Rotational Effects on Radiationless Transition IV: Hyperfine Interaction and Deuterium Isotope Effects[1)]

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The theory of the rotational effects on radiationless transitions in typical azines is extended to include the hyperfine (hf) interaction term, while examining their deuterium (isotope) effects on the decay behaviors after excitation into the rotational levels belonging to their S_{10} levels, i.e. their ground vibrational levels of S_1 states. The Fermi-contact hf term is shown to be enough to endorse the coupling between rotational levels that are different either in symmetries or in some angular-momentum quantum numbers. The deuterium (D) effect is found to be not simply described as a conventional isotope effect: Changes by D substitution are brought about in densities of triplet states and hf coupling terms, as well as molecular symmetry groups. While interpreting the experimental data, modifications of the schemes are made from those presented earlier in this series.

Rotational effects on radiationless transitions in azines such as pyrazine and pyrimidine have been the subject of numerous studies, and further discussion is required by many unexplained results. In this series of Parts I—III,[2—4)] I have tried to interpret the experimental data in a unified form.

In Part I,[2)] the peculiar fluorescence depolarization after R branch excitation of 0_0^0 $^1B_1$ pyrimidine[5,6)] was interpreted by using ΔJ=0 and/or ±1 coupling schemes within a singlet manifold. The hyperfine coupling (hfc) was introduced to assure $|\Delta J|=1$. (However, actual evaluation of the hfc matrix element in this paper indicates $\Delta J=0$ in addition to $|\Delta J|=1$ (Section 2.1).) The importance of the molecular symmetry group (MSG) was also noted.

In Part II,[3)] a general theory of radiationless transitions to describe the rotational effects was presented, by using a Green-function technique on a multiple number of doorway states. According to the formalism and based on molecular-eigenstate (MES) spectra,[7)] the typical intermediate-case (i-c) decay behavior of pyrazine after picosecond-laser excitation into lower rotational levels belonging to its S_{10} level[8)] was examined. What is called axis-switching,[9,10)] i.e., the intensity mixing mechanism between rotational levels due to electronic-state dependencies of Eckart equations (different from the conventional state mixing by the perturbation), was appreciated as a prerequisite for multiple doorway states and was used in a model calculation of this subject. Thus, the *enigma*,[7)] i.e. the difficulty in consistently interpreting the whole experimental data, was solved. (Modification of this theory is also done in this paper (Section 3.3).)

In part III,[4)] the Zeeman effects observed in both the systems (pyrimidine[11—13)] and pyrazine[7,14—17)]) were examined to see the adequacy of the theoretical framework. The results were positive. By choosing a *best* experimental framework with a polarizer set parallel to the magnetic field and assuming an isotropic Zeeman hamiltonian, the Zeeman effect on the formalism was found to be not very significant. Namely, the external magnetic-field effect on the decay behavior was recognized to be an incoherent superposition of $2J+1$ individual processes that were dependent on the quantum number m_J. Experiments with the best framework by taking account of polarization were urged.

In this paper, the theory of the rotational effect on radiationless transitions in typical azines is *extended* to include the hyperfine (hf) interaction term and to examine the deuterium (isotope) effects on the decay behaviors after excitation into the rotational levels belonging to their S_{10} levels. That is, this paper aims at concluding the discussions of the S_{10} levels of the azines, while picking up the data that belong to the title subject but not discussed so far in this series. Therefore, discussions of other compounds as well as of intramolecular vibrational energy redistribution (IVR) and of intramolecular vibration-rotation energy transfer[3)] are left for future study.[18)] This is the reason why *double* subtitles are used. Actually, the former the effects of hfc, have been discussed already in Part I. Hence, in this paper, only its *explicit* matrix element is presented in a form to be compared with that of the Zeeman term in Part III and naturally to introduce the total angular momentum $\boldsymbol{F}=\boldsymbol{N}+\boldsymbol{S}+\boldsymbol{I}$ as another cast. Based on this, a *complementary* discussion to those given in Parts I—III is made, as announced.[2—4)] Therefore, besides discussion of the major subject, i.e. the dynamics of S_{10} levels in deuterium (D) substitutes of both azines, some modifications in the theory are made.

In Section 1, *new* kinds of experimental data as were not discussed in Parts I—III are introduced, such as results on the D effect picked up from a few papers published so far,[12,19—22] and that of the most recent paper on hf interaction in pyrazine,[23] are described briefly. The knowledge of the D effect in condensed phases[19,24] is outlined as well.

A *general* theoretical consideration is made in Section 2 on the influence of D substitution upon the decay of azines. The density of triplet states ρ_t may be the most important factor affected by D substitution. It may also make differences in the values of matrix elements for H_{SO} and $H_{SO}\otimes H_{nBO}$.[2—4,24] The explicit matrix element for the hfc is derived and evaluated to give rise to selection rules that are to be compared with those as stated in the previous papers.[2—4] Furthermore, lowering of symmetry in view of MSG is pointed out, causing skepticism about the use of the perturbational picture for the D effect.

In Section 3, *case-by-case* discussions on the observations in several D substitutes of the azines are made. Actually, the D effect cannot be discussed in terms of the isotope effect in such a systematic way as applied for molecules in the condensed phase. Besides D effects on the density of triplet states and hf terms, MSG is found to play a crucial role. The contribution of the Zeeman effect on these is also discussed to account for the general decay behavior of azines including the data treated in Parts I—III. By the way, successful interpretation of the experimental data, that seem to have been regarded as curious, by this theory may be taken as more evidence to support the theoretical framework of this series. Finally, *re*interpretation of the fast fluorescence decay components for smaller J is made to be consistent with the modified version of the selection rules.

1. Description of the *New* Experimental Data on the Title Subject

The experimental data on the S_{10} levels of azines just correspondent to the title of this paper are described in this Section. Only those that were *not* the subjects for discussion in Parts I—III are picked up.

1.1 Pyrimidine-d_4. The title molecule seems to be the only D substitute of pyrimidine so far reported. Unfortunately, no observation was made (tried?) on the MES spectra of this compound. External magnetic-field effects on the rotational-state dependence of fluorescence in this molecule was examined by Ohta (and Takemura).[12,20] Comparing this to the same kind of experiments on isotopically unmodified pyrimidine (pyrimidine-d_0),[11,12] the major D effect appears to be a decrease in polarization and an increase of the contribution from the quantum beats (qb's). Some complexity such as a partial enhancement of fluorescence (by the magnetic field) is also noted. Somehow, the main factor of the D effect seems to be the increase in the ρ_t.[12]

1.2 Pyrazine-d_n (n=1,3,4). 1.2.1 MES Spectra for n=1,3: Though restricted on a few rotational levels, MES spectra were observed for pyrazine-d_1 and -d_3 (Apparently, the trial for -d_4 failed).[21] The major effect of D substitution is the decrease in intensities depending on the number of D atoms and the rotational quantum numbers, J and K. The effect cannot be simply ascribed to the increase of triplet density of states, ${}^J\rho_t$ as a function of J (Subsection 2.3.2) that obscure the structure.[3] Rather, an actual decrease in intensity and/or increase in the width of the bunch[3] with the J, K dependence should be assumed. This significant J, K dependence was ascribed to the nonradiative decay due to Coriolis coupling.[21,25]

1.2.2 The fast Fluorescence Decay Component for n=4: Felker and Zewail[26] observed the D effect on the fast decay components of pyrazines in a vapor phase. The lifetimes were ca. 110 ps and ca. 80 ps for -d_0 and -d_4, respectively. An *inverse* D effect[27,28] was noted.

1.2.3 External Magnetic-Field Effect for $n=4$: Practically the same kind of experiment was done in pyrazine-d_4[22] as in pyrazine-d_0,[16] using the laser with a coherence time $\tau_c \lesssim 1$ ns[3] for excitation. Though complex, an increase of the i-c behavior by D substitution, due to the increased ρ_t, appears to be predominant. Concerning its Zeeman effect, a novel field-induced mixing between T_1 and T_2 with the $<T_1|H_Z^{(1)}|T_2>$ ($\propto <\pi|\ell_y|n> \neq 0$ by Eq. 2 of Part III) matrix element was suggested.[4,22,24] As a reason for this suggestion, they pointed out the decrease of the lifetime of the slower component caused by the magnetic field. This will be discussed later (Section 3.2.3).

1.3 A New Evidence of hf Interaction in Pyrazine (-d_0). Contribution of the hf interaction in pyrimidine was already noted while interpreting such as distribution patterns of MES's, anisotropic polarization qb's, and polarization decay.[2,5,6,13] In the case of pyrazine, only indirect evidence had been pointed out, in the number (N) or densities (ρ) of MES's and the rate constants of the fast decay components that are almost independent of J (=1—7), probably accompanying depolarization.[3,7,8,29] Recently, however, Willmott and Bitto did quantum-beat spectroscopy using Fourier transform-limited laser pulses and detected anisotropic polarization qb's corresponding to the hf splittings of the order of ca. 500 kHz, for the levels with J=0, 1.[23] Thus, the "enigma" (e.g., too many N) was partially solved as suggested.[3,7]

1.4 The D Effect in Condensed Phase. Not many experiments have been done on the D effect in both azines.[19] Therefore, what we can do is to apply the general theory of the D effect[27,28] upon the information for azines in the condensed phase[19,24] (Section 2.2).

2. Theoretical Framework

This Section is devoted for extending the theoretical framework, presented in Part II and modified slightly in Part III, to apply to the interpretation of the D effect. As introduced, this paper also aims at concluding the discussion of the S_{10} levels of the azines. However, full reformulation of the framework as presented in Part II is not given here. Only factors for modification are discussed. Accumulation of more quantitative data may give us an opportunity to build a fully revised formalism for a better model calculation.

2.1 Effects of the hf Interaction. The importance of the hf interaction has been pointed out already in Part I to account for the $|\Delta J|=1$ coupling. The hf matrix element that may have the largest contribution, i.e., that of a Fermi-contact (F-C) term may be pointed out, as assumed for smaller molecules such as propynal[30] and glyoxal.[31] If we restrict it to a *single* kind of nuclear species (including the environment), the hf hamiltonian (e.g., Eq. 29 of Ref. 31) is approximately represented in terms of tensor operators on total nuclear *and* electron spin angular momentums, ***I*** *and* ***S*** as[32]

$$H_{\mathrm{hfs}} = a_{\mathrm{FC}}\mathsf{T}^{(1)}(\boldsymbol{I})\cdot\mathsf{T}^{(1)}(\boldsymbol{S}). \tag{1}$$

It has to be noted that the assumption of the single nuclear species is only for convenience and not strictly applied to these systems even for pyrazine-d_0 and -d_4. (A ^{14}N nucleus has spin 1.) Therefore, care has to be paid to the actual *use* of the matrix elements derived below. Thence, applying the angular momentum theory,[32] the non-zero matrix element is given as follows:

$$\begin{aligned}
&<t\boldsymbol{v}NKSJm_JIm_IFm_F|H_{\mathrm{hfs}}|t\boldsymbol{v}NKSJ'm_J{}'Im_I{}'Fm_{\mathrm{F}}>=\\
&\quad=a_{\mathrm{FC}}\sum_p(-1)^p(-1)^{I-m_I}\begin{pmatrix} I & 1 & I \\ -m_I & -p & m_I{}' \end{pmatrix}\\
&\quad[I(I+1)(2I+1)]^{1/2}\times\\
&\quad\times(-1)^{J-m_J}\begin{pmatrix} J & 1 & J' \\ -m_J & p & m_J{}' \end{pmatrix}\\
&\quad[(2J+1)(2J'+1)]^{1/2}[S(S+1)(2S+1)]^{1/2}\\
&\quad\times(-1)^{N+S+J+1}\begin{Bmatrix} N & S & J' \\ 1 & J & S \end{Bmatrix};\ S=1.
\end{aligned} \tag{2}$$

By comparing this hf term with the Zeeman term (Eq. 4 of Part III), they are recognized to be practically the same as stated earlier (Part I), i.e. non-zero only within the common rovibrational states $|t\boldsymbol{v}>$ with, e.g. $\Delta J=0$, ±1. Selection rules for the other quantum numbers are $\Delta m_I=0$, ±1 and $\Delta m_J=0$, ±1 dependent on the values of ΔJ and a common parameter $p=0$, ±1 ($\Delta m_I+\Delta m_J=0$, regardless). The only difference is the *natural* introduction of the quantum numbers, F and m_F. (Once hfc was introduced, the system had to be described for these.) Namely, the matrix element is on the basis of nuclear spin-decoupled Hund's case (b),[4,32]

$$|\ t\boldsymbol{v}(((NKS)Jm_J)Im_I)Fm_F>. \tag{3}$$

Therefore, what has been analyzed without invoking the F and m_F quantum numbers[2—4] has to be modified and *re*interpreted as a consequence of incoherent superposition of coherent excitation*s* of block*s* of MES's,[3] expanded on these bases. The conclusions derived in Parts I—III without F and m_F should be regarded as concerned with the averages on these. Thus, qb's due to coherent excitation of states with various F's (and m_F's under the external field) would be automatically introduced. Optical selection rules about these quantum numbers are $\Delta F=0$ ($F\neq0$),±1 and $\Delta m_F=0$ ($m_F\neq0$), ±1 (under the external field).[9] Especially, coherent excitation with $\Delta F=+1$ & -1 is a cause of the anisotropic polarization qb (Section 1.3). If excitation is spread over more eigenstates, polarization decay as dephasing of qb's would be observed, ultimately. This is what was reported and analyzed semi-quantitatively.[2,5,6] However, we cannot proceed further: even if we derive the equations as described above, not much discussion can be made for azines with lack of finer experimental data to compare with the case for the smaller molecules.[30,31] By the way, introduction of various a_{FC}'s as many as the kinds of nuclear species does not much modify the *general* conclusions derived above *and* to be drawn below, in spite of the requirement for more complex equations than these.[32]

With the knowledge acquired in the preceding paragraph, we are now ready to discuss the intensity mixing mechanism assisted by H_{hfs} (H_{SI}) as stated in Part II. Among various alternatives,[31] the *s*-*t*-*t*′-*t*″-*s*′ coupling scheme with $H_{\mathrm{SO}}\otimes H_{\mathrm{vr}}\otimes H_{\mathrm{SI}}\otimes H_{\mathrm{SO}}$, i.e. by a combination of spin-orbit couplings, vibration-rotation interaction, and hyperfine interaction appears to be most important (for the case of pyrimidine).[2—4] This is similar to *one* of the "$\Delta J=1$" schemes shown in Table 1 of Part I.[2] However, the following reservations should be accepted:

(1) Axis-switching between S_0 and S_1 is *not directly* involved in this scheme. Rather, *that* between S_1 and T_1 appears to be important for the evaluation of $\{<s|H_{\mathrm{SO}}|t>\}$, though its effect may not be well distinguished from that of $\{<t|H_{\mathrm{vr}}|t'>\}$.[3]

(2) Accordingly, besides the selection rules on the other quantum numbers, $\Delta J=0$ & ±1 is allowed due to Eq. 2, against $|\Delta J|=1$ in the previous scheme.[2]

(3) Though we now allow different symmetries about Γ_{r} and Γ_{ns} for s and s', we still require the common total symmetry Γ_{int} for them. This is still a severe restriction for levels with lower J. (See, for example, Fig. 1 of Part 1 drawn for the case of pyrimidine; where superscript + of $J_{K_aK_c}$, E$^+$ for $K_c=0$ at three locations should be removed, giving rise to J_{J0}, E with $J=0$—2.)[2] Correspondingly, the following summary of selection rules can be made for the major angular-momentum quantum numbers: (i) $\Delta J=0$, $\Delta N=0$, ±1, and $\Delta K=0$, ±1, ±2 for $\{<s|H_{\mathrm{SO}}|t>\}$;[33] (ii) $\Delta J=0$, ±1, $\Delta N=0$, and $\Delta K=0$ for $\{<t|H_{\mathrm{SI}}|t'>\}$ (Eq. 2), *only* in the case of $\Delta\boldsymbol{v}=0$; (iii) $\Delta J=0$ and $\Delta N=0$ for $\{<t|H_{\mathrm{vr}}|t'>\}$.[2,34] This may be taken as an addendum to Part I.

2.2 D Effects in Molecules without Rotation (in Condensed Phase). The theoretical study on this subject may be regarded as almost finished as can be seen by following many review papers including Refs. 19, 24, and 28. Here, conclusions on both molecules only are described:

(1) Pyrimidine. In this molecule, the Herzberg–Teller (expanded) spin-orbit coupling (HTSOC) mechanism[35]

is usually considered to be predominant, that is, both electronic (matrix elements, $<\mathrm{S}_1|H_{\mathrm{SO}}|\mathrm{T}_1>$) and vibrational (Franck–Condon-weighted density of states) terms decrease upon D substitution (normal D effect).[19,24]

(2) Pyrazine. In this molecule, existence of a T_2 state nearby S_1 is noted at least in polar systems.[36,37] Therefore, the non-Born-Oppenheimer spin-orbit coupling (nBOSOC) term by $H_{\mathrm{SO}}\otimes H_{\mathrm{nBO}}$[2,3] is important to cause the inverse D effect.[24,27,28]

2.3 D Effects for the Isolated Molecules with Rotation. **2.3.1 D Effects on the Axis-Switching:** With lack of experimental data, especially in D substitutes, we cannot discuss this subject quantitatively. However, some decrease in the rotational constants,[19] i.e. in $\Delta E_{kk'}$[3] by D substitution, suggest a non-negligible increase in the axis-switching between *nearby* rotational levels. For, its *total* effect including the $\Delta \boldsymbol{v}\neq 0$ term, i.e. full contribution of axis-switching within the zero-point vibrations in the ground state may not be so significant as in the H_{vr} (Section 4.1 of Part II).[3] This situation is to be compared to the D effect on the energy gap law in the radiationless transition predicting an inverse D effect for smaller ΔE_{if} with i, f representing the initial and final electronic states, respectively (under the Condon approximation).[28]

2.3.2 D Effects on the Triplet Density of States, ${}^J\rho_{\mathrm{t}}$: The conclusion in Section 2.2 is only for the condensed phase and may not be applied for systems not in the statistical-limit case, like both the azines. The most significant is the factor that decides the choice between the small-molecule-limit (s-m-l) case and the intermediate case (i.c.), namely the triplet density of states,[2—4]

$$ {}^J\rho_{\mathrm{t}} \approx \rho^{(J)}/\sigma \approx (3/\sigma)(2J+1)\rho_{\mathrm{v}}. \qquad (4)$$

The major factor subject to the D effect in this equation is the vibrational level density ρ_{v} (increase by a factor of <10 for the small difference of the electronic energy ΔE_{ST}[28] in molecules like both azines[19]) that would bring about the apparent inverse D effect by letting the fast decay component become more significant than qb's.[3] The σ is a (nuclear) symmetry number *not directly* subject to the D effect (Subsection 2.3.4). As to the other factors on the s–t coupling with no dependence on Euler angles,[9] i.e. HTSOC and nBOSOC terms, the conclusions in Section 2.2 still apply.

2.3.3 D Effects as the Effects of hfc: Another aspect to be considered is the D effect observed as that of hf interaction, which is not simply ascribed to the increase of nuclear masses but rather to the properties of the nuclei. It should not be taken as a common D effect as is to be discussed, e.g., by a perturbation theory. Two factors are considered:

(i) Density of States. Lack of a nuclear factor ρ_{I} other than the σ in Eq. 4 is based on the selection rules of $\Delta I=\Delta m_I=0$ in the couplings such as $<s|H_{\mathrm{SO}}|t>$ and $<t|H_{\mathrm{vr}}|t'>$.[2—4,9] However, introduction of hfc, i.e. $<t|H_{\mathrm{SI}}|t'>$ does require the ρ_{I} due to the contribution of $|\Delta m_I|=0$ and 1 besides $|\Delta m_J|=0$ and 1 subject to the common parameter of $|\Delta p|=0$ and 1 and to the restriction of $\Delta m_I+\Delta m_J=0$ with Eq. 2, which is dependent on the nuclear spin $\boldsymbol{I}$ ($I_{\mathrm{D}}=1$, twice of $I_{\mathrm{H}}=1/2$). Therefore, enhancement of the inverse D effect is expected by a factor of $c_{\mathrm{I}}={}^{\mathrm{D}}\rho_{\mathrm{I}}/{}^{\mathrm{H}}\rho_{\mathrm{I}}>1$. This is closely related to the σ and nuclear statistical weights to be discussed in the next Subsection 2.3.4.

(ii) H_{SI} Matrix Elements. With small differences of nuclear magnetic moments indicated by their ratios $2\mu_{\mathrm{D}}/\mu_{\mathrm{H}}\approx 0.61$ ($\lesssim 1$) and $2\mu_{\mathrm{N}}/\mu_{\mathrm{H}}\approx 0.29$ (<1),[32] a little normal D effect is expected for the F–C term (Section 2.1 with Eq. 2). The two tend to cancel each other by the ratio $(\sum_{t''}(v_{t't''}/\Delta E_{t't''}))_{\mathrm{D}}/(\sum_{t''}(v_{t't''}/\Delta E_{t't''}))_H\approx 0.61c_{\mathrm{I}}^2$, as a very crude measure ($v_{t't''}$ representing Eq. 2, Section 2.1; the *effective* numbers of $\{t''\}$ may be assumed to be proportional to ρ_{I}'s). Since little experimental observation (in favor of either of these factors) is available even for smaller molecules, we'll assume a small (inverse) D effect at least in this coupling, as compared to the other dominant factors.

2.3.4 D Effects on $\boldsymbol{\sigma}$ values ($\boldsymbol{\sigma_n}$ and $\boldsymbol{\sigma_{\mathrm{r}}}$): Finally, D effects on the σ values should be discussed. The σ is the factor already introduced in ${}^J\rho_{\mathrm{t}}$ (Eq. 4).[2—4] However, some care must be taken when we discuss the depolarization by the axis-switching, where hfc has the *secondary* contribution (Section 2.1). For that purpose, two kinds of σ's, i.e., σ_{n} *and* σ_{r} for conventional *nuclear* symmetry- *and* novel *rotational* symmetry-numbers (numbers of the allowed symmetries), respectively, are defined in Table 1, besides the values of (nuclear) statistical weights for both azines. These are based on the prescription by Bunker.[9] As discussed in Part I and in this Section 2.1, the σ_{r} is rather important factor in the axis-switching, at least before the contribution of H_{SI} (at $t\lesssim 1$ ns). While the σ used in Eq. 4 corresponds to the σ_{n} named here. Anyway, Table 1 predicts no D effect on the σ values *as long as* the symmetry is common. (See, however, Subsection 3.2.1.) The statistical weights and their relative values in the Table do show a D effect that is partially reflected in the D effect on the densities of the final states in the s-t coupling as mentioned in the preceding subsection, though they are not clearly discernible in the spectral shape (almost degenerate, at low resolution).[9] By the way, this Table is to be compared to Table 1 in Ref. 38, which is based on the rotational subgroup *effectively* isomorphic to the homomorphic MSG used in this series. The statistical weights in this Table (different from those in the review paper[38]) are calculated based on the requirement of quantum mechanics for the symmetry of the total wavefunction Γ_{int} to be either symmetric or antisymmetric for an inversion operation, E^*.[9] However, since

Table 1. MSG's, Statistical Weights, and Symmetry Numbers (σ_n and σ_r) of the Azines

	D_{2h}(M)				C_{2v}(M)				C_s(M)			
	Pyrazine(-d_0)		Pyrazine-d_4		Pyrimidine(-d_0)		Pyrimidine-d_4		Pyrazine-d_1		Pyrazine-d_3	
σ_n	4		4		2		2		1		1	
	A_g	51	A_g	216	A_1	21	A_1	45	A′	216	A′	486
	B_{3g}	27	B_{3g}	162	B_2	15	B_2	36				
	B_{1u}	27	B_{1u}	162								
	B_{2u}	39	B_{2u}	189								
σ_r	4 (A_g, B_{1g}, B_{2g}, B_{3g})				4 (A_1, A_2, B_1, B_2)				2 (A′, A″)			

the ratios of the statistical weights as well as σ_n and σ_r in both Tables are common, little difference is predicted in the schemes described in Section 2.1, according to the group theory. Only the ratio of the statistical weights appears in the observable.[9] (The σ_n is merely an approximate manifestation of the role of the statistical weights with all the ratio set one.)[2—4] Namely, the improvement is in counting the number of states for incoherent superpositions of excitations *and* of its D effect (the last subsection).

The following is a summary of the D effect described in this Section 2 as to be applied for the discussion in the next Section:

(1) Pyrimidine. In spite of normal D effects in electronic and nuclear terms (Section 2.2), the increased ${}^J\rho_t$ would influence the *situation* in the near s-m-l case behavior (towards the intermediate case).[2)]

(2) Pyrazine. An inverse D effect is expected in spite of the small density of states for T_2 nearby S_{10}. Accordingly, the D effect on the nBOSOC mechanism might catch up that of the axis-switching. In the case of pyrazine-d_0, the doorway state as an origin of the fast decay component with the width Γ_d was presumed to be distributed over the bunches with widths $\{\Gamma_s\}$ assuming $\Gamma_d > \Gamma_s$. However, it may not be the case for pyrazine-d_4 with $\Gamma_d \approx \Gamma_s$ predicting more complex behaviors (Section 3.2.2).

3. Application and Remark

Now we are ready to do case-by-case discussions of the experimental data, most of which are picked up from those described in Section 1.

3.1 Pyrimidine-d_n (n=0, 4). With lack of experimental data on the MES spectra of pyrimidine-d_4, quantitative discussions is difficult. The observed D effects, i.e. decrease in polarization and the increase of the contribution from qb's by D substitution can easily be interpreted by the increase of density of states, i.e. of ρ_v assisted by c_I (Section 2.3; σ_n=2 for both d_0 and d_4), using the scheme for the s-m-l case.[2—4]

3.2 Pyrazine-d_n (n=0, 1, 3, 4). In the light of the general discussion in Section 2, it may be almost straightforward for us to make case-by-case discussions for parazines as forestalled in that section. However, some ambiguities can not be avoided because we have *more* parameters than the experimental data. Here, important factors only are pointed out.

3.2.1 D Effect on the J, K Dependence as Seen in the MES Spectra:[21] One of the observations, i.e. dependence on the number of D atoms can easily be interpreted by the increase in the density of states, especially by ρ_v. On the other hand, to interpret the J, K dependence, they were forced to invoke the Coriolis coupling theory that had been used to interpret the rotational effect in the Channel 3 mechanism of benzene.[18,25,39] However, the cited theory including its matrix elements are concerned with the IVR within the singlet manifold hardly involved in the decay of the S_{10} levels, if applied literally. Certainly, Coriolis coupling is possible among triplet levels (coupled to S_{10}). However, it is only a part of the schemes for the well-accepted "complete scrambling" of the triplet levels with ΔJ=0 corresponding to my ${}^J\rho_t$. No evidence for a "partially mixed" triplet state with the K dependence (of the doorway singlet manifold) has been recognized at least for the MES spectra in pyrazine-d_0,[7] as discussed in Part II (the last paragraph of Section 5.4). Actually, H_{SO} matrix elements would greatly reduce the restriction by the Coriolis coupling (ΔJ=0, ΔK=0, ±1, with coefficients dependent on J and K)[21,25,39] with the selection rules of ΔJ=0, ±1 and ΔK=0, ±1, ±2.[33] Then the irreducible representations of rotational wavefunctions included in Table 1 (σ_r portion) are highlighted. The following classification is possible for both pyrazine-d_1 and -d_3 with the C_s(M) symmetry:

$$A' : 0_{00};\ 1_{11}; 2_{20}, 2_{11}, 2_{12};\ \cdots, A'' : 1_{10}, 1_{01};\ 2_{21}, 2_{02};\ \ldots\ .$$

Thus, the weakness of the R(0) band can be interpreted by the (intensity) mixing of the 1_{10} level with the 1_{01} level due to axis-switching.[3] While in the case of the P(2) band, where three levels (1_{10}, 1_{11}, and 1_{01} are excited, one of the level (1_{11}) is coupled *only* with assistance by H_{SI} to *either* 1_{10} and 1_{01} levels (ΔJ=0) *or* such as 0_{00} and 2_{20} levels (ΔJ=±1) (Section 2.1), retaining the intensity in between the P(1) (0_{00}) and the R(0) bunches. Therefore, this D effect can be taken as another evidence of axis switching. In this respect, similar experiments on three kinds of pyrazine-d_2 with

C_{2v}(M) (two) and C_{2h}(M) (one) symmetries (never separated so far ?[15]) are urged. These molecules have common σ_n (=2) and σ_r (=4) values, different from those of pyrazine-d_n with n=0, 1, 3, 4 (Table 1).

3.2.2 Inverse D Effects in the Short Fluorescence Decay Component: As described in Subsection 1.2.2, the clear inverse D effect on the short decay component[26] is noted between pyrazine-d_0 and -d_4. Following the last paragraph of Section 2, nBOSOC is judged to be predominant, at least for higher J ($\gtrsim$10 with enough intermediate states ?).[3] However, for $J<$ 10, we have to be cautious to make any judgement on the complex experimental data.[22] Thus, measurements on the J dependence of the short decay components in the D substitutes of pyrazine, as was done for the d_0,[8] are desired. Since $\Gamma_\mathrm{d}\approx\Gamma_s\gg\Gamma_j$ (the width of the MES j) for this system against the case in pyrazine-d_0 with $\Gamma_\mathrm{d}>\Gamma_s\gg\Gamma_j$, deviation from the double exponential decay would appear to be more significant than the d_0 as discussed in Part II.

3.2.3 D Effects on the External Magnetic-Field Effect on the Decay Behavior of Pyrazines: As just mentioned in the head of this Section 3.2, we cannot thoroughly discuss the experimental data (on this subject) because we have too many parameters. Somehow, the increases in ρ_t and the effects on the nBOSOC scheme as described above are obvious facts to mention. For example, let's examine the D effect on the fluorescence decays following excitation at the P(1) lines of the 0–0 bands (Fig. 5 of Ref. 16 vs. Fig. 5 of Ref. 22). Contributions of both qb's and the fast decay components are more for -d_4 with larger Zeeman effects than -d_0. This can easily be interpreted by the D effect on the density of the triplet states. In this respect, a comment should be made on the proposed field-induced mixing between T_1 and T_2.[22] Since its matrix element appears to be smaller than those of H_nBO and H_SO (between T_1 and T_2) in orders of magnitudes (the electronic components seem to be $<\pi|H_\mathrm{nBO}|n>\gtrsim1$ cm^{-1}, $<\pi|H_\mathrm{SO}|n>\approx1$ cm^{-1}, and $<\pi|H_\mathrm{Z}|n>\approx2\mu_\mathrm{B}H\times$ $<\pi|\ell_y|n>\approx10^{-3}$ cm^{-1} for a typical magnetic field of H=100 G, respectively),[2—4,19,23,28,30,31,40] its effect has to be on the *new* selection rule, e.g., $|\Delta m_\mathrm{S}|=1$ (for the electron-spin component) on the electron-spin decoupled basis.[4,31] However, it can not exceed those by $H_\mathrm{nBO}\otimes H_\mathrm{SO}$ and H_SO (between S_1 and T_1), H_SI and H_Z (within T_1), and so on.[2—4,23,32,40] Accidental closeness (up to $<10^{-3}$ cm^{-1}) between S_{10} and T_{2n} *might* make the $\{<\mathrm{T}_{2vr}|\mathrm{H_Z}|\mathrm{T}_{1v'r'}>;\ \boldsymbol{v}=(n,\{\mathbf{0}\})\}$ terms significant. However, apparent failure to observe the MES spectra cannot be the sole *evidence* to support the closeness. By the way, with the nBOSOC mechanism assisted by the $\{<\mathrm{T}_{1vr}|H_\mathrm{Z}^{(1)}|\mathrm{T}_{1vr'}>\}$ matrix elements (Eq.4 of Part III), there is no a priori reason to invoke field-induced mixing for interpretation of the Zeeman effect on the D effect. As one of the referees pointed out, shortening of the long-lived component of the lifetimes by the magnetic field is taken as evidence for their scheme.[22] Therefore, comments are made on their analysis: (1) Their lifetimes are calculated based on the bi-exponential assumption in spite of experimental conditions that deviate from the ideal intermediate case, e.g. by a laser with the $\tau_\mathrm{c}\lesssim1$ ns. Therefore, the lifetime for the full intermediate condition would be rather close to that at high field (Table 1 of Ref. 22). (2) For the same reason, their components (I_F^f, I_F^s, their Fig. 8; not discussed in this paper) should be treated with care.

3.3 Reinterpretation of the Fast Fluorescence Decay Component (with τ_s) in Pyrazine for $J\lesssim2$. To interpret the *observed* τ_s ($\approx\hbar\Gamma_\mathrm{d}{}^{-1}$) component of pyrazine (-d_0),[8] the intensity-mixing schemes by the axis-switching with the *help* of H_SI has been proposed for $J\lesssim2$ (J=1, 2 (,3), to be more precise) as a cause for the broad doorway state (last paragraph of Section 2).[3] However, the detailed scheme assessed to be most important involves *no direct* axis-switching between S_0 and S_1 (Section 2.1), even with H_nBO. Though the scheme is crucial to interpret various observations such as MES spectra or (hf) qb's, it may not be the *only* cause for the intensity mixing among the optically assigned levels $\{s\}$.[3] Actually, little evidence of the coupling is found for the locations of the $\{s\}$ levels.[3,7] In other words, the *initially* prepared doorway state $\hat{s}_0$ as defined by Eq. 33a of Part II can not be simply represented by the double Lorentzian (Eq. 39 in Part II) for $J\lesssim2$, even as a model (Γ_d *had* to be extremely large), making the isolation of $\hat{s}_0$ practically impossible. Thus, we need an alternative scheme for the interpretation of the fast decay component at least for $J\lesssim2$. Accordingly, what follows can be regarded as an addendum to Part II.

We now propose a *new* scheme for the τ_s component for $J\lesssim2$, where the $\Delta J=0$ scheme is of little use: Coherent excitation into rotational levels *different* in J (by $|\Delta J|$=1) (and K) within the uncertainty width of the laser. The difference, $|\Delta J|$=1 is in accord with the optical selection rule of ΔJ=0, ±1. On the other hand, $\Delta K\neq0$ is mostly through the axis-switching mechanism.[3] Possible candidates for the partners (at the right) in the coherent excitation corresponding to the laser-tuned rotational levels (at the left) are shown below, for the case of J=0—2:

0_{00}–1_{10}; 1_{10}–0_{00}, 1_{10}–$2_{02}(2_{20})$; 2_{20}–2_{02}, 2_{21}–$3_{13}(3_{31})$,
2_{11}–$3_{03}(3_{21})$, 2_{02}–2_{20}, $2_{02}(2_{20})$–1_{10}.

These are picked up considering *both* the selection rules (on angular momentum quantum numbers and the symmetry corresponding to the σ_r portion in Table 1, e.g. as given in the Discussion of Ref. 7 assuming axis-*interchange*[3] between S_0 and S_1) *and* the locations of energy levels.[3] (Schemes containing pairs with energy separations of more than 0.5 cm^{-1} were excluded.) The first two schemes, i.e. those for ΔJ=1 *and* −1 with ΔK=0 correspond exactly to the coherent excitations of P(1) (with Q(1)) *and* Q(1) (with P(1)) bands from the 1_{10} level in the ground vibrational level of the electronic ground state, respectively. Excitation of the P(1) band by the ps laser has simultaneous excitation of the Q(1) band and vice versa (but partially, i.e. only in one of three components). However, they may be too well concealed in the strongly congested Q branch to be distinguished (see below).[3)] The 2_{20}–2_{02} & 2_{02}–2_{20} schemes with $\Delta J=0$ & $\Delta K\neq 0$ are nothing but the axis-switching scheme discussed previously.[3)] The other four schemes with $|\Delta J|=1$ & $\Delta K\neq 0$ are *novel* ones, i.e., those of coherent excitations with $|\Delta J|=1$ assisted by the axis-switching where the states to lend intensities are given in the parentheses. These can *now* interpret all the initial decay components after excitations of the P(n) (n=2, 3) and R(n) (n=1(,2)) bands. Though not evident in the experimental data, contributions of the 1_{10}–2_{02}(2_{20}) *and* 2_{02}(2_{20})–1_{10} schemes would be less significant than those of the 1_{10}–0_{00} *and* 2_{02}–2_{20} schemes, for the case of Q(1)-band *and* Q(2) (or R(1), not P(3))-band excitations, respectively. Most significantly, without the 1_{10}–2_{02}(2_{20}) scheme, the short-lived component after P(2) band excitation by the ps laser[8)] cannot be well interpreted. Since the $0_{00}\leftarrow 0_{00}$ transition is forbidden,[9)] the *observed* short-lived component after "R(0)" band excitation[8)] might be ascribed rather to the transitions in a nearby Q branch, especially to Q(1) with the scheme 1_{10}–0_{00} (See their Fig. 3, which has a subtle peak of the R(0) bands.). The similar schemes may partially contribute to the τ_s components of the levels with $J\gtrsim 3$ (3—5 ?).

Against the case with $\Delta J=0$ like 2_{20}–2_{02}, the excited pair of levels, i.e., doorway states with $|\Delta J|=1$ have little common origins $\{s\}$ of intensity in view of the properties of the photon, ($\boldsymbol{k}$, $\boldsymbol{e}$) with no direct axis-switching scheme.[3)] Therefore, the fast decay process may be described as follows: Right after dephasing of these levels accompanying depolarization, the independent dephasing of the doorway states into the components of the bunches are attained, and so on.[3)] However, the appearance would be practically the same as the case described in Part II. This might also be perceived as a sublation of the scheme by Amirav,[41)] at least for $J\lesssim 2$. *Right* after coherent excitation of the two (or more) doorway states with different J numbers, two (or more) independent decays with lifetimes τ_s and $\{\tau_{\mathrm{b}}{}^s\}$($\approx\hbar\Gamma_s^{-1}$, corresponding to the width of the *bunch*) are observed, followed by the long-lived τ_ℓ component corresponding to $\hbar<\Gamma_j{}^{-1}>$.[3)] This prediction of more than two components of τ_s, $\{\tau_{\mathrm{b}}^s\}$ and $\{\hbar\Gamma_j{}^{-1}$, the lifetime of the MES$\}$ underscore the necessity of observation at the intermediate stage of the decay (Section 5.1 of Part II).

As described above, coherent excitation with $|\Delta J|=1$ is one of the key points that must be included in a future reformulation of the theoretical framework. Also, to avoid possible confusion, one comment should be made about the symmetry of the rovibronic levels, i.e. Γ_{e}, Γ_{v}, Γ_{r}, and so on, that are dependent on the choice of molecular axes (x, y, z) as in the case of a molecular point group: Γ_{r} does not always correspond to the priorities of the rotational axes (a, b, c), which are subject to the axis-interchange and are related to a common asymmetric top label $J_{K_aK_c}$.[3,9)] As to the D effect, the chance for the coherent excitation with $|\Delta J|=1$ will be more for pyrazine-d_n with larger n having a more complex non-exponential decay.

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