# Dual Fluorescence of Pyrazine Cooled in a Supersonic Free Jet

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The fluorescence excitation spectrum of the lowest excited $^1B_{3u}(n\,\pi^*)$ state of pyrazine cooled in a pulsed supersonic free jet was observed. The fluorescence decay of the isolated molecule was also measured in the free jet. The rotationally cooled pyrazine in the collision free condition exhibits extremely large fluorescence quantum yield and dominant slow fluorescence component for low lying vibronic levels. The ratio of the pre-exponential factors of the dual fluorescence decay was examined in terms of the available theory of singlet-triplet mixed state model. It was found that the number of coupled triplet levels obtained from the observed ratio is inconsistent with the calculated excess energy dependence of vibronic density in the triplet state. Remarkable rotational level dependence of the ratio of the pre-exponential factors was observed for the electronic origin, while such a rotational dependence was not found for the lifetime of the slow fluorescence.

The fluorescence decay of low pressure diazabenzene vapor such as pyrazine and pyrimidine is known to be bi-exponential, being composed of a pressure-independent fast decay and of a pressure-sensitive slow one.[1,2] The bi-exponential decay has been explained by a mixed state model proposed by Lahmani *et al.*[3] According to this model, the number of triplet levels coupled to a singlet level plays an important role in decay constant of the slow fluorescence component as well as in the fluorescence quantum yield ratio of the slow and fast components. The experimental results of vibronic energy dependence of the lifetimes and the yield ratio have been found to be in accordance with the prediction based on the model.[1,2] Recently, Baba *et al.*[4] have reported the rotational state dependence of the fluorescence quantum yields for low pressure pyrazine and pyrimidine vapor. The rotational dependence on the nonradiative rate has also been discussed theoretically.[5,6] These studies suggest that critical test of the model should be made for an isolated molecule excited to a particular ro-vibronic state. However, the experimental study under such a critical condition is quite difficult for room temperature vapor of large molecule because of spectral congestion of many rotational levels. Recently, it was shown by many workers[7-11] that the isolated molecule at very low rotational temperature is easily prepared by a supersonic free expansion of the molecule seeded in inert carrier gas. Combining the supersonic free expansion with a narrow band tunable laser, one can study dynamical behaviour of the excited molecule confined in a few ro-vironic level.

In the present study we observed the fluorescence excitation spectrum of the first singlet state of pyrazine ($^1B_{3u}$) in a supersonic free jet seeded in He carrier gas. It was found that the fluorescence quantum yield of the isolated molecule in the jet is extremely large for low-lying vibronic levels compared with the vapor value obtained by extrapolation to zero pressure. The observed lifetimes and the ratio of the pre-exponential factors of a bi-exponential decay were examined in terms of the mixed state model. A remarkable rotational state dependence of the fluorescence decay, which has been observed very recently by ter Horst *et al.*[12] was also found in the present work.

## Experimental

Pulsed supersonic free jets of pyrazine seeded in He gas as a carrier were generated by a pulsed supersonic nozzle described in a previous paper.[13] Visible dye laser pumped by a frequency doubled YAG laser (Quanta-Ray), which is synchronized with the pulsed nozzle, was converted to tunable UV light by a SHG crystal (RDP or ADA), phase matching angle of the crystal being controlled by a microcomputer. Cresyle violet+rhodamine B in ethanol solution (650—635 nm) and rhodamine 640 in ethanol solution (640—610 nm) were used. Spectral resolution of the dye laser was about 0.4 and 1.5 $cm^{-1}$ with and without an etalon, respectively. The supersonic free jet was irradiated by the UV light at 15 mm downstream from the nozzle and the fluorescence was observed from the direction perpendicular to the light beam and to the jet stream. By use of several light baffles, scattered light was reduced to the level not to be detected even at a maximum sensitivity of our detection system. The fluorescence was collected by a lens system ($f=2$) and the image of the fluorescent region in the jet was made on a field lens. Unwanted emission from the shock boundaries in the jet was removed by an adjustable mask which was inserted in front of the field lens, and the fluorescence from isentropic core of the jet was focussed on a photomultiplier (Hamamatsu R562) by a lens.

For the measurement of the fluorescence excitation spectrum, the total fluorescence was detected by the photomultiplier combined with a preamplifier (PAR #115) and a boxcar integrator (Brookdeal 9415) with 1.5 μs gate width. The fluorescence intensity was recorded on a strip chart recorder as a function of the exciting wavelength. For lifetime measurement, a sampling oscilloscope (Tektronix 564B) was used instead of the boxcar integrator. In order to ensure the temporal response of the photomultiplier, a high breeder current (≈10 mA) and a 50 Ω load resistance were used; time resolution was not more than 18 ns. In the case of the lifetime measurement, a solid etalon was inserted in the dye laser cavity to improve the spectral resolution for the excitation. The fluorescence spectra were taken by a monochomater (Nikon P-250) and a photon counting system (Ortec #9302, #9315, and #9325) in a gated mode with 3 μs gate width.

Fluorescence quantum yield of pyrazine in the supersonic jet was estimated by comparing the intensity of fluorescence of the 0-0 band excitation with the corresponding intensity of aniline in the jet. Assuming that the fluorescence quantum

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yield of aniline in the jet is the same as that in vapor at room temperature[14] and taking into account of differences of saturated vapor pressures and integrated absorption coefficients of pyrazine and aniline, the ratio of the fluorescence intensities of two molecules in the jet can be converted into a relative quantum yield of pyrazine with respect to that of aniline.

## Results and Discussion

*Quantum Yield Spectrum.* The fluorescence excitation spectrum of the first excited $^1B_{3u}$ state of pyrazine in a supersonic free jet of helium carrier gas at 4 atm is shown in Fig. 1, together with the room temperature absorption spectrum of pyrazine vapor. The assignments of the vibronic bands were taken from Ref. 15. The band width (FWHM) of the 0-0 band in the supersonic jet was about 4 $cm^{-1}$, from which the rotational temperature of the molecule was estimated to be less than 5 K.

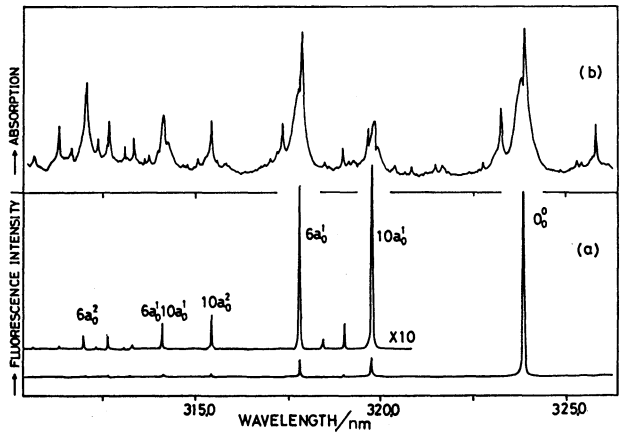


Fig. 1. (a) The excitation spectrum of pyrazine in a supersonic free jet. Saturated vapor of pyrazine at room temperature was seeded in 4 atm He carrier gas. (b) Absorption spectrum in vapor at room temperature.

As is seen from Fig. 1, the excitation spectrum in the free jet shows a rapid decrease of the band intensity with increase of the excess vibrational energy. For example, the 0-0 band is about ten times stronger than that of the $6a^1$ band, while they are comparable in the vapor spectrum. The remarkable difference between the excitation spectrum and the absorption spectrum must be ascribed to a great excitation energy dependence of the fluorescence quantum yield. Although the absorption spectrum of the supersonic jet is not available, it is reasonable to assume that integrated absorption intensities of the individual cold bands in vapor spectrum are proportional to those of the free jet. Since the main cold bands are well isolated in the vapor spectrum, the estimation of their relative integrated intensities should be made with a good accuracy. Using the fluorescence quantum yield of the zero point level obtained by the procedure described in the previous section, we have a quantum yield spectrum of the free jet, which is shown in Fig. 2. The quantum yields of the main vibronic levels are also listed in Table 1.

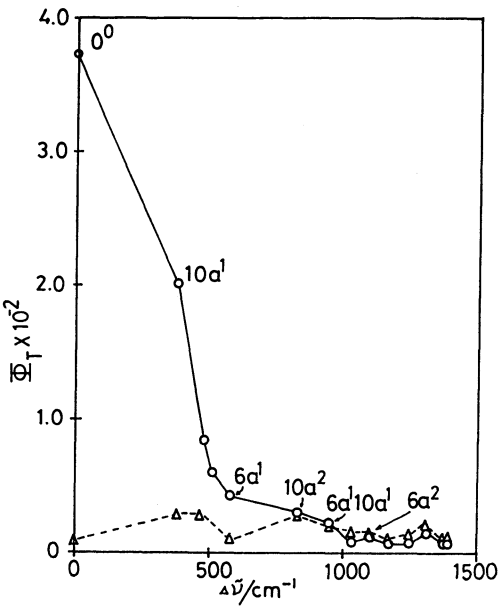


Fig. 2. Fluorescence quantum yield spectrum of pyrazine in a supersonic free jet (—○—). $\Delta\tilde{\nu}$ indicates the energy difference from the electronic origin. For comparison the quantum yield spectrum of 13.3 Pa pyrazine vapor with 2400 Pa isopentane is shown (---△---).

Table 1. Observed quantum yield and lifetime of pyrazine

| Level | $\tilde{\nu}/cm^{-1}$ | $\Phi_T$[a] $\times 10^2$ | $\tau_2$[b]/ns | $\tau_1$[c]/ps | $c_1/c_2$[d] |
|---|---|---|---|---|---|
| $0^0$ | 30876 | 3.7 | 455±10 | 130 | <3 |
| $10a^1$ | 31259 | 2 0 | 264±10 | 125 | 10 |
| $6a^1$ | 31459 | 0.49 | 255±10 | 100 | 43 |
| $10a^2$ | 31709 | 0.35 | 170±15 | 120 | 210 |
| $6a^1 10a^1$ | 31821 | 0.29 | 180±15 | 120 | 240 |
| $6a^2$ | 32043 | 0.11 | 200±20 | 95 | 739 |

a) Quantum yields of the total fluorescence in supersonic free jet. b) Lifetime of the slow fluorescence in supersonic free jet. c) Lifetime of the fast fluorescence in vapor, taken from Ref. 17. d) Ratio of the pre-exponential factors.

The quantum yield of the zero point level is 0.037, which is one order of magnitude larger than the vapor value ($3\times10^{-3}$ at 1.33 Pa in vapor phase) obtained by Frad *et al.*[1] The quantum yield of the free jet rapidly decreases with the excess vibrational energy as seen from Fig. 2 and Table 1. In Fig. 2, the quantum yield spectrum for 13.3 Pa pyrazine vapor in 2400 Pa isopentane is shown for comparison. In contrast to the case of the supersonic jet, the quantum yield is very small ($1\times10^{-3}$) and almost constant over the excess energy region measured, although an appreciable variation is seen at the $10a^1$ level and its combinations.

*Fluorescence Decay from the Vibronic Level.* In our experimental condition of the supersonic free jet, translational temperature is estimated to be 0.5 K and mean collisional time will be greater than 10 μs which is the value for the hard sphere collision with helium atom. Therefore, the fluorescence which decays within

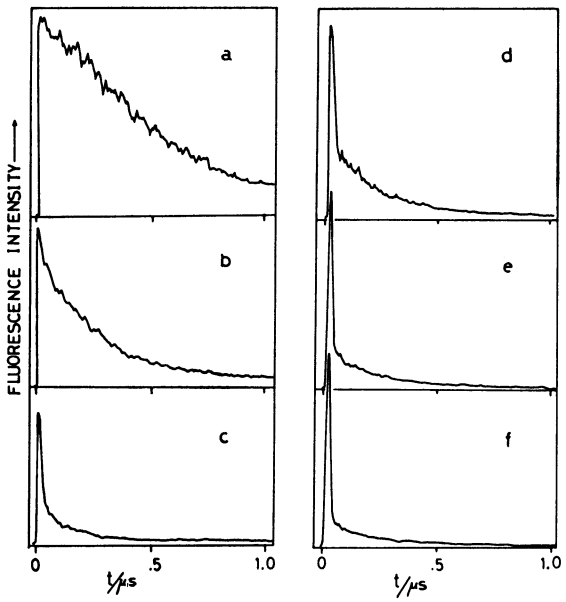


Fig. 3. Oscillogram traces of the fluorescence decay from (a) the electronic origin, (b) $6a^1$ and (c) $6a^2$ of the ultracold pyrazine seeded in 4 atm He gas. Corresponding traces of pyrazine vapor of about 6.65 Pa at room temperature are shown in (d), (e), and (f), respectively.

a time scale less than 10 μs can be regarded as being in a collision free condition.

Oscillogram traces of the fluorescence decay of the jet from several vibronic levels are shown in Fig. 3. The decay from the zero point level was approximately single exponential with lifetime of $455\pm10$ ns (see Fig. 3(a)). On going to the higher vibronic levels, the fast fluorescence component gradually shows up and increases with the excess energy from the zero point level. At a large excess energy the fast component dominates over the slow component (see Fig. 3(c)). The lifetime of the slow component decreases with increase of the excess energy and at $6a^2$ level (excess energy of 1168 $cm^{-1}$) it reduces to a half of the value for the zero point level (see Table 1). On the other hand, in the case of low pressure pyrazine vapor the fluorescence decay is already bi-exponential even for the zero point level as shown in Fig. 3(d). The lifetime of the slow fluorescence in vapor is about 200 ns which is shorter than the value of the jet. The different fluorescence decays between the jet and the low pressure vapor indicate that the slow fluorescence is extremely sensitive to the collisional quenching[16] which still exists in the case of vapor even at extremely low pressure regarded as collision free condition. The lifetime of the slow decay component in the free jet is summarized in Table 1.

Since our detection system is not fast enough to resolve the fast fluorescence decay, the oscillogram traces shown in Fig. 3 do not represent the real decay. Assuming a bi-exponential decay, the fluorescence intensity is given by

$$I_F(t)=I_1(t)+I_2(t)=c_1e^{-t/\tau_1}+c_2e^{-t/\tau_2}, \quad (1)$$

where 1 and 2 refer to the fast and slow components. $c_2$ can be easily obtained by extrapolating the observed $I_2(t)$ into $t=0$. The difference between the oscillogram peak height at $t=0$ and the $c_2$ obtained is defined as $A_1$. Since $\tau_1$ is known to be shorter than $10^{-9}$ s, the $A_1$ value obtained directly from the oscillogram trace is not necessarily equal to $c_1$. By taking a half width $\delta$ of the fast component displayed on the oscillogram trace, the integrated intensity of $I_1(t)$ will be approximately given by $A_1\delta$. On the other hand, the integrated intensity of $I_1(t)$ over a time scale greater than $\tau_1$ can be expressed by

$$\int_0^T I_1(t)\,dt=c_1\tau_1, \qquad T\gg\tau_1. \quad (2)$$

We have, therefore,

$$c_1=\frac{\delta}{\tau_1}\times A_1. \quad (3)$$

$\delta$ was found to be 18 ns from a temporal resolution of our detection system. The lifetime $\tau_1$ of the fast component reported by McDonald and Rice[17] is shown in Table 1. Since no pressure dependence of the fast decay component is observed, it is reasonable to assume that the lifetime of the fast fluorescence of the supersonic jet is the same as that of vapor. The estimated ratios†† $c_1/c_2$ for the individual vibronic bands are shown in the last column of Table 1.

*Rotational Level Dependence of the Fluorescence Decay.* The rotational level dependence of the fluorescence quantum yield has been recently reported by Baba *et al.*[4] for the zero point level of pyrazine. In order to examine the rotational level dependence, we measured the fluorescence decay from various rotational levels of the zero point vibrational level. The measurements

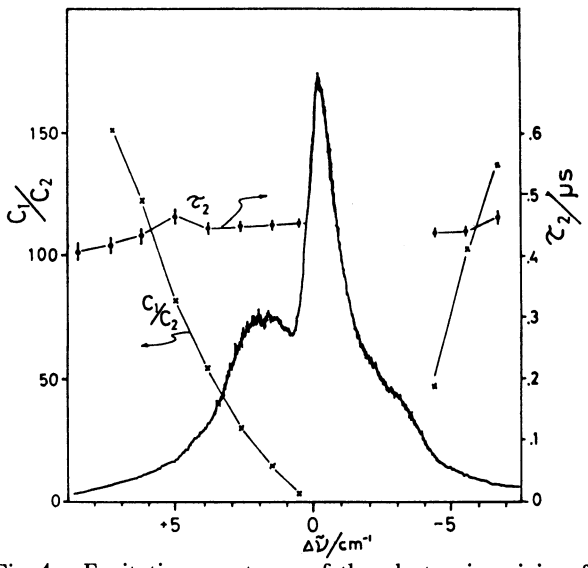


Fig. 4. Excitation spectrum of the electronic origin of pyrazine seeded in 0.05 atm He carrier gas. Lifetime $\tau_2$ of the slow fluorescence decay ($\phi$) and ratio of the pre-exponential factors $c_1/c_2$ ($\times$) are shown superimposedon the excitation spectrum.

†† The vapor value for $6a^1$ band at 31459 $cm^{-1}$ (see Fig. 3(e)) was found to be about 700, which agrees with the value ($10^3$) obtained by Frad *et al.*[1] with the excitation at 31680 $cm^{-1}$.

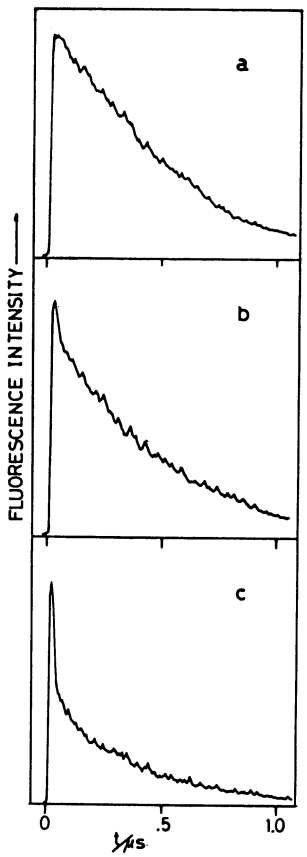


Fig. 5. Rotational dependence of the fluorescence decay from the electronic origin by the excitation of (a) $J'=\approx 1$, (b) $J'=6$—7, and (c) $J'=14$—15.

were made for the supersonic jet with a reduced stagnation pressure of helium gas. In the reduced He pressure, the rotational temperature becomes higher, so that the relatively high rotational levels can also be excited. Excitation spectrum of the 0-0 band under a stagnation pressure less than 0.05 atm of He is actually broad with a rotational envelope as shown in Fig. 4. Rotational temperature was estimated to be higher than 40 K. When the peak at 30876 $cm^{-1}$, which is the Q-branch head, is excited by narrow band UV light of FWHM of 0.4 $cm^{-1}$, a single exponential decay was obtained whose decay constant is the same as that of the jet at a high stagnation pressure (compare Fig. 5(a) and Fig. 3(a)). Tuning the pumping light to the higher energy side (R-branch) of the rotational envelope, a fast component appears prior to the slow component and the ratio of the fast to slow component increases at the far edge of the R-branch. Similar decay was observed also for the P-branch. The typical oscillogram traces are shown in Fig. 5. The results are essentially the same as those reported very recently by ter Harst *et al.*[12]

The observed lifetime of the slow fluorescence component and the ratio of the pre-exponential factors of the fast and slow components ($c_1/c_2$) are given in Table 2. Since the R-branch is well separated from the Q-branch, rotational quantum number $J'$ in the excited state can be roughly assigned for the R-branch with reference to the high resolution vapor spectrum obtained by Merritt and Innes.[18] Although the onset

Table 2. Lifetimes of the slow fluorescence and the ratio of pre-exponential factors of the different rotational levels in the electronic origin

| | $\Delta\tilde{\nu}/cm^{-1}$ [a] | $J'$level | $\tau_2$/ns[c] | $c_1/c_2$[d] |
|---|---|---|---|---|
| R | +8.5 | 20—21 | 411±20 | (138) |
| | +7.3 | 16—18 | 418±20 | 152 |
| | +6.2 | 14—15 | 432±15 | 123 |
| | +5.0 | 12—13 | 461±15 | 82 |
| | +3.8 | 9—10 | 445±15 | 54 |
| | +2.6 | 6— 7 | 450±10 | 30 |
| | +1.5 | 3— 4 | 452±10 | 15 |
| | +0.5 | ≈1 | 456±10 | <3 |
| P | −4.4 | 10—11 | 442±15 | 48 |
| | −5.5 | 14—15 | 441±15 | 104 |
| | −6.7 | 17—18 | 424±20 | 138 |

a) Energy difference from the head of the Q-branch at 30875.8 $cm^{-1}$. b) Estimated rotational quantum number. c) Lifetime of the slow fluorescence. d) Ratio of the pre-exponential factors, by assuming the constant lifetime (130 ps) of the fast fluorescence for the rotational levels.

of the P-branch is congested by overlapping with the Q-branch, the rotational quantum number can be also estimated for the far edge of the P-branch. The estimated $J'$ value are given in Table 2. It is seen from Fig. 4 and Table 2 that the lifetime is almost constant for different $J'$ values, whereas the ratio $c_1/c_2$ greatly increases with increase of $J'$ value.

For the other vibronic bands such as $10a_0^1$ and $6a_0^1$, the detailed lifetime measurements over their rotational structure were not successful because of their small fluorescence quantum yields. However, we could observe increase of the fast component with increase of the rotational temperature of the jet in the broad band (≈1.5 $cm^{-1}$ FWHM) excitation at the peak positions of these vibronic bands. This result may be interpreted as follows. At the low rotational temperature the fluorescence by the broad band excitation arises mainly from a few number of rotational levels with very low $J'$ where the $c_1/c_2$ is small. With increase of the rotational temperature, the fluorescence from the higher rotational levels becomes dominant, resulting in large $c_1/c_2$. Thus, the rotational level dependence of these vibronic bands is concluded to be essentially the same as that of the 0-0 band. According to Baba *et al.*,[4] the change of the fluorescence quantum yield over the rotational levels of the zero point level is ascribed to change of the slow fluorescence component. Their results of the high quantum yield for the low rotational levels are, therefore, consistent with our result of dominant slow component for the low rotational levels.

*Fluorescence Spectrum.* In order to ensure that the slow decay component is actually the fluorescence of pyrazine, we observed the spectrum of the slow decay component in the supersonic free jet. Figure 6 shows the spectrum obtained by excitation at the head of the Q-branch of the 0-0 transition. As seen from Fig. 5(a), only the slow decay component is observed in this excitation. For comparison, the ordinary SVL fluorescence spectrum in vapor at 400 Pa of pyrazine,[15]

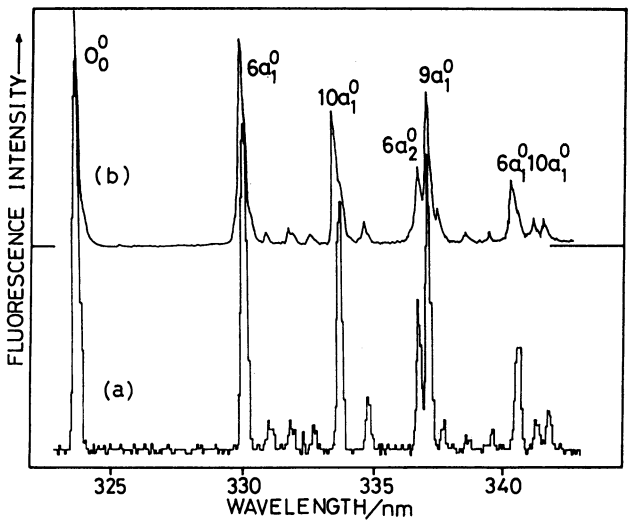


Fig. 6. (a) Fluorescence spectrum of the ultracold pyrazine in a supersonic free jet, being excited at the electronic origin. The slow fluorescence was monitored. (b) Fluorescence spectrum of 400 Pa pyrazine vapor at room temperature. The fast fluorescence was monitored.

which represents practically only the fast component, is shown in the same figure. As seen from the figure, the two spectra are idential with respect to the frequencies and relative intensities of the vibronic bands. Therefore, it is concluded that the slow decay component is really the fluorescence of the molecule.

*Coupled State Density and Fluorescence Lifetime.* The bi-exponential decay of the fluorescence of pyrazine has been interpreted by the model of intermediate strong coupling, where a radiative singlet state strongly interacts with non- or weakly-radiative triplet levels with a relatively large level density.[3] Consider that a single vibronic state $|S>$ in the singlet manifold interacts with $N$ triplet levels $|T>$ through a coupling strength $v_{ST}$. The $|S>$ and $|T>$ levels are assumed to have total energy width $\gamma_S$ and $\gamma_T$, respectively, each of which is composed of radiative and nonradiative contributions. The coupling between the zero order $|S>$ and $|T>$ levels provides $(N+1)$ quasi-stationary molecular eigen states, whose energy levels are distributed within a spectral width $\Delta$ of the exciting light. In the case of coherent excitation of these eigen states by a pulsed light, the time evolution of the wavefunction of the molecule leads to dual fluorescence with fast and slow decay as the result of coherent and incoherent superpositions of the eigen states. In the intermediate case of $|\gamma_S-\gamma_T| \ll \Delta$, the overall fluorescence decay can be approximated by a bi-exponential type given by Eq. 1. The observables in Eq. 1 can be incorporated in the following ways,[1]

$$1/\tau_1 = \frac{\gamma_S}{N} + \gamma_T + \Delta_{ST}, \tag{4}$$

$$1/\tau_2 = \frac{\gamma_S}{N} + \gamma_T, \tag{5}$$

$$c_1/c_2 = N + 1. \tag{6}$$

Since the fast fluorescence is similar to that of the large molecule case, $1/\tau_1$ is dominated by the nonradiative width $\Delta_{ST}$ which is expressed in terms of coupling $v_{ST}$ and the density of state $\rho_T$ in the triplet manifold as far as $v_{ST}\rho_T \gg 1$ is held. Therefore, Eq. 4 can be replaced by

$$1/\tau_1 \simeq \Delta_{ST} = 2\pi\rho_T v_{ST}^2. \tag{7}$$

Thus, the number of interacting levels $N$ is given by

$$N = \pi\Delta_{ST}\rho_T \approx \frac{c_1}{c_2} \quad \text{for } N \gg 1, \tag{8}$$

where Eq. 6 was used. From Eqs. 7 and 8, we obtain

$$\frac{c_1}{c_2} \times \tau_1 = \pi\rho_T. \tag{9}$$

Therefore, $\rho_T$ can be obtained for the individual vibronic levels by using $c_1/c_2$ and $\tau_1$ given in Table 1. $\rho_T$ thus obtained are plotted in Fig. 7 against the excess energy from the origin of $T_1$.

In order to find any correlation between the $\rho_T$ obtained and the density of state in the triplet state, we calculated the state density of the vibrational levels $\rho_T^V$ in $T_1$. The calculation of $\rho_T^V$ was made by the method given by Haarhoff[19] by assuming the same vibrational frequencies of $T_1$ state as those of $S_0$. The result is shown by curve (b) in Fig. 7. $\rho_T^V$ was calculated also by assuming the vibrational frequencies of $S_1$ for those of $T_1$. The calculated result is shown by curve (a) of the same figure. Since the vibrational frequency change upon the excitation from $S_0$ to $T_1$ is generally less significant than the change in the excitation to $S_1$,[20] the curves (a) and (b) are regarded as the maximum and minimum vibronic state densities, respectively.

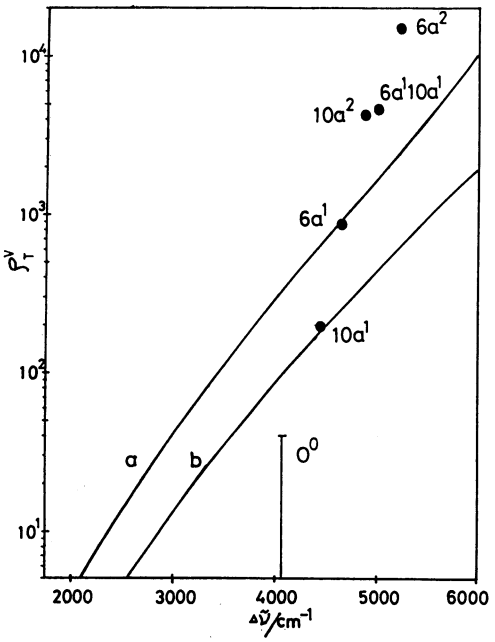


Fig. 7. The triplet state density $\rho_T^V$ (number of levels/cm$^{-1}$) estimated from the $N$ value at the vibronic levels (○) and the calculated vibronic state density $\rho_T^V$ as a function of the excess energy $\Delta\tilde{\nu}$ from the electronic origin of the lowest triplet state. At the electronic origin $0^0$ maximum value is indicated. The vibrational frequencies in the triplet state is assumed at that in the lowest excited siglet state (a) and in the ground state (b).

It is seen from Fig. 7 that the observed $\rho_T$ value agrees with the calculated $\rho_T^V$ for the excess energy region of around 4500 $cm^{-1}$. However, $\rho_T$ is smaller than $\rho_T^V$ for the smaller excess energy region and it is larger for the greater excess energy region. Increase of the observed $\rho_T$ with increase of the excess energy is much rapid than expected from $\rho_T^V$. These facts suggest that the number of coupled triplet levles is not determined simply by the vibronic state of $T_1$. The disagreement between $\rho_T$ and $\rho_T^V$ for the larger excess energy region might be improved by taking into account of the rotational level density which is roughly two orders of magnitude larger than $\rho_T^V$. On the other hand, the fact that $\rho_T$ for the lower energy region is much smaller than the calculated $\rho_T^V$ suggests that there might be a sort of selection rule which selects the interacting levels from the vibronic or ro-vibronic levels of the triplet state.[5]

It is seen from Fig. 4 and Table 2 that the ratio $c_1/c_2$ exhibits a remarkable increase on going to higher $J'$ value in the electronic origin, while the lifetime $\tau_2$ is almost constant over the rotational quantum numberless than $J'=20$. From Eqs. 5 and 6, we have

$$\tau_2 = \frac{c_1/c_2}{\gamma_S + (c_1/c_2)\gamma_T}, \quad \text{for } N \gg 1. \tag{10}$$

A constant value of $\tau_2$ irrespective of various values of $c_1/c_2$ means that $\tau_2$ must be equal to the triplet lifetime $1/\gamma_T$. The triplet lifetime is reported to be the order of $10^{-5}$ s in vapor phase,[1] while $\tau_2 \simeq 450$ ns. Therefore, Eq. 10 is not supported from our experimental results. Since the change of the vibronic or ro-vibronic state density of the triplet state over a range of several wave number around the electronic origin must be very small, we expect no rotational level dependence of $\tau_2$, as it is observed. However, the observed large rotational dependence of $c_1/c_2$ is hard to be explained with the mixed state model proposed by Lahmani *et al.*,[3] suggesting a need of revision of the model.

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