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Collision Induced Perturbations on the Long-lived Fluorescence of Pyrazine in S_1

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Collision induced intersystem crossing (slow fluorescence quenching and phosphorescence induction) from selected vibronic levels of pyrazine in $S_1(n\pi^*, B_{3u})$ was investigated. It was found that slow fluorescence quenching rate at the zero point level exceeds the hard sphere collision rate several times and rapidly approaches it as the excitation energy is increased. On the other hand, phosphorescence induction rate was found to be nearly equal to the collision rate and to have little excitation energy dependence. These differences were discussed on the basis of the collision induced relaxation mechanisms.

In the past decade, the photophysical properties of the electronic excited states of polyatomic molecules in an isolated molecular condition have been studied extensively both from experimental and theoretical points of view and the concept of the intramolecular radiationless transition has been established. On the basis of the understanding of the unimolecular processes, the subsequent problem to be studied seems to be the collision induced intramolecular relaxations which are essentially important in understanding the photochemical reactions. Despite the importance of the collision induced processes, the theoretical interpretation does not seem to be successful yet. This comes from, (1) the lack of the accumulation of the experimental results which are worthwhile to be analyzed theoretically and, (2) the difficulty in dealing with the intermolecular interaction as the perturbation due to the collision.

Spectroscopic and dynamical properties of S_1 ($n\pi^*$, $^1B_{3u}$) pyrazine have been investigated thoroughly by many workers.[1–20)] Individual vibronic levels of S_1 up to 1000 cm^{-1} from the 0-0 band have been assigned by the absorption,[1–7)] SVL fluorescence[13,14)] and pre-resonance Raman scattering works.[8–12)] Under the collision free condition, the fluorescence of pyrazine from the S_1 state exhibits bi-exponential decay that is typical of the intermediate strong coupling molecule as reported by Lahmani *et al.*[16)] In pyrazine, the short-lived component of the fluorescence has the lifetime shorter than 10^{-9} s and the long-lived one is of the order of 10^{-7} s.

When one looks at the effect of collision on the prompt fluorescence, one is able to study the vibrational relaxation within S_1 manifolds. The vibrational mode dependence of V-V transfer rate has been investigated by us on the selected vibronic levels of S_1 pyrazine.[21)]

The long-lived fluorescence derives from the interaction of S_1 with the isoenergetic triplet ro-vibronic levels. The effect of the collision appears on the two optical phenomena, *i.e.*, (1) the quenching of the slow fluorescence and (2) the induction of the phosphorescence from T_1. In the present work, we have investigated the excitation energy dependences of the quenching rate of the slow fluorescence and the induction rate of the phosphorescence under the SVL excitation condition. The amount of the energy loss within the triplet manifolds by a collision has been also obtained under the assumption of the step-ladder relaxation model.

Experimental

As an exciting light source, the second harmonics of a tunable dye laser (Rh-640) pumped by a Molectron nitrogen laser (UV-22) was used. Either RDP or ADA was used as an SHG crystal. The emission intensity was measured by an HTV-R-562 photomultiplier averaged by a boxcar integrator (Brookdeal 9415 and 9425). In order to distinguish fluorescence from phosphorescence, a Nikon P-250 monochromator of 6 nm slit width with a fixed wavelength (345 nm for fluorescence or 390 nm for phosphorescence) was placed in front of the photomultiplier. Moreover, a delay time of the boxcar integrator was adjusted to get the best separation between them. As a collision partner, isopentane whose pressure extends from 0 to 20 Torr (1 Torr= 133.322 Pa.) was added to 2×10^{-2} Torr pyrazine. The gas pressure was measured by a Baratron 222A capacitance manometer. Pyrazine was purified by vacuum sublimations and spectral grade isopentane was used without further purification. The samples were degassed by the freeze-thaw cycles prior to the experiments.

By varying the excitation wavelength up to 1000 cm^{-1} above the 0-0 of S_1-S_0 absorption and the pressure of isopentane, wavelength and pressure dependences of the fluorescence and the phosphorescence were measured by the following procedures. As mentioned above, the fluorescence contains the prompt and slow components. The former component is affected only by adding high pressure gas exceeding 100 Torr. Still the latter one is sensitive to the trivial amount of a foreign gas and is quenched completely in the presence of 20 Torr isopentane. Then, the intensity of the long-lived fluorescence $I_{sf}(P)$ at the pressure $P (P<20$ Torr) is given by

$$I_{sf}(P) = I_{345}(P) - I_{345}(P=20\ \text{Torr}).$$

Where $I_{345}(P)$ is the fluorescence intensity observed at 345 nm with the spectral slit width of 6 nm. The phosphorescence of pyrazine at the pressure P as denoted $I_{ph}(P)$ is dispersed around 390 nm and is overlapped with the fluorescence. By noting the fact that the phosphorescence is induced by collisions, the phosphorescence component is extracted from the total emission observed at 390 nm by the following correction.

$$I_{ph}(P) = I_{390}(P) - I_{345}(P) \times \frac{I_{390}(P=0)}{I_{345}(P=0)}$$

$I_{390}(P)$ is the total (phosphorescence and fluorescence) emis-

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sion intensity at 390 nm and $I_{345}(P)$ is the fluorescence intensity observed at 345 nm at the pressure P. The emission intensity at 390 nm extrapolated at zero pressure $I_{390}(P=0)$ contains only the fluorescence. Thus, the second term of the above equation gives the fluorescence component at 390 nm at the pressure P.

Results and Discussion

The observed fluorescence and phosphorescence intensities against the excitation wavelength and the foreign gas pressure inform us of three physical quantities of the collision induced relaxation. They are, the slow fluorescence quenching rate, the phosphorescence induction rate or the vibrational relaxation rate within the triplet levels and the energy removed per an effective collision. First, the kinetic scheme is given to describe the collision induced relaxation processes from S_1 pyrazine. Then, the experimental results will be discussed on the basis of the kinetic scheme.

The Kinetic Scheme. Temporal behavior of the excited state of an intermediate size molecule like pyrazine has been described quantum mechanically by Lahmani *et al.*[16] van der Werf *et al.*[23] have adopted a kinetic scheme to explain the electronic relaxation of biacetyl. In the present wotk, the kinetic description was used for the evaluation of the above mentioned physical quantities from the experimental data.

Bi-exponential dacay of an excited intermediate size molecule with strong S-T coupling is described by

$$1/\tau_{f1} \simeq \Delta_{ST}, \tag{1}$$

$$1/\tau_{f2} = \bar{\gamma}_n \simeq \bar{\gamma}_S/N + \gamma_T. \tag{2}$$

τ_{f1} and τ_{f2} are the lifetimes of the fast and slow fluorescence, respectively. Δ_{ST} stands for the coupling strength between a vibronic level of the singlet state and N triplet levels. Total decay widths of a S state and a T state are defined as γ and γ which are given as superpositions of individual decay channels by

$$\gamma_S = \Gamma_S + \Delta_{ST} + \gamma_{SS_0}, \tag{3}$$

$$\gamma_T = \Gamma_T + \gamma_{TS_0}. \tag{4}$$

Here Γ_S and Γ_T are the radiative widths of the S and T states, respectively. γ_{SS_0} and γ_{TS_0} indicate the nonradiative decay widths between S and S_0 and between T and S_0, respectively. γ_n represents the total decay width of $(N+1)$ quasistationary states which are formed by the interaction between a S state and N triplet states ($N \approx 10^3$). $\overline{X}$ implies the mean value of the physical quantity X. Because Δ_{ST} is much larger than γ_n, the influence of the collision appears mainly on the $\bar{\gamma}_n$ or γ_T values at relatively low pressure (<20 Torr). That is to say, the collisional perturbation affects only the long-lived fluorescence with a negligible influence on the prompt component as described by

$$\gamma_T(P) = \gamma_T(P=0) + k_q P, \tag{5}$$

where k_q is the quenching rate constant of the slow fluorescence and is obtained by the following Stern-Volmer relation.

$$I_{sf}(P=0)/I_{sf}(P) = 1 + A_f P \tag{6}$$

$$A_f = k_q \tau_{f2} \tag{7}$$

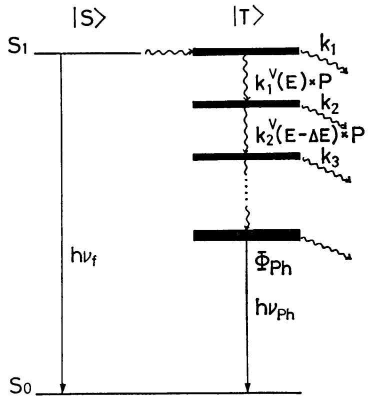

Fig. 1. Step-ladder scheme of vibrational relaxation within triplet manifolds. Symbols are defined in the text.

Here $I_{sf}(P)$ represents the intensity of the slow fluorescence at the pressure P.

It is already known that the phosphorescence of pyrazine is the induced one by collisions after the excitation of a S_1 vibronic level. The pressure dependence of the collision induced phosphorescence intensity informs us of the vibrational relaxation rate within the triplet manifolds and the amount of the removed energy per an effective collision by assuming the step-ladder relaxation model as illustrated in Fig. 1. In the figure, k_i represents the unimolecular decay constant from the triplet manifolds and k_i^v is the collision induced vibrational relaxation rate. ΔE stands for the removed energy by an effective collision. Then, the intensity of the collsion induced phosphorescence at the pressure P is given by

$$I_{ph}(P) = \Phi_{ph} \prod_{i=1}^{n} k_i^v P/(k_i + k_i^v P). \tag{8}$$

Here n is the number of the effective collisions to induce the phosphorescence. Φ_{ph} indicates the quantum yield of the phosphorescence. The reciprocal of the $I_{ph}(P)$ in Eq. 8 can be expanded in the form of the power series of P^{-1} up to the n-th order. k_i values

$$I_{ph}^{-1}(P) = C(1 + \alpha P^{-1} + \beta P^{-2} + \cdots) \tag{9}$$

$$\alpha = \sum_{i=1}^{n} k_i/k_i^v \tag{10}$$

$$\beta = \sum_{i<j} k_i k_j / k_i^v k_j^v \tag{11}$$

can be obtained experimentally only at the initial (i=1) and the final (i=n) level of the step-ladder relaxation from the known slow fluorescence and phosphorescence lifetimes, respectively. k_i for the intermediate step was estimated from the semilogarithmic plot of k_i against the excess energy from T_1. As will be discussed in the later section, the removed energy by a collision was found to be around 1200 cm^{-1}, k_i decreases rapidly as the vibrational relaxation proceeds to the lower step. On the other hand, k_i^v can be assumed to have no appreciable energy dependence as has been found in S_1 pyrazine.[21] Thus, the relation $k_i/k_i^v \gg k_{i+1}/k_{i+1}^v$ may hold for each step. Under these assumptions, Eqs. 10 and 11 can be approximated as

TABLE 1. THE RATE CONSTANTS OF SLOW FLUORESCENCE QUENCHING AND PHOSPHORESCENCE INDUCTION

Level	E	A_f		K_q	A_{ph}		$k_1^{\rm v}$
	cm^{-1}	a)	b)	10^7 s^{-1} Torr^{-1}	a)	b)	10^7 s^{-1} Torr^{-1}
0	30876	18	10.5	6.2	3.3	0.95	1.14
10_a^1	31259	9	8.5	4.2	2.0	0.55	0.94
6_a^1	31459	7.5	3.5	3.5	1.7	0.5	0.79
10_a^2	31709	6.6	—	3.2	1.5	—	0.72
$6_a^1 10_a^1$	31821	3.4	2.6	1.8	1.4	0.4	0.72
6_a^2	32043	2.7	2.2	1.3	1.3	0.3	0.63

a) Our result using isopentane as a collision partner. b) Result using SF_6 as a collision partner by Lahmani *et al.* in Ref. 16.

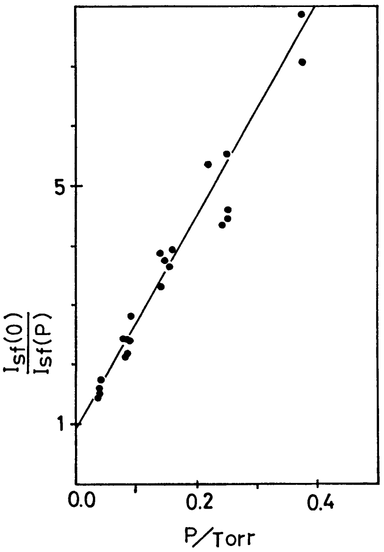

Fig. 2. Stern-Volmer plot of slow fluorescence intensity from the zero point level of S_1. P indicates isopentane pressure. The slope gives the A_f value in Eq. 7.

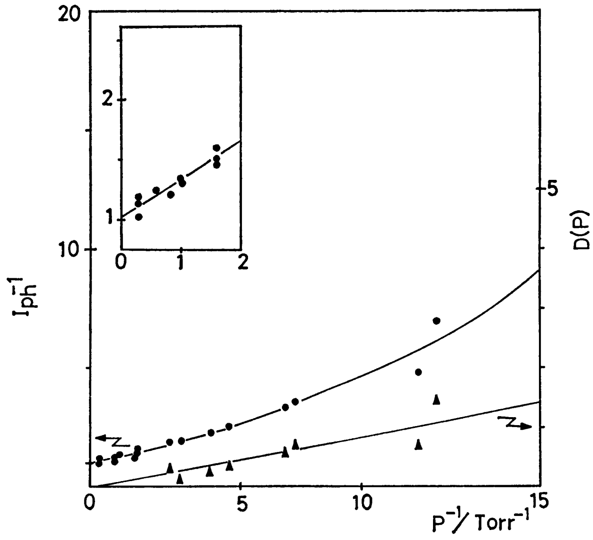

Fig. 3. Phosphorescence induction after the excitation in the zero point level of S_1. I_{ph}^{-1} is plotted against P^{-1} (—●—). The region of 0—2 Torr^{-1} is expanded and its slope gives α value in Eq. 12. The deviation from the linearity is also plotted (—▲—) in the from of the function $D(P)=\{I_{ph}^{-1}-(1+\alpha P^{-1})\}^{1/2}$ and its slope ($\sqrt{\beta}$) gives β value in Eq. 13.

$$\alpha(E) = k_1(E)/k_1^{\rm v}(E), \tag{12}$$

$$\begin{aligned}\beta(E) &= k_1(E)k_2(E-\Delta E)/k_1^{\rm v}(E)k_2^{\rm v}(E-\Delta E)\\ &= \alpha(E)\alpha(E-\Delta E).\end{aligned} \tag{13}$$

First, the reciprocal of the phosphorescence intensity is plotted against the inverse of the pressure. The linear slope and the deviation from the linearity give the values α and β. Because $1/k_1$ is the experimentally observed lifetime of the long-lived fluorescence from a selected vibronic level of S_1, the vibrational relaxation rate $k_1^{\rm v}$ can be evaluated from the α and the k_1 values. In the next step, α and β/α values are plotted against the excitation energy. The energy separation that gives the identical values of α and β/α corresponds to the removed energy ΔE per an effective collision.

The Slow Fluorescence Quenching Rate. By use of the Eqs. 6 and 7, the slow fluorescence quenching rates for the individual vibronic levels of S_1 pyrazine were evaluated on the basis of the observed slow fluorescence intensities $I_{sf}(0)$ and $I_{sf}(P)$. The result is illustrated in Fig. 2 taking the 0-0 band excitation as an example. k_q and A_f values for the individual levels are tabulated in Table 1. One notices easily that k_q values in the excitation around the 0-0 band exceed several times the hard sphere collision value ($\approx 10^7$ s^{-1} Torr^{-1}). Moreover, the value decreases rapidly to reach the hard sphere collision one as the excitation energy is increased.

The Vibrational Relaxation Rate within the Triplet Levels. As the intensity of the slow fluorescence is decreased by collisions, the phosphorescence from T_1 is induced *via* the collision induced vibrational relaxation from the higher triplet levels. Thus, one can evaluate the vibrational relaxation rate from the pressure dependence of the phosphorescence induction. In Fig. 3, the reciprocal intensity of the phosphorescence is plotted against the inverse pressure taking the 0-0 band excitation as an example. The α value that contains the information of two body collision gives us the vibrational relaxation rate within the triplet manifolds. $k_1^{\rm v}$ values obtained from the α values for the individual vibronic levels of S_1 are of the order of the hard sphere collision rate as seen in Table 1. They do not exhibit appreciable variation as the excitation energy is increased, which is in contrast to k_q.

Discussion on the Slow Fluorescence Quenching and the Phosphorescence Induction Mechanisms. As seen in the

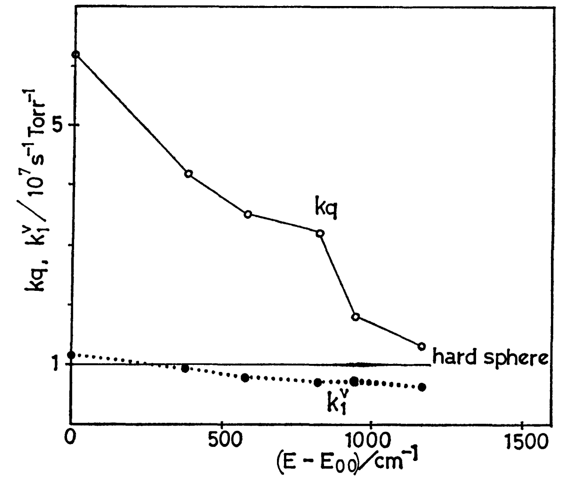

Fig. 4. Excitation energy dependence of the collision induced relaxation rate constant. Slow fluorescence quenching rate k_q(—O—) and phosphorescence induction rate k_1^{v}(···●···) are shown. The calculated hard sphere collision rate (——) is shown for comparison. The ordinate is the rate constant in 10^7 s^{-1} $Torr^{-1}$ scale and the abscissa is the vibrational energy above the zero point level of S_1 in cm^{-1} unit.

previous sections, the evaluated k_1^{v}'s and k_q's differ greatly each other in their magnitudes and excitation energy dependences. This indicates that the quenching of the long-lived fluorescence and the induction of the thermally equilibrated T_1 phosphorescence are caused by different collision processes. As discussed already in the previous section, the slow fluorescence is quenched by the relaxation of the excited molecule from the interaction region of the width Δ_{ST} to the non-interacting one where there is no strong activity of emitting the radiation. Because Δ_{ST} is of the order of 10^{-2} cm^{-1},[16,17] even a single rotational relaxation is enough to cause the slow fluorescence quenching. This may explain the observed large value of k_q in contrast to k_1^{v}. It is also suggested that the optical experiment by the use of an ordinary optical cell at low pressure ($\approx 10^{-3}$ Torr) does not satisfy the isolated molecule condition and that the condition will be met only by a molecular beam. The results of the lifetime measurement of the slow fluorescence of pyrazine under the supersonic expanded beam condition will be published soon.[22]

In going from the lower to the higher energy side, k_q tends to the hard sphere collision value as seen in Fig. 4. Van der Werf *et al.* have found the similar behavior of k_q values in biacetyl and explained it in terms of the overlap of the emitting regions in the higher vibronic levles. However, in pyrazine the overlap cannot be expected in the region up to 1000 cm^{-1} above the 0-0 level of S_1 because each vibronic state in that region is well defined as viewed from the absorption and SVL fluorescence studies. Recently, rotational level dependence of the slow fluorescence has been reported by Baba *et al.*[18] Strong j dependence of the slow fluorescence intensity and decaying rate has been found in the supersonic beam which will be published elsewhere.[22] The excitation energy dependence of k_q values is now under investigation from that point of view.

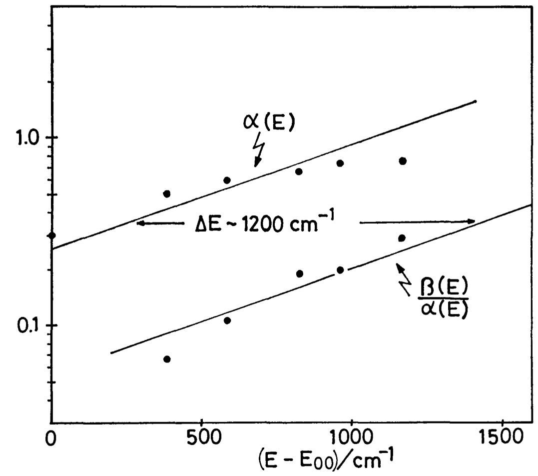

Fig. 5. Vibrational energy removed by an effective collision.

The vibrational relaxation rate k_1^{v} within the triplet mainfolds of pyrazine has the value around the hard sphere collision one as seen in Fig. 4 and Table 1. They are as comparably large as the vibrational relaxation rate within S_1, which is seen in Table 1 of our previous paper.[21] In the figure and table, gradual decrease of k_1^{v} is seen as the excitation energy is increased, which is in conflict to the expectation that k_1^{v} may increase in the higher energy side due to the increase in the vibrational state density and the anharmonicity. It should be noted that k_1^{v} stands for the overall rate of the vibrational relaxation from the level i and contains the relaxation rates of various removed energy even though the effective energy loss ΔE has been evaluated to be 1200 cm^{-1}. The relaxation among the triplet levels both of which are located above the 0-0 of S_1 commences to occur increasingly as the excitation wavelength is increased from the 0-0 to the higher vibronic level of S_1. In that energy region, the non-radiative decay rate estimated from the slow fluorescence lifetime does not exhibit appreciable energy dependence. Thus it is suggested that the $k_i/k_1^{\mathrm{v}}(i \geqq 2)$ terms make non-negligible contributions to α in addition to k_1/k_1^{v} in Eq. 12. This results into the apparent decrease of k_1^{v} in the higher vibronic level excitation.

The Removed Energy by an Effective Collision. In Fig. 5, α and β/α values are plotted against the excitation energy. From that figure, the amount of the energy loss per an effective collision was evaluated to be ≈ 1200 cm^{-1}. The value is qualitatively in agreement with those of biacetyl in the triplet levels[23] and *p*-difluorobenzene in S_1.[24] This gives us the qualitative picture of the relaxation that the excited pyrazine molecule undergoes 3 or 4 effective collisions before it reaches the phosphorescence emitting level of T_1. To confirm the picture, it seems necessary to find a hot phosphorescence from the higher vibronic level of T_1 pyrazine.

Comparison of the Present Results with Those by Lahmani et al. In the work by Lahmani *et al.*,[15,16] A_f and A_{ph} ($=1/\alpha$) values have been evaluated by using

SF_6 as the collision partner. As to the former value, the present result is in good agreement with their result. However, with regard to the A_{ph}, our value exceeds several times that by Lahmani *et al.* This comes from the fact that the collision partner in the present work is isopentane instead of SF_6. In other words the rotational relaxation (or the relaxation of the small energy loss) is insensitive to the shape of the collision partner because the long range interaction governs the relaxation, which is reflected in the large value of k_q. Still, because the vibrational relaxation rate is of the order of the hard sphere collision, the intermolecular coupling that induces the relaxation of the large energy loss of $1200\,\text{cm}^{-1}$ is restricted to the shorter range one which is sensitive to the difference in the molecular shape.

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