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Internal conversion and intersystem crossing in fluoropyridine vapors

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ABSTRACT

Fluorescence, fluorescence excitation, biacetyl-sensitized phosphorescence excitation and absorption spectra of three fluoropyridines (2-fluoropyridine, 6-fluoropyridine and 2,6-difluoropyridine) have been measured in the vapor phase. The quantum yields of the $S_1 \rightarrow T_1$ intersystem crossing of these fluoropyridines have been determined by means of a sensitized biacetyl phosphorescence method based on intermolecular T–T energy transfer. It is shown that the main nonradiative process in these fluoropyridines is the internal conversion $S_1 \rightarrow S_0$, which may include possible photochemical decomposition processes. It is shown that the internal conversion rates increase almost exponentially with increasing excitation energy, while the increase of the $S_1 \rightarrow T_1$ intersystem crossing rates is not significant.

1. Introduction

Pyridine is known as a prototype of heterocyclic molecules, the S_1 state of which has been assigned as (n,π^*) in nature [1]. It was reported that pyridine and methyl-substituted pyridines also exhibit extremely weak emission in the vapor phase, which have been assigned to the $^1(n,\pi^*)$ fluorescence [2–4]. Although the S_1 state of pyridine is of (n,π^*) type, the nature of the S_1 state is known to change depending on the substitution position on the ring and substituted group. The S_1 state of some of fluorine substituted pyridines has been assigned as (π,π^*) in nature.

In a previous paper, it was shown that 2- and 3-fluoropyridine (2- and 3-FP, respectively) exhibit weak fluorescence from S_1 [5]. The fluorescence quantum yields were shown to decrease significantly with increasing the excitation energy. This observation indicates that the nonradiative rate constant from S_1 increases as the excitation energy increases. However, it is not clear whether the main nonradiative process from S_1 is the internal conversion or intersystem crossing. In order to obtain a deeper insight into the nonradiative processes of fluorine-substituted pyridines, it must be of importance to determine the intersystem crossing quantum yields of fluoropyridines.

In the present work, the fluorescence, fluorescence excitation and absorption spectra of 2- and 3-FP and 2,6-difluoropyridine (2,6-DFP) vapors have been measured, along with the excitation spectra of the biacetyl-phosphorescence sensitized by energy transfer from triplet fluoropyridines. The intersystem crossing quantum yields of these molecules have been determined by means of a sensitized biacetyl phosphorescence method based on the intermolecular T–T energy transfer. The main nonradiative process from S_1 is shown to the internal conversion to S_0, which may include possible photochemical decomposition processes. The $S_1 \rightarrow S_0$ internal conversion and $S_1 \rightarrow T_1$ intersystem crossing rate constants were evaluated as a function of excitation energy for these fluoropyridines.

2. Experimental

2- and 3-FP and 2,6-DFP obtained from Tokyo Chemical Industries, Japan (TCI) were purified by means of trap-to-trap distillation under vacuum. Diacetyl obtained from TCI was used as a sensitizer. The samples were degassed by repeating freeze–thaw cycles in an all-glass made vacuum system equipped with a diffusion pump. The pressures of the sample vapors were always kept blow the saturation pressures at the temperatures employed in the present study. We have first determined the vapor pressures of the fluoropyridines and biacetyl at different temperatures by measuring the absorption intensities. The used optical cell possesses two side arm reservoirs for storing one of fluoropyridines and biacetyl separately. The pressure of fluoropyridines and biacetyl were then determined by the temperature of the side arm reservoirs. The sample cell containing fluoropyridine and biacetyl vapors was then isolated from the reservoirs, the contents were trapped by liquid nitrogen, and the cell was sealed off. By measuring the optical densities of fluoropyridine and biacetyl vapors in the cell, we determined the pressures below the saturation pressure. In this way, biacetyl pressure was changed from 10 to 100 Torr with keeping the pressure of 2- or 3-FP vapor almost constant. Details of the sample preparation are described in a foregoing paper [6]. During the measurement, temperature of the sample cell was controlled by a thermostated cell holder. For most of the emission measurement square 10-mm path length quartz cells were used.

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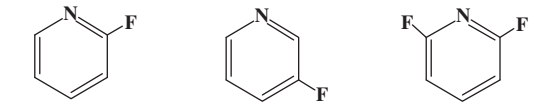

Absorption spectra were measured with a Shimadzu UV-2550 spectrophotometer and the emission and excitation spectra were measured with a Spex Fluorolog-3 (Model 21-SS) spectro photometer. The latter photometer, designed especially for the measurements of weak emission signals, is equipped with a double-grating excitation monochromator, a high-pressure 450-W Xenon lamp as an excitation-light source and a photomultiplier tube (Hamamatsu R928-P) in an electric-cooled housing operated in photon-counting mode to detect weak signals. Two reflecting mirrors were placed beside the sample cell to intensify the emission signals [7]. Excitation spectra were corrected for the spectral intensity distribution of the exciting light with an aqueous solution of rhodamine B as a quantum counter. The emission spectra were corrected for the sensitivity of the detection system by comparing the measured spectrum with the real spectrum using β-naphthol in acetic acid–sodium acetate buffer solution as a standard. Fluorescence quantum yields were determined by comparing the corrected fluorescence spectra of the samples with that of quinine in sulfuric acid used as a standard, which is assumed to have a fluorescence quantum yield of 0.51 [8].

3. Results and discussion

Fluorescence spectra of 2-FP and 2,6-DFP vapors following the excitation into the S_1 origins are shown in Figs. 1a and 1b, respectively. The spectra show the maxima at about 35 000 and 34 000 cm^{-1}, respectively, for 2-FP and 2,6-DFP vapors. Fluorescence spectrum of 3-FP vapor is weak, but is shown in a previous paper [5]. The fluorescence spectral shapes remained almost unchanged upon varying the buffer gas pressure up to 300 Torr or addition of air up to 760 Torr. Each of the fluorescence spectra is situated in the region adjacent to the corresponding absorption

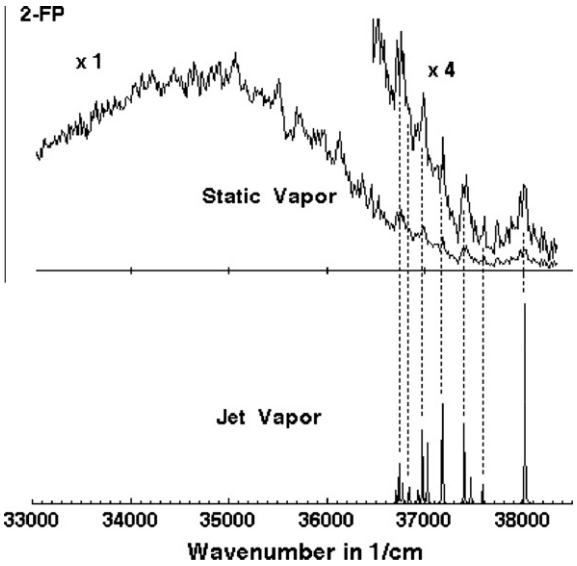

Fig. 1a. Fluorescence spectra of 2-FP in the static vapor phase (upper panel) and in a jet (lower panel). The spectrum in a jet is obtained from the data in Ref. [9].

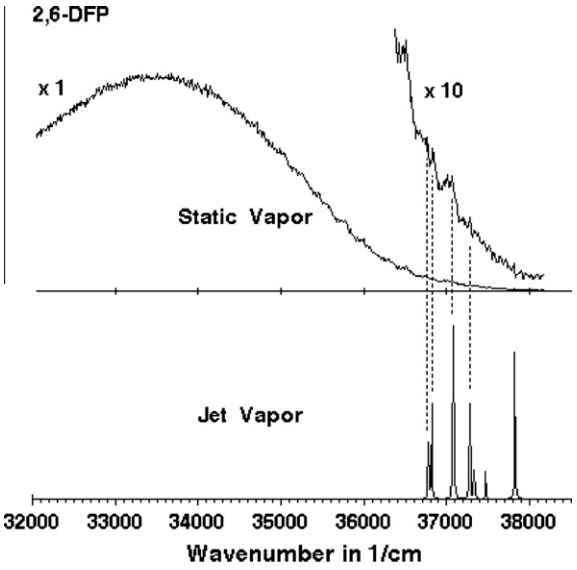

Fig. 1b. Fluorescence spectra of 2,6-DFP in the static vapor phase (upper panel) and in a jet (lower panel). The spectrum in a jet is obtained from the data in Ref. [10].

spectrum. Closer inspection of the fluorescence spectra of 2-FP and 2,6-DFP vapors reveals the presence of weak bands. These weak bands correspond well to those observed in a jet, although the correspondence is seen only vaguely for 2,6-DFP vapor [9,10].

Figs. 2a, 2b and 2c show the absorption, corrected fluorescence excitation and corrected biacetyl-sensitized phosphorescence excitation spectra of 2-, 3-FP and 2,6-DFP vapors, respectively, at about 10 Torr as measured with 0.2 nm excitation bandwidth. The measured absorption spectra agree well with those reported previously [11–13]. It is seen in Figs. 2a, 2b and 2c that the excitation and sensitized phosphorescence excitation spectra of each molecule agrees well with the corresponding absorption spectrum so far as the locations of the vibronic bands are concerned, indicating that the fluorescence originates from the sample molecule itself. It is seen that the excitation and sensitized phosphorescence excitation intensities decrease significantly with increasing the excitation

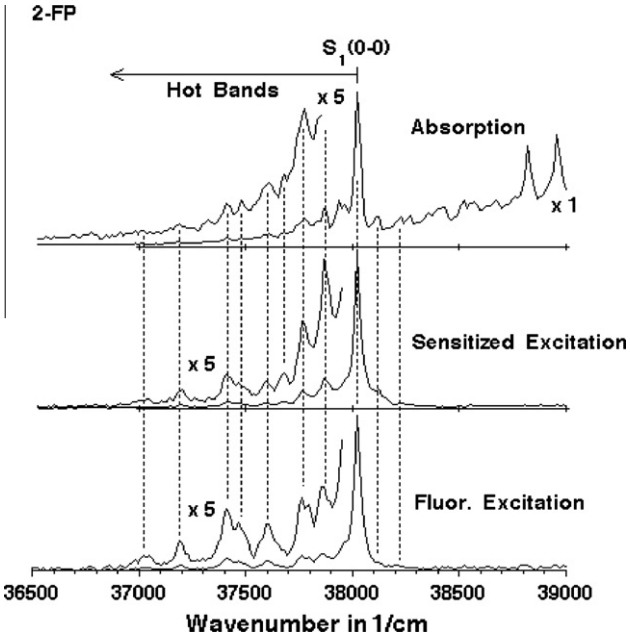

Fig. 2a. Absorption, biacetyl-sensitized phosphorescence excitation and fluorescence excitation spectra of 2-FP vapor.