May, 1988] © *1988 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 61, 1787—1788 (1988)* 1787

Phosphorescence Excitation Spectra in the Singlet-Triplet Absorption Region of Pyrazine and Pyrimidine Vapors

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(Received December 23, 1987)

Synopsis. Phosphorescence excitation spectra in the $S_0 \rightarrow T_1$ absorption region of pyrazine and pyrimidine have been observed in the vapor phase at room temperature. In pyrimidine vapor, the origin of the $S_0 \rightarrow T_1$ transition has been determined to be at 350.42 nm, and the T_1 state is assigned to the $n\pi^*$ state.

Relaxation dynamics in the triplet states of pyrazine and pyrimidine in the vapor phase seems to be extremely different from the dynamics in rigid media. For example, the phosphorescence quantum yields of these molecules in the vapor phase are much smaller than those in rigid media,[1-3] indicating that a fast nonradiative process occurs in T_1 only in the vapor phase. This suggests that there is a difference in electronic property and/or molecular geometry between the T_1 states of the isolated molecules and the molecules in rigid media. However, these problems remain unsettled.

The purpose of this note is to report the phosphorescence excitation spectra in the $S_0 \rightarrow T_1$ absorption region of pyrazine and pyrimidine in the vapor phase at room temperature. The T_1 states of both compounds are well-known to be of the $n\pi^*$ type in low temperature matrices.[4] In pyrimidine vapor, however, the possibility was suggested that the T_1 state is the $\pi\pi^*$, since the radiative lifetime evaluated from the yield and decay of the phosphorescence in the vapor phase is more than ten times as long as that in a rigid glass.[2] In this note, therefore, the assignment of the T_1 state of pyrimidine vapor is discussed, based on the rotational contour of the absorption band. The excitation spectrum of pyrazine vapor is compared with the absorption spectra.[5,6]

Experimental

The excitation light source is a pulsed dye laser (Lambda Physik FL2002), pumped by a XeCl excimer laser (Lambda Physik EMG 103 MSC). The intensity of phosphorescence dispersed by a monochromator was measured by using a photon counting detection system which is equipped with a circuit for a time-gated high voltage imposed on the photomultiplier (TGHV circuit).[7] With this system, the scattered light is eliminated, and the number of photons which are emitted from the sample in a certain time range after a pulse excitation can be counted. Emission decays were also measured by using the above-mentioned TGHV circuit and a photon counting lifetime apparatus equipped with a time-to-amplitude converter. In the present experiments, the phosphorescence at 390 nm emitted in the time range from 4 μs to 50 μs after pulse excitation was monitored to obtain the excitation spectra and decays of phosphorescence for the two compounds studied.

Results and Discussion

Figure 1 shows the phosphorescence excitation spectrum of pyrazine vapor. The phosphorescence lifetime of pyrazine, which is independent of the excited level, was determined to be ca. 60 μs, in agreement with the result of excitation into S_1.[1] The absorption spectrum of the $S_0 \rightarrow T_1$ transition of pyrazine vapor was observed by Innes and Giddings by using a 70 m absorption path.[5] They reported that the structure of the 0–0 band is predominantly of a parallel type, indicating that the direction of the transition dipole is perpendicular to the molecular plane, i.e., T_1 is the $n\pi^*$ state. Later, the $S_0 \rightarrow T_1$ absorption spectrum of pyrazine vapor was remeasured by Fischer,[6] and recently the $S_0 \rightarrow T_1$ transition in a supersonic jet was detected with a multiphoton ionization technique.[8,9] In the present spectrum, the strong band at 372.77 nm is assigned to the $S_0 \rightarrow T_1$ origin, and the strong bands at 625 and 1140 cm^{-1} above the origin are assigned to the $6a_0^1$ and $9a_0^1$ bands, respectively. Thus, the observed excitation spectrum is essentially the same as the absorption spectrum reported by Fischer, except that the intensity ratios between the 0–0 and the $6a_0^1$ bands in both spectra are different from each other. As is seen in Fig. 2(a), the 0–0 band exhibits a parallel-type rotational contour, in agreement with the report by Innes and Giddings.

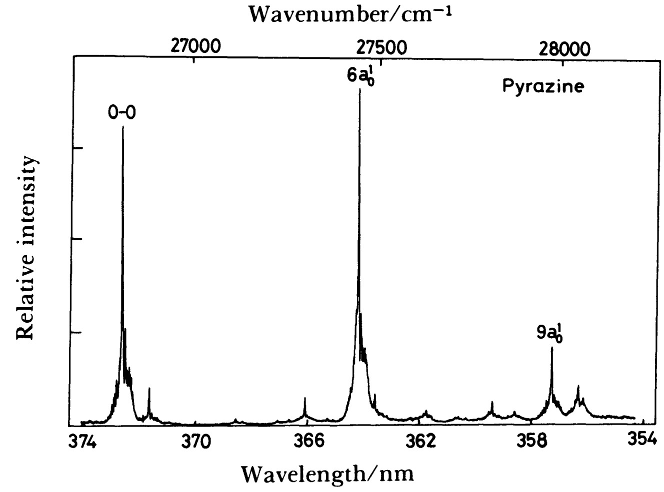

Fig. 1. Phosphorescence excitation spectrum in the $S_0 \rightarrow T_1$ absorption region of pyrazine vapor. The sample pressure is 2 Torr (1 Torr≈133.322 Pa). The 0–0 band is at 372.77 nm.

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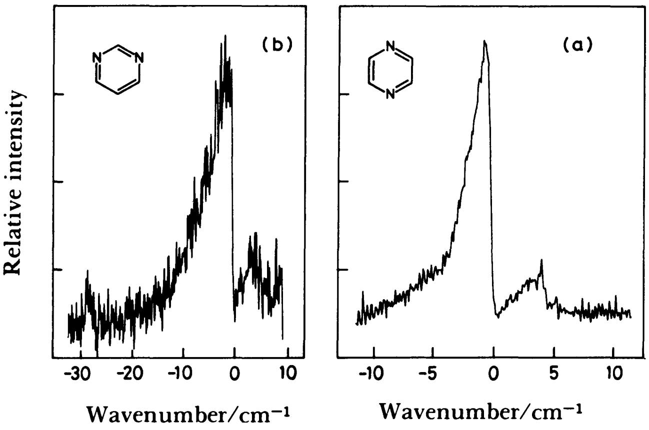

Fig. 2. Rotational contour of the 0–0 band belonging to the $S_0 \rightarrow T_1$ transition of pyrazine (a) and pyrimidine (b) vapors at room temperature.

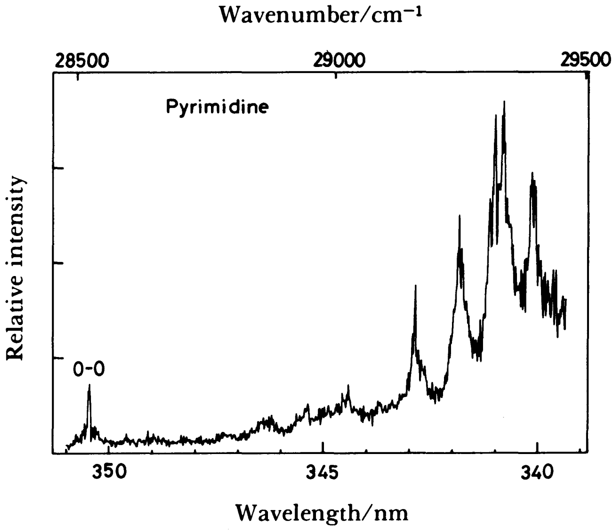

Fig. 3. Phosphorescence excitation spectrum in the $S_0 \rightarrow T_1$ absorption region of pyrimidine vapor at ca. 5 Torr. The 0–0 band is at 350.42 nm.

Figure 3 shows the phosphorescence excitation spectrum in the $S_0 \rightarrow T_1$ absorption region of pyrimidine vapor. The phosphorescence lifetime was determined to be ca. 60 μs, in fair agreement with the previous result of excitation into S_1.[2] In the previous paper,[2] the vibrational structure of the phosphorescence spectrum of pyrimidine vapor observed with excitation into S_1 was analyzed by assuming tentatively that the phosphorescence band at 350.5 nm corresponds to the 0–0 band of the $T_1 \rightarrow S_0$ transition. It is seen in Fig. 3 that in the excitation spectrum a distinct band exists at 350.42 nm, which is in good agreement with 350.5 nm. From these observations we are naturally led to the conclusion that the band at 350.42 nm in the phosphorescence excitation spectrum is the 0–0 band for the $S_0 \rightarrow T_1$ transition of pyrimidine vapor. If the T_1 state of pyrimidine vapor is the $\pi\pi^*$ type, the 0–0 band for the $S_0 \rightarrow T_1$ transition is expected to exhibit a perpendicular-type rotational contour which is similar to the contour observed for the $10a^1_0$ band belonging to the $S_0 \rightarrow S_1$ transition of pyrazine.[10] As is shown in Fig. 2(b), however, the 0–0 band of pyrimidine vapor exhibits a parallel-type rotational contour. Therefore, the T_1 state of pyrimidine vapor is assigned to the $n\pi^*$ state, as in the case of pyrazine.

In pyrazine, the spectral shapes of the $S_0 \rightarrow T_1$ excitation spectra in the vapor phase and in a rigid glass are analogous to each other.[11] However, the excitation spectrum of pyrimidine vapor shown in Fig. 3 is not analogous to the $S_0 \rightarrow T_1$ absorption spectrum of crystal.[12] The excitation (absorption) spectrum of pyrimidine vapor shows more complicated structure for excess energies of more than 600 cm^{-1} above the $S_0 \rightarrow T_1$ origin, as is seen in Fig. 3. The energy separation between S_1 and T_1 of pyrimidine is as small as ca. 2500 cm^{-1}. Then, the intense bands lying above 600 cm^{-1} from the origin may be attributed to the hot bands associated with transitions to S_1 from higher vibronic levels of S_0.

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