The multiphoton ionization spectrum of jet-cooled pyrimidine in the 3p Rydberg and 3B1(π*,n) states

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The multiphoton ionization spectrum of jet-cooled pyrimidine in the 3p Rydberg and $^3B_1$ (π^*,n) states

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Abstract

Resonance-enhanced multiphoton ionization (REMPI) has been applied to study the $n \to 3p$ Rydberg transition of pyrimidine (jet-cooled sample and mass resolved spectrum). Only the one component, the $3p_z(B_2)$, appears in the $(2 + 1)$ REMPI and the active vibrations are $v_{6a} = 622$, $v_1 = 946$, and $v_{9a} = 1116 \text{ cm}^{-1}$. The symmetry of the state was determined by polarization measurements (linear, circular polarization). The first (π^*,n) $^3B_1$ triplet state appears as a one-photon resonance in the three-photon ionization process.
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Keywords: Pyrimidine; 1,3-Diazine; REMPI; Rydberg states; Triplet; Mass spectrum

1. Introduction

Pyridine and the diazines (pyridazine, pyrimidine, and pyrazine) have a variety of singlet and triplet states, both (π^*,n) and (π^*,π) that are experimentally accessible in the 3–10 eV absorption region [1–7]. Some Rydberg states are also detectable in the absorption spectrum as sharp bands at energies above 6 eV. Resonance-enhanced multiphoton ionization (REMPI) is a powerful spectroscopic technique, capable to reveal or to discriminate Rydberg transitions from valence transitions. For pyridine and the diazines, transitions to some Rydberg states have been recorded/identified by REMPI spectroscopy. Specifically, Turner et al. [8] identified, by $(2 + 1)$ REMPI-static cell, the $n \to 3s$ Rydberg transition of pyridine and pyrazine. Bolovinos et al. [9] detected the $n3s$ transition of pyrimidine. For pyridazine, the $n3s$ Rydberg state has been located by Philis [10]. In a resent work [11], Tsubouchi and Susuki reported the energies of the $n3p$ Rydberg states for pyridine

($3p_x$, $3p_y$, and $3p_z$), pyridazine ($3p_z$), and pyrazine ($3p_y$, $3p_z$).

In the REMPI spectrum of pyrazine [8], the first triplet state $^3B_{3u}$ was also detected (372.8 nm) as a one-photon resonance in a three-photon ionization process. Villa et al. [12] demonstrated that the (π^*,n) $^3B_{3u} \leftarrow {}^1S_0$ $(1 + 2)$ REMPI transition of pyrazine can be detected in a supersonic molecular beam. For the other two diazines and for pyridine, the $(1 + 2)$ REMPI detection of the first (π^*,n) triplet state has not yet been reported. Of course, the first (π^*,n) $S_1 \leftarrow S_0$ transition of pyridine (origin at 287.52 nm) and of diazines (origin of pyridazine at 374.65 nm, of pyrimidine at 321.76 nm, and of pyrazine at 323.79 nm) can be easily detected by $(1 + 2)$ REMPI (jet-cooled and mass resolved) [13].

The purpose of this article is to investigate the $n3p$ Rydberg states of pyrimidine using $(2 + 1)$ REMPI spectroscopy (jet-cooled sample, mass resolved spectrum). Orbital n is the antisymmetric $n_-(b_2)$ molecular orbital. The $n_- \to 3p$ excitation has three states-components: $A_2(3p_x)$, $A_1(3p_y)$, and $B_2(3p_z)$. Only the one component has been detected in the VUV absorption spectrum at ~ 6.97 eV [2,4,14]. The symmetry of this state must be

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A_1 or B_2 (A_2 is one-photon forbidden). Using the polarization behavior of the two-photon process (linearly and circularly polarized light) we show that this state is the B_2. The lowest (π^*,n) triplet transition, $^3B_1 \leftarrow {}^1S_0$ [15–17], is also detected as a one-photon resonance [(1 + 2) REMPI].

2. Experimental

Vapors of pyrimidine (99% purity, Aldrich) and argon (250 kPa) were expanded into a vacuum chamber through a 10 Hz pulsed valve of 0.50 mm orifice diameter (General Valve, Iota One). The sample tube and the valve were held at ~45 °C by a wire resistance-heater. The supersonic molecular beam was crossed by a focused UV laser beam ($f = 7.5$ cm lens, power of the UV laser ~1 mJ/pulse) at about 4 cm downstream from the orifice. The UV laser beam (tuned range 341–358 nm) was produced from a nanosecond Nd:YAG pumped dye laser (Lambda Physik, Scanmate 2EC-400) with LC7100 dye and a frequency-doubling BBO III crystal. A pulse generator (SRS, model DG535) synchronized the laser pulse to the jet. The REMPI mass-selected spectrum was recorded on a PC as a function of laser wavelength by gating the parent ion ($m/z = 80$) with a boxcar integrator (SRS 250). A time-of-flight mass spectrometer (R.M. Jordan, Wiley-McLaren type, 1 m field-free region) separated the m_i ions. The mass spectra were recorded on a LeCroy 9310C digital oscilloscope. For the production of circularly polarized light,

a 1/4 wave retardation plate was used. The quality of the circular polarization was optimized by observing the elimination of the H_2O^+ ion signal in the laser induced mass spectrum. Ashfold et al. [18] observed, for the first time, the $4s \leftarrow 1b_1$ Rydberg transition of water in a $(3 + 1)$ REMPI experiment using laser light in the 355 nm region. This $(3 + 1)$ REMPI spectrum is strong in linearly polarized light and completely disappears in circularly polarized light [18]. Therefore, by adding a very small amount of water in the sample holder we were able to check the quality of circular polarization.

3. Results and discussion

3.1. Laser induced mass spectrum

Fig. 1 depicts the mass spectra induced by the nanosecond pulsed laser at the wavelength of 355.25 nm [(A) for circularly and (B) for linearly polarized light]. This wavelength corresponds to the position of the first peak (0_0^0 of the $n \rightarrow 3p$) in the $(2 + 1)$ REMPI spectrum of pyrimidine (see Fig. 2). The parent peak ($m/z = 80$) gains intensity when the laser beam is circularly polarized and is 1.5 times stronger compared to the mass spectrum induced by linear polarization. For the $C_2H_n^+$ peaks ($m/z = 24$–28) this factor is not obvious and the reason is that these peaks are also present (not with the same intensity as in Fig. 1) when the laser wavelength is out of resonance (for example, at 354 nm). At 354 nm, the intensity of the $m/z = 24$, 25, and 27 peaks is about 2/3 of that shown in Fig. 1B and
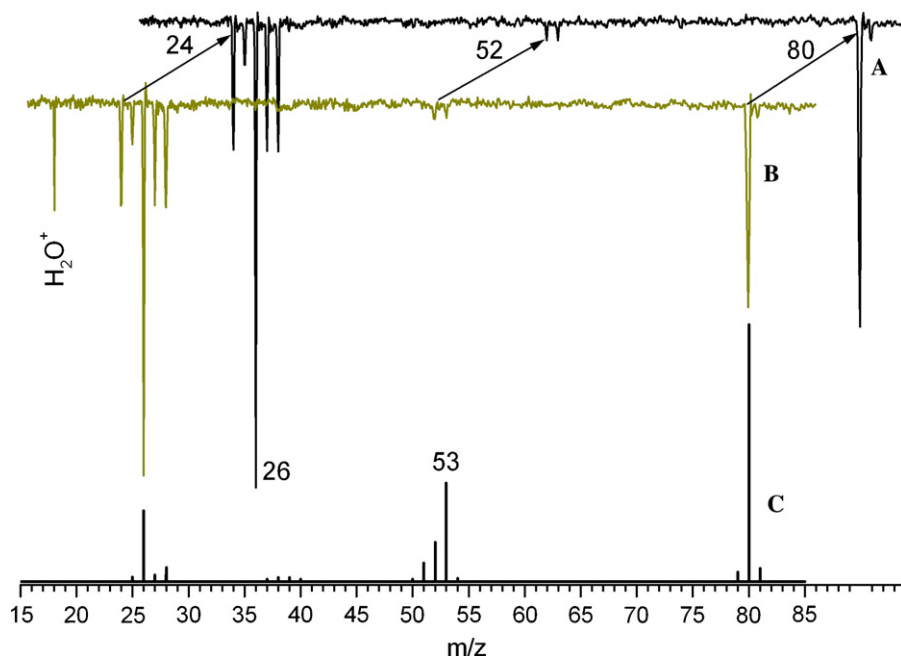

Fig. 1. Pyrimidine mass spectrum induced by 355.25 nm nanosecond dye laser using (A) circular polarization and (B) linear polarization. For the appearance of the H_2O^+ ion in (B) and its complete attenuation in (A) see the experimental part. For comparison, the normal (70 eV) electron impact ionization mass spectrum is included as (C) [19].
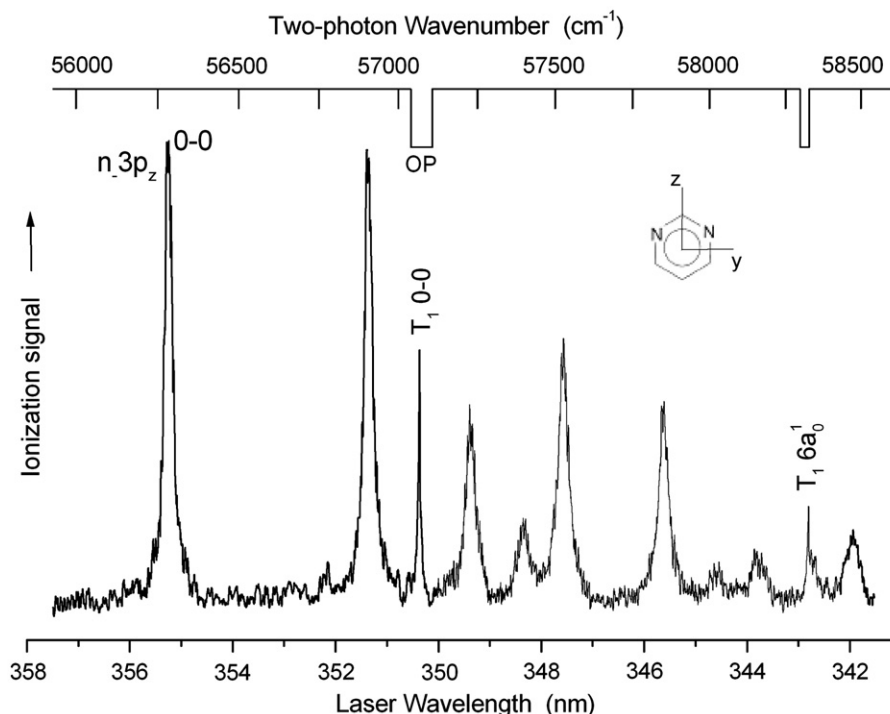
Fig. 2. REMPI spectrum of jet-cooled pyrimidine (linearly polarized laser). The two sharp peaks, marked by T_1, are (1 + 2) REMPI and all the other peaks are (2 + 1) REMPI.

the intensity of $m/z = 26$ is about the 1/4, respectively. The C^+ ion is also present at the resonant and nonresonant wavelengths. The H_2O^+ ion is an impurity and disappears when the laser light is circularly polarized. The electron impact mass spectrum of pyrimidine, as given by NIST [19], is included in Fig. 1 for comparison. The $m/z = 53$ ($C_3H_3N^+$) is one of the main peaks in the EI mass spectrum but it is just above the noise level in the nanosecond laser induced mass spectrum. This ion most probable corresponds to N-ethynyl-methylimine ($HC\equiv C-N=CH_2$)$^+$ or to acrylonitrile ($H_2C=CH-C\equiv N$)$^+$. The fragmentation mass pattern shows that photodissociation of pyrimidine is also taking place (from the valence $^1A_1$ $\pi\pi^*$ state, two-photon absorption) yielding the neutral fragments $HCN + C_3H_3N$ and, during the same laser pulse, C_3H_3N is ionized. The $C_3H_3N^+$ ion must have a large absorption cross section and by multiphoton absorption gives the background signals at $m/z = 24$–28 and 12. The HCN and C_3H_3N neutral fragments have been observed in the photodissociation of pyrazine with UV light [20]. Certainly, the $C_3H_3N^+$ ion is also formed from the pyrimidine ion (pyrimidine REMPI), by the ladder switching mechanism, and it is immediately photodissociated yielding mostly the $C_2H_2^+$ ($m/z = 26$) ion.

3.2. REMPI spectrum

Fig. 2 is the recorded REMPI spectrum ($m/z = 80$) of jet-cooled pyrimidine. Two very sharp peaks are present at 350.36 and 342.80 nm. The position of these peaks

coincides with the origin of the lowest triplet state $^3B_1$ and the $6a_0^1$ vibronic level, respectively, as were measured by laser induced phosphorescence of jet-cooled pyrimidine [15]. Therefore, the $^3B_1 \leftarrow {}^1S_0$ transition of pyrimidine is detectable by (1 + 2) REMPI spectroscopy. The other peaks (Fig. 2) are interpreted as a two-photon transition to the $3p$ Rydberg state (2 + 1 REMPI). This interpretation is secured, since the VUV absorption spectrum of pyrimidine shows "sharp" peaks in the 178 nm region [2,4,14]. The present experiment gives the 0–0 transition at $2 \times 28\,141$ cm^{-1} =

Table 1
Vibrational energies and assignments of peaks recorded in the REMPI spectrum of pyrimide

Laser λ (nm)	Energy (cm^{-1})	Δv (cm^{-1})	Assignment
355.25	$2 \times 28\,141$	0	0–0 $3p_z(^1B_2)$
351.37	$2 \times 28\,452$	622	$6a_0^1$
350.36	$28\,534$	0	0–0 $T_1(^3B_1)$
349.39	$2 \times 28\,614$	946	1_0^1
348.35	$2 \times 28\,699$	1116	$9a_0^1$
347.56	$2 \times 28\,764$	1246	$6a_0^2$
345.62	$2 \times 28\,925$	1568	$1_0^1 6a_0^1$
344.58	$2 \times 29\,012$	1742	$9a_0^1 6a_0^1$
343.83	$2 \times 29\,076$	1870	$6a_0^3$
342.80	$29\,163$	629	$6a_0^1 T_1$
342.71	$2 \times 29\,171$	2060	$1_0^1 9a_0^1$
341.93	$2 \times 29\,237$	2192	$1_0^1 6a_0^2$

In the ground cationic state of pyrimidine the vibrational frequencies are $v_{6a} = 636$, $v_1 = 954$, and $v_{9a} = 1126$ cm^{-1} [23].

56 282 cm^{-1} (6.977 eV). Using polarization measurements (linearly and circularly polarized laser) we found that the intensity I of the 0–0 band increases under circular polarization and the ratio $\Omega = I_{circ}/I_{lin} = 3/2$. This means [21,22] that the symmetry of this state is B_2 and not A_1. The adiabatic ionization potential of pyrimidine is 75 261 cm^{-1} [23] and using this value, the quantum defect of this state is $\delta = 0.60$. The vibrational analysis of the $n_- \rightarrow 3p_z(B_2)$ transition is given in Table 1. For the assignment of the bands, we have taken into consideration the vibrational frequencies of the ground cationic state of pyrimidine (ZEKE photoelectron spectroscopy) [23] and the original proposal of Parkin and Innes [2]. There is no evidence of another $3p$ component in the region that Table 1 covers.

Acknowledgment

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