reported that the lifetime remains constant, while the fluorescence is quenched by a factor of three.

An interpretation of the behaviour of the A_+/A_- ratio was given by Felker et al. [3], who mentioned that in a magnetic field the selection rule for singlet-triplet coupling is $\Delta J = 0, \pm 1$ [6,7], thus allowing for a threefold increase in the number of coupled triplets (we recall that the $^1\text{B}_{3u} \nu' = 0, J' = 0$ state of pyrazine is known to couple to about 13 triplet states in zero field [2,8]).

In this work we extend the measurements to high fields (up to 50 kG). We find again that the total emission intensity drops by a factor of three in a mag-

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netic field, while the fluorescence lifetime remains unchanged. Particular attention is paid to a collisional contribution to the decrease of the quantum yield in a magnetic field, as collisional relaxation might give a trivial explanation for the threefold decrease of the emission intensity. We find that collisions are of minor importance. A puzzling feature is that the decay time is hardly dependent on the magnetic field. This complicates the interpretation, which has to be given in terms of purely intramolecular effects and which should account both for the decrease in quantum yield and the constancy of the fluorescence lifetimes.

2. Experimental

We have used two experimental configurations, denoted set-up 1 and set-up 2. In both configurations excitation took place by frequency doubling the output of a Lambda Physik FL2002E dye laser (bandwidth 1 GHz, pulse duration about 3 ns) pumped by a Moletron UV1010 nitrogen laser.

Set-up 1 (high magnetic field set-up). The geometry of the molecular beam, the exciting laser beam and the magnetic field is shown in fig. 1. A pulsed nozzle was mounted in the evacuable bore of a superconducting magnet (Siemens SUMA 60/72/110). The jet stream was in the direction of the magnetic field. The excitation beam crosses the molecular beam at 25 to 30 mm from the nozzle (diameter 1 mm). The laser beam travels perpendicular to the magnetic field; its polarization was also perpendicular to the field. The fluorescence was detected in the direction of the magnetic field using a quartz fiber. The set-up was such that the influence of the magnetic field on photomultiplier operation is rather mild. The fluorescence intensities reported are corrected for the effect of the magnetic field on the photomultiplier sensitivity, using stray light from the exciting laser pulse as calibration. The system was pumped using an Edwards ES4000 rotary pump.

Set-up 2 (low magnetic field set-up). The vacuum chamber was pumped by an 18B3A Edwards vapor booster pump, backed by an Edwards ES4000 rotary pump. A Helmholtz coil was mounted in the vacuum chamber. Here the magnetic field was pulsed synchronously with the nozzle. The timing was facili-

Fig. 1. Scheme of the high magnetic field set-up. 1: helium dewar; 2: superconducting coil; 3: molecular beam; 4: hollow tubes through which the laser beam enters and leaves the vacuum chamber; 5: mirrors; 6: quartz fiber.

tated by measuring on an oscilloscope the voltage across a small resistor in series with the coil. The magnetic field values are accurate to $\pm 15\%$.

3. Results and discussion

The main features of the experimental results obtained in this work can be summarized as follows: (a) the rotational contour does not change as a function of the magnetic field, (b) the intensity of every rotational branch decreases by a factor of three for fields larger than 300 G and (c) the fluorescence lifetime is not dependent on the magnetic field strength. In the remaining part of this paper we will present the experimental results obtained in more detail, and discuss its interpretation.

Figs. 2a,b show the total emission across the rotational contour without a magnetic field and in a field of 40 kG. Apparently the rotational branches do not broaden in a magnetic field. This is easily understood: in a magnetic field the set of zero-field triplet

Fig. 2. Excitation spectra of the $^1B_{3u} 0_0^0$ transition recorded in a magnetic field of: (a) $H = 0$ G, (b) $H = 40$ kG. The Q-branches are scaled to the same height, but the actual intensity in high field is $1/3$ of the zero-field intensity.

states [1,2,8] shifts away, but a new set of triplet states becomes resonant. Provided the singlet-triplet interaction does not increase in a magnetic field, the overall linewidth of the rotationally resolved branches does not broaden. We therefore conclude that the intramolecular interaction between the singlet state and the triplet states is not magnetically sensitive.

We further note that the relative intensities remain the same for all fields. However, the *absolute* intensity decreases by a factor of three for fields larger than 300–500 G (we cannot set such low fields accurately in the high magnetic field set-up 1). We emphasize that this decrease also occurs for the P(1) line. If the field strength is gradually increased to higher values (up to 50 kG), we find that the fluorescence intensity remains constant to within $\pm 15\%$. The puzzling feature in the decay measurements is that the overall decay constant of the slow component does not depend on the magnetic field strength. A similar result has been reported by Matsumoto et al. [4,5].

In the high-field set-up 1 the lifetime is 110 ± 25 ns

for all rotational branches. Evidently, this lifetime is collisionally shortened (the lifetime should be at least 400 ns [2,8,14]). We could hold collisions responsible for the threefold decrease of the emission intensity in the following way. Consider the zero-order $^1B_{3u}$ state having a decay rate constant $G = G_r + G_{nr}$. Dilution of this decay rate constant over N triplet states results in the decay rate constant of a single state (denoted ME): $G_{ME}(H = 0) = G/N$. Adding to this decay rate a collisional decay rate constant G_c that transfers population of a ME to a nonradiative and/or long-living vibronic triplet state in the $^3B_{3u}$ state, we get $G_{ME}(H = 0) = G/N + G_c$. In a magnetic field we then have $G_{ME}(H > 0) = G/3N + G_c$, and consequently the quantum yield in zero field ($G_r/N/G_{ME}(H = 0)$) will become $(G_r/3N)/G_{ME}(H)$. Clearly, the quantum yield drops by a factor of three in magnetic field if $G_c \gg G/N$. As G/N is about 1 MHz, this condition seems to be clearly fulfilled in the high-field set-up.

To learn more about the effect of collisions, we studied them separately in the low magnetic field set-up 2, where we can achieve rotational temperatures between 0.5 and 30 K [9]. We find that A_+ remains comparatively unaffected up to $H = 160$ G, but decreases by a factor of three at a field in the vicinity of 300 G. The relative ratio $\{A_+(160)/A_+(160)\}/\{A_+(0)/A_+(0)\} \approx 3$ depends somewhat on J' . We measured A_+/A_- up to $J' = 4$; the range is restricted by the Boltzmann factors in the ground state at a temperature of about 1 K. These results agree with those of Matsumoto et al. [4]. The above relative ratio is somewhat dependent on collisions, but the collisional dependency generally does not exceed the variation found between the different J' . The emission intensity for every rotational branch (including $J' = 0$) decreases by a factor of about three in a magnetic field even at the lowest rotational temperatures examined. The relative intensity of the branches with and without a magnetic field depends only slightly ($\pm 10\%$) on the temperature. The decay rate constant of the slow component generally shows some variation as a function of magnetic field under collision-free conditions. The rate constant occasionally increases at a particular field (compare fig. 3a and fig. 3b), but decreases in case of another field strength. In general, no systematic trend could be found toward either a larger or smaller value. On the basis of these results we conclude that the threefold decrease

Fig. 3. Decay of the slow component of the R(1) transition at zero field (upper trace) and $H \approx 160$ G (lower trace), measured in the low-field set-up 2. The fast component has been omitted in order to facilitate comparison of the decays of the slow component.

in emission intensity in a magnetic field is not due to collisions and arises from a purely intramolecular effect.

This decrease of the quantum yield in a magnetic field under collision-free conditions can be interpreted in the following simple way. We will refer to the following as interpretation 1. We start with the zero-order singlet state S_1 having a total decay rate constant $G = G_r + G_{nr}$, where G_{nr} is the nonradiative decay to the ground state manifold (in fact we have shown this decay to be rotationally dependent through Coriolis coupling [9]). The S_1 state is coupled to N zero-order triplet states, which we assume to have a nonradiative decay constant g (the zero-order triplet decay rate constant g was originally introduced by Amirav and Jortner [10]). We then have for the decay rate constant of a ME roughly $G_{ME} = G/N + g$. In a magnetic field the decay rate becomes $G_{ME} = G/3N + g$ where we take into account the increase of the number of coupled triplet levels from N to $3N$. Since

the decay rate constant does not depend in a systematic way on the magnetic field strength, we could conclude that g dominates over both G/N and $G/3N$, while g is also magnetic insensitive. However, the conclusion that $g \gg G/N$ has to be rejected for low J' (< 5) considering:

(a) The value obtained for G and the individual values of g of each ME obtained from direct lifetime measurements of individual MEs. In fact it was found that $G \lesssim G/N$ for $J' = 0$ [8] ^{#1}.

(b) The good agreement between calculated and observed intensities of rotational branches in the work of de Lange et al. [9]. Here the rotational dependence of the quantum yield was studied. The approach used and the quantitative agreement obtained independently support the conclusion that $g \lesssim G/N$ for low J' .

Let us therefore consider another explanation. We will refer to this as interpretation 2. Suppose that g is magnetic field dependent; i.e., $g = g(H)$. We will also assume that g saturates; i.e., that for sufficiently large magnetic fields $g(H) = bg(H=0)$, where b is a constant. Such a situation is rather common [7]. In zero magnetic field we then have for the decay $G_{ME}(H=0)$ of an individual ME:

$$G_{ME}(H=0) = G/N + g(0). \quad (1)$$

The total emission intensity at zero field of a rotational branch is given by

$$I_{tot}(H=0) \propto (G_r/N)/G_{ME}(H=0), \quad (2)$$

where " $\propto$ " means proportional to. In the case of magnetic fields H larger than the saturation value H_s , we have instead of eq. (1):

$$G_{ME}(H) = G/(3N) + bg(0), \quad (3)$$

and instead of eq. (2)

$$I_{tot}(H) \propto (G_r/3N) / G_{ME}(H). \quad (4)$$

^{#1} In this work the fluorescence decay rate constant of an individual ME was compared to its relative intensity under steady-state conditions. Deviations from a linear relationship between the decay rate constant and the intensity of an ME indicates the size of g . However, in this work the contribution of collisional effects to g were not considered, despite the fact that the rotational temperature is not extremely low (> 4 K). Especially in the case of weak lines a collisional contribution to the decay rate constant will result in a relatively large apparent width of the zero-order triplet states.

Using the experimental observations $G_{ME}(H=0) \approx G_{ME}(H)$ we can equate eq. (1) and eq. (3); i.e.,

$$G/N + g(0) \approx G/(3N) + bg(0), \quad (5)$$

from which we obtain

$$g(0) \approx \{1/(b-1)\}2G/(3N). \quad (6)$$

Using $G \approx 10$ MHz, $N \approx 10$ (these values pertain to $J' = 0$ [2,5,6]), and $b = 3$ (as discussed below), we find $g(H=0) \approx 0.3$ MHz as a typical value. However, this interpretation is also not very satisfactory for numerous reasons. The main objection is that for $J' \geq 5$ it was concluded by de Lange et al. [9] that $g \gg G/N$, in accordance with the results and interpretation of Amirav and Jortner [10]. But $g \gg G/N$ immediately implies that for $J' \geq 4$ the lifetime should become considerably shorter in magnetic fields, which is not observed.

In summary, we note that interpretation 1 works well for high J' (but not for low J'), while the reverse holds for interpretation 2. We are therefore forced to conclude that the zero-order triplet rate constant g consists of both a magnetic field dependent part $g_1(H)$ and a magnetic field independent part g_2 ; i.e., $g(H) = g_1(H) + g_2$. A rough estimate for the value of $g_1(H)$ can be obtained by considering the experimental observation $G_{ME}(H) \approx G_{ME}(H=0)$. We then obtain $2g_1(H=0) \approx 2G/(3N)$; i.e., $g_1(H=0) \approx 0.3$ MHz, where we have used $g_1(H) \approx 3g_2(H=0)$. Using a typical value for g of about 1 MHz [8], we find for g_2 about 0.7 MHz. Note that for high J' , where [6,7]

$$G_{ME} = G/N + g + G_c \approx g + G_c, \quad (7)$$

the decay rate constant g increases from 1 MHz in zero field to 1.6 MHz in high field. This small shortening of the lifetime of high- J' states in a magnetic field is obscured by collisional lifetime shortening G_c^{-1} which inevitably accompanies the higher rotational temperatures necessary for populating high J'' in the ground state.

In closing our reasoning we have to show that our argument given under interpretation 1 is still consistent if g is the dominant part of the decay rate constant of G_{ME} and the singlet amplitude is not distributed equally over the triplet states. As pointed out by Amirav and Jortner [10] expressions for the fluorescence intensity like eq. (2) become slightly different.

They obtain for the quantum yield Y [10]

$$Y = G_T/(G_{ME}N_{eff}). \quad (8)$$

In the above equation N_{eff} is the effective dilution factor defined in ref. [10] and replaces N in eqs. (2) and (4). Obviously, in a magnetic field N_{eff} increases threefold, and thus Y decreases threefold (G_{ME} , given by eq. (8), hardly changes as discussed above).

Having obtained some consistency in the observation that (a) the quantum yield decreases by a factor of three in a magnetic field, and (b) the collision-free as well as the collisional lifetime is unaffected by the magnetic field, we now turn to a discussion of the interpretation. Here we are hampered by the fact that the width of the zero-order triplet states is yet unclear. Amirav [11,12] has proposed (on the basis of absorption and excitation spectra) that there are additional states (the "grass" in terminology of Amirav), but this suggestion has been ruled out by the results of Meerts and co-workers [13]. Matsumoto et al. [4] have proposed that the triplet states are coupled to a very dense manifold of another triplet state. In our opinion, the existence of another triplet state is very unlikely as there is no evidence of another singlet state in the vicinity or below the $^1B_{3u}$ state.

The original aim of the present study was to explore the possibility that the width g of the zero-order triplet states arises from collisional relaxation. It was noted that the fluorescence lifetime is very sensitive to collisions, which is entirely reasonable considering that the average spacing of the triplet manifold is 300 MHz. In other words, rather minute interactions between the pyrazine and the carrier gas could give significant collisional relaxation^{#2}. If the width of the zero-order triplet states solely arises from collisional relaxation then the quantum yield at low J' (in particular the P(1) branch) would not change in a magnetic field at sufficiently low temperatures. In fact, the quantum yield changes even at the lowest temperatures we could achieve (0.5-1 K). Thus, the most important conclusion from the present study is that the width g of the triplet states is at least due to a *purely*

^{#2} Many results reported have been claimed as obtained under collision free conditions, but decay rates reported often contained large (30-100%) collisional contributions. Obviously, the experimental conditions under which the rotational and translational temperatures are sufficiently low are rather severe.

intramolecular interaction. As argued above, we are then forced to the odd conclusion that this width consists both of a part sensitive as well as a part insensitive to a magnetic field. Considering the minute value of the magnetic field sensitive part of the width g (only 300 kHz), we suggest that it arises from coupling of the zero-order triplet state to the ground state manifold (one might expect that this decay rate will also increase by a factor of three if a single spin sub-level of the nonrotating molecule is coupled to the ground state manifold [7]). We suggest that the part insensitive to the magnetic field (about 700 kHz) originates from intramolecular vibrational relaxation within the triplet manifold.

Summarising, it has been shown that (a) the strength of the singlet-triplet coupling in the B_{3u} states is not dependent on a magnetic field, (b) the zero-order width of the triplet states is due to purely intramolecular relaxation and does not arise solely from collisions, and (c) the zero-order width g of the triplet states consists both of a magnetic field sensitive part (with a typical value of about 0.3 MHz at zero field) and a magnetic field insensitive part (with a typical value of about 0.7 MHz). For low J' this width is not the dominating part of the total width for those MEs which are responsible for the vast majority of the fluorescence intensity [8]. However, in a magnetic field this may not be the case.

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