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VIBRATIONAL RELAXATION IN THE LOWEST SINGLET EXCITED STATE OF PYRAZINE

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Collision-induced intramolecular vibrational energy transfer from selected vibronic levels of pyrazine was investigated in the lowest singlet excited state(B_{3u}, $n\pi^*$). In 0-0, $10a_0^1$, and $6a_0^1$ excitations it was found that ν_{16b}(234 cm^{-1} in S_1, b_{3u}) is the efficient energy accepting mode.

Vibrational relaxation in polyatomic molecules has been an important subject for understanding the dynamics of the collisional process. In contrast to many works$^{1)}$ in the ground electronic state, as to the V-V energy transfer in the excited electronic states, only few studies have been made for polyatomic molecules. Parmenter et al. and Rice et al. made precise investigations on the vibrational relaxation in S_1($\pi\pi^*$) state of benzene$^{2)}$ and aniline$^{4)}$, and found several interesting aspects of the energy flow, i.e. an enormously large value of the relaxation rate and the selective energy flow through ν_{16} mode. S_1 state of pyrazine is $n\pi^*$ in character. The absorption and fluorescence spectra have a well resolved fine structure and were analyzed completely$^{5)}$, so the molecule is suitable for the investigation of collision-induced intramolecular V-V energy flow from the selected vibronic levels.

The second harmonics of the dye laser(Rhodamine 640) pumped by a frequency doubled YAG laser(5 Hz, 10 ns) was used as an exciting light source with 0.1 nm band width(fwhm). The fluorescence spectra were measured by a Nikon P250 monochromator with 0.3 nm resolution. The fluorescence was detected by an HTV R562 photomultiplier and was averaged by a boxcar integrator(Brookdeal 9415 and 9425).

The V-V energy transfer rate was determined by the following experimental procedure. First, the fluorescence spectra of 2.5 Torr pyrazine from individual vibronic bands of S_1-S_0 absorption were measured. Then, the fluorescence spectra were recorded by adding isopentane as a collision partner to the sample. In the spectra with the foreign gas, the emission bands from vibrationally relaxed levels were observed. As isopentane pressure was increased, the intensity of the relaxed fluorescence was increased. From these experimental data, V-V energy transfer rate from a particular vibronic level to the other one was determined by a simple kinetic model.

Pyrazine(Pz) in S_1 state has two components of fluorescence, i.e. short-lived one($\tau_{f.1}$<1 ns) and long-lived one($\tau_{f.2}$~several hundred ns). At the pressure higher than 1 Torr, the long-lived component completely disappears through the process of collision-induced intersystem crossing(C.I.I.S.C.) and only the prompt component is seen in the fluorescence[7]. When isopentane(M) of 10 to 800 Torr is added to the Pz vapor(more than 1 Torr), only single collision is at most expected between Pz and M within the S_1 lifetime of Pz. Then, the kinetic scheme can be described analogously to that of ref. 2). Making several reasonable assumptions, the steady state treatment gives Eq. (1),

$$\frac{[Pz(S_1,i)]}{[Pz(S_1,j)]} = \frac{k_v(j) + k_e^{isc}(j)}{k_v(i-j)} + \frac{\tau_{f.1}^{-1}(j)}{k_v(i-j)} \times \frac{1}{[M]} \tag{1}$$

where $k_v(i-j)$ denotes the collision-induced V-V energy transfer rate from the i-th to the j-th vibrational level and $k_v(j)$ is the overall V-V transfer rate from the j-th level. $k_e^{isc}(j)$ is the C.I.I.S.C. rate of the short-lived component from the j-th level which is the missing term in ref. 2).

The level populations in Eq. (1) are connected with the fluorescence intensities by Eq. (2).

$$\frac{[Pz(S_1,i)]}{[Pz(S_1,j)]} = \frac{k_r(j)}{k_r(i)} \times \frac{I_f(i)}{I_f(j)} \tag{2}$$

Here $k_r(i)$ stands for the radiative rate of the i-th level and $I_f(i)$ represents the observed relative fluorescence intensity from the i-th level.

There has been no precise measurement on the fluorescence quantum yields($\Phi_{f.1}$) and lifetimes of individual vibronic bands of Pz S_1-S_0 absorption. According to the recent work by Yamazaki[8], at the zero point level $\tau_{f.1}$ and $\Phi_{f.1}$ is ca. 0.1 ns and 1.29×10^{-3}, respectively. And $\Phi_{f.1}$ decreases gradually in going from 0-0 to higher energy side, while $10a_0^1$ band shows remarkably large fluorescence yield. So, $k_r(i)$ were taken constant(1.29×10^7 sec^{-1}) over the individual vibronic bands except $10a_0^1$ and its combination band whose k_r values were taken as 2.4×10^7 sec^{-1}. This seems to be reasonable because ν_{10a} band has a different electronic character from other vibronic bands through the strong vibronic interaction between $S_1(n\pi^*)$ and $S_2(\pi\pi^*)$. Thus, the V-V energy transfer rate from the i-th to the j-th vibrational level($k_v(i-j)$) was experimentally determined by the use of Eqs. (1) and (2) combined with the above assumptions.

0-0 excitation; In the 0-0 excitation, the V-V energy flow is only endoenergetic and the evaluated $k_v(i-j)$ value should be corrected for the Boltzmann factor.

$$k_v(i-j) = k_v'(i-j) \times \exp(-\frac{\Delta E}{kT})$$

Here ΔE is the energy separation between two vibrational levels and k_v' is exactly proportional to the V-V transition probability. The energy flow map from the zero point level is shown in Fig. 2-(1). The k_v and k_v' values are tabulated in Table 1. One notices the se-

Fig. 1. Fluorescence spectra of $10a_0^1$ excitation. 2.5 Torr pyrazine (A) No added gas. (B) 810 Torr isopentane. Main bands and vibronic levels are assigned by ref. 5).

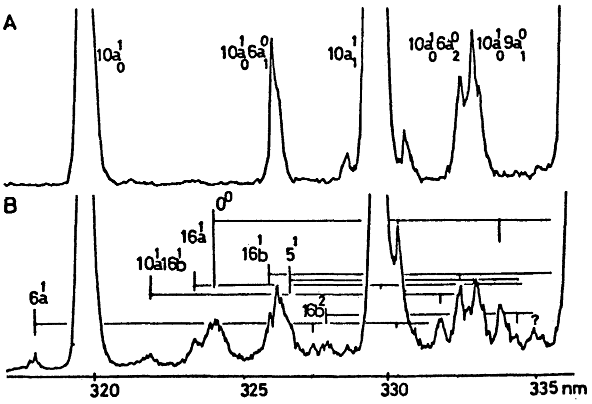
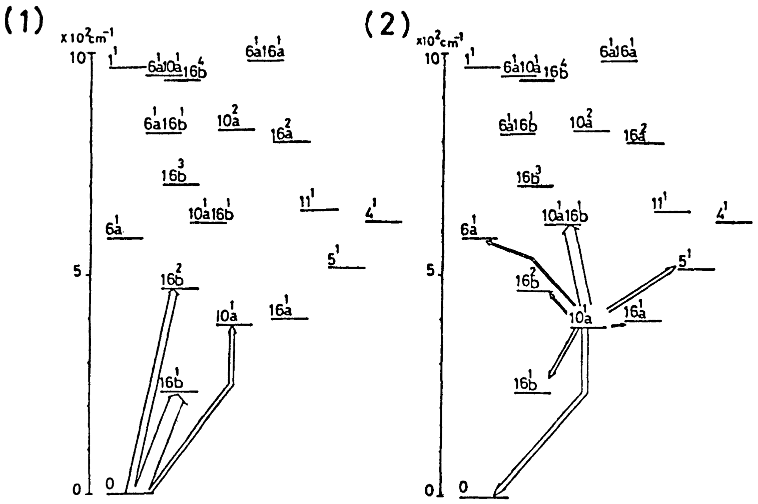


Fig. 2. Energy flow map. Energy flow from (1) zero point level, from (2) $10a^1$ level. The magnitude of the rate is shown by the width of arrow. The vibrational assignment is due to ref. 5) and two-photon result in ref. 6).



lective energy flow by ν_{16b} (234 cm^{-1}, b_{3u}) mode.

$10a^1_0$ excitation; The observed spectra and the energy flow map are illustrated in Fig. 1 and Fig. 2-(2), respectively. The observed V-V channels are $6a^1$, $10a^1 16b^1$, $16a^1$, 0-0, $16b^1$, $5^1$and $16b^2$. Especially the vibrational relaxation from $10a^1$ to $10a^1 16b^1$ is selectively efficient(Table 1). Even compared with the efficiencies of V-V transfer to isoenergetic levels such as $16a^1$ and $16b^2$, the efficiency of this path is much higher.

$6a^1_0$ excitation; In this case spectral congestion prevents us from analyzing quantitatively the result. However the V-V transfer from $6a^1$ to $6a^1 10a^1$ was found to be a dominant path.

Table 1. V-V energy transfer rate constant*

Final Level	ΔE(cm^{-1})	k_v(i-j)	k_v'(i-j)	k_v(i)	k_{sv}
0-0 excitation					
$16b^1$	234	8.9	27.		
$10a^1$	383	0.95	5.7		
$16b^2$	467	1.2	11.		
				11.	17.
$10a^1_0$ excitation					
0-0	-383	6.5	6.5		
$16b^1$	-149	3.5	3.5		
$16a^1$	16	1.9	2.0		
$16b^2$	84	1.7	2.5		
5^1	134	2.5	4.7		
$6a^1$	200	1.	2.5		
$10a^1 16b^1$	234	3.9	12.		
				21.	19.

* The rate constants are shown in $\times 10^6$ sec^{-1} $Torr^{-1}$ unit.

Total V-V transfer rate; total rates are also shown in Table 1. $k_v(i)(=\sum_j k_v(i-j))$ are nearly equal or somewhat smaller compared with k_{sv} obtained by the Stern-Volmer relationship, and the total rates are somewhat larger than the collision rate 1×10^7 sec^{-1} $Torr^{-1}$ given by the hard sphere approximation. It means that a single collision between excited Pz and isopentane induces V-V energy transfer.

Several tendencies are presented by the analysis of the result, and they are summarized as follows.

(1) In the excitations to the individual vibronic levels of S_1 pyrazine, ν_{16b} was found to be a dominant energy accepting vibration. The tendency is quite similar to those of benzene$^{2)}$ and aniline$^{4)}$.

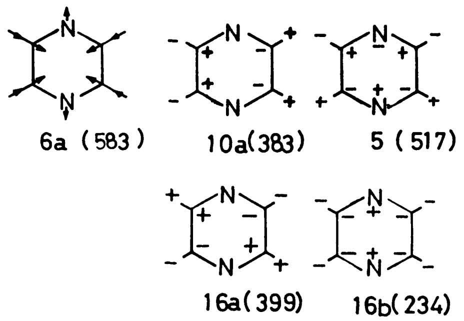


Fig. 3. Vibrational modes and their frequencies in S_1 state of pyrazine. Vibrational frequencies in S_1 are illustrated in cm^{-1} unit, in parentheses.

(2) The overall vibrational relaxation occurs even by a single collision, which is clearly seen in the large values of $k_v(i)$ or k_{sv}.

Several vibrational modes active in the pyrazine S_1-S_0 absorption are shown in Fig. 3. ν_{16b} is the out-of-plane ring bending vibration(b_{3u} symmetry) and this may imply that Pz-M interaction is stronger in face-to-face orientation than in head-to-head one. In order to understand the selectivity of ν_{16b} among other out-of-plane vibrations, the theoretical treatment applying long range Van der Waals interaction between Pz and M is now underway. As to the large values of $k_v(i)$ or k_{sv}, the electronic configuration in the excited state may induce strong interaction between excited Pz and M as indicated by Parmenter et al.$^{3)}$

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