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Measurement of Singlet-Triplet Absorption Spectrum of Pyridazine by a Sensitized-Phosphorescence Excitation Method

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Synopsis. The $S_0 \rightarrow T$ absorption spectrum of pyridazine was measured by means of sensitized-phosphorescence excitation in EPA rigid-glass solution at 77 K. Its intensity was found to be much lower than that of the corresponding spectrum of pyrazine.

The phosphorescence of pyridazine has not been observed as yet, although its intersystem-crossing quantum yield is of the same order of magnitude as the yields of strongly phosphorescent pyrazine and pyrimidine.[1)] It may be presumed that a slow rate of radiative decay of the triplet state, compard with its radiationless decay, is responsible for the non-phosphorescent property of pyridazine.

Hochstrasser and Marzzacco[2)] measured $S_0 \rightarrow T$ absorption of pyridazine crystal at 4.2 K, where S_0 and T denote the ground singlet and excited triplet states respectively, and they evaluated the rate constant for the radiative triplet decay (k_P). According to their results, the k_P value for pyridazine is of the same order of magnitude as those for pyrazine and pyrimidine, and the 0–0 band of the $S_0 \rightarrow T$ absorption of pyridazine is located at 412.5 nm. Recently, however, Innes *et al.*[3)] reported that pyridazine vapor gives $S_0 \rightarrow T$ absorption with the 0–0 band at 445 nm.

In the present study, the $S_0 \rightarrow T$ absorption of pyridazine in rigid-glass solution was measured by a method based on sensitized-phosphorescence excitation (SPE). In the SPE method, a triplet energy donor and an acceptor are used. Only the donor molecule is excited, and an excitation spectrum is obtained by monitoring the sensitized phosphorescence emitted from the acceptor triplet produced by triplet-triplet energy transfer. The SPE spectrum thus obtained corresponds to the donor absorption spectrum. Note that the SPE spectrum can be measured even when the donor gives no phosphorescence, and that the SPE method has a high sensitivity compared with the absorption method. In this study pyridazine was used as energy donor and naphthalene-d_8 as acceptor.

Experimental

Pyridazine (Nakarai Chemical Co.) was carefully purified by repeated vacuum distillation. Pyrazine (Nakarai Chemical Co.) and naphthalene-d_8 (E. Merck Co.) were purified by vacuum sublimation. EPA (5: 5: 2 parts by volume of ethyl ether, isopentane, and ethyl alcohol) was used as solvent. The acceptor concentration was fixed, while the donor concentration was widely changed. All the sample solutions were degassed by repeated freeze-thaw cycles.

The SPE spectra were measured at 77 K with a high-resolution, high-sensitivity emission spectrophotometer equipped with a photon-counting detector and a phosphoroscope. The SPE spectra were corrected for the spectral intensity of the light source and monochromator system.[4)]

The quantum yield of the donor triplet is either equal to or less than unity according as the donor molecule is photoexcited in the wavelength region of $S_0 \rightarrow T$ or $S_0 \rightarrow S$ absorption; in the latter case the yield is identical with the intersystem-crossing yield. Allowance was made for this difference in quantum yield[5)] to obtain the SPE spectrum which, throughout the two wavelength regions, has an intensity proportional to the absorption intensity represented by the molar extinction coefficient (ε). The intensity of the excitation spectrum at a certain wavelength in the $S_0 \rightarrow S$ absorption region was then equated to the ε value at that wavelength to convert the excitation spectrum to the absorption spectrum.

Results and Discussion

In order to confirm the validity of the present method, we first observed the SPE spectrum for a system of pyrazine (donor) and naphthalene-d_8 (acceptor). The resulting absorption spectrum of pyrazine is compared in Fig. 1 with the absorption spectrum derived from the usual phosphorescence excitation (PE) spectrum which was measured with pyrazine alone. The two spectra are in good agreement with each other.

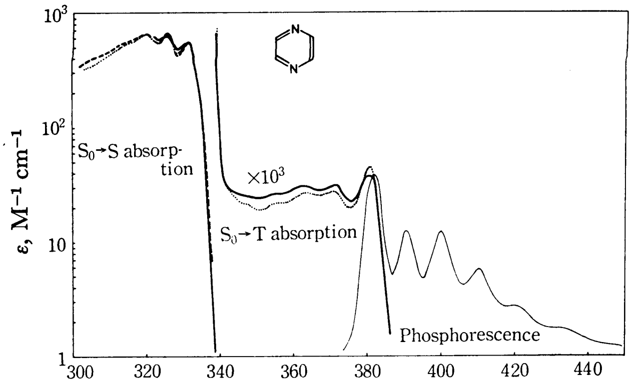

Fig. 1. Absorption and phosphorescence spectra of pyrazine in EPA at 77 K. Solid and dotted lines depict the absorption spectra derived from SPE and PE spectra, respectively. Broken line shows the usual $S_0 \rightarrow S$ absorption spectrum. Scale of intensity in the phosphorescence spectrum is linear.

An example of the SPE spectrum obtained for the system of pyridazine and naphthalene-d_8 is given in Fig. 2 with solid lines (a). The PE spectrum which was measured under the same conditions (except for the absence of pyridazine) as in the measurement of the SPE spectrum (a) is also shown in Fig. 2 with dotted lines (b). The PE spectrum (b) ranging from 385 to 470 nm corresponds to the $S_0 \rightarrow T$ absorption of naphthalene-d_8. Comparison of the spectra (a) and (b) shows

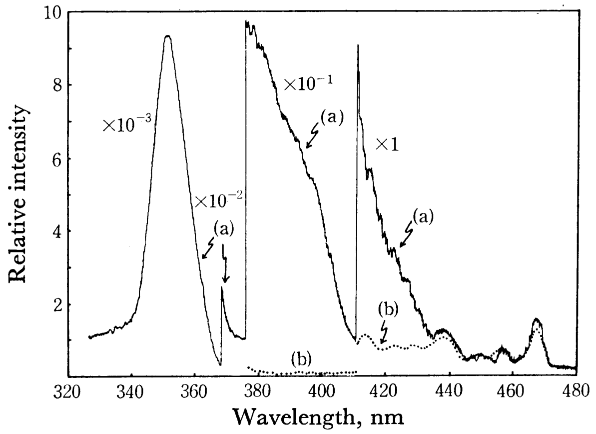

Fig. 2. Uncorrected chart of SPE and PE spectra.
(a) SPE spectrum of 0.1 M pyridazine and 0.06 M naphthalene-d_8 pair in EPA at 77 K; (b) PE spectrum of naphthalene-d_8 under the same conditions.

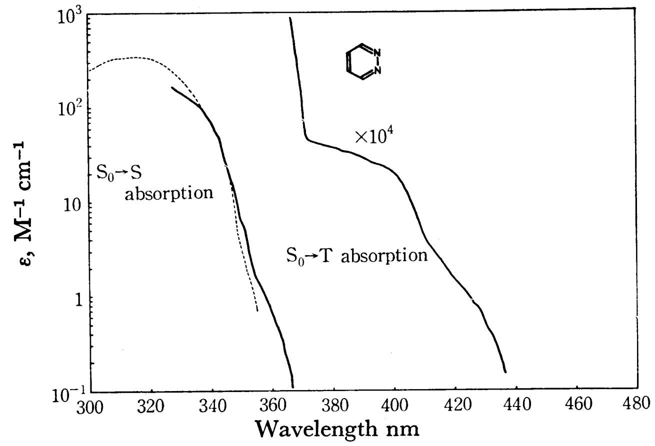

Fig. 3. Absorption spectrum of pyridazine in EPA at 77 K. Solid line, spectrum obtained by the SPE method; broken line, the usual $S_0 \rightarrow S$ absorption spectrum.

that the SPE spectrum between 435 and 470 nm originates actually from the direct $S_0 \rightarrow T$ excitation of naphthalene-d_8. Subtraction of the spectrum (b) from the spectrum (a) yields the true SPE spectrum, which in turn leads to the absorption spectrum of pyridazine through the procedure described before; the results are shown in Fig. 3.

In Fig. 3 the absorption occurring in a region of 370—440 nm can be assigned to an $S_0 \rightarrow T$ transition. Alternatively, one may imagine that it consists of two transitions which are to be called $S_0 \rightarrow T_1$ and $\rightarrow T_2$ in order of increasing energy. Theoretically, ${}^1A_1 \rightarrow {}^3B_1(n, \pi^*)$ and ${}^1A_1 \rightarrow {}^3A_2(n, \pi^*)$ transitions are possible for the C_{2v} pyridazine molecule.[2,3] The $S_0 \rightarrow T_1$ transition may then be related to the 445 nm absorption reported by Innes *et al.*,[3] and the $S_0 \rightarrow T_2$ to the 412.5 nm absorption by Hochstrasser and Marzzacco.[2] The values of ε_{max} for the $S_0 \rightarrow T_1$ and $\rightarrow T_2$ transitions are about 5×10^{-5} and 2×10^{-3} M^{-1} cm^{-1}, respectively. In either case the ε_{max} value is much smaller than the corresponding value for pyrazine (3×10^{-2} M^{-1} cm^{-1} from Fig. 1).[6] If, in this way, the $S_0 \rightarrow T$ absorption of pyridazine involves two transitions, the phosphorescence must originate from the lower triplet state, T_1. Then, it follows from the intensity of the $S_0 \rightarrow T_1$ absorption that k_P of pyridazine is as small as 0.16 s^{-1}. It may be noted that k_P of pyrazine is estimated to be 110 s^{-1} from its $S_0 \rightarrow T$ absorption intensity.

The lack of phosphorescence in pyridazine may thus be attributed, at least in part, to the fact that its lowest excited triplet has a relatively small k_P value.

References

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5) The intersystem crossing quantum yield, Φ_{ISC} used is 0.33 for pyrazine and 0.2 for pyridazine in EPA at 77 K. The former value was determined from our unpublished work by the same method as used in Ref. 1. The latter is taken from Ref. 1. These values are equal to the ones reported by Cohen and Goodman (*J. Chem. Phys.*, **46**, 713 (1967)).

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