

# The Mechanism of Occurrence of Dual Fluorescence in Intermediate Case Molecules as Viewed from Rotational Effects

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Fluorescence decays of jet-cooled pyrazine excited at various positions of rovibronic transitions within the 0–0 band were measured by the use of a pulsed dye laser pumped by an excimer or a nitrogen laser. The experimental data thus obtained on the number ( $N$ ) of the triplet states coupled to the initially excited singlet rovibronic state were analyzed and interpreted by the aid of computer simulation using an asymmetric rotor program. The results indicate that the extraordinarily great variation of  $N$  with excitation energy and unreasonably small values of  $N$  hitherto reported in the literature can be understood in terms of the conventional theory based on the singlet–triplet mixed state model which has been developed for elucidating the mechanism of the occurrence of dual fluorescence in intermediate case molecules.

**KEY WORDS:** Dual fluorescence; intermediate case molecule; fluorescence decay; rotational effect; pyrazine; supersonic jet.

## INTRODUCTION

Under collision-free conditions, molecules with intermediate case level structure, such as pyrazine<sup>1,2</sup> and pyrimidine<sup>3–5</sup>, are known to exhibit dual fluorescence consisting of fast and slowly decaying components, which give one and the same spectrum. The decay of the fluorescence can thus be expressed in the form:

$$I_F(t) = C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2) \quad (1)$$

where  $I_F(t)$  means the fluorescence intensity as a function of time. Here, and from now on, the subscripts 1 and 2 refer to the fast and slow fluorescence components, respectively. Hence,  $\tau_1 < \tau_2$  in Eqn (1).

The biexponential decay of fluorescence in intermediate case molecules has been interpreted theoretically in terms of a singlet-triplet mixed state model. This model was first proposed by Lahmani, Tramer, Tric and Delory<sup>6,7</sup>, and was adopted by several groups of authors<sup>2-5,8-11</sup>. The basic ideas underlying the mixed state model are as follows<sup>6</sup>: (i) coherent excitation of mixed states, which result from coupling of an excited singlet (ro)vibronic state with a manifold of triplet (ro)vibronic states, prepares the singlet (ro)vibronic state concerned; (ii) owing to phase mismatching or dephasing, the initially prepared singlet (ro)vibronic state exhibits a fast exponential decay; (iii) this decay is followed by a quasiexponential slow decay due to a superposition of incoherent decays of individual mixed states.

The present paper deals with two problems concerning the mechanism of occurrence of the dual fluorescence in intermediate case molecules. One problem is that a new mechanism has recently been proposed by Kommandeur and his research group<sup>12</sup> to explain the results of their experiments on the effect of molecular rotation on the dual fluorescence. Their mechanism involves light scattering and is entirely different from the singlet-triplet mixed state mechanism by Lahmani *et al*<sup>6</sup>. The other problem is concerned with the number of triplet states to which the initially prepared singlet state is effectively coupled. According to the mixed state mechanism, this number ( $N$ ) should be significantly larger than unity. However, the values of  $N$  reported by more than a few authors for some excited rovibronic states of intermediate case molecules are close to, or even smaller than, unity.

In order to settle these problems, the details of which are given in the next section, we have re-examined the fluorescence characteristics of pyrazine under collision-free conditions in a supersonic jet, and have analyzed the resulting experimental data by the aid of computer simulation using an asymmetric rotor program.

## DETAILS OF THE PROBLEMS

Let us consider an intermediate case molecule<sup>4-6</sup>. The lowest excited singlet electronic state and a lower-lying triplet electronic state of the

molecule will be called  $S_1$  and  $T$ , respectively. A vibronic state in  $S_1$ , which can be reached by optical excitation from the ground state, and a manifold of vibronic states in  $T$  will be denoted by  $|S\rangle$  and  $\{|T^j\rangle\}$ , respectively. The total energy widths of  $|S\rangle$  and  $|T\rangle$ , denoted by  $\gamma_S$  and  $\gamma_T$ , respectively, are written as:

$$\gamma_S = \Gamma_S + \gamma_S^{NR} \quad (2)$$

$$\gamma_T = \Gamma_T + \gamma_T^{NR} \quad (3)$$

where  $\Gamma_S$  and  $\Gamma_T$  represent radiative widths, and  $\gamma_S^{NR}$  and  $\gamma_T^{NR}$  represent non-radiative widths,  $\Gamma_T$  and  $\gamma_T^{NR}$  being assumed to be independent of  $j$ . The coupling of  $|S\rangle$  and  $\{|T^j\rangle\}$  leads to the following quasistationary mixed states:

$$|n\rangle = \alpha_n |S\rangle + \sum_{j=1}^N \beta_{nj} |T^j\rangle \quad (4)$$

with  $n = 1, 2, \dots, N + 1$ . As was mentioned previously,  $N$  is the number of triplet vibronic states  $\{|T^j\rangle\}$  to which  $|S\rangle$  is effectively coupled. Owing to the above coupling, broadening of the  $|S\rangle$  level occurs to give a linewidth denoted by  $\Delta_{ST}$  (fwhm). On the assumption that the triplet vibronic states  $\{|T^j\rangle\}$  are uniformly spaced and that the coupling matrix elements are constant, independent of the index  $j$ , the broadening is represented by a Lorentzian line shape. In such a case,  $\Delta_{ST}$  is given by

$$\Delta_{ST} = 2\pi\nu_{ST}^2 \rho_T \quad (5)$$

where  $\nu_{ST}$  is the constant coupling matrix element, and  $\rho_T$  is the density of the vibronic states  $\{|T^j\rangle\}$ . In the foregoing descriptions, it has been presumed that  $\nu_{ST}\rho_T \gg 1$  (strong coupling). In the case of the Lorentzian line broadening, the number of effectively coupled triplet states,  $N$ , is given by

$$N = 1/2\pi\rho_T\Delta_{st} \quad (6)$$

which, using Eqn (5), is rewritten as<sup>6,10,13</sup>:

$$N = \pi^2 V_{ST}^2 \rho_T^2 \quad (7)$$

The excited state which is initially prepared by coherent excitation

of the set of mixed states  $\{|n\rangle\}$  is identical with the zero-order singlet state  $|S\rangle$ . The subsequent change in  $|S\rangle$  content of the excited state can be described approximately as a sum of two exponential decays, corresponding to fast (coherent) and slow (incoherent) decays, as given by Eqn (1).

We assume here that  $N \gg 1$  and  $\Delta_{ST} \gg \gamma_S$ . The former relation follows from Eqn (7) and the relation  $V_{ST}\rho_T \gg 1$ , and the latter is known to be valid for pyrazine<sup>13</sup>, pyrimidine<sup>13</sup> and *s*-triazine<sup>14</sup>. It can then be shown that the lifetimes,  $\tau_1$  and  $\tau_2$  in Eqn (1), and the quantum yields,  $\Phi_1$  and  $\Phi_2$ , for the fast and slow fluorescence are expressed as follows:

$$\tau_1 = \hbar/(\Delta_{ST} + \gamma_S) \quad (8)$$

$$\tau^2 = \frac{\hbar}{\gamma_S/N + \gamma_T} \quad (9)$$

$$\Phi_1 = \Gamma_S/(\Delta_{ST} + \gamma_S) \quad (10)$$

$$\Phi_2 = \frac{\Gamma_S/N}{\gamma_S/N + \gamma_T} \quad (11)$$

The number  $N$  can be related to the pre-exponential factors  $C_1$  and  $C_2$  appearing in Eqn (1); namely:

$$N = C_1/C_2 \quad (12)$$

Furthermore, combination of Eqns (8)–(11) yields:

$$N = \frac{\tau_2\Phi_1}{\tau_1\Phi_2} \quad (13)$$

It may be noted here that integration of the first and second terms on the right-hand side of Eqn (1) with respect to  $t$  between 0 and  $\infty$  gives  $C_1\tau_1$  and  $C_2\tau_2$ , which correspond to  $\Phi_1$  and  $\Phi_2$ , respectively.

In the foregoing theoretical treatment, we have regarded the coupling states  $|S\rangle$  and  $\{|T^j\rangle\}$  as vibronic without giving due consideration to the role of molecular rotation in the singlet–triplet coupling or in the electronic relaxation. However, the experimental value of  $\rho_T$  is often too large to match the triplet vibronic density evaluated theoretically<sup>2-5,8-10</sup>. For this reason, some authors have taken the molecular rotation into account.

McDonald *et al.*<sup>10</sup>, for instance, advanced the following view. At the modestly high energy levels in the triplet manifold reached *via* the

intersystem crossing, various non-rigid body couplings lead to extensive scrambling of rotational states of different  $K'$ . Here, the quantum numbers of the total rotational angular momentum and its projection on the top axis (for a symmetric top molecule) are denoted by  $J$  and  $K$ , respectively, and the prime refers to the electronically excited state. On account of the rotational scrambling mentioned above and of the strong prohibition due to the conservation of nuclear spin symmetry, one must multiply the triplet vibrational state density by  $(2J' + 1)/\sigma$  to count completely all the states in the triplet which are coupled to one singlet vibronic state with a rotational quantum number of  $J'$ , where  $\sigma$  is the symmetry number of the molecule.

If the view of McDonald *et al.* is valid, the states  $\{|T^j\rangle\}$  as well as the state  $|S\rangle$  should be regarded as rovibronic. In Eqns (5)–(7), accordingly,  $\rho_T$  should be considered to represent the density of the rovibronic states;  $\rho_T$  can then be expressed in the form:

$$\rho_T = \frac{2J' + 1}{\sigma} \rho_{Tv} \quad (14)$$

where  $\rho_{Tv}$  is the density of the vibronic states.

Furthermore, by means of high-resolution emission spectroscopy, Baba *et al.*<sup>15</sup> observed that the fluorescence quantum yields of pyrazine and pyrimidine vapors vary greatly with the rotational level excited. Since then, several groups of authors<sup>11,13,14,16–35</sup> have investigated the rotational level dependence of the fluorescence decays and/or yields for azabenzene vapors. Most of the results of these investigations can be explained on the theory of Lahmani *et al.*<sup>6</sup>, if we assume that only the slow component of fluorescence depends on the rotational level excited and that the scrambling of the rotational levels occurs.

Thus, the following appear to have been established: (1) The dual fluorescence from intermediate case molecules can be explained in terms of the singlet–triplet mixed state model; (2) only the slow fluorescence component is affected by molecular rotation. As has been mentioned, however, at least two problems remain to be settled.

Kommandeur and his coworkers<sup>20</sup> studied fluorescence characteristics of pyrazine in a supersonic jet, excited at various rovibronic transitions within the 0–0 band, using a pulsed and frequency-doubled dye laser as an exciting light source (pulse duration, several nanoseconds). The bandwidth of the laser ( $<0.1 \text{ cm}^{-1}$ ) is such that the individual rovibronic absorption lines in the  $P$  and  $R$  branches, each of

which is characterized by  $J'$  and is a superposition of all possible  $\Delta K = 0$  transitions, can be resolved. They observed that the ratio of the pre-exponential factors  $C_1/C_2$  (Eqn (1)) increases linearly with increasing  $J'$ .

In addition to the above observation, Kommandeur *et al.*<sup>20</sup> found an interesting fact concerning the behavior of the magnitude of  $C_1/C_2$ . According to these authors, the value of  $C_1/C_2$  resulting from excitation at the top of an absorption line in the  $P$  or  $R$  branch is an order of magnitude smaller than the one resulting from excitation at the bottom between that line and a neighboring line. Furthermore, on the side of the absorption line, the  $C_1/C_2$  ratio has a value intermediate between those at the top and bottom. They observed such behavior of  $C_1/C_2$  for various lines belonging to the  $P$  and  $R$  branches up to  $P(4)$  and  $R(9)$ , the numbers in the parentheses denoting the  $J''$  values of the ground state.

According to Eqn (12), the above experimental results mean that the number of coupled levels  $N$  varies by a factor of more than 10 within a narrow wave number range of  $0.2 \text{ cm}^{-1}$ . Kommandeur regarded this as highly improbable, and considered that the fast component cannot be due to biexponential decay arising from intermediate case level structure, as it is conventionally understood from the viewpoint of the theory by Lahmani *et al.* Thus, he proposed an entirely new mechanism, i.e. the fast component actually originates from non-resonant light scattering (NRLS)<sup>12</sup>. In his view, the azines, including pyrazine, are basically small molecules, and most of the experiments on the decay and quantum yield of the fast component can be explained when NRLS is included.

Recent experiments on the emission decay of pyrazine with picosecond time resolution have shown that the fast component is a real fluorescence and is not due to light scattering<sup>11,35</sup>. The question will then be raised as to how one can explain the experimental results of Kommandeur *et al.*<sup>20</sup>. It should be pointed out in this connection that the explanation by Kommandeur is based on the presumption that pyrazine can be treated satisfactorily as a symmetric top. In our opinion, the pyrazine molecule is actually an asymmetric top, and the deviation from the symmetric top may have an unexpectedly large effect on electronic relaxation processes in that molecule<sup>17</sup>.

We now turn to the problem of the number ( $N$ ) of effectively coupled triplet states. This number is of crucial importance in the

**Table I** Values of  $N$  from different sources for the 0-0 band of pyrazine

Excitation line <sup>a</sup>	Position <sup>b</sup> (cm <sup>-1</sup> )	$J'$	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII		
R(0)	0.41	1	25	62	49	14	290	(48)	~0	2	6	0.6	1.5	15		
R(1)	0.81	2	36	49	21	21	349	(80)	~0	6	8	0.8	1.6	24		
R(2)	1.22	3	44	91	266	129	924	(112)	0.1	10	7	1.0	2.2	38		
R(3)	1.62	4	58					(144)	0.3	15	10	1.2	3.1	50		
R(4)	2.01	5	98		449	200	817	176	0.5	21	12	1.6	4.1			
R(5)	2.41	6	124	337	429	188	630	208	0.7	27	15	1.9	5.1			
R(6)	2.80	7			647	281	817	240	0.9	34	17	2.5	6.2			
Excitation bandwidth (cm <sup>-1</sup> )			0.1	0.5	0.5	0.5	0.5	1	0.2	0.4	0.5	0.06	0.25			
Temperature (K)			3	<10	10	1	298	30	10	>40	2					
Reference			This work						13	34	18	23	26	31	11	22

<sup>a</sup> Numbers in parentheses denote the  $J''$  values of the ground state.<sup>b</sup> Calculated by means of symmetric top approximation.

theory of Lahmani *et al.*, as has been shown previously. For a molecule belonging to the intermediate case, the relation  $N \gg 1$ , or at least  $N > 1$ , should be satisfied. The values of  $N$  that have been reported by several groups of authors for pyrazine are widely different from one another and, in some cases, the  $N$  values are smaller than unity. The situation can be seen by reference to Table I, in which the reported values of  $N$  are collected.

The value of  $N$  may change with the sample conditions such as pressure and temperature and also with the instrumental conditions such as the pulse duration or spectral bandwidth of the exciting light. Furthermore, the apparent value of  $C_1/C_2$  would change with the response time or the time resolution of the detector system employed. In this study, therefore, we have directed particular attention to these experimental conditions.

## EXPERIMENTAL

The experimental apparatus for measuring fluorescence–excitation spectra and fluorescence decays in a pulsed supersonic jet has been described elsewhere<sup>36</sup>. Pyrazine vapor of about 5 Torr seeded in helium (several hundred Torr) was expanded into a vacuum chamber at about  $10^{-5}$  Torr through the 400- $\mu\text{m}$  orifice of a nozzle.

In order to carry out selective excitation into rovibronic levels characterized by the rotational quantum number  $J'$ , a tunable dye laser (Lambda Physik FL 2002 E) pumped by a XeCl excimer laser (Lambda Physik EMG 103 MSC) and combined with an angle-tuned etalon (free spectral range =  $1 \text{ cm}^{-1}$ ) was used as an exciting light source with rhodamine 640 as the dye. The frequency of the dye laser was doubled by a potassium dihydrogenphosphate (KDP) crystal. The resulting ultraviolet (UV) pulses, which were used for exciting the sample, have a duration of 10 ns and an effective bandwidth of  $0.1 \text{ cm}^{-1}$ . The wavelength of the UV light was scanned with a  $0.02 \text{ cm}^{-1}$  step by using a portable computer (Olivetti M10).

A tunable dye laser (Moletron DL14) pumped by a nitrogen laser (Moletron UV22), which is the same as the one used as an excitation source in our previous experiments under bulk gas conditions<sup>13</sup>, was also employed in the present experiments to investigate the temperature dependence of the fluorescence characteristics under the same

experimental conditions. The UV pulses generated by a KDP crystal have a duration of 3 ns and a bandwidth of  $0.5 \text{ cm}^{-1}$ , as reported previously<sup>13</sup>.

The laser beam crossed the supersonic jet, synchronized with the laser with a repetition rate of 20 Hz, at 22 mm downstream from the nozzle. The fluorescence was viewed at right angles to the direction of propagation both of the laser beam and of the jet beam. The total fluorescence was monitored with a photomultiplier (Hamamatsu Photonics R106) to obtain the fluorescence excitation spectra and fluorescence decays. The detector system was the same as described in previous papers<sup>13-16,36</sup>. The laser wavelength was tuned to a given position within the absorption spectrum in the following way: the laser is scanned with a  $0.02 \text{ cm}^{-1}$  step and the fluorescence–excitation spectrum is recorded until the top of a rovibronic absorption line or the bottom between two neighboring lines is reached. Since, in the latter case, the fluorescence was very weak, the intensity of the scattered light, which can be evaluated by trapping the sample using liquid nitrogen, was reduced to a reasonably low level by using UV filters (Toshiba UV35 and UV37).

## SIMULATION

The absorption and fluorescence–excitation spectra and the average of the rotational quantum number  $J'$  for the excited state  $S_1$ ,  $\bar{J}'$ , as a function of excitation frequency  $\nu$  were simulated by using, unless otherwise stated, an asymmetric rotor program<sup>17</sup>. Here  $\bar{J}'$  is defined as:

$$\bar{J}' = \frac{\sum J' f(J', K'_a, K'_c, \nu, T)}{\sum f(J', K'_a, K'_c, \nu, T)}$$

where  $f(J', K'_a, K'_c, \nu, T)$  is the probability that a molecule is excited into a rotational level with rotational quantum numbers  $J'$ ,  $K'_a$  and  $K'_c$  at an excitation frequency of  $\nu$  and at a temperature of  $T$ ; the sum is taken over all the appropriate values of  $J'$ ,  $K'_a$  and  $K'_c$ . Detailed procedures for simulation are described below.

First, the frequency and intensity are calculated for each of the rovibronic absorption transitions by the use of the following rotational constants reported by Innes *et al.*<sup>37</sup>:  $A'' = 0.21285$ ,  $B'' = 0.19767$  and  $C'' = 0.10249 \text{ cm}^{-1}$  for the zero point vibrational level in  $S_0$ ;  $A' =$

0.21122,  $B' = 0.19678$  and  $C' = 0.10113 \text{ cm}^{-1}$  for the same level in  $S_1$ . Then, a certain number of points are taken which are uniformly spaced along the  $\nu$  axis between  $-5$  and  $5 \text{ cm}^{-1}$  (or between  $-30$  and  $30 \text{ cm}^{-1}$ ), with 0 taken at the band origin. At each point, i.e. at each frequency  $\nu$ , the intensities of rovibronic absorption transitions whose energies lie in the excitation bandwidth with its center at that point are summed up on the assumption that the exciting light has a triangular band shape; a simulated absorption spectrum is thus obtained.

Since the quantum yield of the fast component of fluorescence is known to be independent of the rotational level excited<sup>13</sup>, the excitation spectrum of the fast fluorescence can be regarded as identical to the absorption spectrum. On the other hand, the quantum yield of the slow component of fluorescence depends on the rotational level excited, and is proportional to  $(2J' + 1)^{-1}$ <sup>13,17,34</sup>. In addition, the fluorescence of pyrazine is dominated by the slow component at low temperatures<sup>34</sup>, e.g.  $<30 \text{ K}$ . Accordingly, the excitation spectra of pyrazine at temperatures below  $10 \text{ K}$  were simulated by calculating the corresponding absorption spectra after each of the intensities of the rovibronic transitions concerned was multiplied by  $(2J' + 1)^{-1}$ .

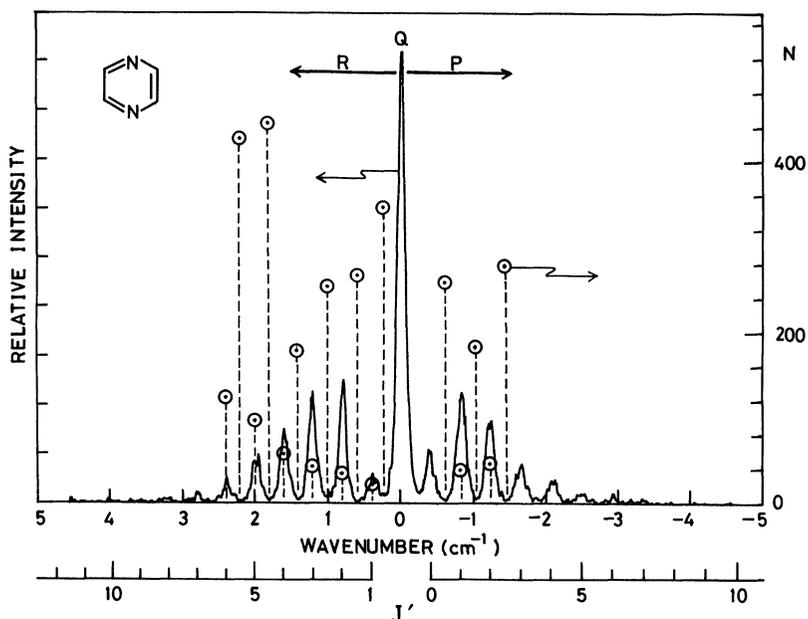
The average quantum number  $\bar{J}'$  as a function of  $\nu$ , which may be called a  $\bar{J}'$  spectrum, was simulated in a manner similar to those in which the absorption and excitation spectra were calculated.

When the pyrazine molecule was treated as an approximately symmetric top, a computer program was used which is similar to the asymmetric rotor program described above<sup>17</sup>. In such a case, mean rotational constants  $\bar{B}'' = (A'' + B'')/2$  and  $\bar{B}' = (A' + B')/2$  were used.

## RESULTS

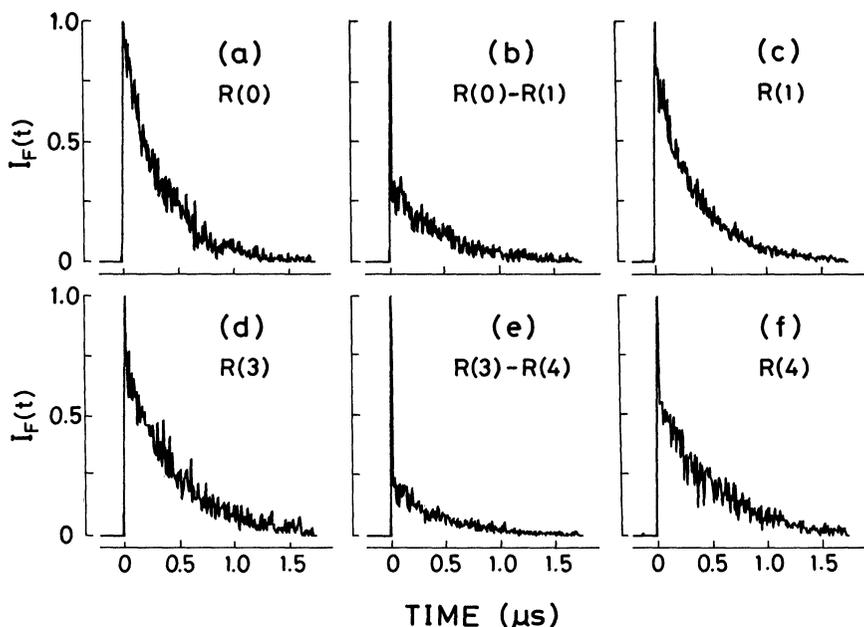
All the results given below are concerned with the fluorescence generated by excitation within the 0-0 absorption band of jet-cooled pyrazine. For the results shown in Figures 1-3, the excitation bandwidth is  $0.1 \text{ cm}^{-1}$  and the rotational temperature of pyrazine is estimated to be  $3 \text{ K}$  (*see below*); for the results shown in Figures 4-6, the bandwidth is  $0.5 \text{ cm}^{-1}$ .

Figure 1 shows the fluorescence-excitation spectrum, together with the values of  $N$  for various excitation positions. These  $N$  values were determined from the fluorescence decays following excita-



**Figure 1** Fluorescence-excitation spectrum (—) and values of  $N$  ( $\odot$ ) for the 0-0 band of jet-cooled pyrazine at 3 K. Stagnation pressure of the carrier gas (He) is 540 Torr, and excitation bandwidth is  $0.1 \text{ cm}^{-1}$ . The band origin denoted by 0 is at  $30875.79 \text{ cm}^{-1}$ . The values of  $J'$  shown at the bottom are calculated by means of symmetric top approximation<sup>13</sup>.

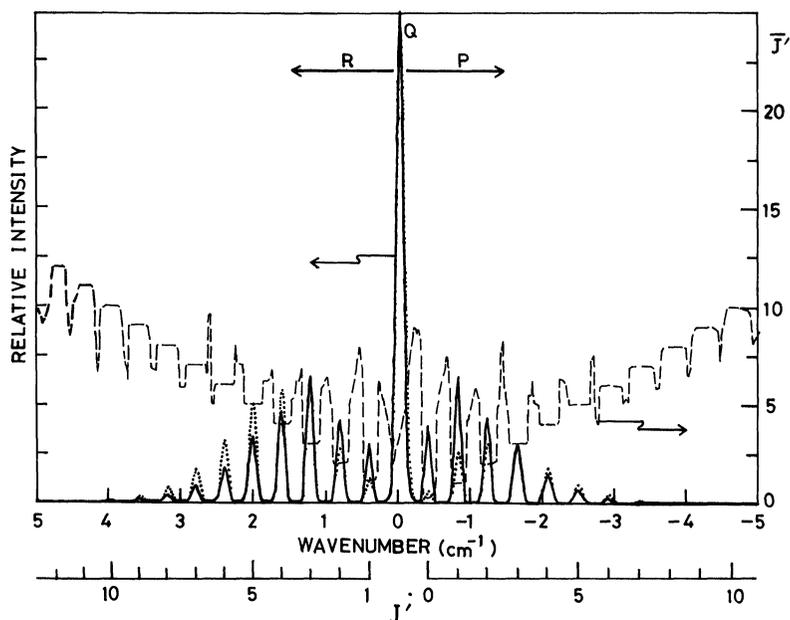
tion at the tops of the absorption lines and at the bottoms between the neighboring lines. Some examples of the fluorescence decays are shown in Figure 2. For each of the observed decay curves, the integrated fluorescence intensities were evaluated which are to be assigned to the fast and slow fluorescence components, and the ratio between the resulting integrated intensities was regarded as the fluorescence quantum yield ratio,  $\Phi_1/\Phi_2$ . The value of  $\Phi_1/\Phi_2$  was then multiplied by the lifetime ratio  $\tau_2/\tau_1$  to give  $N$  according to Eqn (13). With the collision-free pyrazine molecule, both the  $\tau_1$  value<sup>11,13</sup> and the  $\tau_2$  value<sup>13,25,26,30</sup> are known to be practically independent of the excitation position within the 0-0 absorption band; the lifetime values used in this study are as follows:  $\tau_1 = 100 \text{ ps}$ <sup>10,11,34,35,38</sup> and  $\tau_2 = 400 \text{ ns}$ <sup>13,25,26,34</sup>. It may be noted that the  $\tau_2$  values obtained in the present experiments (see Figure 2) fall in the range 390–430 ns.



**Figure 2** Fluorescence decays following excitation at different positions within the 0-0 band of jet-cooled pyrazine at 3 K. Excitation positions:  $R(0)$ , the top of absorption line  $R(0)$ ;  $R(0)-R(1)$ , the bottom between absorption lines  $R(0)$  and  $R(1)$ ; other symbols have analogous meanings. The experimental conditions are the same as in Figure 1.

As is seen in Figure 1, the values of  $N$  vary markedly according to whether the excitation position is tuned to the top or to the bottom of the absorption lines belonging to both the  $P$  and the  $R$  branch.

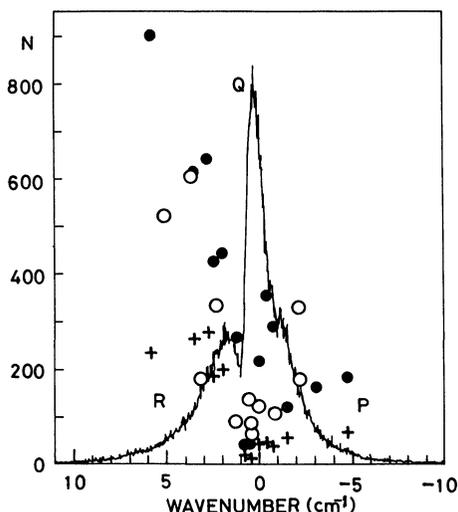
Absorption and fluorescence-excitation spectra were simulated by the use of the asymmetric rotor program described in the preceding section. The spectral bandwidth was taken as  $0.1 \text{ cm}^{-1}$ , while the temperature was changed from 2 to 10 K. The shapes of both spectra are sensitive to the temperature. It was found that the observed and calculated excitation spectra agree reasonably well with each other at 3 K. Figure 3 shows calculated absorption and excitation spectra for a bandwidth of  $0.1 \text{ cm}^{-1}$  and a temperature of 3 K. Under the same conditions, the average value of  $J'$ , i.e.  $\bar{J}'$ , was calculated as a function of excitation wave number, yielding a  $\bar{J}'$  spectrum. The results are also shown in Figure 3.



**Figure 3** Simulated absorption (.....), fluorescence-excitation (—) and  $f'$  (---) spectra for the 0-0 band of pyrazine at 3 K. Excitation bandwidth is  $0.1 \text{ cm}^{-1}$ . See Figure 1 for the values of  $J'$ .

In order to facilitate comparison with previously reported values of  $N$  (Table I)<sup>13</sup>, additional  $N$  values for jet-cooled pyrazine were determined from decay curves that were measured with a greater excitation bandwidth of about  $0.5 \text{ cm}^{-1}$ , using the nitrogen laser as a pumping light source. The procedure for determining  $N$  is based on Eqn (13), and is the same as that described in the case of the smaller bandwidth of  $0.1 \text{ cm}^{-1}$  (Figure 1). The  $N$  values thus determined are shown in Figure 4 with open circles; in this case, the rotational temperature is estimated to be somewhat lower than 10 K.

In connection with the experimental results given in Figure 4, calculations of  $\bar{J}'$  at different temperatures were performed as a function of excitation wave number, with the bandwidth fixed at  $0.5 \text{ cm}^{-1}$ , using the asymmetric and symmetric rotor programs. The results are shown in Figures 5 and 6, respectively.

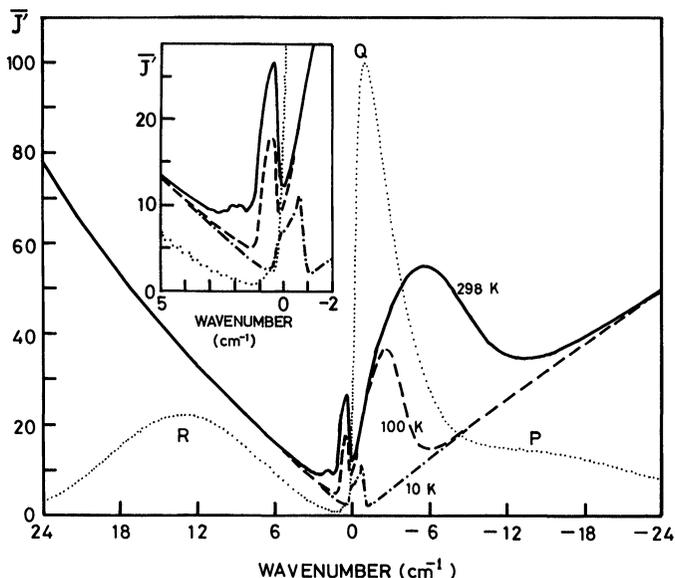


**Figure 4** Fluorescence-excitation spectrum (—) and values of  $N$  ( $\circ$ ) observed for the 0-0 band of jet-cooled pyrazine ( $<10$  K). Stagnation pressure of the carrier gas (He) is 410 Torr, and excitation bandwidth is  $0.5\text{ cm}^{-1}$ . The values of  $N$  at 10 and 1 K calculated by Eqn (18) are represented by  $\bullet$  and  $+$ , respectively.

## DISCUSSION

In the present experiments, the values of  $N$  were determined on the basis of Eqn (13). It is to be recalled, however, that the fundamental equations such as Eqns (8)–(13) for intermediate case molecules hold when the pulse duration ( $\tau_{\text{pd}}$ ) or the coherence time of the exciting light is sufficiently shorter than  $\tau_1$  given by Eqn (8), i.e. when the coherence bandwidth of the exciting photon is sufficiently greater than  $\Delta_{ST} + \gamma_S$ . Furthermore, Eqn (12) is valid only if the ratio  $C_1/C_2$  is obtained from the fluorescence decay which is measured by means of a detector system with a sufficiently fast response. The value of  $N$  which is determined either from Eqn (12) or from Eqn (13) using the data obtained under the ideal instrumental conditions mentioned above, can be regarded as “intrinsic” in the sense that it represents the number  $N$  which is inherent to the molecular level  $|S\rangle$  concerned and is given by Eqns (6) or (7).

Here we are interested in the intrinsic number  $N$  and also in the

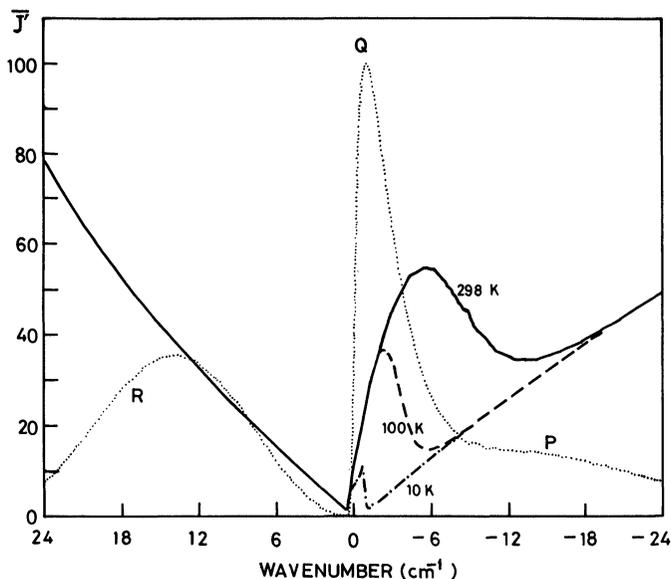


**Figure 5** Simulated  $\bar{J}$  spectra for the 0-0 band of pyrazine at different temperatures: —, 298 K; ---, 100 K; ·····, 10 K. The simulated absorption spectrum at 298 K (·····) is also shown for reference. Excitation bandwidth is  $0.5 \text{ cm}^{-1}$  in every case.

intrinsic lifetime of the fast fluorescence, i.e.  $\tau_1$  given by Eqn (8). In general, however, it is very difficult to determine directly and precisely these intrinsic quantities under perfect coherent excitation and perfect response. Thus, for pyrazine, if the pulse duration  $\tau_{pd}$  is of the order of 1 ns, i.e. if the coherence bandwidth of the exciting light is smaller than  $\Delta_{ST} + \gamma_S$ , then the apparently observed  $\tau_1$  value will become equal to the value of  $\tau_{pd}$  which is evidently larger than the intrinsic  $\tau_1$  value ( $\sim 100$  ps). Also, the observed ratio  $C_1/C_2$  will become correspondingly small compared with the intrinsic value of  $C_1/C_2$ . These arguments apply to the present experiments as well as to the experiments by some other authors (see Table I).

In our previous paper<sup>13</sup>, we pointed out the following: when the coherence bandwidth of the exciting light is  $\zeta(\Delta_{ST} + \gamma_S)$ , with  $\zeta$  being smaller than unity (narrow coherence bandwidth),  $I_F(t)$  in Eqn (1) is changed to  $I'_F(t)$  which is expressed approximately in the form:

$$I'_F(t) = \zeta C_1 \exp(-\zeta t/\tau_1) + C_2 \exp(-t/\tau_2) \quad (8)$$



**Figure 6**  $J'$  spectra simulated by means of symmetric top approximation for the 0-0 band of pyrazine at different temperatures: —, 298 K; ---, 100 K; -·-·-, 10 K. The absorption spectrum at 298 K (·····) simulated by the same approximation is also shown for reference. Excitation bandwidth is  $0.5\text{ cm}^{-1}$  in every case.

where  $C_1$ ,  $\tau_1$ ,  $C_2$  and  $\tau_2$  are the same as those given in Eqn (1). Thus, for the fast component of fluorescence the pre-exponential factor is reduced to  $\zeta C_1$  and the lifetime is lengthened to  $\tau_1/\zeta$ , but for the slow component both quantities remain unchanged. As a result, in the case of narrow coherence bandwidth excitation, the number of effectively coupled triplet states,  $N'$ , is given by

$$N' = \zeta C_1 / C_2 = \zeta N \quad (16)$$

On the other hand it follows from Eqn (15) that, on narrowing the coherence bandwidth of the exciting light, both  $\Phi_1$  and  $\Phi_2$  remain unchanged<sup>13</sup>. Accordingly, if  $\Phi_1/\Phi_2$  is evaluated from data on the fluorescence spectrum or decay obtained by narrow coherence bandwidth excitation, and if the values of intrinsic lifetime  $\tau_1$  and  $\tau_2$  are known, the intrinsic number  $N$  can be found from Eqn (13).

The data for  $N$  shown in Figure 1, along with the decay data given in Figure 2, clearly indicate that there is a marked tendency for  $N$  to be

particularly large when the excitation is made at the bottom between two neighboring absorption lines. This observation is the same as that reported by Kommandeur *et al.*<sup>20</sup>, except that their  $N$  values, which were obtained by a different method, are smaller than ours by a factor of about 10.

The variation of the observed  $N$  value with excitation energy (Figure 1) appears to be closely related to the variation of the  $\bar{J}'$  value calculated by means of computer simulation (Figure 3). In fact,  $\bar{J}'$  shows minima at the tops of absorption lines and maxima at the bottoms between successive lines.

For the  $0^0$  vibronic state of pyrazine,  $\tau_1$  is nearly independent of the rotational level excited. It then follows from Eqn (8) that  $\Delta_{ST}$  is also independent of the rotational level, since  $\Delta_{ST} \gg \gamma_S$ . Therefore, substituting Eqn (14) into Eqn (6) yields:

$$N \propto (2J' + 1) \quad \text{or} \quad N \propto (J' + 1/2) \quad (17)$$

Here  $\rho_{Tv}$  is assumed to be a constant for a given vibronic state. Thus, except for the constant term of  $1/2$ ,  $N$  is proportional to the quantum number  $J'$ , which may be replaced by  $\bar{J}'$ . Evidently, this linear (or approximately proportional) relation between  $N$  and  $\bar{J}'$  favors the fact that  $N$  and  $\bar{J}'$  vary in similar ways across the 0-0 vibronic band (Figures 1 and 3).

It should be emphasized here that, if the pyrazine molecule is treated as a symmetric top,  $\bar{J}'$  will increase simply as the excitation wave number increases in the  $R$  branch (decreases in the  $P$  branch), i.e. in this case,  $\bar{J}'$  cannot be particularly large at the bottoms of the successive absorption lines. This fact is one material reason why Kommandeur considered that the theory of the intermediate case molecule by Lahmani *et al.* does not apply to pyrazine.

Since the pyrazine molecule is actually an asymmetric top, mixing must occur among rotational levels which the molecule would have if it were a symmetric top. As a result, the vibronic band concerned may have a complicated rotational structure in which a large number of weak, irregular transitions to rotational levels of high  $J'$  are superimposed on the regular transitions associated with the "parent" symmetric top. This is the reason why the calculated  $\bar{J}'$  spectrum shows the complex pattern seen in Figure 3.

In this way the observed variation of  $N$  across the vibronic band can be understood in terms of Eqn (17), which is based on the  $S$ - $T$  mixed

state model, without resorting to such a new theory as Kommandeur proposed. Closer inspection of Figures 1 and 3, however, will reveal that quantitatively a deviation occurs from the linear relation between  $N$  and  $\bar{J}'$ —for excitation at the tops of the absorption lines, an approximately linear relation is found to exist between  $N$  and  $\bar{J}'$ , but the  $N$  values at the bottoms are evidently larger than those inferred, using Eqn (17), from the  $N$  values at the tops. One of the reasons for this deviation is probably that our simulation is not satisfactory enough to produce quantitatively good results.

We now proceed to the discussion of the number of effectively coupled triplet states,  $N$ . In Table I the  $N$  values obtained in the present experiments for jet-cooled pyrazine (columns I and II) are given, together with those reported in the literature (columns V–XII). The values of  $N$  in Table I are confined, for the sake of simplicity, to those obtained by excitation in the  $R$  branch region. The values in columns I and II were taken from the experimental data shown in Figures 1 and 4, respectively. The values of  $N$  are found to be widely different, as has been pointed out.

The  $N$  values in column V for the bulk gas of pyrazine at room temperature (298 K)<sup>13</sup> were obtained by us under the same instrumental conditions as those in column II—nevertheless, it is seen that those in column II are significantly smaller than those in column V. The question will then be raised as to whether or not the difference between the  $N$  values is caused solely by the difference between the temperatures of the samples.

Let the low temperature of the jet sample be denoted by  $T_1$ , and the high temperature of the bulk gas sample by  $T_2$ . If it is assumed that Eqn (17) holds, then for a given excitation wave number the number  $N$  at  $T_1$  is related to that at  $T_2$  as follows:

$$N(T_1) = \frac{2\bar{J}'(T_1) + 1}{2\bar{J}'(T_2) + 1} N(T_2) \quad (18)$$

with  $T_2$  fixed at 298 K, the values of  $N(T_1)$  were calculated for  $T_1 = 10$  and 1 K, using the values of  $\bar{J}'$  as given in Figure 5 and also the values of  $N(T_2)$  given in column V of Table I; for the details of the  $N(T_2)$  values, see Figure 8 in Baba *et al*<sup>13</sup>. The results shown in Figure 4 as well as in columns III and IV of Table I indicate that the experimental  $N(T_1)$  values (open circles in Figure 4 and column II of Table I) fall roughly between  $N(T_1 = 10 \text{ K})$  and  $N(T_1 = 1 \text{ K})$ . This means that the difference

in  $N$  between the jet and bulk gas samples is largely attributable to the difference in temperature between the two samples.

As is seen from Figure 6, the  $\bar{J}'-\tilde{\nu}$  curves (with  $\tilde{\nu}$  denoting excitation wave number) at different temperatures are practically the same in the  $R$  branch region, except for the positions very near the band origin, and  $\bar{J}'$  increases monotonously with increasing  $\tilde{\nu}$ . If, therefore, the pyrazine molecule is regarded as a symmetric top, Eqn (18) will predict that  $N(T_1)$  is practically equal to  $N(T_2)$ ; in other words,  $N$  does not depend on temperature. On the other hand, in the case of the asymmetric top (Figure 5),  $\bar{J}'$  for  $\tilde{\nu} < 5 \text{ cm}^{-1}$  in the  $R$  branch region increases with increasing temperature, and at higher temperatures the  $\bar{J}'-\tilde{\nu}$  curves varies in a complicated manner, giving two minima (at  $\tilde{\nu} \approx 0$  and  $\approx 2 \text{ cm}^{-1}$  for 298 K). Such behavior of  $\bar{J}'$  as a function of  $\tilde{\nu}$  and  $T$  accounts for our experimental observation<sup>13</sup> that, at high temperatures,  $N$  has relatively large values and varies in a somewhat complicated manner even in the region of the  $R$  branch which is isolated from the  $Q$  and  $P$  branches.

The  $N$  data in the remaining columns, VI–XII, of Table I were all obtained for jet-cooled pyrazine. The values of  $N$  in column VI were calculated by the use of an empirical relation<sup>34</sup> between  $N$  and  $J'$ :

$$N = 16(2J' + 1) \quad (19)$$

Amirav and Jortner<sup>34</sup> derived this equation by combining an empirical relationship between the absolute fluorescence quantum yield of pyrazine and  $J'$  with the theoretical relationships given by Eqns (10) and (11) of this paper. These authors measured the fluorescence quantum yields using a chaotic light source for excitation. They assumed that Eqn (19) holds for  $J' = 5-22$ . The values in parentheses in column VI result from application of Eqn (19) to cases in which  $J'$  is smaller than 5. The  $N$  values in column VI are found to agree roughly with the corresponding values obtained in the present study (columns I and II).

In contrast to this, the  $N$  values in columns VII–XI, which were all obtained by evaluating the ratios  $C_1/C_2$  directly from crude fluorescence decay curves, are one to three orders of magnitude smaller than the values obtained by the present authors and by Amirav and Jortner, the latter values being considered to represent (approximately) the intrinsic  $N$  values. Owing to the slow response of the detector systems employed, the crude decay curves mentioned above led to  $C_1$  values

smaller than the true ones. Furthermore, although the  $N$  data in columns IX and XI were obtained using picosecond laser pulses for excitation, the data in columns VII, VIII and X were obtained using nanosecond laser pulses. Evidently, therefore, in the latter three cases the crude decay curves cannot give the intrinsic values of  $C_1/C_2 (=N)$ . These arguments account for the fact that the  $N$  values in columns VII–XI are much smaller than the intrinsic values.

We now turn our attention to the  $N$  values in column XII, which were derived from the spectra of the molecular eigenstates (ME) of  $S_1$  pyrazine. The ME spectra were measured by Kommandeur and colleagues<sup>21,22</sup> under high resolution conditions ( $10^{-3} \text{ cm}^{-1}$ ). The values in column XII are the numbers of rovibronic states counted in their ME spectra. Taking account of possible  $\Delta K = 0$  transitions, Kommandeur and colleagues<sup>22</sup> divided the above numbers by  $2J' - 1$  (in the case of the  $R$  branch) to obtain the  $N$  values with which we are concerned in Table I. However, with the resolution and sensitivity in their spectral measurements, some of the eigenstates may possibly have been missed from the ME spectra. In addition, if the symmetric top approximation is employed, the energy separation between successive  $\Delta K = 0$  transitions in pyrazine is estimated to be less than  $10^{-3} \text{ cm}^{-1}$  for  $R(1) - R(3)$ <sup>13</sup>. It is then conceivable that the  $\Delta K = 0$  transitions were not resolved under their experimental conditions. In view of these circumstances, the values given in column XII have not been divided by  $2J' - 1$ . It is seen that these  $N$  values in column XII are significantly large compared with those in columns VII–XI.

Lastly, mention should be made of the polarization of the fluorescence from azabenzenes including pyrazine. It has been found recently that the fluorescence of these molecules exhibits polarization, the characteristics of which depend on the initially excited rotational level<sup>33</sup>. In general, therefore, in such experiments as were designed in the present study, the polarization effect must be taken into account. We have examined this effect by measuring the decays of the parallel and perpendicularly polarized components of fluorescence from jet-cooled pyrazine. The results indicate that, so far as the excitation within the 0–0 absorption band is concerned, there is no significant difference between the two decay curves observed. This means that the fluorescence polarization has practically no effect on the experimental results obtained in the present study and hence on the conclusions derived from these results.

## CONCLUSION

Analyses of the results of the present experiments on pyrazine as a typical representative of intermediate case molecules have revealed that the two problems concerned in this paper, i.e. the extraordinarily great variation of  $N$  with excitation energy and unreasonably small values of  $N$  hitherto reported in the literature, can be understood at least qualitatively within the framework of the conventional theory based on the  $S$ - $T$  mixed state model.

It should be emphasized that, in order to investigate the effects of molecular rotation on electronic relaxation phenomena, one must treat the pyrazine molecule exactly as an asymmetric top, without assuming it to be an approximately symmetric rotor. This observation is important especially when the position of the exciting light is close to the band origin.

## Acknowledgment

This work was partly supported by a Grant-in-Aid for Scientific Research (59430003) from the Ministry of Education, Science and Culture.

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