Electronic Relaxation Processes from Single Vibronic Levels in the $S_1(n, \pi^*)$ State of Pyridine Vapor

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The rate constants of radiative decay (k_F), internal conversion (k_{IC}), and intersystem crossing (k_{ISC}) for single vibronic levels in the $S_1(n, \pi^*)$ state of pyridine-d_0 and -d_5 vapors have been determined from measured fluorescence quantum yields (Φ_F), intersystem crossing quantum yields (Φ_{ISC}), and picosecond fluorescence lifetimes. The Φ_{ISC} values are fairly constant in the region of lower excess vibrational energy (<1000 cm^{-1}), while the Φ_F values are particularly large for vibronic levels involving non-totally symmetric vibrations, ν_{16b} and ν_{10a}. The latter observation is attributed to both an increase of k_F and a decrease of k_{IC} and k_{ISC} (relative to the zero-point level) for the ν_{16b} levels ($16b^2$ and $16b^2 6a^1$), and to an increase of k_F for the ν_{10a} levels. The relative values of k_F are discussed using the Herzberg-Teller theory of vibronic coupling. The values of k_F for $16b^1$ and $16b^2$ are significantly larger than that for the zero-point level, though no absorption band corresponding to $16b_0^1$ can be observed. In both pyridine-d_0 and -d_5, the value of k_{IC} is as large as 1.7×10^{10} s^{-1} even for the zero-point level, which is more than twice the k_{ISC} value for the same level.

In previous papers,[1] we reported the results of experimental studies on the excitation-energy dependence of nonradiative electronic relaxation in pyridine vapor. It was shown that the fluorescence quantum yield of pyridine is almost constant in the neighborhood of the zero-point vibrational level of the $S_1(n, \pi^*)$ state and decreases rapidly as the vibrational energy in excess of the zero-point energy, ΔE, becomes higher than 800 cm^{-1}. This observation was interpreted as due to an increase in rate of the internal conversion $S_1 \rightsquigarrow S_0$. In these studies, however, on account of the extreme weakness of the fluorescence of pyridine, the bandwidth of the exciting light employed was so great (>100 cm^{-1}) that the individual vibronic bands could hardly be resolved.

In the present study, we have re-examined the fluorescence and intersystem-crossing quantum yields of pyridine-d_0 and -d_5 with a small excitation bandwidth of ≈ 1 cm^{-1}, using a high-resolution laser spectrophotometric system. The resulting data, along with the picosecond fluorescence lifetimes obtained using a mode-locked dye laser, have made it possible to determine precisely the rate constants for the radiative and nonradiative processes that start from single vibronic levels in the S_1 state of pyridine-d_0 and -d_5. In the absorption spectrum of pyridine, the long-wavelength tail of the $S_2 \leftarrow S_0$ absorption has a significant intensity in the $S_1 \leftarrow S_0$ absorption region. The present paper is concerned with a region of ΔE lower than 1600 cm^{-1} where the contribution of $S_2 \leftarrow S_0$ absorption is relatively small.

The vibrational analyses of the $S_1 \leftarrow S_0$ absorption spectra of pyridine-d_0 and -d_5 were made, respectively, by Sponer and Stücklen[2] and Shukla *et al.*[3] More recently, Mochizuki *et al.*[4] analyzed vibronic bands of the pyridines, and showed that the $\nu_{10a}(a_2)$ vibration induces a vibronic interaction between $S_1(^1B_1)$ and $S_2(^1B_2)$ states. The band at $\nu_{0-0}+139$ cm^{-1} of pyridine-d_0 was assigned by Jesson *et al.*[5] to an overtone of the $16b(b_1)$ mode with two quanta, *i.e.* $16b_0^2$. (Jesson *et al.* adopted a wavenumber of 138 cm^{-1} instead of 139 cm^{-1}). Mochizuki *et al.*[6] had a doubt about this assignment, because they could not observe any progression involving the ν_{16b} vibration in their single vibronic level (SVL) fluorescence spectrum from the $16b^2$ level. In the present study, attention was directed to the role of these non-totally symmetric vibrations in the electronic relaxation processes in pyridine.

Experimental

Pyridine-d_0 (Merck, Uvasol) was allowed to stand over potassium hydroxide for a few days, and was fractionally distilled under a stream of nitrogen. Pyridine-d_5 (Aldrich, Spectrograde) and biacetyl (Nakarai Chemicals, G. R.) were purified by repeated distillation under reduced pressure. Sulfur hexafluoride (SF_6, Seitetsu Chemicals, 99.65%) was used as an inert foreign gas without further purification.

Absorption spectra and excitation spectra of fluorescence or sensitized phosphorescence were measured simultaneously at room temperature with a high-resolution laser spectrophotometric system, the details of which were described in previous papers.[7] In this system, a pulsed dye laser (Molectron DL14) pumped by a nitrogen laser (Molectron UV22) is used as a light source. The dye laser is operated by the use of a mixture of Coumarin 495 and Rhodamine 6G, and the frequency is doubled by a KDP crystal to generate UV laser pulses with a repetition rate of 20 pulses/s, a spectral bandwidth of about 0.5 cm^{-1}, and a pulse duration of 3 ns. A somewhat wide spacing was taken between the successive wavelengths of the laser light, so that the overall resolution was about 1 cm^{-1} for both absorption and excitation spectra. All the emission measurements were made by the use of 35 mm square quartz cells.

For obtaining the fluorescence quantum yield (Φ_F), the fluorescence spectrum was measured and corrected for the spectral sensitivity of the emission monochromator-photomultiplier system. The absolute Φ_F value of pyridine-d_0 or -d_5 was determined for excitation at the 0–0 band of the $S_1 \leftarrow S_0$ absorption by comparing the corrected fluorescence spectrum of the pyridine with that of quinine sulfate in (1/2) M sulfuric acid (1 M=1 mol dm^{-3}), which has a Φ_F value of 0.51.[8]

The intersystem-crossing quantum yields (Φ_{ISC}) of the pyridines were determined by means of the sensitized-biacetyl-phosphorescence method based on T–T energy transfer.[9] To a mixture of 0.5 Torr (1 Torr=133 Pa) of pyridine-d_0 or -d_5 (donor) with 0.5 Torr of biacetyl (acceptor) was added 160

Torr of SF_6. Under such high pressure conditions, the energy transfer takes place from the thermally equilibrated T_1 levels of the donor to the isoenergetic triplet levels of the acceptor, irrespective of the initially excited singlet level of the donor. The energy transfer is followed by rapid vibrational relaxation into the thermally equilibrated triplet of biacetyl, from which the biacetyl phosphorescence is emitted. The intensity of the sensitized biacetyl phosphorescence (I_p) was measured following excitation of the donor at 0–0 band of its $S_1 \leftarrow S_0$ absorption. On the other hand, for a mixture composed of 0.5 Torr of biacetyl and 160 Torr of SF_6, the intensity of biacetyl phosphorescence ($I_p{}^0$) was measured by exciting biacetyl at 453 nm, *i.e.*, at the 0–0 band of its $S_1 \leftarrow S_0$ absorption. The Φ_{ISC} value of biacetyl is known to be unity when excitation is made at long wavelengths including 453 nm.[10] The Φ_{ISC} value of the donor can then be obtained by comparing I_p with $I_p{}^0$ after the usual corrections are made.

The pressure of the pyridines was determined from the absorption intensity, while that of biacetyl was determined by measuring the intensity of its phosphorescence excited at 453 nm; biacetyl vapor is known to give a definite phosphorescence quantum yield when it is excited at this wavelength and at a pressure higher than 1 Torr.[10]

For measuring the excitation spectra, the fluorescence was monitored through filters, UV-D35 (Toshiba) and 2,6-lutidine (25% by volume) in hexane, and the sensitized phosphorescence was monitored through a cut filter, VY-45 (Toshiba). The excitation spectra were corrected for the spectral intensity distribution of the exciting laser light and for the inner filter effect. Relative values of Φ_F and Φ_{ISC} at various excitation positions were obtained by taking the ratios of the intensities of the corrected excitation spectra to the intensities of the corresponding absorption spectra. By combining the resulting relative yields with the absolute quantum yield which had been determined, as mentioned earlier, at a particular excitation position for the fluorescence or sensitized phosphorescence, the absolute values of Φ_F and Φ_{ISC} were obtained as a function of excitation energy for pyridine-d_0 and -d_5.

The fluorescence lifetimes (τ_F) of pyridine-d_0 and -d_5 were obtained by using a synchronously-pumped, mode-locked dye laser[11] as an exciting light source. The details of the experiments have been reported elsewhere.[12]

Results

Figures 1(a) and 2(a) show, respectively, the $S_1 \leftarrow S_0$ absorption spectra of pyridine-d_0 and -d_5 in the vapor phase. Band assignments are given in the figures and also in Table 1, where FR means Fermi resonance. These assignments are the ones made by Mochizuki *et al.*[4] except for the bands involving the ν_{16b} vibration, the assignments of which are taken from a paper by Jesson *et al.*[5]

The spectrum of pyridine-d_0 consists mainly of bands that correspond to fundamentals, overtones, or combinations of two totally symmetric vibrations $\nu_{6a}(a_1)$ and $\nu_{12}(a_1)$, which in the excited state S_1 have frequencies of 542 cm^{-1} (ν_{6a}') and 995 cm^{-1} (ν_{12}'). The progression $6a_0^n$, starting with the 0–0 band ($n=0$), is seen to be most prominent. Note that the 0–0 band is located at 34769 cm^{-1}. Some other bands are observed which

Table 1. Quantum yields, lifetimes, and radiative and nonradiative rate constants for pyridine-d_0 and -d_5 vapors

Compound	Vibronic level[a)]	$\Delta E^{b)}$ / cm^{-1}	Φ_F / 10^{-5}	Φ_{ISC}	τ_F / ps	k_F / 10^6 s^{-1}	k_{IC} / 10^{10} s^{-1}	k_{ISC} / 10^{10} s^{-1}
Pyridine-d_0	0	0	5.9	0.30	42	1.40	1.67	0.71
	$16b^1$	59[c)]	9.4	0.22	41	2.29	1.91	0.53
	$16b^2$	139	11.9	0.28	60	1.98	1.20	0.47
	$16b^3$	237[c)]	10.6	0.24				
	$10a^1$	331	8.3	0.24	34	2.44	2.23	0.71
	$16b^4$	347[c)]	10.9	0.26				
	$16b^5$	464[c)]	8.4	0.30				
	$6a^1$	542	7.0	0.30	42	1.67	1.67	0.71
	$16b^26a^1$	681	12.8	0.27	54	2.37	1.36	0.49
	$10a^16a^1$	864	6.3	0.15	35	1.80	2.43	0.43
	12^1	995	7.0	0.23	35	2.00	2.21	0.65
	$6a^2$	1084	6.3	0.20	38	1.66	2.10	0.53
	$10a^16a^2$	1406	3.0	0.08	30	1.00	3.07	0.27
	12^16a^1	1537	2.7	0.06	28	0.96	3.36	0.21
	$6a^3$	1626	0.9	0.03				
Pyridine-d_5	0	0	6.0	0.30	42	1.43	1.66	0.72
	$16b^2$	118	12.0	0.31	50	2.40	1.38	0.62
	$10a^1$	253	8.2	0.28	40	2.05	1.80	0.70
	FR ($6a^1$	510	10.0	0.30	34	2.94	2.06	0.88
	$10a^2$)	560	9.7	0.29	45	2.16	1.57	0.65
	12^1	954	7.7	0.23	30	2.57	2.56	0.77
	FR ($6a^2$	1075	6.2	0.15				
	$16b^212^1$)	1082	2.5	0.07				
	FR ($10a^212^1$	1465	11.0	0.13	34	3.24	2.56	0.38
	$6a^112^1$)	1516	6.1	0.10				

a) See Figs. 1 and 2 for the absorption transitions which lead to the vibronic levels in this column. The 0–0 band for pyridine-d_0 is located at 34769 cm^{-1} and that for pyridine-d_5 at 34950 cm^{-1}. b) From Ref. 4 except for c). c) From Ref. 5.

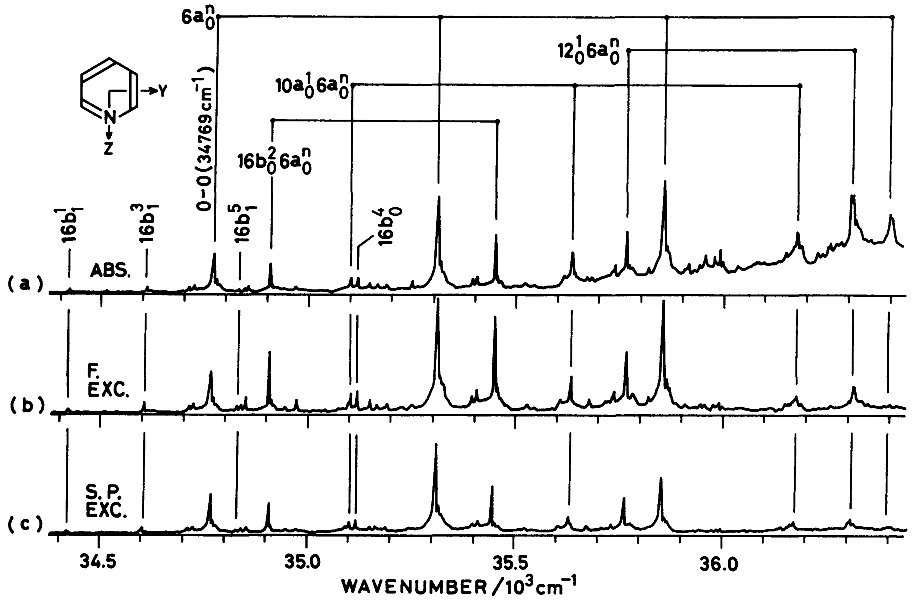

Fig. 1. (a) Absorption spectrum, (b) fluorescence excitation spectrum, and (c) sensitized biacetyl phosphorescence excitation spectrum for pyridine-d_0 vapor. The pressures of pyridine-d_0: (a) 5.4, (b) 0.5, and (c) 1.0 Torr. In the case of (c), 0.8 Torr of biacetyl and 160 Torr of SF_6 are added to the pyridine-d_0 vapor. In the notation of vibronic transitions, the superscript and subscript denote the vibrational quantum numbers in the S_1 and S_0 states, respectively.

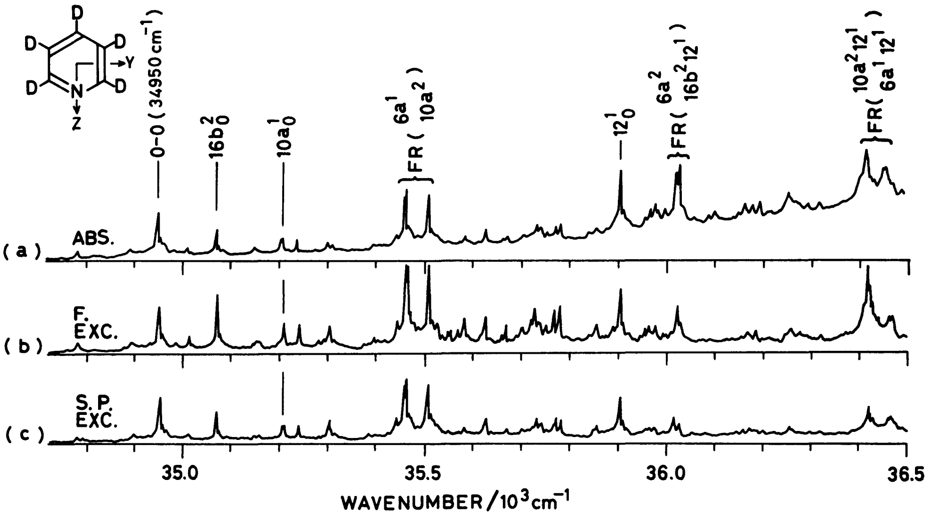

Fig. 2. (a) Absorption spectrum, (b) fluorescence excitation spectrum, and (c) sensitized biacetyl phosphorescence excitation spectrum for pyridine-d_5 vapor. The pressures of pyridine-d_5: (a) 7.6, (b) 1.8, and (c) 0.8 Torr. In the case of (c), 1.1 Torr of biacetyl and 160 Torr of SF_6 are added to the pyridine-d_5 vapor. In the notation of vibronic transitions, the superscript and subscript denote the vibrational quantum numbers in the S_1 and S_0 states, respectively.

involve non-totally symmetric vibrations, $\nu_{16b}(b_1)$ and $\nu_{10a}(a_2)$. Thus the bands at $\nu_{0-0}+139$ cm^{-1} and $\nu_{0-0}+331$ cm^{-1} can be assigned to $16b_0^2$ and $10a_0^1$, respectively. The combination band $16b_0^2 6a_0^1$ and weak hot bands $16b_1^n$ ($n=1$, 3, 5) also appear in the spectrum. A progression in ν_{6a}', denoted by $10a_0^1 6a_0^n$ in the figure, starts with the $10a_0^1$ band. On the other hand, the absorption spectrum of pyridine-d_5 does not show any regular progressions of bands. This is due mainly to the occurrence of Fermi resonance, as is seen in Fig. 2(a). The 0-0 band is located at 34950 cm^{-1} in this case.

Figures 1(b) and 1(c) show the excitation spectra of the fluorescence and sensitized biacetyl phosphorescence for pyridine-d_0, and Figs. 2(b) and 2(c) the same spectra for pyridine-d_5. Band positions in these excitation spectra agree very well with those in the corresponding absorption spectra, indicating that the observed fluorescence and sensitized phosphorescence originate from pyridine-d_0 or -d_5 itself. It was confirmed that no change in shape of the fluorescence excitation spectra occurs upon adding the foreign gas, SF_6, up to 160 Torr. In Figs. 1 and 2, it can be seen at a glance that, so far as the lower excitation energy region is concerned, the sensitized phosphorescence excitation spectrum is similar to the absorption spectrum, but that the fluorescence excitation spectrum is substantially different from the absorption spectrum in intensity distribution. In fact, in the fluorescence excitation spectra of pyridine-d_0 and -d_5, some bands which involve the ν_{16b} mode have particularly high intensities.

The values of fluorescence quantum yields (Φ_F) and of the intersystem-crossing quantum yields (Φ_{ISC}) from various vibronic levels are shown in Table 1, and the excess vibrational energy (ΔE) dependence of Φ_F and Φ_{ISC} is illustrated in Figs. 3 and 4. These yield values were determined according to the method described in the preceding section. As is seen in Figs. 1 and 2, each of the bands is characterized by a peak. However, the peak is accompanied by a background which is due to superposition of the rotational contours of neighboring bands and, at higher frequencies, also to overlap of the tail of the $S_2 \leftarrow S_0$ absorption. In the evaluation of Φ_F and Φ_{ISC}, therefore, care was taken to eliminate the contribution of the background to the spectral intensity.[13] It is seen from Figs. 1—4 that the values of Φ_F are significantly large for levels involving the ν_{16b} mode, *i.e.*, $16b^2$ and $16b^2 6a^1$ of pyridine-d_0 and $16b^2$ of pyridine-d_5. The value of Φ_F for the $10a^1$ level is about 1.4 times that for the zero-point level in both molecules. In pyridine-d_0, Φ_F rapidly decreases as ΔE exceeds about 1100 cm^{-1}. In pyridine-d_5, the values of Φ_F for the Fermi resonance levels are larger than that for the zero-point level except for the level at 1082 cm^{-1}. On the other hand, the values of Φ_{ISC} for both pyridine-d_0 and -d_5 are fairly constant regardless of the nature of the vibronic level in the lower ΔE region (<1000 cm^{-1}). In the case of pyridine-d_0, Φ_{ISC} is found to decrease rapidly in the higher ΔE region.

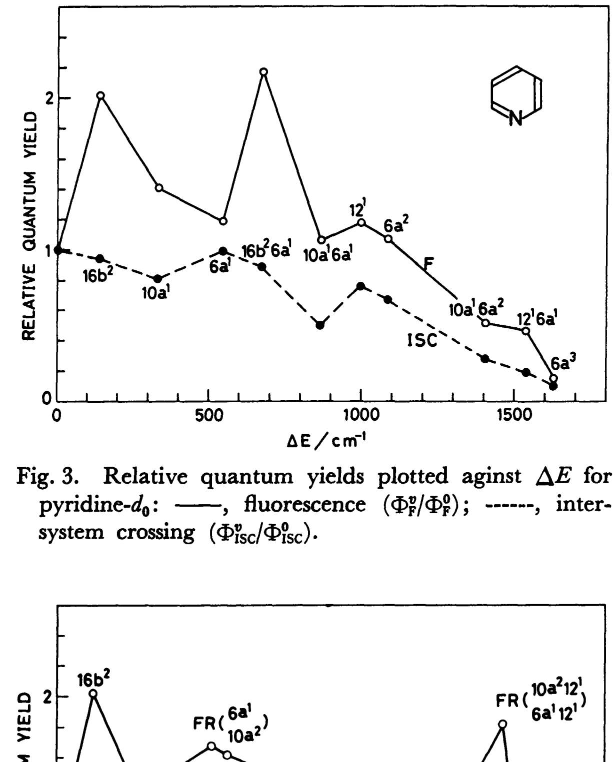

Fig. 3. Relative quantum yields plotted aginst ΔE for pyridine-d_0: ——, fluorescence (Φ_F^v/Φ_F^0); ------, intersystem crossing ($\Phi_{ISC}^v/\Phi_{ISC}^0$).

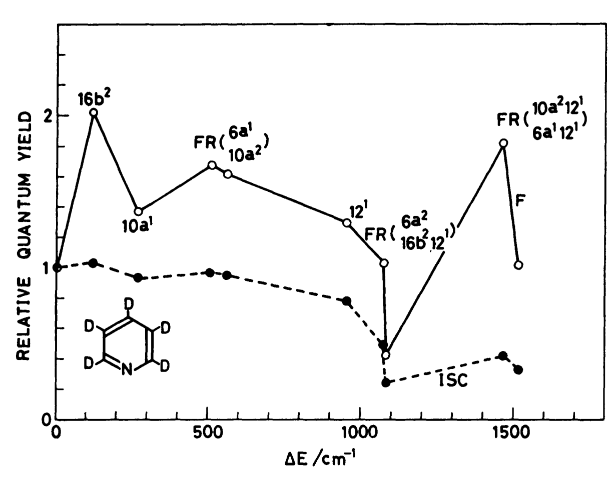

Fig. 4. Relative quantum yields plotted against ΔE for pyridine-d_5: ——, fluorescence (Φ_F^v/Φ_F^0); ------, intersystem crossing ($\Phi_{ISC}^v/\Phi_{ISC}^0$).

The observed fluorescence lifetimes (τ_F) of pyridine-d_0 and -d_5 are summarized in Table 1. When ΔE increases, τ_F does not decrease monotonously, but varies in a characteristic way. The lifetimes for $16b^2$ and $16b^2 6a^1$ levels are seen to be notably long.

Discussion

Since pyridine is considered to belong to the statistical limit rather than to the intermediate case,[1,12] the experimental results described in the preceding section can be analyzed on the basis of a simple kinetic scheme. Suppose that the pyridine molecule is excited into a vibronic level v in the S_1 state. The molecule will then relax through radiative and nonradiative decay processes. The rate constant for the radiative fluorescence decay is denoted by k_F^v, and those for the $S_1 \rightsquigarrow S_0$ internal conversion and the $S_1 \rightsquigarrow T$ intersystem crossing are denoted by k_{IC}^v and k_{ISC}^v, respectively. So far as lower excitation energies are concerned, nonradiative processes other than the latter two processes may safely be neglected in the case of pyridine, because the quantum yield of the photochemical reaction in pyridine vapor is known to be negligibly low, as was described in a previous paper.[1] The quantum yield of the fluorescence (Φ_F^v) and that of the intersystem crossing (Φ_{ISC}^v) from a vibronic level v can thus be expressed as $\Phi_F^v = k_F^v/(k_F^v + k_{IC}^v + k_{ISC}^v)$ and $\Phi_{ISC}^v = k_{ISC}^v/(k_F^v + k_{IC}^v + k_{ISC}^v)$. The radiative rate constant k_F^v is given by

$$k_F^v = \Phi_F^v/\tau_F^v, \qquad (1)$$

where τ_F^v represents the lifetime of the fluorescence from v. The nonradiative rate constants can be written as

$$k_{IC}^v = k_F^v(1 - \Phi_F^v - \Phi_{ISC}^v)/\Phi_F^v, \qquad (2)$$

$$k_{ISC}^v = k_F^v \Phi_{ISC}^v/\Phi_F^v. \qquad (3)$$

On the basis of Eqs. 1—3, the rate constants k_F^v, k_{IC}^v, and k_{ISC}^v were determined from the experimental values of τ_F^v, Φ_F^v, and Φ_{ISC}^v, with the results summarized in Table 1. The relative values of the rate constants, k_F^v/k_F^0, k_{IC}^v/k_{IC}^0, and k_{ISC}^v/k_{ISC}^0, are shown in Figs. 5 and 6, the values for the zero-point level ($v=0$) being normalized to unity.

An increase of the quantum yield of fluorescence from an excited vibronic level will result, in general, from an increase of the radiative rate and/or a decrease of the nonradiative rate. We first consider pyridine-d_0. For

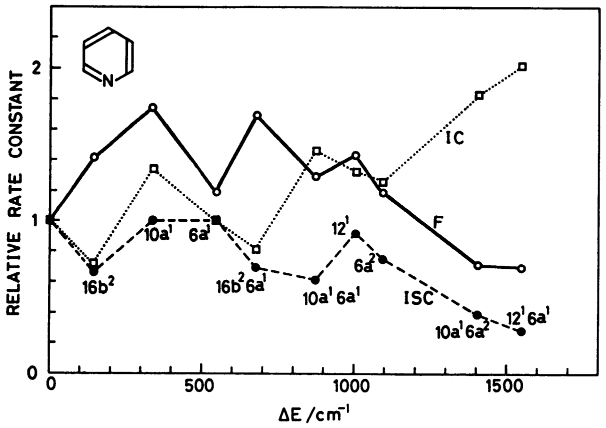

Fig. 5. Relative rate constants plotted against ΔE for pyridine-d_0: ——, k_F^v/k_F^0; ······, k_{IC}^v/k_{IC}^0; ------, k_{ISC}^v/k_{ISC}^0.

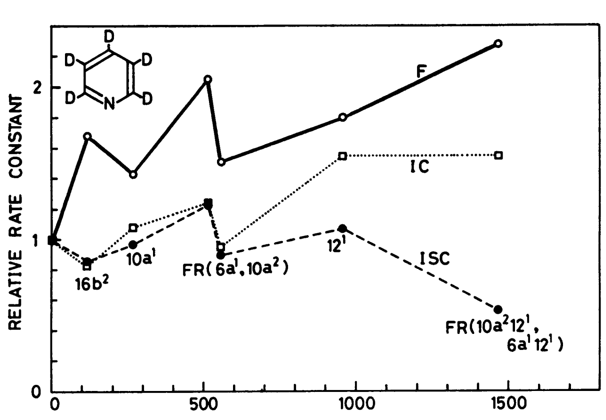

Fig. 6. Relative rate constants plotted against ΔE for pyridine-d_5: ——, k_F^v/k_F^0; ······, k_{IC}^v/k_{IC}^0; ------, k_{ISC}^v/k_{ISC}^0.

its 16b² level, k_F^v is 1.41 times as large as k_F^0, while the values of k_{IC}^v and k_{ISC}^v are about 70% of the values of k_{IC}^0 and k_{ISC}^0. These relations existing among the rate constants account for the finding that Φ_F^v is particularly large for the 16b² level ($\Phi_F^v/\Phi_F^0=2.02$). The 16b²6a¹ level is in a similar situation, as is seen from Table 1 and Fig. 5. For the 10a¹ level, Φ_F^v is significantly larger than Φ_F^0, *i.e.*, $\Phi_F^v/\Phi_F^0=1.41$. This observation is interpreted as due solely to the fact k_F^v/k_F^0 is as large as 1.74. Note that in this case k_{IC}^v/k_{IC}^0 and k_{ISC}^v/k_{ISC}^0 are greater than or equal to unity. Inspection of the kinetic data given in Table 1 will reveal that the relatively high values of Φ_F for the 16b² and 10a¹ levels of pyridine-d_5 be explained in essentially the same manner as the corresponding values of pyridine-d_0.

Since the $S_1(^1B_1)$ state of the pyridine molecule is of an (n, π^*) type, the rate of the radiative decay from S_1 may be noticeably enhanced by the vibronic interaction. Let us first discuss vibronic levels involving the ν_{10a} vibration after the method adopted by Yamazaki, Fujita, and Baba[14] in their discussion about the radiative rate constant of the fluorescence of pyrazine. According to these authors, the ratio of the radiative rate constant for the $10a^j$ level to that for the zero-point level, *i.e.*, $k_F(10a^j)/k_F^0$ is given by

$$\frac{k_F(10a^j)}{k_F^0}=\frac{1+(\zeta/u)(2j+1)}{1+\zeta/u}, \tag{4}$$

where ζ is the ratio of the intensity of the $10a_0^1$ absorption band to that of the 0–0 absorption, and u is a numerical factor introduced to allow for the difference between ν_{10a}' and ν_{10a}'', which denote the frequencies of ν_{10a} in S_1 and S_0, respectively. Equation 4 is based on the Herzberg-Teller theory of vibronic coupling. From the integrated intensities for the rotational contours of the $10a_0^1$ and 0–0 absorption bands, ζ is determined to be 0.28 for pyridine-d_0 and 0.24 for pyridine-d_5. There is a great difference between ν_{10a}' and ν_{10a}''. In fact, $\nu_{10a}'=331\ \text{cm}^{-1}$ and $\nu_{10a}''=886\ \text{cm}^{-1}$ for pyridine-d_0, while $\nu_{10a}'=253\ \text{cm}^{-1}$ and $\nu_{10a}''=690\ \text{cm}^{-1}$ for pyridine-d_5. By the use of these frequency values, the numerical factor u is calculated to be 0.30 for pyridine-d_0 and 0.29 for pyridine-d_5. These data lead to the results that $k_F(10a^1)/k_F^0=1.97$ and 1.91 for pyridine-d_0 and -d_5, respectively. The corresponding experimental values are 1.74 and 1.43, so that in either case the calculated value is higher than the experimental. However, in view of the fact that no allowance has been made for the mixing of vibrational modes due to the Duschinskii effect, which is likely to occur between ν_{10a} and ν_{16a} in pyridine,[6] as well as for the anharmonicity of the ν_{10a} vibration,[4] it may be said that the theoretical results obtained from Eq. 4 account, to a good extent, for the experimental data on the radiative rate constants.

As is seen in Table 1, the ν_{16b} vibration, the out-of-plane "boat" vibration, seems to have an effect on k_F which is similar to the one observed for the ν_{10a} vibration. In the case of ν_{16b}, however, if an equation analogous to Eq. 4 is used, $k_F(16b^j)/k_F^0$ is estimated to be unity regardless of j. The reason for this is that the ratio ζ between the intensities of $16b_0^1$ and 0–0 absorption bands is zero, because no absorption band can be observed which is to be assigned to $16b_0^1$. In contrast to the above theoretical estimation, the experimental values of k_F for both 16b¹ and 16b² levels are significantly larger than k_F^0, as is seen from Table 1.

Mochizuki *et al.*[6] recently reported that the SVL fluorescence spectrum from "the 16b² level" of pyridine-d_0 or -d_5 is essentially the same as the corresponding fluorescence spectrum from the zero-point level except for a relative shift by 139 cm⁻¹ in pyridine-d_0 and by 118 cm⁻¹ in pyridine-d_5, and that no fluorescence band is observed which is to be related to the ν_{16b} vibration. Accordingly, they pointed out that one cannot decide whether the absorption band at $\nu_{0-0}+139\ \text{cm}^{-1}$ (or $\nu_{0-0}+118\ \text{cm}^{-1}$) should be assigned as a cold band like $16b_0^2$ or as a hot band of an unknown vibration. In a later report, on the basis of the absorption spectrum measured in a supersonic cold beam, these authors showed that the band in question must be regarded as a cold one.[15] To sum up it may be said that the assignments involving the ν_{16b} vibration, given by Jesson *et al.*[5] for some absorption bands at lower frequencies of pyridine-d_0 and -d_5, are considered to be reasonable, but that the spectral or kinetic properties associated with these bands appear to be unusual.

Another point to be noted is that the values of k_F for some vibronic levels involving totally symmetric vibrations 6a and 12 are observed to be larger than k_F^0. At present, we are not in a position to give an adequate explanation for the above observation. It is possible, however, that a higher energy singlet state having the same symmetry as S_1 may be vibronically coupled to S_1 through mode 6a or 12 to enhance the rate of the radiative decay from the vibronic levels in question.

The Φ_{ISC} value of pyridine vapor is obviously smaller than unity even for the zero-point level and decreases with increasing ΔE, in marked contrast to pyrazine and pyrimidine vapors whose Φ_{ISC} values are known to be close to unity over a wide range of ΔE.[14] This is due to the fact that in pyridine k_{IC} is more than twice as large as k_{ISC} even at the zero-point level, whereas in pyrazine and pyrimidine k_{IC} is much smaller than k_{ISC}. The anomalously large k_{IC} value in pyridine, which is responsible for the extreme weakness of its fluorescence, suggests that there should be a strong vibronic coupling between $S_1(n, \pi^*)$ and S_0. The detailed mechanism of such a coupling, however, remains· to be elucidated.

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