

Study of the 3s Rydberg State of Pyrimidine by Multiphoton Ionization Spectroscopy

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The 3s Rydberg state of pyrimidine is seen as a two-photon resonant structure on its three-photon ionization spectrum. The vibrational structure is analyzed and compared with the VUV absorption and photoelectron spectra. © 1987 Academic Press, Inc.

I. INTRODUCTION

The use of tunable dye lasers to produce resonance enhanced multiphoton ionization (REMPI) spectra is a powerful method to investigate molecular energy levels. This method is particularly well suited for detecting molecular Rydberg states (*I*) which live long enough, compared with the valence states, to have a high probability of ionization by the photons of the exciting laser pulse.

In this paper we present the three-photon ionization spectrum of pyrimidine in the dye laser wavelength range 355–395 nm. The multiphoton ionization (MPI) spectra of other azabenzenes have been reported in the same wavelength region (2, 3). The structure seen in our MPI spectrum is attributed to the two-photon excitation of the 3s Rydberg state. This state was seen weakly in VUV absorption spectra a long time ago (4, 5) but it was given a different 0–0 and vibrational assignment, probably because the 0–0 transition cannot be easily seen in one-photon absorption spectra.

It is well established by now from photoelectron (PES) and MPI spectroscopy, as well as theoretical calculations, that the highest occupied molecular orbital of the group of azabenzenes is an *n*-type orbital (6, 7). For pyrimidine, in addition, the *n* → 3s (¹*A*₁ → ¹*B*₂) transition is symmetry allowed in both one- and two-photon excitation.

II. EXPERIMENTAL DETAILS

The experimental setup used in the present work consisted of a cross-shaped, copper-gasketed, stainless-steel static cell, bakable to 200°C. Two of its ports were used as entrance and exit windows for the laser beam, the exit window being set at the Brewster angle for minimum reflection of the laser beam. The third port, at right angle to the laser beam direction, was used for the support of two parallel ~1-cm plate electrodes being ~1 cm apart and located at the center of the cell. The fourth port could be used for observation of fluorescence emission. A liquid nitrogen trap was installed between the cell and a diffusion pump, allowing background pressures of better than 1×10^{-6}

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mbar to be achieved. The outgas accumulation in the cell was vanishingly small over the periods of time needed to complete a series of measurements.

The output from a XeCl excimer laser (Lumonics TE-860-3) pumped dye laser (Lumonics EPD-330) was focused on a spot between the plate electrodes by a quartz lens of 4-cm focal length. The photoelectron pulse resulting from the MPI process was amplified by an electron avalanche in the sample gas caused by an external electric field (200–300 V/cm) applied between the electrodes. The resulting signal was detected with a charge-sensitive preamplifier (ORTEC 142A), averaged with a boxcar integrator (Stanford Research Systems SR 250), and recorded on a chart recorder (J-J Instruments CR 6525). The laser wavelength was calibrated by means of a 60 cm monochromator (Jobin Yvon HRP) and its total uncertainty was $\sim 0.5 \text{ \AA}$ ($\sim 8 \text{ cm}^{-1}$ in two-photon energies). The laser bandwidth was measured also with the same monochromator and it was $\sim 0.1 \text{ \AA}$. The dyes we used were DMQ (355–370 nm), BPBD (370–385 nm), and QUI (380–395 nm) and they were bought from Lambda Physik.

The power dependence of the resonant MPI signal was found to be almost quadratic for pulse energies from 0.2 to 2 mJ (measured with a Gentec ED-200 joulemeter). Typical pulse energies used were $\sim 1 \text{ mJ}$ in the maximum of the dye profiles.

Pyrimidine had a 98% purity and was bought from Koch-Light. It was degassed by repeated freeze–pump–thaw cycles and used without further purification. Typical gas pressures in the cell ranged from 0.5 to 1 mbar and were measured with an MKS baratron head (Type 221 A).

The spectra reported here were not corrected for varying laser intensity. The gain profile of the various dyes was measured with a fast photodiode (Instrument Technology ITL-TF1850), the boxcar integrator, and the chart recorder. These profiles are shown in Fig. 1b.

III. RESULTS AND DISCUSSION

The MPI spectrum of pyrimidine is shown in Fig. 1a. The sharp bands have a linewidth of $\sim 50 \text{ cm}^{-1}$ which is indicative of their Rydberg nature. Similar linewidths have been reported for the MPI Rydberg spectra of the other azabenzenes (2, 3) and can be attributed to the expanded rotational selection rules for two-photon transitions at room temperature (3).

Most of the peaks show a splitting of 1–2 \AA , which can be attributed to rotational structure and/or Fermi resonances. Fermi resonances appear also in the first $n-\pi^*$ transition of this molecule (8). Cold MPI spectra in a supersonic jet will clarify this structure.

The broad background under the peaks is due to the nonresonant three-photon ionization. This was checked by seeing that the ratio of the intensity of the peaks to the intensity of the underlying background increased by decreasing the dye laser power. In addition, this background was present for all wavelengths and followed the dye profile intensity. Since the total MPI signal is the sum of resonant and nonresonant terms, which have different laser intensity dependences, we cannot apply any power correction to the observed spectra.

The strongest peak is the one at $\lambda = 3863.5 \text{ \AA}$, which corresponds to a two-photon transition energy of $51\,753 \text{ cm}^{-1}$. This transition was seen in the one-photon VUV

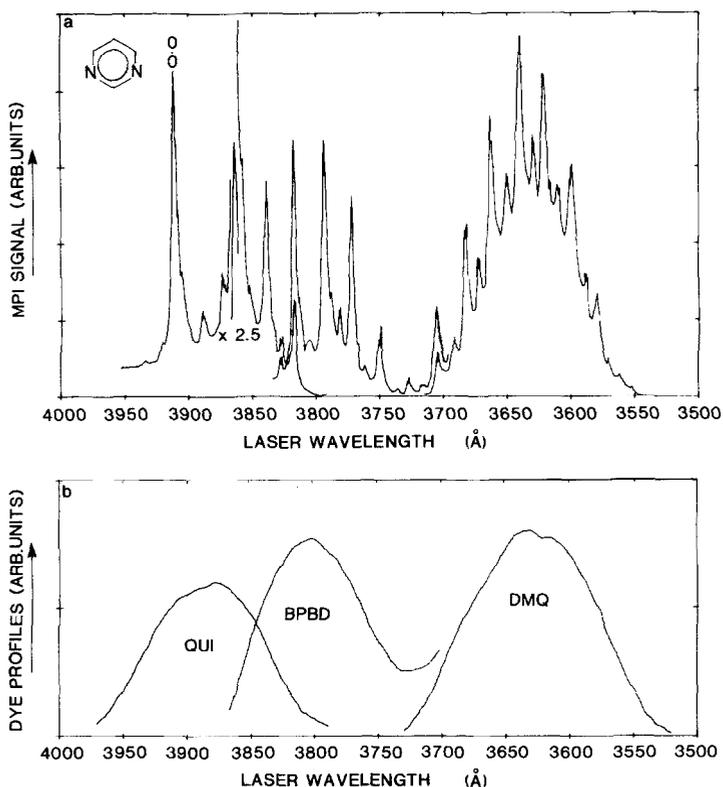


FIG. 1. (a) Two-photon resonant MPI spectrum of pyrimidine. Peak heights do not represent relative intensities. (b) Dye profiles. There is no correlation of the intensities among the different dyes.

absorption spectrum (4) and it was assigned to the 0-0 component of the 3s Rydberg band (5). In our spectrum there appears another strong peak further to the red at $\lambda = 3911 \text{ \AA}$ (two-photon transition energy = $51\,124 \text{ cm}^{-1}$).

The comparable intensities of these two transitions and their two-photon energy difference of 629 cm^{-1} leads us to assign the lower peak to the 0-0 transition in contrast to the previous assignment (5). The higher peak is due then to the excitation of the $6a$ vibration [ground state frequency (9) 677 cm^{-1}]. Such an assignment can be supported by the similarity, in terms of band intensities and frequency assignment, of the corresponding pyrazine MPI spectrum (2). In addition by operating the QUI dye to its limits ($\sim 4 \text{ mJ}$ at the maximum of the dye profile) we could just see a weak transition at a two-photon distance of $\sim 677 \text{ cm}^{-1}$ lower than the assigned 0-0 one. This is obviously the $6a_1^0$ hot band.

Having found the 0-0 transition, we performed an almost complete vibrational analysis of the observed spectrum. The results of this analysis are given in Table I, where the symmetry and numbering of different modes is based on the assignment of Innes *et al.* (9). The more than one vibrational states that are proposed for the higher energy peaks imply assignments less secure than those of the lower energy peaks.

TABLE I
Vibrational Energies and Assignments for Pyrimidine

Laser λ (Å)	$2\nu_{\text{vac}}$ (cm^{-1})	$\Delta(2\nu_{\text{vac}})$ (cm^{-1})	Assignment
3911	51124	0	0-0
3889	51413	289	$6a_0^0 1_1^1$
3873	51626	502	?
3863.5	51753	629	$6a_0^1$
3839	52083	959	1_0^1
3827	52246	1122	$9a_0^1$
3817.5	52376	1252	$6a_0^2$
3805	52542	1424	$8a_0^1$
3793.5	52708	1584	$6a_0^1 1_0^1$
3781	52882	1758	$6a_0^1 9a_0^1$
3771.5	53015	1891	$6a_0^3$; 1_0^2
3760.5	53170	2046	$6a_0^1 8a_0^1$; $1_0^1 9a_0^1$
3749	53333	2209	$6a_0^2 1_0^1$
3747	53362	2238	$9a_0^2$
3735	53519	2395	$6a_0^2 9a_0^1$; $1_0^1 8a_0^1$
3726	53662	2538	$6a_0^4$; $1_0^2 6a_0^1$; $9a_0^1 8a_0^1$
3717	53792	2682	$6a_0^2 8a_0^2$
3704.5	53974	2850	1_0^3 ; $6a_0^3 1_0^1$; $8a_0^2$
3691.5	54163	3039	$1_0^2 9a_0^1$; $6a_0^3 9a_0^1$
3682	54304	3180	$6a_0^5$; $1_0^2 6a_0^2$
3671.5	54459	3355	$9a_0^3$; $1_0^2 8a_0^1$
3662.5	54592	3468	$6a_0^4 1_0^1$; $1_0^3 6a_0^1$
3650.5	54771	3647	$6a_0^4 9a_0^1$; $9a_0^2 8a_0^1$
3640	54930	3806	1_0^4 ; $6a_0^6$; $6a_0^3 1_0^2$
3628	55112	3988	$1_0^3 9a_0^1$; $6a_0^1 9a_0^3$
3620	55234	4110	$1_0^3 6a_0^2$; $6a_0^5 1_0^1$
3610	55387	4263	$6a_0^5 9a_0^1$; $8a_0^3$
3599	55556	4432	$1_0^4 6a_0^1$; $6a_0^4 1_0^2$; $6a_0^7$
3587	55742	4618	$6a_0^2 9a_0^3$
3579	55866	4742	$1_0^3 6a_0^3$; $6a_0^6 1_0^1$; 1_0^5
3570	56028	4899	$6a_0^6 9a_0^1$
3561	56165	5041	$1_0^4 6a_0^2$; $6a_0^5 1_0^2$

TABLE II

Frequency Values and Symmetry of Vibrations in the $n \rightarrow 3s$ Rydberg Transition of Pyrimidine

Frequency values from (MPI) spectra (cm^{-1})	Frequency values from (OP) spectra ⁽⁵⁾ (cm^{-1})	Frequency values from (PE) spectra ⁽⁵⁾ (cm^{-1})	Frequency values in ground state ⁽⁹⁾ (cm^{-1})	Assignment ⁽⁹⁾ and symmetry ⁽⁹⁾
635	633	653	677	6a (a_1)
959	950	984	991	1 (a_1)
1122	1106	1209	1147	9a (a_1)
1424	1441	-	1569	8a (a_1)

The vibrational structure is built on the 1, 6a, 8a, and 9a totally symmetric vibrations and their combinations. We should note that the photoelectron vibrational structure is attributed to the same three main vibrations 1, 6a, 9a, while the weaker 8a vibration is assigned only in the one-photon absorption spectrum (5). Table II gives the frequency values of the different vibrations which appear in one-photon (OP) (5), MPI, and PES (5) spectra, as well as their ground state values (9). The 1, 6a, and 9a vibrations appear also in the pyrazine MPI 3s Rydberg spectrum (2).

We also observe from Fig. 1a and Table I that the strongest peaks are due to the 1 and 6a vibrations only, while the weaker peaks are due to transitions where 9a and/or 8a vibrations are active, too.

The term value of our assigned 0-0 band is $24\,037\text{ cm}^{-1}$ [I.P. = 9.32 eV (10)], which is close to the 3s term values of benzene and other azabenzenes (2, 3). The "absence" of this transition from the one-photon spectrum might be due either to a strong valence-Rydberg state mixing or/and to increased radiationless deexcitation. These reasons together with a weaker Franck-Condon overlap factor, which is expected from the extended vibrational contour of the observed states (indicating a position change of the minimum of the 3s electronic state relative to the ground state minimum), could explain the weak, if not absent, 0-0 band in the one-photon spectra.

IV. CONCLUSIONS

The two-photon resonant three-photon ionization spectrum of the 3s Rydberg state of pyrimidine has been obtained. The 0-0 transition is further to the red than that assigned until now on the basis of one-photon absorption spectra. This molecule also shows strong vibrational activity built on the main 1, 6a, and 9a vibrations.

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