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FLUORESCENCE SPECTRUM OF PYRIMIDINE VAPOR FROM THE ZERO-POINT VIBRATIONAL LEVEL OF $^1B_1(n, \pi^*)$ STATE

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The fluorescence spectrum of pyrimidine vapor which originates from the zero-point vibrational level of the $^1B_1(n, \pi^*)$ state has been measured. Most of the strong bands can be explained in terms of three totally-symmetric vibrations: ν''_{6a}, ν''_{12}, and ν''_{9a}. No phosphorescence was observed from pyrimidine vapor at various pressures.

Vapor-phase emission spectra of aza-aromatics have recently attracted considerable attention in relation to the mechanism of intramolecular radiationless transition. At a sufficiently low vapor pressure, emission may be observed which originates from a single vibronic level (SVL) of an isolated molecule. Along this line, Lahmani et al.[1,2] investigated the vapor-phase emission of pyrazine, and Jordan and Parmenter[3] reported fluorescence spectra from two different SVL's of pyridazine. It was noted that pyridazine vapor did not show any phosphorescence[3] in contrast to the pyrazine vapor. This situation is similar to the case of the emission of these molecules in the condensed phase.[4] As regards pyrimidine (1, 3-diazabenzene), Logan and Ross[5] have reported a vapor-phase fluorescence spectrum without vibrational analysis; their spectrum was obtained by using only the 313.2 nm mercury line for excitation. Since the emission spectrum from a SVL is strongly dependent upon the vibronic level excited,[2,3] it is indispensable for a thorough understanding of the vibrational structure to measure the fluorescence spectrum from the zero-point level.

The purpose of this communication is to report the SVL fluorescence spectrum from the zero-point vibrational level of the $^1B_1(n, \pi^*)$ state, the lowest excited singlet (S_1), of pyrimidine vapor and to present the results of analysis of its vibrational structure.

Fluorescence spectra of pyrimidine vapor were measured by a photon-counting emission spectrophotometer[6] equipped with a 150-W xenon lamp as an excitation light source and a Hamamatsu TV R-585 photomultiplier. The dark current was 0.5 count/sec without cooling the photomultiplier. The fluorescence measurement was carried out for 6 torr of pyrimidine vapor at 18 °C. Under these conditions, the

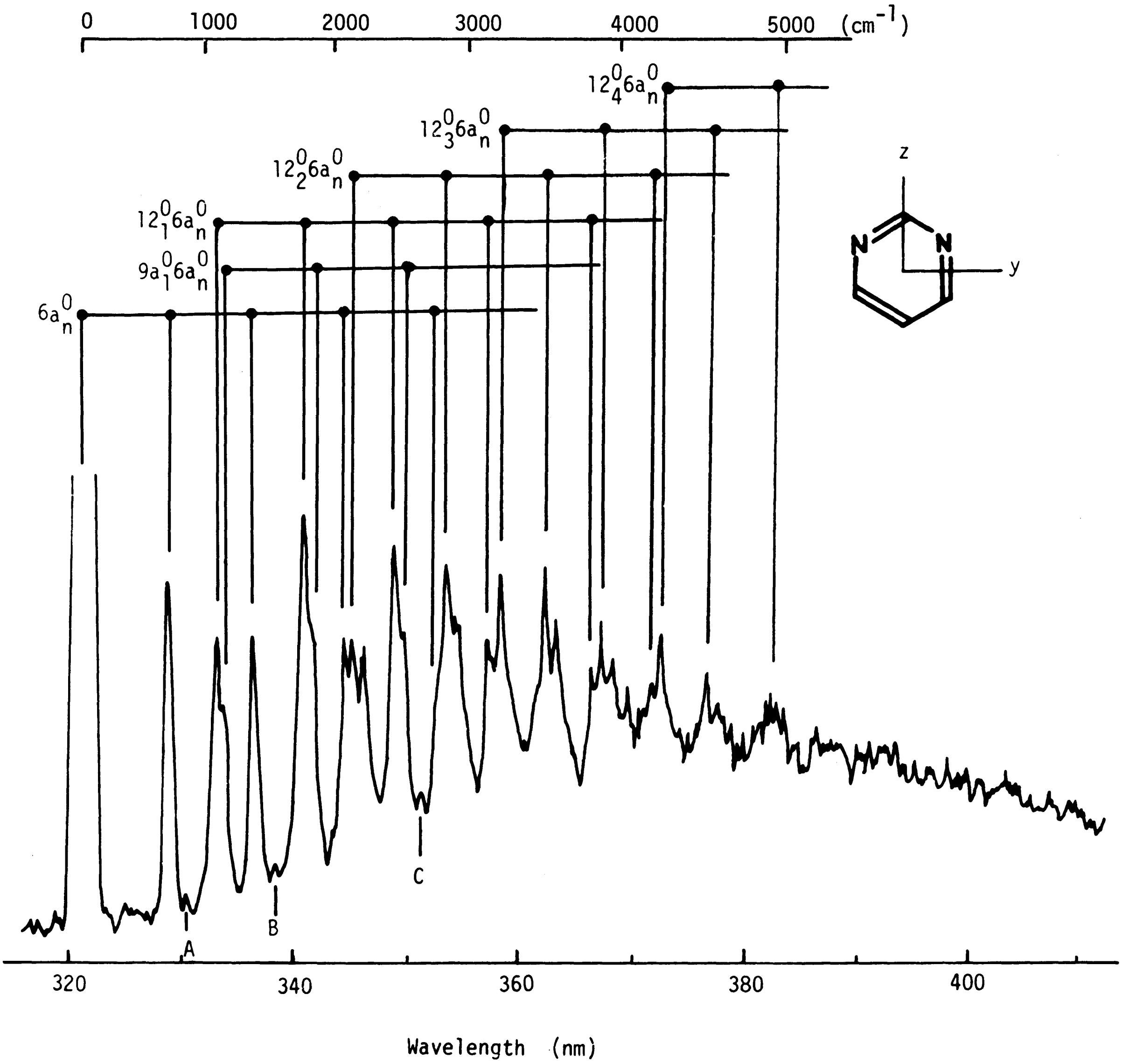

Fig. 1. Fluorescence spectrum of pyrimidine vapor at a pressure of 6 torr obtained by excitation at the 0–0 absorption band (321.5 nm) with a bandwidth of 100 cm^{-1}. The bandwidth of the detection monochromator is 50 cm^{-1}.

Table 1. Vibrational Analysis of the Fluorescence Spectrum of Pyrimidine Vapor

ν (cm^{-1})a)	Displacement (cm^{-1})		Assignment c)	ν (cm^{-1})a)	Displacement (cm^{-1})		Assignment
	Obs.	Calc.b)			Obs.	Calc.b)	
31067	0	0	origin	28324	2743	2708	$6a^0_4$
30390	677	677	$6a^0_1$	28248	2819	2807	$12^0_2 6a^0_1$
30216	851	870	$17a^0_1$ (A)	28180	2887	2888	$12^0_1 9a^0_1 6a^0_1$
29996	1071	1065	12^0_1	27952	3115	3096	$12^0_1 6a^0_3$
29937	1130	1146	$9a^0_1$	27855	3212	3195	12^0_3
29703	1364	1354	$6a^0_2$	27581	3486	3484	$12^0_2 6a^0_2$
29524	1543	1547	$17a^0_1 6a^0_1$ (B)	27501	3566	3565	$12^0_1 9a^0_1 6a^0_2$
29308	1759	1742	$12^0_1 6a^0_1$	27268	3799	3773	$12^0_1 6a^0_4$
29252	1815	1823	$9a^0_1 6a^0_1$	27201	3866	3872	$12^0_3 6a^0_1$
29034	2033	2031	$6a^0_3$	26874	4193	4161	$12^0_2 6a^0_3$
28946	2121	2130	12^0_2	26796	4271	4260	12^0_4
28864	2203	2211	$12^0_1 9a^0_1$	26541	4526	4549	$12^0_3 6a^0_2$
28640	2427	2419	$12^0_1 6a^0_2$	26108	4959	4937	$12^0_4 6a^0_1$
28571	2496	2500	$9a^0_1 6a^0_2$	25904	5163	5226	$12^0_3 6a^0_3$
28445	2622	2612	$17a^0_1 12^0_1 6a^0_1$ (C)				

a) Wavenumbers with an accuracy of ± 10 cm^{-1}.

b) Calculated with the vibrational frequencies taken from Refs. 8) and 9).

c) For bands (A), (B), and (C), see also Fig. 1.

mean time between collisions is longer by a factor of ten than the fluorescence lifetime estimated from the quantum yield and radiative lifetime.7) Pyrimidine (Tokyo Kasei Kogyo) was purified, just before use, by vacuum distillation in the presence of barium oxide.

The fluorescence spectrum with respect to excitation at the 0–0 absorption band (321.5 nm) is shown in Fig. 1. The vibrational analysis can be made on the basis of the infrared and Raman spectral data.8,9) The numbering of normal modes follows the one used by Innes et al.10) The principal structure of the zero-point fluorescence spectrum is rather simple as in pyrazine1,2) and pyridazine.3)

The wavenumbers and assignments of fluorescence bands are listed in Table 1. Most of the strong bands can be explained in terms of three totally-symmetric vibrations in the ground electronic state: ν''_{6a}, ν''_{12}, and ν''_{9a}. In particular, the long progressions in the ν_{6a} and ν_{12} vibrations make dominant contributions to the fluorescence spectrum.

In the present analysis of vibrational structure, the ν''_{12} mode plays an important role. This in turn leads to some modification of the vibrational assignment proposed earlier by Innes et al.[8)] for the absorption spectrum of pyrimidine vapor. They assigned the band represented by D in Fig. 2 to ν'_{8a}, i. e., to $8a^1_0$. The corresponding band $8a^0_1$ (ν''_{8a} = 1569.7 cm^{-1})[10)] cannot be found in the fluorescence spectrum, and a fairly strong band, 12^0_1, appears instead. It is, therefore, concluded that in the assignment of the absorption spectrum by Innes et al. ν'_{8a} should be changed with ν'_{12}. It may be noted that Innes et al. also suggested that the assignments of ν'_{8a} and ν'_{12} might need to be interchanged.

According to the new assignment, in the fluorescence and absorption spectra of diazines, the ν_{12} vibration is active only in pyrimidine; no vibronic bands related to ν_{12} are found in pyrazine and pyridazine.[2,3)] This must be associated with the fact that the ring bending vibration ν_{12} is totally symmetric only in pyrimidine; it is a b_{1u} mode in pyrazine (D_{2h}) and a b_2 in pyridazine (C_{2v}). On the other hand, although ν_{8a} is totally symmetric in all three diazines, it is not active in pyrazine and pyridazine[2,3)] as well as in pyrimidine.

In the absorption spectrum of pyrimidine vapor (Fig. 2), a doublet is observed at about 314 nm. This doublet with a separation of 56 cm^{-1} was regarded by Innes et al.[8)] as a Fermi doublet due to the interaction of ν'_{6a} and $2\nu'_{16b}$.

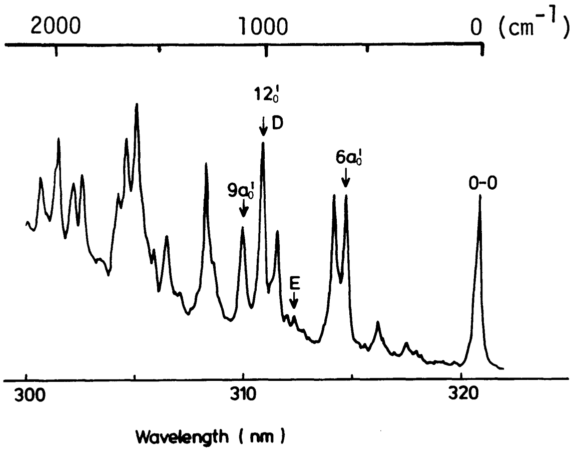

Fig. 2. Absorption spectrum of pyrimidine vapor. This spectrum, measured with a Cary 15 spectrophotometer, corresponds to the low-resolution spectrum of Innes et al.[8)] The assignments follow the ones in Ref. 8) except for 12^1_0 which is based on the present study.

However, only a very narrow band $6a_1^0$ is observed in the fluorescence spectrum. Therefore, even if the Fermi resonance should occur in the ground state, the separation of the doublet would be considerably smaller than that in the upper state.†

The other prominent bands due to the ν''_{9a} vibration and its combinations correspond fairly well to the analogous bands in the absorption spectrum.

A band of low intensity (band A in Fig. 1) is observed at 851 cm^{-1} from the origin, along with its combination bands with ν''_{6a} and ν''_{12} (band B and C). Since these bands are very weak compared with totally-symmetric bands, they must involve a nontotally-symmetric mode and borrow their intensity through vibronic coupling. It may be assumed that the coupling occurs between the $^1B_1(n, \pi^*)$ state and the next higher singlet state, $^1B_2(\pi, \pi^*)$. The symmetry species of the perturbing vibration is then a_2 (out-of-plane). In the case of pyrimidine (C_{2v}), there are two vibrations of a_2 type: ν''_{16a} ring bending mode (394 cm^{-1}) and ν''_{17a} CH bending mode (870 cm^{-1}). The band at 851 cm^{-1} can thus be assigned to ν''_{17a} fundamental. Similarly, the nontotally-symmetric vibration observed in the fluorescence spectrum of pyrazine vapor is of a CH bending mode.1,2,11,13) Concerning the ν'_{17a} vibration in the upper state, no information is available in the literature. In the absorption spectrum of pyrimidine vapor, the band represented by E in Fig. 2 might be assigned to the ν'_{17a} fundamental with a displacement of 834 cm^{-1} from the origin. This band was disregarded by Innes et al.

The vibrational structure in the fluorescence spectrum mentioned above is essentially the same as that observed for a mixed crystal of pyrimidine with benzene.12) The analysis of the spectrum of this mixed crystal at 4.2 K shows that the emission originates exclusively from the zero-point vibrational level. In the measurement of vapor-phase fluorescence, the excitation at the 0—0 absorption band should simultaneously give rise to v—v transitions such as $16b_1^1$ and $16a_1^1$ to an extent determined by a Boltzmann distribution. However, the observed emission spectrum involves no vibronic bands which are to be attributed to fluorescence from vibrational levels other than the zero-point level.

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† According to the fluorescence spectrum of a mixed crystal of pyrimidine with benzene at 4.2 K, reported by Hochstrasser and Marzzacco,12) the Fermi resonance between ν''_{6a} and $2\nu''_{16b}$ appears to be very weak.

It should be noted that no phosphorescence was observed from the pyrimidine vapor. According to the prediction from the $S_1 - T_1$ separation in a condensed phase ($\sim$2500 cm^{-1}), phosphorescence could occur in a region lower in energy than 28600 cm^{-1}. In pyrazine, the relative intensities of fluorescence and phosphorescence are known to change significantly with increasing vapor pressure.1,2) In the case of pyrimidine, the spectral pattern of the vapor emission (Fig. 1) was not changed by increasing the vapor pressure of pyrimidine from 1 to 10 torr and even by adding isopentane as a foreign gas up to 300 torr.

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