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TWO NEARBY ELECTRONIC STATES OF PYRIDAZINE

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Fluorescence excitation spectrum, SVL fluorescence spectra, MPI excitation spectrum in supersonic jet condition and absorption spectra in solvents at 4.2 K have been measured for the near UV transition of pyridazine. All support the interpretation that there exist two electronic states and their separation is 373 cm^{-1} in the gaseous state.

The vibrational structure of the 370 nm absorption spectrum of pyridazine vapor due to n,π* transition is so complicated that its unique analysis is quite difficult. The complexity probably arises from congestion of four excited n,π* states expected in the near UV region.[1)] Recently Ransom and Innes[2)] pointed out from their study of the absorption spectrum that the band at 27021 cm^{-1}, which is located 373 cm^{-1} higher in frequency than the 0-0 band of the lowest excited $^1B_1(n,\pi^*)$ state (26649 cm^{-1}), should be assigned as the 0-0 band of the electronic transition to a second $^1B_1(n,\pi^*)$ state. In the present study, four kinds of experiments have been carried out to examine the interpretation by Ransom and Innes. They are the fluorescence excitation spectrum, the single vibronic level (SVL) fluorescence spectra from the various vibronic levels, the absorption spectra in solvent at 4.2 K and the multiphoton ionization (MPI) excitation spectrum in a supersonic free jet. All the results obtained seem to support the interpretation that the band at 27021 cm^{-1} is the 0-0 band of the second n,π* electronic transition.

Sample pressure of about 0.4 kPa was employed for the measurement of the SVL fluorescence and the fluorescence excitation spectra. A Molectron scanning dye laser with about 1 cm^{-1} half width which was pumped by a Molectron nitrogen laser (600 kW) was used as an exciting light source. The dye used was PBD (Exciton) which covers the region of 360 to 380 nm. The SVL fluorescence spectra were obtained by a Nalumi 0.75 m monochromator combined with an HTV R-562 photomultiplier and a Boxcar integrator (Brookdeal 9415/9525). The spectral FWHM was about 0.3 nm. The fluorescence excitation spectrum was measured by collecting the fluorescence by a lens and was detected by a photomultiplier (1P28) after passing through a cut-off filter (Corning V-Y42 or V-Y44). The effect of the filter on the observed spectral intensity was found to be very small. The intensity of the exciting laser light was monitored by a photodiode with a sample-hold circuit. The continuous light source for the absorption spectra at 4.2 K was provided by 150 W xenon lamp. Cyclohexane and benzene were used as solvents. The MPI spectrum of pyridazine in a supersonic free jet was obtained by the method reported in Ref. 3.

The fluorescence excitation spectrum of pyridazine vapor is shown in Fig. 1

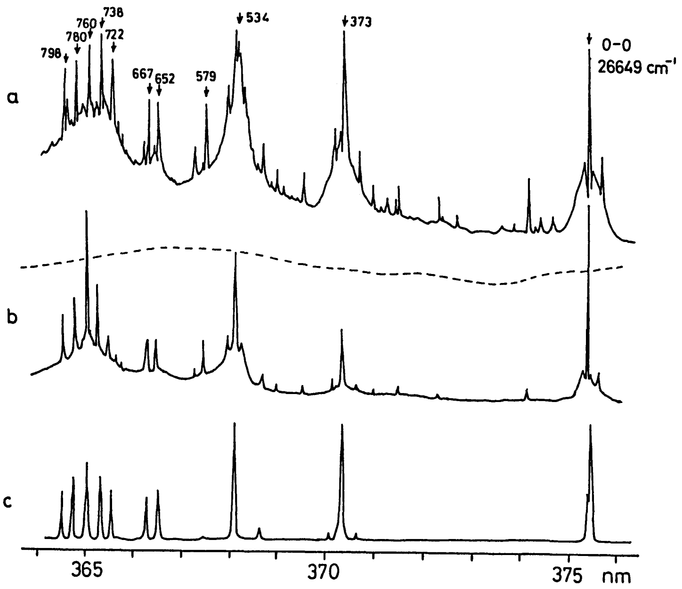

Fig. 1. Absorption spectrum (a), fluorescence excitation spectrum (b) of pyridazine vapor at room temperature and one photon resonance two photon ionization excitation spectrum (c) of ultracold pyridazine molecule prepared by supersonic free expansion. The broken curve shows the exciting laser intensity.

Table 1. Relative quantum yields of main vibronic bands[(a)]

Displacement from the 0-0 band/cm^{-1}	Emission Intensity / Optical Intensity[(b)]
0	1.0
373	0.3
534	0.5
579	0.5
652	0.5
667	0.4
722	0.2
738	0.3
760	0.7
780	0.4
798	0.4

(a) Errors of the ratios are ±15 %.
(b) Values relative to that of 0-0 band.

together with the absorption spectrum. All main vibronic bands have central sharp Q branch and they belong to the B_1 species of C_{2v} symmetry.[1)] In order to discriminate cold bands from hot bands, the absorption spectrum of the ultracold molecule in the vapor phase prepared by supersonic free expansion[4)] was measured in the form of one-photon resonance two-photon ionization excitation spectrum. The result shows that all the strong bands except the band at 0+579 cm^{-1} are cold bands (see Fig. 1c). Table 1 gives the ratios of emission intensity of the excitation spectrum to optical density of the absorption spectrum for main cold bands. The ratios can be regarded as the relative fluorescence quantum yields of the individual vibronic bands. As is seen from the table, the 0-0 band exhibits the highest quantum yield, while the band at 0+373 cm^{-1} has a very low quantum yield. The quantum yields of the other bands assume various values between those of the 0-0 and 0+373 cm^{-1} bands. In the case of pyrazine where the vibronic interaction between the two low lying excited singlet states is strong, the vibronic bands responsible for the coupling have larger quantum yields whereas other bands have almost the same value.[5)] On the other hand, quantum yields of the various vibronic levels of pyrimidine[6)] show gradual decrease with increasing vibrational energy. The behavior of pyridazine is peculiar compared with pyrazine and pyrimidine and can be considered to be the consequence of the strong mixing between the vibronic states of two nearby S_1 and S_2 states.

The single vibronic level fluorescence spectra generated by pumping the absorption bands indicated by arrows in Fig. 1a have been measured and some of them

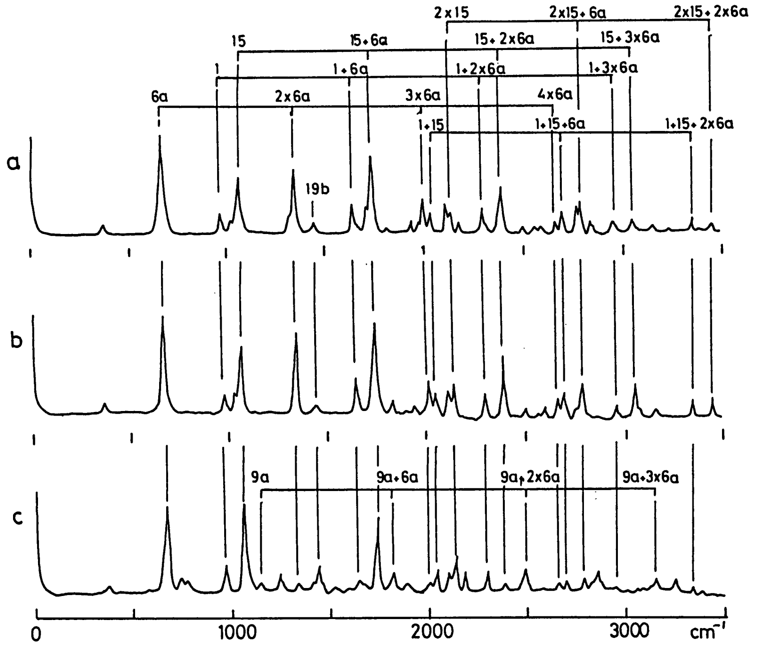

Fig. 2. Fluorescence spectra generated by pumping (a) 0-0, (b) 0+373 cm^{-1} and (c) 0+534 cm^{-1} absorption bands. Lord's numbering was used for the ground state frequencies.[8)]

are shown in Fig. 2. The fluorescence spectra obtained by the 0-0 and 0+373 cm^{-1} band excitation are very similar as seen from Figs. 2a and 2b. They have a long progression of the ground state 6a vibration (665 cm^{-1}) with similar intensity distributions. Similar results were also reported by Jordan and Parmenter.[7)] Since 6a is the totally symmetric vibration with lowest frequency and the excited state 6a vibration appears strongly in the absorption spectra of other azines, the absorption band of 0+373 cm^{-1} might be assigned to $6a^1_0$ of S_1. However, this assignment is denied from the condideration of Franck-Condon factor, because the intensity distribution of the 6a progression should be different between the spectra originating from the zero-point and 6a vibrational levels of the excited state. On the other hand, in the fluorescence spectrum generated by pumping the band at 0+534 cm^{-1} (Fig. 2c), the intensity distribution of the 6a progression differs greatly from that of the spectrum of the 0-0 band excitation, leading to the assignment of this band to $6a^1_0$ of S_1. Thus, no reasonable correspondence with the ground state totally symmetric vibration can be made for 373 cm^{-1} unless an abnormally great frequency change in the electronic transition is assumed. We prefer, therefore, to assign the 0+373 cm^{-1} band to the electronic origin of S_2 in accordance with the assignment by Ransom and Innes. The similarity of the fluorescence spectra by the 0-0 and 0+373 cm^{-1} band excitation suggests that the molecular structures of S_1 and S_2 are very similar. The absorption band at 0+738 cm^{-1} is assigned to $9a^1_0$ from its SVL fluorescence spectrum. The SVL fluorescence spectra obtained by pumping the other absorption bands were complicated and definite assignmemts for the absorption bands could not be obtained.

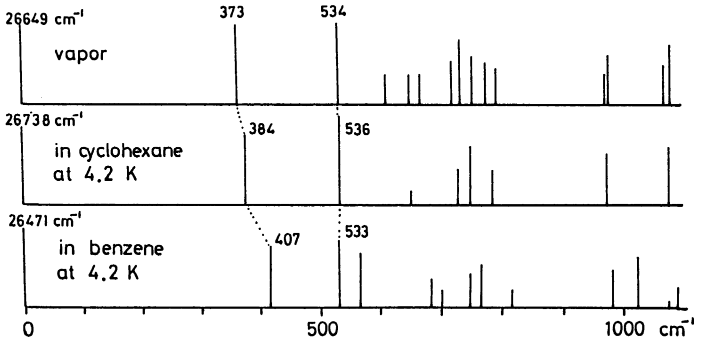

Fig. 3. Effects of solvents (cyclohexane, benzene) at 4.2 K on the 0+373 cm^{-1} and 0+534 cm^{-1} bands.

Figure 3 shows the absorption spectra of the vapor and of solutions in cyclohexane and benzene at 4.2 K. The effect of solvent is rather large for the 0+373 cm^{-1} band compared with that of the 0+534 cm^{-1} band. This is also consistent with the interpretation that the 0+373 cm^{-1} band belongs to S_2.

All the results obtained from four kinds of measurements support the interpretation that there exist two n,π* electronic states separated by 373 cm^{-1} in the spectral region around 370 nm. The complexity of the 370 nm absorption spectrum is concluded to be due to strong coupling between the vibronic states of these two nearby electronic states.

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