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Rotational Effect on Radiationless Transition I: Fluorescence Depolarization in Pyrimidine[26]

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Fluorescence depolarization after R branch excitation of 0_0^0 $^1B_1$ pyrimidine was interpreted by utilizing $\Delta J=0$ and/or ± 1 coupling schemes within a singlet manifold through triplet rovibronic levels where spin-orbit, vibration-rotation, and hyperfine interaction terms are involved. These schemes are suggested to be useful interpreting the intermediate-case phenomena observed in this kind of molecules.

Many studies have been devoted to elucidate the mechanisms of the radiationless transition in the S_1 state of pyrazine, a typical intermediate-case (i-c) molecule, including its rotational level dependence.[1] However, no agreement is reached at, so far, Among the theories, four streams have apparently survived in the papers reported by the present author,[2] by Sekiguchi et al.[3] derived from that by McDonald et al.,[4] by Drave and Kommandeur,[1] and by Amirav.[5] One of the reasons for the difficulty of settlement seems to be the complexity of the case of pyrazine itself. So, the author has turned attention to another system, pyrimidine which indicates a transition from small-molecule-limit (s-m-l) to intermediate cases depending on the experiments.

Chapter **I** is devoted to describing the experimental data on the title subject i.e. those exposed in the papers by two groups.[6a,7] In the next chapter, hamiltonians employed for description are presented which give rise to various types of (doorway) singlet states and (dark) triplet states as well as their coupling schemes. A major part of this paper is contained in chapter **III** where the mechanism of the fluorescence depolarization is discussed stepwise. Extension to the intermediate case will briefly be described in the final chapter, which is actually an Introduction to part II of this series.

I. Description of the Reported Data

Here, time variation in the polarization of fluorescence after R branch excitation of pyrimidine as reported by the two groups is described.

The first report on this subject was made by Ohta et al.[6a] who measured the decay of the polarized fluorescence after R(0) band excitation within the 0–0 band of the $S_1 \leftarrow S_0$ transition in pyrimidine under the external magnetic field of 0—130 G (1 G=10^{-4}T). By extrapolating the field effect, they interpreted the polarization change at zero magnetic field as a beat pattern with a frequency of about 0.7 MHz and ascribed it to a sort of internal magnetic-field (hyperfine, hereafter denoted as hf) effect.[6]

Subsequently, Wang and Lim[7] reported similar experiments on R(n) band excitation for n=0—4. The $P(t)$ curve (time variation of the polarization i.e. $[I_{\parallel}(t)-I_{\perp}(t)]/[I_{\parallel}(t)+I_{\perp}(t)]$ for R(0) (in their Fig. 3) is just correspondent to the $I_{\parallel}(t)-I_{\perp}(t)$ curve given by Ohta et al. (Fig. 2 with H=0),[6a] though t>0.8 μs portion is missing in the former. They analyzed the $P(t)$ curve into two components: the shorter one which decays in a time shorter than the fluorescence lifetime and the longer one which is almost constant during the fluorescence lifetime. As to n dependence, two facts are noted: (1) The time for the polarization (short component) decay decreases with increasing n, (2) while the $P(0)$ value decreases to the value which is in intermediate between the regular and statistical limits.[8] They ascribed these observation to any rotation-dependent perturbation which mixes the singlet states of different K quantum numbers (via triplet levels).

Now, my own description will be made about experimental data observed by the two groups: Imagine the $P(t)$ curve for t=0—1.5 μs after R(0) excitation by combining the two kinds of curves mentioned above, its pattern would be just like that of a fading humming (or howling), namely one of the typical i-c patterns of dephasing accompanying quantum beats and partial rephasing, reminding us of a simulated fluorescence decay pattern after excitation of pyrazine via P(1) portion of the $S_1 \leftarrow S_0$ 0_0^0 transition.[9] Thus, though the total fluorescence decay curve is described as that of an s-m-l case, the polarization process is rather described as an i-c phenomenon. This interpretation may be regarded as a sublation of those by the both groups. Another fact to be noted is a slight discrepancy between two kinds of experimental data: $P(t)$ values calculated from $I_{\parallel}(t)$ and $I_{\perp}(t)$ values by Ohta et al.[6] are slightly smaller than those given by Wang and Lim.[7] This may be ascribed to the difference in the qualities of their lasers (vide infra).

II. Theory

In this chapter, hamiltonians to describe radiationless transitions ranging from s-m-l to intermediate cases are presented in reduced forms suitable for pyrimidine. The whole theoretical architecture which starts from identification of the hamiltonian for each system will be developed in Part II.[2] Briefly, what distinguishes this theory from the others[1,3-5] is in the fact that plural number of doorway (singlet) states $\{s\}$ are considered to be involved. The states $\{s\}$ and corresponding (dark) triplet states $\{t\}$ are defined as eigenfunctions of a hamiltonian:

$$H^0 = H_0 + PVP;\ P = 1 - \sum_s |s\rangle\langle s| - \sum_t |t\rangle\langle t|, \qquad \text{(1a)}$$

where $\{s\}$ carry almost all the absorption intensity from a ground (g) state in the concerned wavelength region, induced by the radiation-molecule interaction, H_{gs}^{int}.[10] Therefore, they may be interpreted as rotational levels belonging to a vibronic state spectroscopically assigned. The perturbation for the s-t coupling to induce time-development is then given as

$$H' = V - PVP. \qquad \text{(1b)}$$

The choice of V was the major subject in the Ref. 10. For azines including pyrimidine, the next definition would be adequate at least in the zeroth order:

$$H_0 = H_{\text{e,PSABO}} - H_{\text{ivr}}^e + H_{\text{v}}{}^e + H_{\text{r}}{}^e + H_{\text{S}}^{(e)} + H_{\text{I}}^{(e)};$$

$$V = H_{\text{ivr}}^e + H_{\text{nBO}} + H_{\text{SO}} + H_{\text{vr}}^e + H_{\text{rS}}^{(e)} + H_{\text{SI}}^{(e)}. \qquad \text{(2)}$$

Here, the subscripts e, v, r, S, and I represent the electronic, vibrational, rotational, electron-spin, and nuclear-spin parts respectively. The hamiltonian with the superscript e is different for each electronic state e.[11] While, the superscript (e) indicates that concerned hamiltonians are usually described as effective hamiltonians.[11] The terms with PSABO, ivr, nBO, SO, and vr correspond to the portions on pure-spin adiabatic Born–Oppenheimer approximation,[12] intramolecular vibrational-energy redistribution,[12] non-Born–Oppenheimer interaction,[12] spin-orbit interaction,[11,12] and vibration-rotation interaction,[11] respectively. The H_{vr}^e may further be partitioned into centrifugal distortion (H_{cd}^e) and Coriolis (H_{Cor}^e) terms.[2,11] $H_{\text{rS}}^{(e)}$ and $H_{\text{SI}}^{(e)}$ are for rotation-electron spin and electron spin-nuclear spin couplings, respectively and introduces a hyperfine-structure (hfs) term, with minor contribution of nuclear spin-nuclear spin interaction $H_{\text{II}}^{(e)}$ contained in $H_{\text{I}}^{(e)}$.[11] Though, the hfs term is one of the smallest among perturbations mentioned here, it plays the important role in the s-t coupling of pyrimidine for fluorescence depolarization (vide infra). The reason why $H_{\text{S}}^{(e)}$ and $H_{\text{I}}^{(e)}$ containing spin-spin interaction terms ($H_{\text{SS}}^{(e)}$ and $H_{\text{II}}^{(e)}$) are allocated to H_0 is as follows: The eigenfunction of H_0 is then represented by the product $\Phi_{\text{e}}^e \Phi_{\text{v}}^{ev} \Phi_{\text{r}}^{er} \Phi_{\text{S}}^{(e)} \Phi_{\text{I}}^{(e)}$ i.e. in a well-partitioned form. Actually, choice of V does not matter in view of complementarity principle of quantum mechanics as long as we introduce higher order terms through the PVP operator.[10] What to be noted here is existence of the superscript e which plays an essential role in the i-c molecules. Namely, $H_{\text{r}}{}^e$ and $H_{\text{r}}{}^{e'}$ terms are partially composed of $V_{\text{vr}}^{e'}$ and V_{vr}^e terms, respectively,[2] due to electronic-state dependencies of Eckart equations.[11]

In the s-m-l case, we are sometimes encountered with molecular eigenstates (MES's), whose hamiltonian belonging to an exact molecular hamiltonian:

$$H_{\text{M}}{}^0 = H_0 + V. \qquad \text{(3)}$$

In general, MES's are represented as complex linear combinations of wavefunctions belonging to either H^0 or H_0 i.e. those of $\{s\}$ and $\{t\}$ or $\{s_0\}$ and $\{t_0\}$, respectively. However, if the effect of V (the major term being H_{SO} for azines) is small, MES's may be approximately represented as $|\hat{s}\rangle \sim |s\rangle \sim |s_0\rangle$ and $|\hat{t}\rangle \sim |t\rangle \sim |t_0\rangle$. This situation belongs to a weak-coupling case, to say more precisely, a weakly-coupled s-m-l case.[13] Pyrimidine's case is, however, not always consistent with this description.

By utilizing the hamiltonians (1)—(3), we can now apply the general theory of radiationless transitions[12] to the present case: s-m-l to i-c behaviors either described by $H_{\text{M}}{}^0$ or dominated by H'/V, respectively.[2]

III. The Mechanism of Fluorescence Depolarization

This chapter is devoted to interpreting the experimental facts described in chapter **I**, namely dual nature (s-m-l vs. intermediate cases) of the fluorescence decay and depolarization processes. To do this, it is essential to identify the rovibronic levels involved in these experiments i.e. zeroth-order S_1 and T_1 levels, which may be regarded as $\{s_{(0)}\}$ and $\{t_{(0)}\}$, respepctively, defined in the last chapter. On the basis of these levels, the time development can be described.

1. The $\{s\}$-$\{t\}$ coupling scheme. The title scheme shown in Fig. 1 was made for the above purpose; only levels required to describe the decay after R(0), R(1), and P(3) excitations being indicated. The sparsely distributed levels ($\{s\}$) at the left-hand side belong to the $S_{1,0}$ state with naming and symbols assigned according to the prescription written by Bunker: Rotational levels are assigned on an oblate- and near-symmetric-rotor representation by the symbol $J_{K_aK_c}$: P^{sgn}.[11] For example, 1_{11}: O^+ represents a wavefunction (wf) very close to $2^{-1/2}(|J=1,\ k_c=1\rangle + |J=1,\ k_c=-1\rangle)$ with $K_c = |k_c| = 1$ (odd) to which the unique assignments of symmetry species under the molecular symmetry group (MSG), $C_{2v}(M)$ are given for rotational ($\Gamma_r = A_2$), rovibronic ($\Gamma_{\text{rve}} = B_2$), nuclear spin ($\Gamma_{\text{ns}} = A_1$), and internal ($\Gamma_{\text{int}} = B_2$) wf's, respectively. According to the partity requirement of Γ_{int} being either B_1 or B_2, only this combination is allowed by $B_1(\Gamma_{\text{ve}}) \times A_2(\Gamma_r) \times A_1(\Gamma_{\text{ns}}) = B_2(\Gamma_{\text{int}})$. The level locations are reproduced by using the rotational constants for the zeroth-order rotational levels in the $S_{1,0}$ manifold. They are estimated from molecular-eigenstate (MES) spectra assuming a weakly-

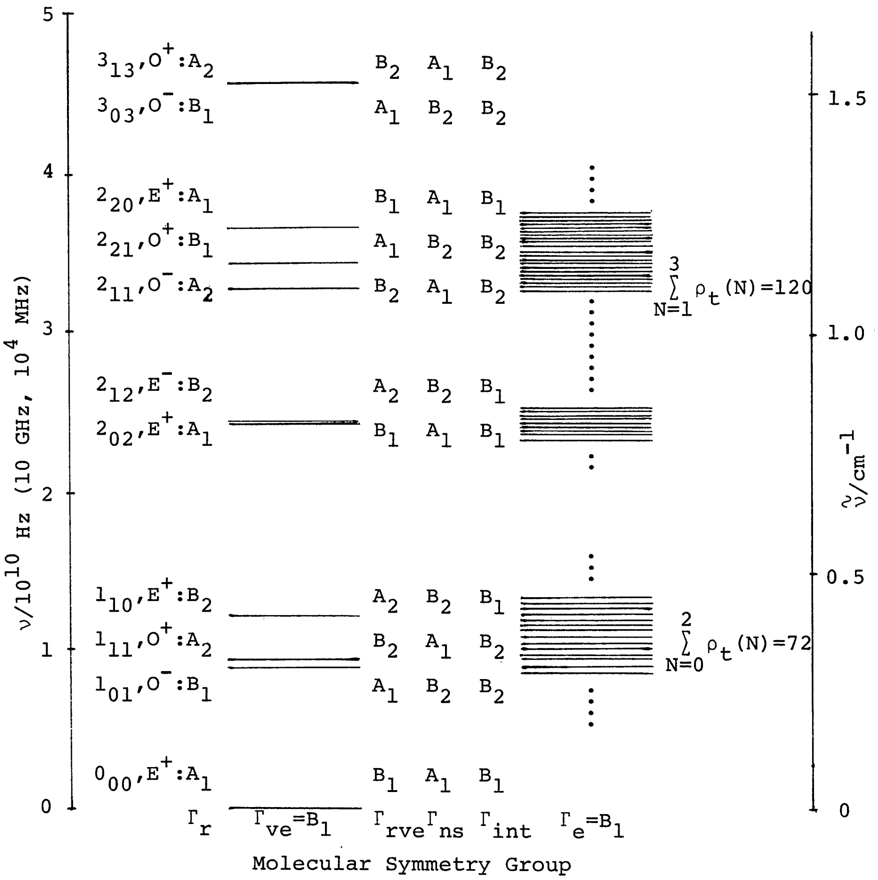

Fig. 1. The {s}-{t} coupling scheme for the case of R(0), R(1), and P(3) band excitation of pyrimidine within the $S_{1,0}$ manifold.

coupled s-m-l case, some strongly-perturbed levels being omitted from the fitting.[14] Though several hyperfine (hf) components may be assumed for each rotational level drawn in the figure, only a part of them are allowed to be existent by the parity restriction.[11] Somehow, the hf splittings are much smaller than the width of the line drawn in the figure. For, their energies are zeroth-order values with extremely small splittings derived from the H_{II} term (vide supra, the superscripts *e*, (*e*) are abbreviated hereafter).

More densely distributed levels ({*t*}) at the right-hand side represent triplet levels which may be directly coupled with the singlet levels. The level density is counted as $\rho_t^{(J)}=\sum_{N=J-1}^{J+1}\rho_t(N)$ with $\rho_t(N)=(2N+1)\rho_v$ for $J\geq1$, where N and ρ_v represent rovibronic-angular-momentum quantum number and density of states of the triplet vibronic levels, respectively. Here, the loosest selectivity ($\Delta N=0$, ±1 only) was taken into account. While, $\rho_t^{(0)}=\rho_t(1)=3\rho_v$ by $\boldsymbol{J}=\boldsymbol{N}+\boldsymbol{S}$ with $J=0$ and $S=1$. Thus, $\rho_t^{(J)}=3(2J+1)\rho_v$ for all J e.g. $\rho_t^{(1)}=72/\text{cm}^{-1}$ using the estimated value of $\rho_v=8/\text{cm}^{-1}$ by Spears and El-Manguch.[15] Since more severe selectivities are actually imposed on the coupling e.g. both Γ_{int} and total angular momentums (F, m_F) have to be conserved,[11] the effective level density may be reduced as low as one tenth of the above value rationalizing the weak-coupling assumption (at least for the MES's $\{\hat{s}\}$ dominated by *s* character).

2. Depolarization Scheme. Now, we'll seek for the depolarization scheme i.e. for the *s*–{*s'*} coupling scheme where *s* (e.g. 1_{10} in case of R(0) excitation) represents an initially prepared (optically selected/doorway/zeroth-order) singlet level while {*s'*} represent the other levels which may contribute to the depolarized fluorescence after coupling, in view of a time-dependent-perturbation theory. For, without this scheme, no polarization change can be introduced; the mere *s*–{*t*} coupling giving rise to intensity variation only, due to population change of the *s* level with a constant *P* value. One candidate for this may be considered to be a $1_{10}\rightarrow1_{11}$ scheme, in case of R(0) excitation, which is apparently in conformity to the proposal by Wang and Lim.[7] For, if we assume pure *c* parallel transitions for both absorption and emission processes, the change of *P* from ~1/2 to ~−1/3 is derived for full (100%) conversion of the above scheme by simple integration over Euler angles, under the symmetrical-top assumption.[8,11,16,17] However, it is not the case in actuality due to complete forbiddeness (Not only Γ_r's but also Γ_{int}'s are different from each other.). Thus, $1_{10}\to 2_{02}$ and $1_{10}\to 0_{00}$ schemes with $\varDelta J=1$ and -1, respectively, are left for the candidate. P values of the final levels 2_{02} and 0_{00} with $m_J=0$ are calculated to be $-1/2$ and 0, respectively, under the fore-mentioned assumptions contributing to the depolarization. In order to make a thorough account of this problem, it is the most adequate to set a secular equation on all the rovibronic levels concerned as drawn in the Fig. 1 that would give MES's. If this could be performed, the depolarization may be described as dephasing of the doorway state s (e.g. 1_{10} state) into MES's which contain both $\{s'\}$ and $\{t\}$ components (vide infra).[1–5,9,10,12] For that purpose, all the matrix elements on perturbing terms like H_{SO}, H_{vr}, and $H_{\mathrm{hfs}}\sim H_{\mathrm{SI}}\sim\sum_i a_i \boldsymbol{S}\cdot\boldsymbol{I}_i$ have to be evaluated. However, this is not easy due to lack of detailed informations i.e. is a kind of work which has to go far beyond the simulation made by Konings et al..[14b] For, they apparently failed to precisely reproduce the ultra high-resolution spectrum patterns, on the assumption of a single doorway state s. Therefore, we'll make up the schemes based on perturbational treatment.

In Table 1, all possible schemes are tabulated. The values of $\varDelta E_{ss'}$ are taken from Fig. 1. On the other hand, little information is available about off-diagonal matrix elements of perturbations H_{SO}, H_{SI}, H_{vr}, and H_{asym}: Matrix elements of H_{SO} between S_1 and T_1 electronic wf's are set to be smaller than those of glyoxal[18] i.e.$\lesssim 10^{-1}$ cm^{-1} by considering the difference in n orbitals between carbonyl compounds and azines; namely $v_{\mathrm{st}}\approx 10^{-2\pm1}$ cm^{-1}. For, n-orbital in the C=O group has more p character and more localized than azines.[19] The same is applied for H_{SI} and H_{vr}.[18,19] Matrix elements of H_{asym} are evaluated on the spectroscopical data.[14] As discussed above, the $\varDelta J=0$ scheme for $n=0$ ($J=1$) is forbidden and $\varDelta J=1$ schemes are required for depolarization after R(0) excitation. Among three kinds of schemes, the last fourth-order term seems to be the most effective because many $\{t, t', t''\}$ combinations are available with significant contributions judging from the level distribution in Fig. 1. In contrast, the contributions of the lower order schemes are minor due to very little chance for either the $\{t\}$ level or the $\{t, t'\}$ combination to be effectively involved.

Also included in the Table is the other kind of schemes available for $J\geq 2$: For example, a 2_{20}: E^+ level is coupled with a 2_{02}:E^+ level either directly or through $\{t\}$ levels, because they belong to common symmetry species ($\Gamma_r=\mathrm{A}_1$, $\Gamma_{\mathrm{rve}}=\mathrm{B}_1$, $\Gamma_{\mathrm{ns}}=\mathrm{A}_1$, and $\Gamma_{\mathrm{int}}=\mathrm{B}_1$). Among them, the second order scheme with two H_{SO} matrix elements and the H_{vr} scheme i.e. the first two schemes are expected to play predominant roles over the last two schemes i.e. those containing the matrix element of either H_{SI} or H_{asym} (if we regard it as a perturbation). This is not the case for the other levels

Table 1. Depolarization "Scheme" after R(n) Band Excitation

for $n=0$ (1_{10} level)

$\varDelta J=0$ scheme; not available (1_{10}—×—1_{11})

$\varDelta J=(\pm)$ 1 schemes: $\varDelta E_{ss'}\lesssim 0.4$ cm^{-1}

$$s\overset{H_{\mathrm{SO}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\underset{\longleftrightarrow}{\{t\}}\overset{H_{\mathrm{SI}}(\varDelta J=1)}{\rule{4em}{0.4pt}}\{s'\}\text{: } v_{st}\lesssim 0.1\ \mathrm{cm}^{-1};\ v_{s't}\lesssim 10^{-3}\ \mathrm{cm}^{-1}$$

or

$$s\overset{H_{\mathrm{SO}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\{t\}\overset{H_{\mathrm{SI}}(\varDelta J=1)}{\rule{4em}{0.4pt}}\{t'\}\text{:}\overset{H_{\mathrm{SO}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\{s'\}\text{: } v_{st},\ v_{st'}\lesssim 0.1\ \mathrm{cm}^{-1};\ v_{tt'}\lesssim 10^{-3}\ \mathrm{cm}^{-1}$$

$$s\overset{H_{\mathrm{SO}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\{t\}\overset{H_{\mathrm{vr}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\underset{\longleftrightarrow}{\{t'\}}\text{:}\overset{H_{\mathrm{SI}}(\varDelta J=1)}{\rule{4em}{0.4pt}}\{t''\}\overset{H_{\mathrm{SO}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\{s'\}\text{: } v_{st},\ v_{s't''}\lesssim 0.1\ \mathrm{cm}^{-1};\ v_{tt'}\lesssim 0.1\ \mathrm{cm}^{-1};\ v_{t't''}\lesssim 10^{-3}\ \mathrm{cm}^{-1}$$

or

for $n\geq 1$ (levels with $J\geq 2$)

$\varDelta J=0$ scheme (major): $\varDelta E_{ss'}\gtrsim 0.1$ cm^{-1}

$$s\overset{H_{\mathrm{SO}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\{t\}\overset{H_{\mathrm{SO}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\{s'\}\text{: } v_{st},\ v_{s't}\lesssim 0.1\ \mathrm{cm}^{-1}$$

$$s\overset{H_{\mathrm{vr}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\{s'\}\text{: } v_{ss'}\lesssim 10^{-2}\ \mathrm{cm}^{-1}$$

$$s\overset{H_{\mathrm{SO}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\underset{\longleftrightarrow}{\{t\}}\overset{H_{\mathrm{SI}}(\varDelta J=0)}{\rule{4em}{0.4pt}}\{s'\}\text{: } v_{st}\lesssim 0.1\ \mathrm{cm}^{-1};\ v_{s't}\lesssim 10^{-3}\ \mathrm{cm}^{-1}$$

or

$$s\overset{H_{\mathrm{asym}}(\varDelta J=0)}{\rule{5em}{0.4pt}}\{s'\}\text{: } v_{ss'}\lesssim 10^{-3}\ \mathrm{cm}^{-1}$$

$\varDelta J=(\pm)$ 1 schemes; as given for $n=0$

i.e. for 2_{21}: O^+, 2_{11}: O^-, and 2_{12}: E^- levels, higher order schemes being required (See Fig. 1). In case of $J \geq 4$, there always exists at least one rotational level with the common symmetry species within sublevels of the common J. However, care has to be taken of the larger $\varDelta E_{ss'}$ values for larger J as well as on the other selectivities.[11,18,20]

3. Classification of the MES's. Since the assessment of the coupling scheme are made in the preceding section, we'll discuss the nature of MES's with reference to the observed MES spectra. As for the $\hat{s}$ level, content of the s component may be safely estimated as more than 50% judging from the successful assignments of the stronger bands to $\{s_0\}$ i.e. to $\{\hat{s}\}$ consistent with the estimated rotational constants (with some exceptions). Nevertheless, depolarization phenomena[6,7] as well as Zeeman effects in both frequency domain[14] and time domain[6] experiments indicates non-negligible contribution of $\{s'\}$ and $\{t\}$ components depending on m_S, m_I, and m_F quantum numbers. However, hfs was too small to be measured in MES spectra[14] only indirectly evidenced in quantum beat frequencies.[6] As to the $\{\hat{t}\}$ state,[13] scrambling is expected to be strong enough to make the distribution of $\{s\}$ contents fairly random. Actually, the pair model[13] frequently used for the weak-coupling case can not be applied for pyrimidine as indicated in the observed randomly-distributed $\{\hat{t}\}$ levels with more $\{s\}$ characters.[14] Therefore, $\{\hat{t}\}$ levels with any $\{s\}$ characters are existent as densely as drawn in Fig. 1, possibly randomly but widely distributed.

4. Interpretation of the Polarization Decay. If all the concerned MES's are given precisely and all the experimental conditions e.g. the laser frequency and its qualities including the coherence width ($\varDelta\nu_c$) are set, the fluorescence decay process may be described as a consequence of incoherent and coherent excitation of MES's. Namely, several groups of superimposed MES's are considered to decay independently to give rise to observed polarization decay patterns as time-dependent vector sums of contributions from s and $\{s'\}$.[2] However, this procedure can not be applied for the present case still due to lack of informations. Therefore, we are forced to make up some model schemes depending on the experiments e.g. depending on the n value of R(n). Somehow, even this kind of trial had been made for polyatomic molecules of this size neither for pyrimidine[6,7] nor for the simpler molecule like propynal.[21] For the latter molecule, group theory (on the angular momentum) was applied without referring to singlet levels rendering depolarization.[21]

Firstly, we'll consider the case of $n=0$ observed by the two groups. In both experiments, the optically prepared level is uniquely described as the zeroth-order 1_{10} level. For, no other level is optically accessible in those wavelength regions with $\varDelta\tilde{\nu} \approx 0.1$[6] or 0.03[7] cm^{-1} for the molecule in the ground level, $S_{0,0}$ (0_{00}). To say more precisely, hf components belonging to the active (s) level have to be considered. These components are almost degenerate due to minor contribution of H_{II} (vide supra). In order for the s state to be prepared, $\varDelta\tilde{\nu}_c$ of the laser may be required to be as much as ($\lesssim$) 1 cm^{-1} with a corresponding coherence length of $\tau_c \sim 10$ ps. For, the distribution region of MES's with the s character in pyrimidine is considered to be larger than that of pyrazine (~8,000 MHz for the $J=0$ level)[22] due to the difference in ρ_v, if we assume v_{st} coupling matrix elements between S_1 and T_1 are common for both molecules at least in the order-of-magnitude. This condition is also not satisfied in the present experiments, however, $\varDelta\nu_c$'s being narrower. Therefore, going back to the initial description, the observed polarization decays have to be interpreted as incoherent superposition of the decays of those states built up as coherent superpositions of the hf components of some $\hat{s}$ and $\{\hat{t}\}$ levels, whose distribution is different for each laser shot. This is commonly encountered situation when we use incoherent lasers not under transform-limited condition.[2,5] Separation between these levels are estimated as follow: $\varDelta E^{\hat{s}}_{\mathrm{hfs}} < 10^{-3}$, $\varDelta E^{\hat{t}}_{\mathrm{hfs}} \sim 10^{-3}$, and $\varDelta E_{\hat{s}\hat{t}} < 0.1$ cm^{-1} by examining the data of "quantum beat",[6,7] Zeeman effects,[6,14] and the energy-level distribution in Fig. 1, respectively. Therefore, by applying the dephasing theory,[1–5,9,10,12] immediate (as fast as 10^{10} s^{-1}) depolarization contributed from $\{\hat{t}\}$ levels and slow depolarization ($\ll 10^8$ s^{-1}) with quantum beat frequencies of $<10^2$ MHz corresponding to the energy differences between hf components of the $\hat{s}$ level are expected, consistent with the observation. Mixing of a few percent of [s, $\{s'\}$] states into $\{\hat{t}\}$ levels through the s-t coupling by the H_{SO} term is enough for interpretation of the immediate depolarization. While, the slow depolarization is accounted by using the fourth order $|\varDelta J|=1$ scheme in Table 1 where mixing of $\{s'\}$ into $\hat{s}$ as much as 10% is assumed depending on hf components. Accordingly, the difference in $P(t)$ values between the two groups' mentioned in Chapter **I** is easily ascribed to the difference in the number of $\{\hat{t}\}$ states involved: the constant component of the $P(t)$ decay is smaller in case more $\{\hat{t}\}$ levels with more $\{s'\}$ characters are excited by the wider laser ($\varDelta\tilde{\nu}_c \lesssim 0.1$ cm^{-1})[6] than those of the other group ($\lesssim 0.03$ cm^{-1}).[7]

In the case of R(1) branch excitation, situation is fairly different from that of R(0). For, the band is actually composed of three kinds of transitions restricted by $\varDelta J=1$, $\varDelta K_c=0$, and the parity selectivity.[11,14] Namely, the prepared doorway states are of 2_{20}, 2_{21}, and 2_{11} types which are different from one another in the MSG representation and the pseudo-parity. Therefore, the observed decay behavior has to be interpreted as a superposition of at least three (disregarding hfs) decays; The decay behaviors of 2_{21} and 2_{11} levels (averaged over $m_J=0, \pm1$) are described just like the 1_{10} level because the same kind of matrix elements appear to be working. Thus, final levels connected by $\Delta J=\pm 1$ schemes i.e. pairs of (3_{13}, 1_{11}) and (3_{03}, 1_{01}) levels with $m_J=0$, ± 1 contribute to the depolarized fluorescence in average. While for the 2_{20} level, new kinds of matrix elements i.e. $\Delta J=0$ schemes in Table 1 are now at work, the final level being 2_{02} ($P<0$ averaged on $|m_J|=0$, 1). The most important scheme among these is of the s-t-s′ coupling with the H_{SO} matrix elements. Then, even without the help of H_{SI}, immediate depolarization is realized, contributed from some $\{\hat{t}\}$ containing $\{s'\}$ characters as much as 10%. Direct mixing of $\{s'\}$ in $\hat{s}$ by the H_{vr} coupling at a few percent level may also have some contributions. The chances for this kind of schemes to be involved would be larger for larger J, because the number of possible kinds of symmetry species is restricted even accounting the pseudo-parity.[1,11] Actually, for $n\geq 3$ i.e. for $J\geq 4$, all the K ($K_a K_c$) sublevel is coupled with at least another sublevel with $\Delta J=0$ (vide supra). Furthermore, t level density increases in parallel with J by $\rho_t^{(J)}=3(2J+1)\rho_v$ as illustrated in Fig. 1 for $J=1$ and 2 (section **III-1**). This does not, however, completely exclude the contribution of the H_{hfs} term because some of the levels (e.g. with $K_c=J$) are energetically isolated[14] and/or have zero H_{SO} matrix elements,[20] letting the contribution of $\Delta J=\pm 1$ schemes non-negligible as may be evidenced in the observation of the slow component even after $J=4$.[7]

Finally, the case of P(3) excitation is briefly discussed where no polarization decay is evidenced.[7] In this case all the $|J_{K_aK_c}, m_J>$ level with $J=2$ is practically reached at by the selectivities of $\Delta J=-1$, $\Delta K_c=0$, and $\Delta m_J=0$.[11] Thus, $<P>(\gtrsim)0$ right after excitation with little room for depolarization consistent with the observation. This is a general consequence for the molecule with the c parallel transition (vide supra).[8]

IV. Extension to Intermediate Case

The experimental data so far discussed are all what are described as in the s-m-l case in the sense that the doorway state s was not coherently excited (vide supra). Now, let's seek for the experimental data to be described as "rotationally-resolved" i-c phenomena in pyrimidine. Not so many data are available so far in spite of the fact that the molecule has been described as an i-c molecule for long time.[6,7,14,23] As to the 0–0 transition, a decay cucrve after excitation at a Q branch peak measured at room temperature may be adequate. It is, however, contributed from various J levels with $<J>\sim 30$.[23] Though polarization data are also reported in this case,[23] it is left for future study because the situation is complicated.[24] In short, this case can not be interpreted as a simple intermediate-case phenomenon, though the argument for the P(3) case may partially be applied. For, an ensemble average has to be considered. At higher vibrational levels, the intermediate case is now reached with excess energies of ~5,000 cm^{-1} even for smaller J.[23] In this case, the depolarization rate is almost close to the decay rate of the fast fluorescence decay component. In other words, a common dephasing process is involved in both total decay and depolarization of the fluorescence. This is to be regarded as a typical phenomenon of an i-c molecule. At levels with higher excess energies, the average coupling constant between the rovibronic levels of S_1 and T_1 becomes smaller in parallel with the increase of ρ_v. Therefore, the energy distribution of MES's with the s character becomes narrower compared to the s-m-l case letting coherent excitation of the s state by the laser (~0.1 cm^{-1}, 10 ns; $\tau_c>10$ ps) more feasible. The short fluorescence (polarization) decay process is then described as dephasing of the s state into MES's containing both $\{t\}$ and $\{s'\}$ components which are optically inaccessible by the laser chosen for exitation. Accompanied with dephasing of the s component, the $\{s'\}$ components now appear as origins of the depolarized fluorescence as is consistent with observation. This is a tentative interpretation, however. For, if we try to interpret the i-c behavior in pyrazine, we have to take note of another important aspect: Wider band width (>0.1 cm^{-1}) has to be used to cover whole area of the band assigned by $\Delta J=0$, ± 1 and $\Delta K_c=0$ selection rules with contributions of up to $(2J+1)$ K (K_aK_c) sublevels.[1-5] Then, the notion of the unique doorway state s becomes no longer adequate. For, the $\{s'\}$ states with the same symmetry as the s state contribute not only to the emission but also to the absorption processes through the $\Delta J=0$ schemes, though this intensity borrowing was usually interpreted as due to mixing by the perturbing term H_{asym}.[3] Thus, excitation can now be distributed over whole MES's retaining the common symmetry species and the "J" number after several back and forth between $\{s\}$ and $\{t\}$ levels during fluorescence decay.[2] For example, by applying the scheme in Fig. 1, it is now well understood that the number of triplet levels coupled to the singlet level s is in parallel with J.[1-5] To say precisely, the effective density of states (for dephasing) is calculated to be ${}^J\rho_t\sim\rho_t^{(J)}/\sigma=(3/2)(2J+1)\rho_v$ with $\sigma(=2)$ being the symmetry number[1,11] (for pyrimidine).

More detailed arguments including interpretations of many other experimental data e.g. a polarization decay curve of the $J=2$, zero-point vibrational level of ${}^1B_{1u}$ pyrazine,[25] as well as proposal of new kinds of experiments will be given elsewhere.[2,24]

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