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Rotational State Dependence of the External Magnetic Field Effect on the Fluorescence of Pyrimidine-d_4 at the S_1 Origin

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External magnetic field effects on the intensity and decay of the fluorescence of pyrimidine-d_4 have been examined with excitation at the individual rotational lines of the 0−0 band belonging to the $S_0 \rightarrow S_1$ transition. The fluorescence is quenched by a magnetic field with a tendency that the efficiency of quenching becomes higher with increasing J' of the excited level, except for the R(0) and P(2) line excitations. The fluorescence lifetime, which tends to increase with increasing J' at zero field, is also affected by the magnetic field. A good correlation is found between the field dependence of the fluorescence intensity and the field dependence of the fluorescence lifetime; the lifetime becomes longer when the fluorescence quenching becomes larger or vise versa. Field-induced quantum beats are observed on some rotational line excitations, and the fluorescence intensity and lifetime largely change at the field strengths where these beats are induced. The magnetic field effects are interpreted in terms of the singlet−triplet mixed-state model.

1. Introduction

The fluorescence of the molecules which have an intermediate case level structure composed of singlet−triplet (S−T) mixed states is affected by an external magnetic field (H), as confirmed in aza aromatic compounds.[1] In all these compounds, magnetic quenching of the fluorescence saturates at high fields, and the efficiency of quenching depends on the rovibrational level excited. The magnetic quenching has been explained by the mechanism that the external magnetic field mixes spin sublevels (fine structure levels) belonging to a single rotational level and consequently mixes sublevels belonging to different rovibrational levels of the triplet states. It has been proposed that the efficiency of magnetic quenching depends on the level density of the triplet state coupled to the singlet state at zero field. In fact, the increase of the excess vibrational energy and the increase of the total angular momentum (J') of the excited level, both of which lead to an increase of the level density of the triplet state coupled to the singlet state, enhance the efficiency of magnetic quenching.

The mechanism of the S−T interaction in a deuterated molecule is expected to be the same as in the protonated one except that the vibrational level density of the triplet state may be larger in the deuterated one than in the protonated one, when the excess vibrational energies above the S_1 origin are the same. As reported earlier,[2] however, an anomalous magnetic field dependence both of the intensity and of the lifetime of fluorescence was found at the R(0) excitation of the 0−0 band, belonging to the $S_0 \rightarrow S_1$ transition of pyrimidine-d_4; H induces fluorescence *enhancement* and lifetime shortening, in contrast with the magnetic quenching of fluorescence. The question remains unsettled whether the fluorescence of pyrimidine-d_4 following excitation at rotational lines other than R(0) also shows a different magnetic field dependence from the protonated pyrimidine.

In the present study, the external magnetic field dependence of the intensity and decay of fluorescence in pyrimidine-d_4 is examined not only at the R(0) line but also for other individual rotational lines belonging to the 0−0 band of the $S_0 \rightarrow S_1$ transition in a supersonic jet. It is confirmed that the magnetic field effect on the fluorescence of pyrimidine-d_4 at the S_1 origin is well interpreted by using the mechanism which has been deduced from the experiments of pyrimidine-h_4 and other aza aromatic molecules with intermediate level structures composed of S−T mixed states.

2. Experimental Section

Pyrimidine-d_4 donated by Professor Koyanagi was used in the present experiments.

Optical measurements were carried out under collision-free conditions in a supersonic jet by using the same experimental apparatus and procedures as reported in our previous papers.[3,4] The frequency of a dye laser (Lambda Physik FL2002E), pumped by a XeCl excimer laser (Lambda Physik EMG103 MSC), was doubled by a KDP crystal. The generated UV light with about 0.1-cm^{-1} spectral width and about 10-ns duration was used for excitation. A molecular beam was expanded into a vacuum chamber through a pulsed nozzle with a diameter of 0.4 mm, and the sample was excited 22 mm downstream from the nozzle. Wavelength calibration of the dye laser scanning system was achieved by recording the fluorescence excitation spectrum of iodine vapor.

The fluorescence decay and intensity were measured by using a digital memory (Iwatsu DM901) and a homemade integrator, respectively. A traditional orthogonal geometry was used: the molecular beam proceeds along the X axis; excitation light propagates along the Y axis; the fluorescence was monitored in the Z direction; the external magnetic field (H) was applied along the Z axis. Unless otherwise noted, the excitation light is linearly polarized along the X axis, and undispersed fluorescence at wavelengths longer than 350 nm was monitored with a polarization analyzer oriented to transmit emission whose vector is 45° from the X and Y axes, i.e., the sum of the intensities of parallel and perpendicularly polarized components were monitored.

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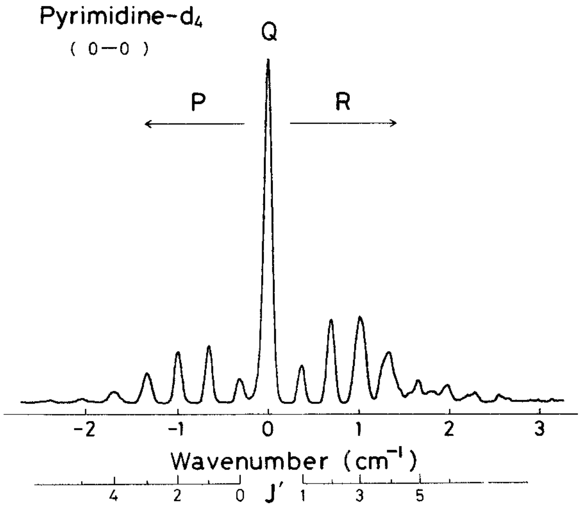

Figure 1. Fluorescence excitation spectrum of pyrimidine-d_4 along the rotational contour of the 0−0 absorption band belonging to the $S_0 \rightarrow S_1$ transition. The band origin denoted by 0 is at 31 188.4 cm^{-1} (see the text).

3. Results and Discussion

3.1. Rotational Analysis of the Jet-Cooled Fluorescence Excitation Spectrum. The fluorescence excitation spectrum of pyrimidine-d_4 observed in a supersonic jet is shown in Figure 1. The spectrum shows a characteristic parallel band rotational structure, as in the case of pyrimidine-h_4.

The rotational energies for the vibrationless levels of both the ground state (S_0) and of the S_1 state are given by the following expression for an oblate symmetric top:[5]

$$E(J,K) = BJ(J + 1) + (C - B)K^2$$

The relevant selection rules for the parallel transition are

$$\Delta K = 0 \qquad K = 0, \quad \Delta J = \pm 1$$

$$\Delta K = 0 \qquad K \neq 0, \quad \Delta J = 0, \pm 1$$

The K level structure cannot be resolved in our spectra, as the difference $(C' - B') - (C'' - B'')$ is very small. Here, the prime and double prime indicate the S_1 and S_0 states, respectively. Consequently, the following simple combination differences were used to verify the rotational numbering and calculate the rotational constants of B' and B'':

$$\Delta E'' = R(J - 1) - P(J + 1) = 4(J + {}^1\!/_2)B''$$

$$\Delta E' = R(J) - P(J) = 4(J + {}^1\!/_2)B'$$

B' and B'' of pyrimidine-d_4 at the S_1 origin were determined to be 0.177 ± 0.002 and 0.178 ± 0.002 cm^{-1}, respectively. Although these constants were obtained in the small range of J, the present value of B'' is nearly the same as the average value of the rotational constants reported for the S_0 state.[6] The band origin, denoted by 0 in Figure 1, is determined to be 31 188.4 cm^{-1}, which is also identical with the one reported by Innes et al.[7]

3.2. Rotational State Dependence of the Fluorescence Lifetime at Zero Field. The fluorescence of the 0^0 pyrimidine-d_4 observed in a jet shows a nearly single-exponential decay composed of only the slow component, in contrast with a bulk gas experiment,[8] and some decays are superimposed by quantum beats. The evaluated lifetime of the slow fluorescence at zero field depends on the rotational level excited, as is shown in Table 1. To explain the rotational state dependence of the fluorescence lifetime, we introduce the following S−T mixed-state model.

The molecular eigenstates of the S_1 state of pyrimidine can be expressed by S−T mixed states resulting from the coupling between the zero-order singlet rovibronic state, $|S\rangle$, and the manifold of the zero-order triplet states, $\{|T_j\rangle\}$:

$$|n\rangle = a_n|S\rangle + \sum b_n^{\,j}|T_j\rangle \tag{1}$$

where $n = 1, 2, ..., N_{\text{eff}} + 1$, and N_{eff} is the effective number of rovibronic states $|T_j\rangle$ coupled to $|S\rangle$.

Applying the S−T mixed-state model to the intermediate case (several hundreds $\geq N_{\text{eff}} \gg 1$), Lahmani et al.[9] have shown that the lifetime of the slow component of fluorescence, denoted by τ_F, is roughly given by

$$\tau_F = \hbar/\gamma = \hbar(\gamma_S/N_{\text{eff}} + \gamma_T)^{-1} \tag{2}$$

where γ_S and γ_T are the total line widths of $|S\rangle$ and $|T_j\rangle$, respectively. Here, the following assumptions are employed: the line widths of the mixed states can be substituted by the average value of γ; the line widths of the zero-order triplet states are the same (γ_T). The quantity N_{eff} is given by the inverse of the time-averaged probability of finding the system in $|S\rangle$; $N_{\text{eff}} + 1 \equiv 1/\sum_n |a_n|^4$.[10,11] The quantum yield of the slow component, denoted by Φ_F, is

$$\Phi_F = \Gamma_S/(\gamma N_{\text{eff}}) \tag{3}$$

where Γ_S represents the radiative width of $|S\rangle$.

Equations 2 and 3 show that both τ_F and Φ_F vary with N_{eff}. As mentioned in a previous paper,[12] the classification into the following three cases is useful: (i) $\gamma_S/N_{\text{eff}} \gg \gamma_T$; (ii) $\gamma_S/N_{\text{eff}} \approx \gamma_T$; (iii) $\gamma_S/N_{\text{eff}} \ll \gamma_T$. In case i, τ_F depends on N_{eff}, but Φ_F is nearly independent of N_{eff}. In case iii, it is vice versa. In case ii, both τ_F and Φ_F vary with N_{eff}, i.e., τ_F increases while Φ_F decreases, as N_{eff} increases. In pyrimidine-h_4, Φ_F and τ_F were shown to depend on the rotational level excited.[13−15] This rotational state dependence was confirmed to be primarily governed by the rotational-level dependence of N_{eff}; i.e., N_{eff} increases with increasing J'. At the smallest value of N_{eff}, Φ_F shows a large maximum and τ_F shows a shallow minimum. Thus, the 0^0 pyrimidine-h_4 is considered to belong to an intermediate between cases ii and iii. It has been found that the 0^0 pyrazine belongs to case iii[13,15] and that the 6^1 and 6^2 *s*-triazine belong to case ii.[12] As is shown in Table 1, there is a tendency that τ_F of pyrimidine-d_4 increases with increasing J' of the excited level. This tendency, which agrees with the one observed in pyrimidine-h_4 or *s*-triazine, is well understood by assuming that N_{eff} increases with increasing J' of the excited level. The fluorescence quantum yield of pyrimidine-d_4 is also expected to increase with decreasing J' of the excited level.

The rotational state dependence of N_{eff} has been attributed to K scrambling in the triplet manifold following intersystem crossing (ISC).[12−16] The level density of the triplet state coupled to S_1, ρ_T, may be written as the product of the vibrational level density ($\rho_T{}^{\text{vib}}$) and the rotational factor (R_T); i.e., $\rho_T = \rho_T{}^{\text{vib}}R_T$. If K scrambling occurs in the triplet manifold following ISC in pyrimidine-d_4, as in the case of pyrimidine-h_4, the excited level of S_1 with a specific rotational quantum number of J' and K' can couple with the triplet levels having different values of K, though the values of J' must be conserved at zero field. Then, R_T is considered to be proportional to $2J' + 1$. For the K scrambling to be complete (where R_T is proportional to $2J' + 1$), however, the vibrational level density of the triplet state may

TABLE 1: Fluorescence Lifetime at Zero Field ($\tau_F(0)$) and at 158 G ($\tau_F(158)$) and the Classification of the Field Dependence of the Lifetime for Various Rotational Lines of the 0−0 Band Belonging to the $S_0 \rightarrow S_1$ Transition of Pyrimidine-d_4[a]

excitation position	P(6)	P(5)	P(4)	P(3)	P(2)	P(1)	R(0)	R(1)	R(2)
J'	5	4	3	2	1	0	1	2	3
$\tau_F(0)$	920	930	785	790	885	740	760	750	780
$\tau_F(158)$	970 (1050)[b]	975	950	780	730	745 (800)[c]	680	760	920
class	+	+	+	0	−	0	−	0	+

[a] τ_F at the field strengths where field-induced quantum beats are found are shown in parentheses. The values of τ_F are in units of ns. [b] The value at 70 G. [c] The value at 142 G.

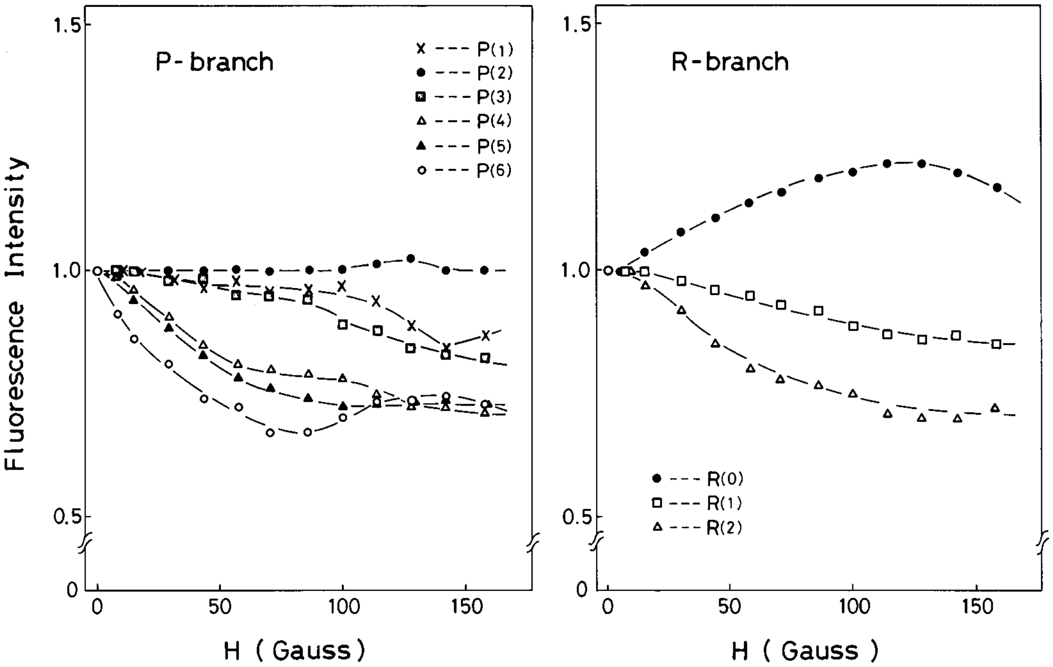

Figure 2. Plots of the fluorescence intensity (I_F) as a function of the field strength (H) at various rotational line excitations of the 0−0 band. The excitation lines of the P-branch transition (left) are as follows: (×) P(1); (●) P(2); (□) P(3); (△) P(4); (▲) P(5); (○) P(6). The excitation lines of the R-branch transition (right) are as follows: (●) R(0); (□) R(1); (△) R(2). The fluorescence intensity at zero field is normalized to unity in each case.

have to be large enough; i.e., a large number of ρ_T^{vib} is necessary to achieve the systematic J' dependence. As is shown in Table 1, τ_F at P(2) and R(0) is larger than the one at P(3) and R(1), respectively, which implies that N_{eff} at the rotational levels with $J' = 1$ is larger than that at $J' = 2$. This lack of systematic J' dependence of τ_F at zero field may come from the small value of ρ_T^{vib} at the S_1 origin.

3.3. Rotational State Dependence of the Magnetic Field Effect. The fluorescence intensity (I_F) of pyrimidine-d_4 is affected by H. The values of I_F are plotted in Figure 2 as a function H at various rotational lines belonging to the P or the R branch of the 0−0 absorption band of the $S_0 \rightarrow S_1$ transition. These intensities were obtained by integrating a full decay with excitation at the peak of the spectrum shown in Figure 1. The fluorescence is quenched by H, except for the R(0) and P(2) line excitations, and there is a tendency that the efficiency of quenching becomes higher with increasing J' of the excited level. This tendency agrees with the above-mentioned rotational state dependence of τ_F at zero field in the sense that both show similar J' dependence. I_F does not always decrease monotonically with increasing H even when fluorescence is quenched by H. For example, a minimum of I_F is observed at ~140 G at P(1) and at ~70 G at P(6) (see Figure 2).

As is shown in Figure 3, τ_F is also affected by H. Figure 4 shows plots of τ_F as a function of H on the excitation at the individual rotational lines of the 0−0 band. The field dependence of τ_F is roughly classified into three cases: (1) τ_F increases with increasing H; (2) τ_F is nearly independent of H; (3) τ_F decreases with increasing H. Case 3 is found only at the rotational levels with $J' = 1$, i.e., at R(0) and P(2). Cases 1 and 2 correspond to the excitations where fluorescence is quenched by H. Actually, case 1 corresponds to the rotational levels with high J', i.e., at R(2), P(4), P(5), and P(6), while case 2 corresponds to the levels with low J' of 0 or 2, i.e., P(1), P(3), and R(1). These classifications of cases 1−3 are denoted by +, 0, and −, respectively, in Table 1. A comparison between the field dependences of I_F and τ_F implies that magnetic quenching of fluorescence and lengthening of τ_F are in pairs and fluorescence enhancement and shortening of τ_F are in pairs. At ~140 G of P(1) and ~70 G of P(6), where I_F shows a minimum, τ_F shows a maximum (cf. Figures 2 and 4). This relation also supports the conclusion that an external magnetic field which induces a fluorescence quenching induces lifetime lengthening. The values of τ_F at a high field of 158 G are also given in Table 1 for the individual rotational lines, together with the zero-field value.

The observed magnetic quenching of fluorescence is well interpreted in terms of the spin-decoupling mechanism, as in the case of other aza aromatic molecules.[1,17−19] In the triplet states, a given rotational level with N is split into three different spin sublevels (fine structure levels) with $J = N + 1$, N, and $N - 1$. These levels are denoted by F_1, F_2, and F_3, respectively. The splitting of these sublevels at zero field results from spin−spin interaction and/or spin−rotation interaction. Here, the number of the rovibrational levels of the zero-order triplet states is denoted by p. According to the selection rule at zero field, i.e., $\Delta J = 0$, only one sublevel can couple with a given singlet state at zero field. At high fields, spin sublevels can be mixed.

Then, a single rotational level of the singlet state can couple with all the spin sublevels of the triplet state, as not just with one sublevel at zero field. Thus, H plays a role to increase $N_{\rm eff}$. Since $\Phi_{\rm F}$ is inversely proportional to $N_{\rm eff}$, magnetic quenching is expected to be induced.

The model Hamiltonian can be constructed by using a $(3p + 1) \times (3p + 1)$ matrix in terms of the zero-order basis. This matrix is written in block form as

$$\mathbf{H}_{\rm am} = \begin{vmatrix} \epsilon_{\rm S} & f_1 & f_2 & \cdots & f_p \\ \bar{f}_1 & \epsilon_1 & 0 & \cdots & 0 \\ \bar{f}_2 & 0 & \epsilon_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \bar{f}_P & 0 & 0 & \cdots & \epsilon_p \end{vmatrix} \qquad (4)$$

where $\epsilon_{\rm S}$ is the energy of $|{\rm S}\rangle$. f_p is the row matrix given by $(0,0,\upsilon_p)$ by assuming that at zero field, $|{\rm S}\rangle$ interacts only with the $\rm F_3$ component of $|{\rm T}_p\rangle$. Here, υ_p is the zero-field coupling strength, and $\bar{f}_p$ is the column matrix given by the transpose of f_p. The eigenvalues and eigenvectors of the S−T mixed states can be obtained by diagonizing the above matrix both in the absence and in the presence of H, if the fine splittings of each triplet level and the coupling strength of the S−T interaction are known. The composition of ϵ_p, which is a 3×3 matrix, is given as follows:[1]

$$\epsilon_p = \begin{vmatrix} E^p{}_{{\rm F}_2} + \dfrac{\alpha M_J}{N(N+1)} & \alpha\beta_1 & \alpha\beta_2 \\ \alpha\beta_1 & E^p{}_{{\rm F}_1} + \dfrac{\alpha M_J}{N+1} & 0 \\ \alpha\beta_2 & 0 & E^p{}_{{\rm F}_3} - \dfrac{\alpha M_J}{N} \end{vmatrix} \qquad (5)$$

where $E^p{}_{{\rm F}_1}$, $E^p{}_{{\rm F}_2}$, and $E^p{}_{{\rm F}_3}$ are zero-field energies of the fine structure levels of $|{\rm T}_p\rangle$. The coupling constants α, β_1, and β_2 are given by

$$\beta_1 = -\frac{1}{N+1}\left[\frac{N[(N+1)^2 - M_J{}^2]}{2N+1}\right]^{1/2}$$

$$\beta_2 = -\frac{1}{N}\left[\frac{(N+1)(N^2 - M_J{}^2)}{2N+1}\right]^{1/2}$$

$$\alpha = g\mu_{\rm B}H \qquad (6)$$

where g, $\mu_{\rm B}$, and H represent the spin g factor, Bohr magnetron, and applied magnetic field, respectively.

If the locations of zero-order triplet states, the coupling strengths, and the fine structure splittings are known, it is possible to simulate the magnetic field dependence both of $\tau_{\rm F}$ and $\Phi_{\rm F}$, i.e., $I_{\rm F}$, since the line width of the mixed state (γ_n) and $\Phi_{\rm F}$ are given by $|a_n|^2\gamma_{\rm S} + \sum_n|b_n|^2\gamma_{\rm T}$ and $\sum_n|a_n|^4\Gamma_{\rm S}/\gamma_n$, respectively.[1] Unfortunately, a quantitative discussion seems to be impossible since the locations of the triplet states as well as the coupling strengths are difficult to precisely determine. However, the above equations indicate that a magnetic field mixes not only the spin sublevels of the single rovibronic level but also the sublevels belonging to different rovibronic levels of the triplet states through the interaction of these triplet states to the same singlet state; i.e., H plays a role to increase $N_{\rm eff}$, as mentioned above. This type of mixing among different rovibrational levels becomes stronger as the energy of the sublevels which are uncoupled with the singlet state at zero field is closer to $\epsilon_{\rm S}$, which is called isoenergetic intermanifold mixing (IIS).[11] $N_{\rm eff}$ can be shown to be increased by a factor of 3 by high fields, if the assumptions which are employed to derive eqs 2 and 3 are used. Further, the efficiency of mixing among spin sublevels, which is directly related to the efficiency of magnetic quenching of fluorescence, is considered to become larger with increasing $N_{\rm eff}$ since an increase of $N_{\rm eff}$ plays a role to decrease the average energy separation among spin sublevels, as demonstrated in our model calculation.[1] It is considered that the efficiency of magnetic quenching is determined by $\rho_{\rm T}$ at zero field. The tendency that the efficiency of the magnetic quenching of fluorescence becomes higher with increasing J' is well understood by assuming that $N_{\rm eff}$ increases with increasing J'. In fact, $\tau_{\rm F}$ at zero field shows a tendency that $N_{\rm eff}$ increases with increasing J' of the excited level. It should be added that the efficiency of magnetic quenching, however, reaches the ceiling. When $N_{\rm eff}$ at zero field is extremely large, the average energy separation among spin sublevels becomes small accordingly, but the average coupling strength of IIS decreases because of the large density of rovibrational levels sharing the $|{\rm S}\rangle$ component.[11]

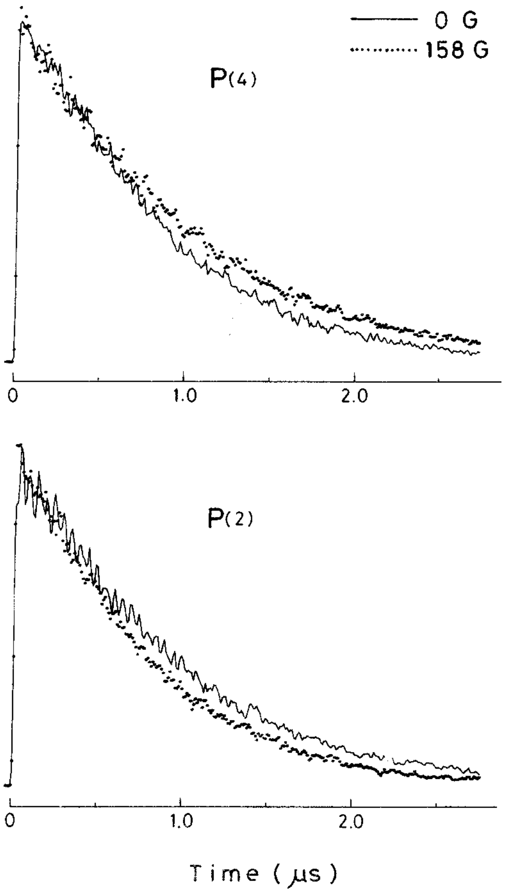

Figure 3. Fluorescence decays observed at zero field (solid line) and at 158 G (dotted line) on excitation at the P(2) line (lower) and P(4) line (upper).

As mentioned previously, the relation between $\gamma_{\rm S}/N_{\rm eff}$ and $\gamma_{\rm T}$ for the 0^0 pyrimidine-d_4 is considered to be an intermediate between case ii and case iii. The fact that both magnetic quenching of fluorescence and lifetime lengthening occur for most excitations is well understood by assuming that $N_{\rm eff}$ is increased by H (see eqs 2 and 3). The relation of the field dependence between $\Phi_{\rm F}$ and $\tau_{\rm F}$ at R(0), which shows the anomalous field dependence, is also understood by assuming that $N_{\rm eff}$ is exceptionally decreased by H for this excitation. However, it must be confessed that the field dependence is not

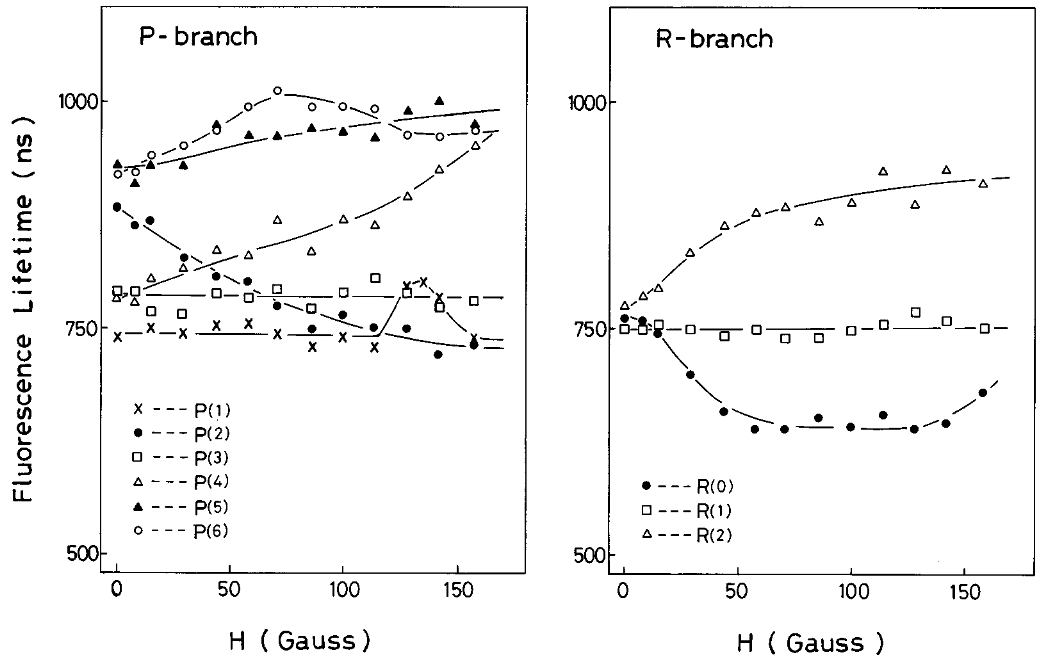

Figure 4. Plots of the fluorescence lifetime (τ_F) as a function of the field strength (H) at various rotational line excitations. The excitation lines of the P-branch transition (left) are as follows: (×) P(1); (●) P(2); (□) P(3); (△) P(4); (▲) P(5); (○) P(6). The excitation lines of the R-branch transition (right) are as follows: (●) R(0); (□) R(1); (△) R(2).

always interpreted only in terms of $N_{\rm eff}$. At P(3) and R(1), where rotational levels with $J' = 2$ are excited, $N_{\rm eff}$ is regarded as increased by H since I_F monotonically decreases with increasing H (see Figure 2). When γ_S and γ_T are independent of H, therefore, τ_F is expected to become longer with increasing $N_{\rm eff}$. In contrast with the expectation, τ_F is nearly independent of H at these excitations (see Figure 4). Thus, the results at P(3) and R(1) imply that a field-induced change in γ_T occurs in some case, in addition to the field-induced change in $N_{\rm eff}$.

As is shown in eq 2, τ_F approaches the lifetime of the zero-order triplet state as $N_{\rm eff}$ increases. As is shown in Figure 4, the τ_f values at higher rotational levels approach ~1 μs as H increases. Then, the triplet lifetime of pyrimidine-d_4 at the S_1 origin seems to be ~1 μs on average. At the S_1 origin, the triplet lifetime of pyrimidine-h_4 is reported to be about ~1 μs.[13-15] Thus, there is no remarkable deuterium effect on the triplet lifetime. The lack of deuterium effect for the triplet lifetime at the S_1 origin of pyrimidine is very different from pyrazine, where the triplet lifetime of pyrazine-d_4 at the S_1 origin is about twice as large as that of pyrazine-h_4.[20,21]

The field dependence of fluorescence at the excited levels with $J' = 1$ prepared by the R(0) or P(2) excitation seems to show that $N_{\rm eff}$ is reduced by H at these levels, in contrast with other rotational levels. Fluorescence decay at the R(0) excitation exhibits polarization quantum beats having frequencies of 5.3, 7.0, 9.4, 10.5, and 13.3 MHz between hyperfine components of S−T mixed states.[2,22] In these beats, the phase of the parallel polarized component is opposite to that of the perpendicularly polarized one. The molecular quantum beat which is independent of the polarization is also observed with a frequency of 20 MHz.[22] This frequency corresponds to the energy separation between two mixed states composed of the levels with $J' = 1$, $K' = 0$. The quantum beat corresponding to the latter beat is also observed for the P(2) excitation (see Figure 3). Unfortunately, the hyperfine quantum beats observed at R(0) are too complicated to be analyzed at present, but the large splittings of the hyperfine components probably come from a large admixture of triplet state(s) in the optically excited state. The Zeeman splittings of the hyperfine beats could not be observed, but the frequencies of the polarization quantum beats become lower with increasing H and converge to 2.7 MHz at around 120 G. The polarization quantum beat observed at ~120 G at R(0) is assigned to the Zeeman quantum beat whose frequency corresponds to the energy splitting between Zeeman sublevels with $M_J' = \pm 1$ of the S−T mixed state of $J' = 1$. In fact, the polarization beat of pyrimidine-d_4 at 120 G seems to be essentially the same as the Zeeman quantum beat of pyrimidine-h_4 observed at the R(0) excitation.[22] Above 120 G, the beat frequency becomes higher with increasing H, as expected from the usual Zeeman quantum beats. The fact that the frequency of the Zeeman quantum beat at 120 G is much smaller than the frequencies of the hyperfine quantum beats observed at zero field seems to suggest that the triplet nature of the excited state becomes weaker with increasing H, i.e., the coupling strength of the S−T interaction seems to be reduced by H, probably because of a field-induced shift of the triplet state. Then, it may be said that $N_{\rm eff}$ becomes smaller with H since $N_{\rm eff}$ is proportional to the square of the coupling strength. Thus, the field dependence of the polarization quantum beats also seems to show that $N_{\rm eff}$ decreases with H. As is shown in Figures 2 and 4, the field dependence of I_F (and τ_F) at R(0) is very different from that at P(2). This result implies that there is a strong K dependence for the rotational level of $J' = 1$. On the other hand, I_F (and τ_F) at R(1) and P(3) varies with H in the same way and so do R(2) and P(4), suggesting that the K dependence is very small at these excitations.

I_F and τ_F do not always monotonically vary with H; for P(1), at around 140 G, I_F bounces up and τ_F bounces down, and the same behavior is observed at 70 G for P(6). Furthermore, quantum beats are observed at these field strengths. Figure 5 shows fluorescence decays and their Fourier transforms for the P(1) excitation at different strengths. The quantum beats with a frequency of 4.7 and 6.3 MHz are observed at 142 G, and these beats are observed only around 140 G. The former frequency is independent of H, while the latter frequency slightly shifts to the blue (about 0.4 MHz) by changing H. A full explanation for the field-induced quantum beats as well as the nonmonotonic field dependence of I_F and τ_F cannot be given

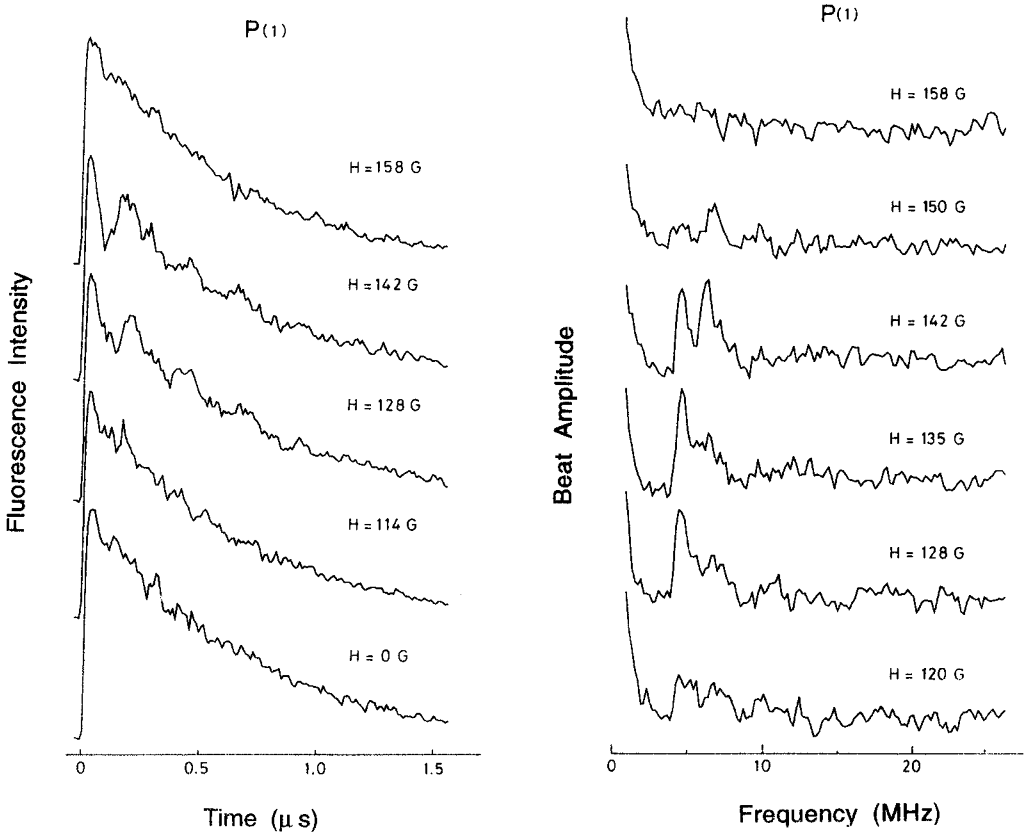

Figure 5. Magnetic field dependence of the fluorescence decay following excitation at the P(1) line (left) and the Fourier transforms of the decay at various values of H from 120 to 158 G (right).

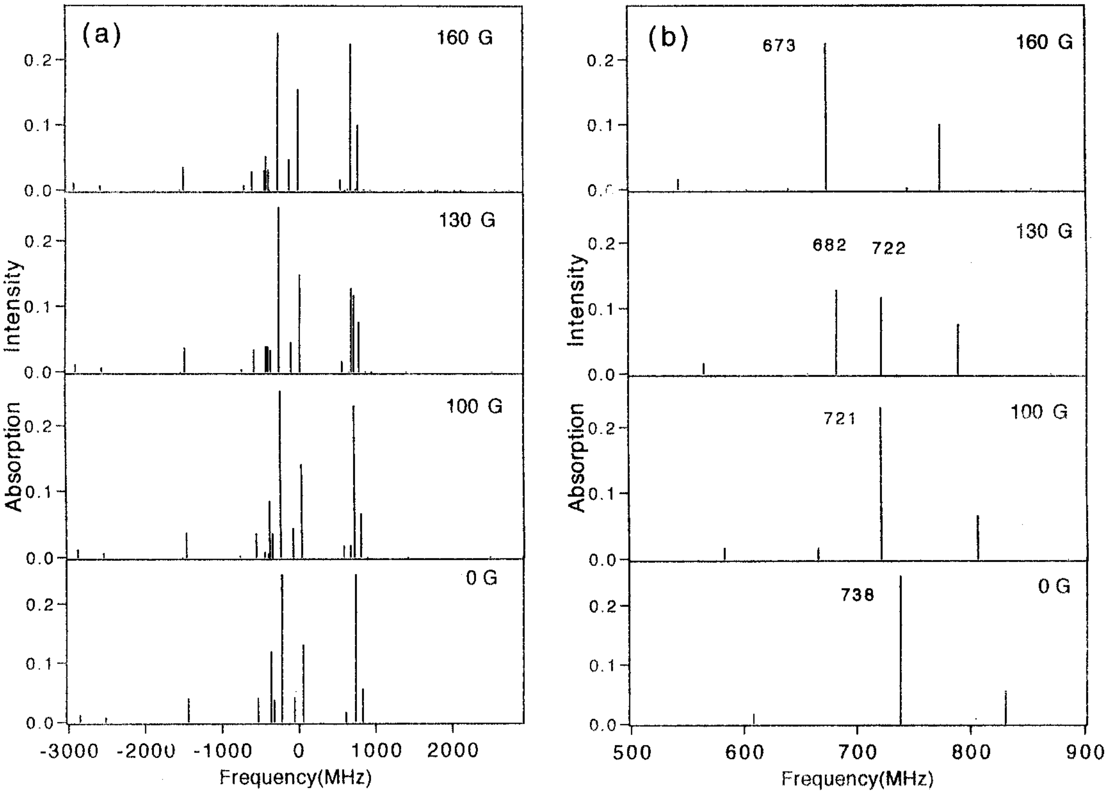

Figure 6. Simulated absorption spectra at 0, 100, 130, and 160 G by using the set of parameters for the pyrazine. The whole spectra are shown in a, and an expanded view from 500 to 900 MHz is shown in b.

by eqs 2 and 3. However, our model calculation carried out for pyrazine with eqs 4−6 seems to give a clue to understand the field dependence at P(1) and P(6).[1] Eigenvalues and the eigenvectors of the mixed states have been calculated as a function of H by using the locations of the zero-order triplet states and the coupling strengths of the S−T interaction given by Lawrance and Knight,[23] which were derived by analyzing the data of the ultrahigh-resolution spectra of the P(1) band of the $S_0 \rightarrow S_1$ transition of pyrazine. In the calculation, F_3 components of the triplet states with $N = 1$ and $M_J = 0$ located at −2821.5, −2495.4, −1380.5, −518.7, −340.9, −304.1, −90.7, −8.8, 436.7, 619.7, and 816.3 MHz were assumed to interact with the S_1 origin (0 MHz) with the coupling strengths of 289.3, 228.4, 287.0, 84.0, 53.8, 75.9, 129.5, 127.5, 422.7, 79.0, and 56.0 MHz, respectively.[1] It was also assumed that $E^p{}_{F_2} - E^p{}_{F_1} = E^p{}_{F_1} - E^p{}_{F_3} = 1$ GHz for all the triplet levels. The field dependence of the fluorescence intensity was examined by comparing $\sum_n |a_n|^4$, i.e., $(N_{\mathrm{eff}} + 1)^{-1}$, at different values of H with the zero-field value. Note that Φ_F is proportional to $\sum_n |a_n|^4$ when the decay rates of the S−T mixed states are independent of H and can be substituted by the average value. According to the calculation, Φ_F does not decrease monotonically with H and shows some fluctuation. For example, Φ_F decreases with increasing H and has a minimum around 130 G. As H further increases, Φ_F increases and has a maximum around 160 G and again decreases with further increasing H. The absorption spectra simulated with the same parameters are shown in Figure 6 for 0, 100, 130, and 160 G. These spectra show that the minimum of Φ_F at 130 G is attributed to a distribution of the absorption intensity into a plural number of mixed states. It can be easily imagined that coherent excitation into closely lying mixed states whose absorption intensities are similarly strong, e.g., absorption lines at 682 and 722 MHz in Figure 6, will lead to the appearance of the quantum beat with a frequency of 40 MHz. At the same time, the overall decrease in the coefficients of $|a_n|^2$ (i.e., the increase in N_{eff}), which comes from a distribution of the absorption intensity, results in the lengthening of τ_F, when γ_T is larger than γ_S (see eq 2).

A similar situation seems to occur for the P(1) excitation of 0^0 pyrimidine-d_4 at around 140 G and for P(6) at 70 G, because the level spacings of the zero-order triplet states and the S−T coupling strengths are not uniform. It may be said that the absorption intensity is accidentally distributed into more mixed states at these field strengths; N_{eff} accidentally increases, and hence, fluorescence quenching and lifetime lengthening occur. Thus, the field-induced quantum beats as well as the complicated field dependence of I_F and τ_F can be explained by the lack of uniformity both in the locations of zero-order triplet states and in the coupling strength, as reproduced in the model calculation carried out with parameters given for the P(1) line of pyrazine.

4. Summary

The rotational state dependence both of the fluorescence lifetime at zero field and of the magnetic field dependence of the fluorescence intensity and lifetime in 0^0 pyrimidine-d_4 is semiquantitatively understood by assuming that N_{eff} depends both on the rotational level excited and on the magnetic field. There is a tendency that N_{eff} increases with increasing J' of the excited level and with increasing H, except for the rotational levels prepared through the R(0) and P(2) excitations. Except for the rotational levels with $J' = 1$, the efficiency of magnetic quenching of fluorescence tends to become higher with increasing J' of the excited level. This tendency agrees with our previous conclusion that the efficiency of magnetic quenching becomes higher with increasing N_{eff}. A field-induced fluorescence enhancement and lifetime shortening are observed for the $J' = 1$ rotational levels prepared by the R(0) and P(2) line excitations, and this anomalous field dependence is interpreted by assuming that N_{eff} is exceptionally decreased by H. Field-induced quantum beats as well as fluctuations of field dependence of I_F and τ_F are attributed to a lack of uniformity both in the distribution of zero-order triplet states and in the coupling strength of the S−T interaction.

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