Vibronic-Level Dependence of the Radiative Decay Rate in Pyrazine and Pyrimidine Vapors: Re-examination under High Spectral Resolution

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Synopsis. The radiative decay rate constants (k_F) for vibronic levels in S_1 of pyrazine and pyrimidine were derived by using the quantum yields measured under the conditions of SVL excitation. The vibronic level dependence of k_F in pyrazine can be explained by the Herzberg-Teller theory.

Pyrazine and pyrimidine are prototypes of intermediate-case molecules and their fluorescence emissions consist of two components, fast and slow fluorescence, in the vapor phase at low pressure. The vibronic coupling through the ν_{10a} vibration in the S_1 state of pyrazine was studied by Yamazaki *et al.*[1,2] From quantum yields and lifetimes measured for the fast fluorescence, they derived the radiative decay rate constants for individual vibronic levels, and compared these experimental decay constants with theoretical ones obtained on the basis of the Herzberg-Teller theory. They concluded that the theory overestimates the rate constants for levels involving the ν_{10a} vibration. However, their quantum yields were obtained with the spectral resolution ($\approx 20\,\mathrm{cm}^{-1}$) insufficient for exciting single vibronic levels (SVL) separately,[1] while their lifetimes were obtained with significantly higher resolution.[2] We have newly measured the SVL fluorescence quantum yields for pyrazine and pyrimidine in the vapor phase with narrow-band excitation ($\approx 0.5\,\mathrm{cm}^{-1}$) and re-examined the magnitude of the vibronic coupling in pyrazine. In this study we are solely concerned with the fast fluorescence; hereafter it will be simply called fluorescence.

Experimental

The apparatus and the method for optical measurements were the same as described previously;[3,4] the exciting laser pulse has a bandwidth of $\approx 0.5\,\mathrm{cm}^{-1}$. The sample vapors were at moderately high pressures (17.0 mTorr† pyrazine +12.2 Torr SF_6, and 156 mTorr pyrimidine+36 Torr SF_6), where the slow component is quenched completely and the fast is free from collision.[3] Since the excitation spectra were obtained by monitoring a part of the total fluorescence intensity, a correction was made so that the ratio of the actually monitored intensity to the total might be constant for all the bands studied.

Results and Discussion

Figure 1 shows absorption and fluorescence-excitation spectra for pyrazine. Owing to the high resolution, vibronic bands (*e.g.*, $10a_0^1$ and $6a_0^1 16b_1^1$) are well separated from one another and even their band contours are discernible to a certain extent. The relative fluorescence quantum yield for each SVL was obtained by comparing the integrated intensity of the band, related to the SVL, in the excitation spectrum with that of the corresponding absorption band. In either case the contribution of the underlying continuum due to the overlapping of the other bands was subtracted from the integrated intensity.

The SVL fluorescence quantum yields (Φ_F) of pyr-

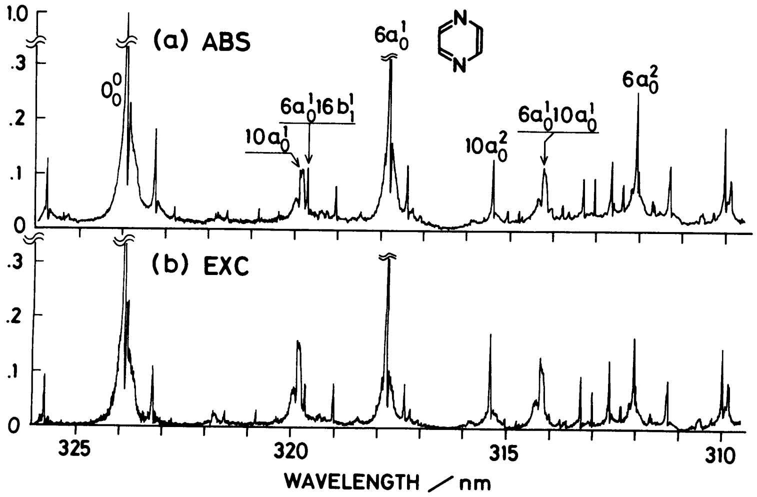

Fig. 1. Absorption spectrum (a) and fluorescence excitation spectrum (b) for pyrazine. In each spectrum, the peak height of the 0_0^0 band is normalized to unity. The peak heights of the $6a_0^1$ band in the absorption and excitation spectra are 0.74 and 0.50, respectively. The excitation spectrum has been corrected for the variation of the exciting laser intensity, but in this spectrum the correction described in the text has not been made.

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† 1 Torr≈133.322 Pa.

Table 1. Quantum yields, lifetimes and radiative rate constants

	Level	Φ_F	τ_F[b)]	k_F^{exp}[c)]	k_F^{theor}[d)]
		10^{-4}	ns	$10^6 s^{-1}$	$10^6 s^{-1}$
Pyrazine	0^0	1.4[a)]	0.12	1.2	1.2
	$10a^1$	3.3	0.15	2.2	2.0
	$6a^1$	1.5	0.11	1.4	1.2
	$10a^2$	3.4	0.16	2.2	2.8
	$6a^1 10a^1$	3.3	0.13	2.5	2.0
	$6a^2$	2.0	0.11	1.9	1.2
Pyrimidine	0^0	39[a)]	2.8	1.4	
	$6a^1$	18	2.0	0.90	
	$6b^2$	14	1.9	0.74	
	1^1	9.6	1.6	0.60	
	12^1	15	1.9	0.79	
	$6a^2$	9.7	1.3	0.75	
	$6a^1 12^1$	9.1	1.4	0.65	
	12^2	7.8	1.4	0.56	
	$6a^2 12^1$	9.1	1.4	0.65	

a) The absolute Φ_F value for the 0^0 level was determined by reference to the data in Ref. 3. b) The lifetimes for pyrazine were taken from Ref. 2, and those for pyrimidine were newly measured in this study with an excitation bandwidth of $\approx 0.5\ \mathrm{cm}^{-1}$. c) Experimentally obtained k_F. d) Theoretically obtained k_F; the relative values of k_F originally obtained from the theory were placed on an absolute scale by fitting $k_F^{\mathrm{theor}}(0^0)$ to $k_F^{\mathrm{exp}}(0^0)$.

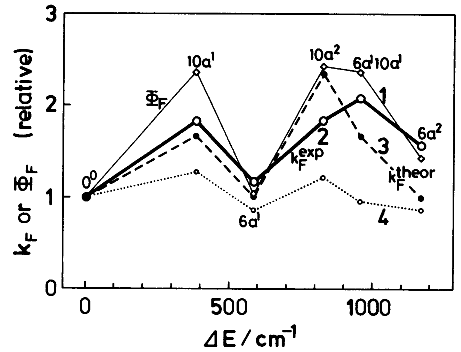

Fig. 2. Relative values for Φ_F and k_F plotted against ΔE for pyrazine: (1) Φ_F; (2) k_F^{exp}; (3) k_F^{theor}; (4) k_F, obtained in a low resolution experiment. Values in (1)—(3) were obtained in this study and those in (4) were taken from Ref. 2.

azine are given in Table 1, and a plot of Φ_F against the excess vibrational energy (ΔE) is shown in Fig. 2 by a lean solid line. The values of Φ_F for the levels involving $10a^j$ (Φ_F^j) are significantly larger than that for the 0^0 level (Φ_F^0), *i.e.*, $\Phi_F^j/\Phi_F^0 \gtrsim 2$ for $j \geq 1$. The ν_{10a} (b_{1g}) vibration can induce vibronic coupling between $S_1(^1B_{3u})$ and $S_2(^1B_{2u})$. Since the transition from S_0 to S_2 has a much larger oscillator strength, levels involving $10a^j$ will show larger radiative decay rate constants (k_F), and hence larger Φ_F values, than do the other vibronic levels. It is to be noted, however, that large Φ_F values may result not only from large k_F values but also from small total decay constants, as pointed out by Yamazaki *et al.*[2)]

The values of k_F were obtained by combining the values of Φ_F measured in the present study with the lifetimes (τ_F) reported by Yamazaki *et al.*[2)] (Table 1). As is shown in Fig. 2 with a thick solid line, the resulting k_F values vary with ΔE more widely than those obtained from the low resolution study[2)] (shown by a dotted line). The values of k_F, like those of Φ_F, are obviously large for the levels involving $10a^j$, *i.e.*, $k_F^j/k_F^0 \gtrsim 2$ for $j \geq 1$. This is a direct manifestation of the vibronic coupling through the ν_{10a} vibration.

We treat the vibronic-level dependence of k_F in pyrazine by means of the Herzberg-Teller theory[5)] assuming the harmonic oscillator approximation for the ν_{10a} vibration. Although ν_{10a} is known to be anharmonic,[6)] the anharmonicity is not large enough to produce a significant effect on the following discussion.[1)] The radiative decay rate constant for the $10a^j$ level relative to that for the zero-point level is given by[1)]

$$\frac{k_F^j}{k_F^0} = \frac{1+(\zeta/u)(2j+1)}{1+\zeta/u}, \tag{1}$$

where j is the quantum number of ν_{10a}, ζ the intensity ratio of the $10a_0^1$ absorption band to the 0_0^0, and u is a numerical factor equal to 0.346 in this case. Yamazaki *et al.*[1)] derived $\zeta=0.23$ for pyrazine from a high resolution spectrum. We obtained $\zeta=0.18$ by excluding the underlying continuum, although 0.23 was obtained by including it. The value of k_F calculated theoretically by using $\zeta=0.18$ is plotted against ΔE, with the result shown in Fig. 2 by a broken line (see also Table 1). It is seen that with respect to k_F the present experimental result agrees fairly well with what is predicted by the simple Herzberg-Teller theory.

For pyrimidine, the experimental k_F value, obtained in the same manner as k_F of pyrazine, was found to decrease roughly monotonically up to $\Delta E \approx 2500\ \mathrm{cm}^{-1}$ (Table 1), as in the case of the low resolution study, indicating that the vibronic levels in S_1 pyrimidine are not appreciably perturbed by vibronic coupling.

References

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