

The electronic states of pyrimidine studied by VUV photoabsorption and electron energy-loss spectroscopy

F. Ferreira da Silva,^a D. Almeida,^a G. Martins,^a A. R. Milosavljević,^b
B. P. Marinković,^b S. V. Hoffmann,^c N. J. Mason,^d Y. Nunes,^a G. Garcia^{ef} and
P. Limão-Vieira^{*ad}

Received 5th January 2010, Accepted 10th March 2010

First published as an Advance Article on the web 28th April 2010

DOI: 10.1039/b927412j

The electronic state spectroscopy of pyrimidine C₄H₄N₂ has been investigated using both high resolution VUV photoabsorption in the energy range 3.7 to 10.8 eV (335 to 115 nm) and lower resolution electron energy loss in the range 2 to 15 eV. The low energy absorption band, assigned to the (π^*) $\leftarrow 7b_2(n_N)$ ($1^1B_1 \leftarrow 1^1A_1$) transition, at 3.85(4) eV and the vibrational progressions superimposed upon it have been observed for the first time, due to the availability of a high-resolution photon beam (0.075 nm), corresponding to 3 meV at the midpoint of the energy range studied. Vibronic coupling has been shown to play an important role dictating the nature of the observed excited states, especially for the lowest 1^1B_1 state. The 2^1B_1 state is proposed to have its origin at 7.026 eV according to the vibrational excitation reported in this energy region (7.8–8.4 eV). New experimental evidence of 4^1A_1 state with a maximum cross section at 8.800 eV is supported by previous *ab initio* quantum chemical calculations. Rydberg series have been assigned converging to the three lowest ionisation energy limits, 9.32 eV (2^2B_2), 10.41 eV (2^2B_1) and 11.1 eV ($2^2A_1 + 2^2A_2$) with new members reported for the first time and classified according to the magnitude of the quantum defects (δ). Additionally, the absolute differential cross section for inelastic electron scattering has been measured for the most intense band from 6.9 to 7.8 eV assigned to $1\pi\pi^*$ ($3^1A_1 + 2^1B_2$).

1. Introduction

It is now well established that a large amount of the energy deposited in the biological environment by ionising radiation, may be channelled into the biomolecular constituents,¹ such that the incident radiation liberates large numbers of low energy secondary electrons along the ionisation track. The resulting secondary electron energy distribution reveals that the majority of these secondary electrons have an energy below the ionisation threshold of most biomolecules and can induce significant amounts of both single and double strand breaks in cellular DNA.² Therefore, this electron induced degradation process may provide a doorway to mutations or induce cell death.³ Low energy electrons may also excite biomolecular targets through inelastic collisions and populate electronically

excited states which may subsequently decay with the production of ‘radicals’ whose chemical reactivity may strongly influence the local site chemistry. Though, interest in the electronic state spectroscopy provides key insights into photo-induced dissociation with applications in modelling biological relevant spectroscopic processes. Pyrimidine (1,3-diazine), C₄H₄N₂, belongs to the group of diazine ring molecules that may be used as a chemical or molecular model for the single nucleosides (thymine, cytosine and uracil) in nucleic acids. Hence a study of the photoabsorption spectroscopy and electron interactions with pyrimidine may provide an insight into the damage induced in larger biomolecules by ionising radiation.

UV photoabsorption by C₄H₄N₂ has been studied on several previous occasions^{4,5} and some electron energy loss spectra and *ab initio* multi-reference configuration interaction calculations have been reported.⁶ In addition, Knight *et al.*⁷ have carried out extensive analysis of the emission spectra, obtained by exciting selectively a number of vibronic levels in the lowest excited ($\pi^* \leftarrow n$) singlet state, while several calculations on symmetry adapted cluster-configuration interaction (SAC-CI)⁸ and equation of motion coupled-cluster methods (STEOM-CC),^{9–12} have been reported with high levels of accuracy. Moreover, *ab initio* quantum chemical studies of the vertically excited singlet states of pyrimidine have been performed by Malmqvist *et al.*,¹³ Billes *et al.*¹⁴ have measured and calculated vibrational frequencies at the Møller–Plesset perturbation and DFT levels. Two-photon

^aLaboratório de Colisões Atômicas e Moleculares, CEFITEC, Departamento de Física, FCT Universidade Nova de Lisboa, 2829-516 Caparica, Portugal. E-mail: plimaovieira@fct.unl.pt; Fax: +351-21 294 85 49; Tel: +351-21 294 85 76

^bLaboratory for Atomic Collision Processes, Institute of Physics, Pregrevica 118, 11080 Belgrade, Serbia

^cInstitute for Storage Ring Facilities, Aarhus University, Ny Munkegade, DK-8000, Aarhus C, Denmark

^dCentre of Molecular and Optical Sciences, Department of Physics and Astronomy, The Open University, Walton Hall, Milton Keynes, UK MK7 6AA

^eInstituto de Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano 113-bis, 28006 Madrid, Spain

^fDepartamento de Física de los Materiales, UNED, Senda del Rey 9, 28040 Madrid, Spain

spectra of the lowest electronic states have been analyzed by means of response theory calculations by Luo and co-workers.¹⁵ Åsbrink *et al.*¹⁶ reported the photoelectron spectrum of pyrimidine and other azabenzenes up to 25 eV, where the lowest ionisation energy was attributed to the removal of an electron from the nitrogen lone pairs. More recently, electronic state resolved PEPICO spectroscopy of pyrimidine has been reported by Plekan *et al.*¹⁷

The high resolution of the VUV photoabsorption spectra presented in this paper complements these previous optical studies and by combining such measurements with advanced theoretical calculations we can, for the first time, interpret the electronic state spectroscopy of C₄H₄N₂ below the lowest ionization energy.

2. Brief summary of the geometry and electronic configuration of pyrimidine, C₄H₄N₂

Pyrimidine, C₄H₄N₂, has C_{2v} symmetry in its electronic ground state and its 24 fundamental vibrational frequencies are labelled according to ref. 14. The outermost valence molecular orbital electron configuration in the electronic ground state (1¹A₁) can be represented as: ... (1a₂)² (11a₁)² (2b₁)² (7b₂)².⁶ The highest occupied molecular orbital (HOMO) has been identified as having n_N character; Åsbrink *et al.*¹⁶ have reported 7b₂ and 11a₁ as the lone pairs, while Bolovinos and co-workers⁵ have ascribed 2b₁ and 1a₂ as π character orbitals. Moreover, these latter authors have also identified the lowest unoccupied molecular orbital (LUMO) as π*(3b₂). On the basis of the convergence of Rydberg series observed by optical absorption, Palmer *et al.*⁶ have made use of the first four ionisation energies of pyrimidine ascribed to ²B₂, ²B₁, ²A₁ + ²A₂, with the corresponding vertical and adiabatic values (VIE/AIE), 9.73/9.32, 10.41/10.41, 11.23/11.10 and 11.39 eV, respectively. These values are in reasonable agreement with the AIE obtained in Åsbrink *et al.*'s¹⁶ photoelectron experiments. In the present work, Palmers' AIEs of 9.32 (7b₂)⁻¹, 10.41 (2b₁)⁻¹ and 11.10 eV (11a₁)⁻¹ have been used to calculate the quantum defects associated with transitions from the HOMO to Rydberg orbitals (Section 4.3). Recent theoretical studies have shown strong overlapping of the lowest Rydberg states with valence states resulting in complex intensity distribution in the electronic spectrum.^{9,11–13}

3. Experimental procedure

3.1 VUV photoabsorption

The present high-resolution VUV photoabsorption spectrum of pyrimidine was recorded using the UV1 beam line of the ASTRID synchrotron facility at Aarhus University, Denmark (Fig. 1–8). The experimental apparatus has been described elsewhere.¹⁸ Briefly, synchrotron radiation passes through a static gas sample and a photomultiplier is used to measure the transmitted light intensity. The incident wavelength is selected using a toroidal dispersion grating with 2000 lines/mm providing a resolution of 0.075 nm, corresponding to 3 meV at the midpoint of the energy range studied. For wavelengths below 200 nm (energies above 6.20 eV), helium is flushed through the

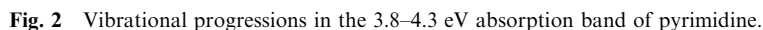
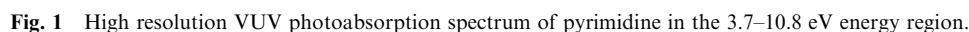
small gap between the photomultiplier and the exit window of the gas cell to prevent any absorption by air contributing to the spectrum. The sample pressure is measured using a capacitance manometer (Baratron). To ensure that the data is free of any saturation effects, absorption cross-sections are measured over the pressure range 0.007–0.750 Torr, with typical attenuations of less than 10%. The synchrotron beam ring current is monitored throughout the collection of each spectrum and background scans are recorded with the cell evacuated. Absolute photoabsorption cross sections were then obtained using the Beer–Lambert attenuation law:

$$I_t = I_0 \exp(-n\sigma x) \quad (1)$$

where I_t is the radiation intensity transmitted through the gas sample, I_0 is that through the evacuated cell, n the molecular number density of the sample gas, σ the absolute photoabsorption cross section, and x the absorption path length (25 cm). The accuracy of the cross section is estimated to be $\pm 5\%$. Only when absorption by the sample is very weak ($I_0 \approx I_t$), does the error increase as a percentage of the measured cross section.

3.2 Electron energy loss

Electron energy loss spectra have been measured at the Institute of Physics, Belgrade, using a cross beam experimental setup which has been described previously.¹⁹ Briefly, a non-monochromatic electron beam produced by an electron gun crossed a molecular beam produced by a non-magnetic stainless steel needle perpendicularly. The scattered electrons were then retarded and focused by a four-element cylindrical electrostatic lens into a double cylindrical mirror analyzer (DCMA). After being selected by energy, the electrons were focused by a three-element cylindrical lens into a single channel multiplier, working in a single counting mode. The highest energy resolution was limited by the initial thermal spread of incident electrons to be about 0.5 eV. The accuracy of the incident electron energy was determined to be ± 0.4 eV. The electron gun could be rotated around the gas needle over the range of scattering angles from -40° to 130° . The uncertainty of the angular scale was found to be better than $\pm 0.5^\circ$, while the angular resolution was estimated to be $\pm 2^\circ$. The base pressure was about 3×10^{-7} mbar and the operating pressure was in the range $(2-5) \times 10^{-6}$ mbar. All electron energy loss measurements were performed in a constant pass energy mode, by ramping the retarding potential at the entrance of DCMA. The energy loss scale was calibrated using the position of the elastic peak. Absolute differential cross section (DCS) for inelastic electron scattering were obtained using the recently published absolute elastic DCSs for pyrimidine²⁰ and inelastic/elastic intensity ratio recorded in our EEL spectrum at each scattering angle. The effect of the transmission function of the electron energy analyser was checked against EEL measured for Ar under the same experimental conditions, according to known absolute cross sections for elastic and inelastic scattering. During the measurements, the whole gas-handling system (sample container, pipes, and needle) was slightly heated (50–60 °C) to provide stable experimental conditions and to improve the signal.



photoabsorption of pyrimidine in the 2–15 eV energy range. The experimental photoabsorption spectrum for the pyrimidine molecule, as determined by the electron impact method (2–15 eV) is shown in Fig. 9. The high resolution cross section, obtained through an optical method (application of the Beer–Lambert law) in the range 3.7–10.8 eV has also been included in Fig. 9. Within the respective error bars (5% in the optical case and approximately 10% in the electron impact method), the agreement between the two sets of data is reasonable good.

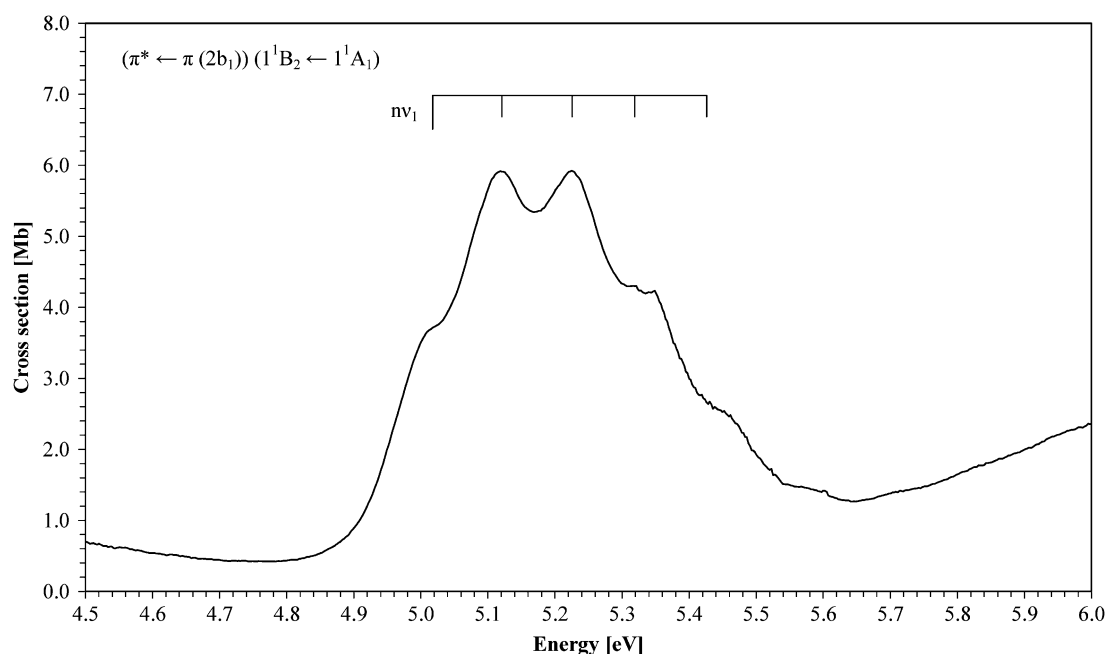


Fig. 3 Vibrational progressions in the 4.5–6.0 eV absorption band of pyrimidine.

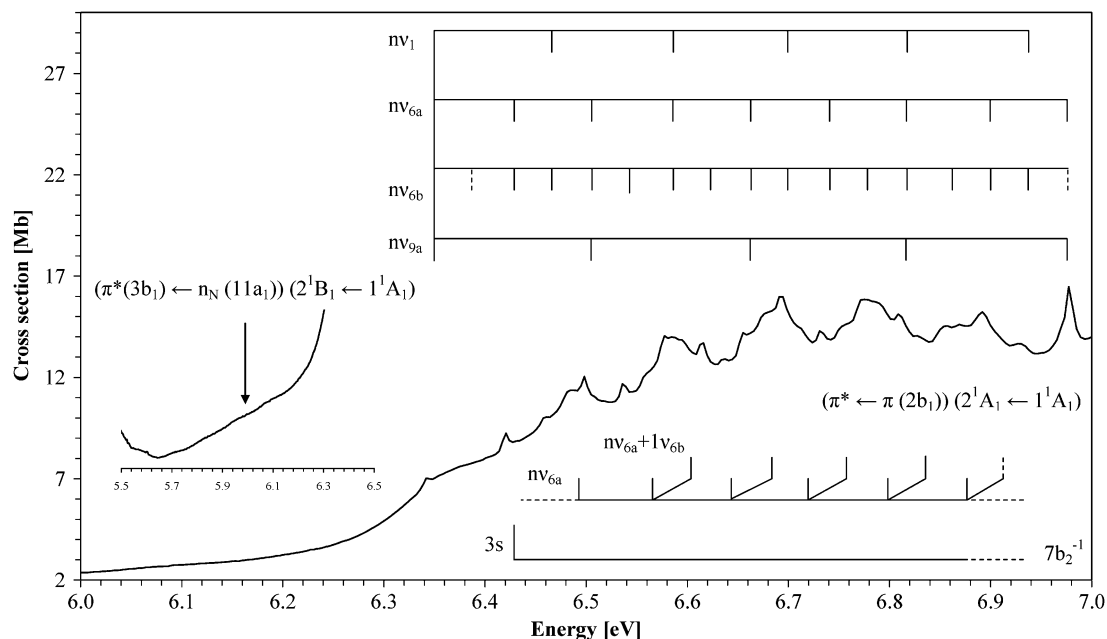


Fig. 4 Vibrational progressions in the 6.0–7.0 eV absorption band of pyrimidine.

3.3 Pyrimidine samples

The liquid samples used in the VUV and EEL measurements were purchased from Sigma-Aldrich with a minimum purity of $\geq 99\%$. The samples were degassed by a repeated freeze–pump–thaw cycle.

4. VUV photoabsorption and EELS results and discussion

The present full range of the VUV photoabsorption spectrum of pyrimidine, $C_4H_4N_2$, is shown in Fig. 1. All the fine

structures observed in the present spectrum are better resolved than in any previous work and several members of the Rydberg series are assigned for the first time. The major absorption bands can be classified mainly as valence transitions of $(\pi^* \leftarrow n_N)$ and $(\pi^* \leftarrow \pi)$ character and members of Rydberg series converging to the three lowest ionisation energies. The present data indicates that the electronic transitions have mixed valence-Rydberg character, which is in clear agreement with previous work. The singlet-singlet hot-bands (< 3.854 eV) in the spectrum give information on the low-frequency vibrations, several of them

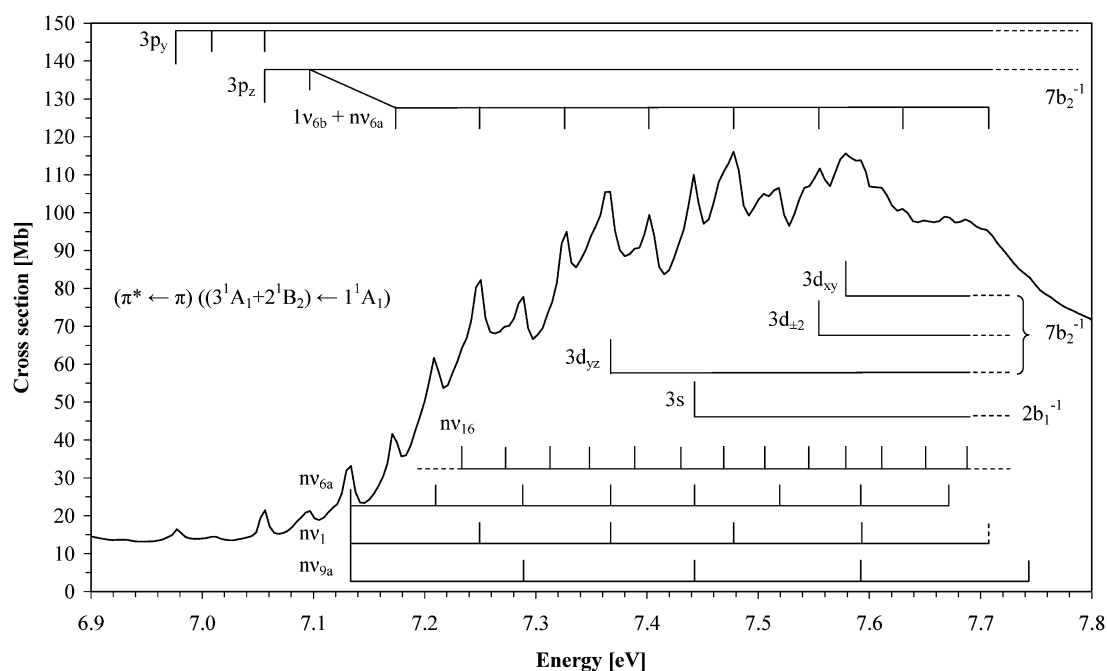


Fig. 5 Vibrational progressions in the 6.9–7.8 eV absorption band of pyrimidine.

being vibronically active (section 4.2). To avoid congestion, some of the fine structure above 3.854 eV and that extending to the ionisation limits in the pyrimidine spectrum, primarily coupled with Rydberg transitions, have not been labelled in the figures.

The symmetry forbidden ($\pi^*(3b_2) \leftarrow n_N(7b_2)$, $1^1A_2 \leftarrow 1^1A_1$) transition reported by Palmer *et al.*⁶ at ~ 4.7 eV, using a near-threshold electron energy loss spectroscopy, has also been detected in the VUV absorption measurements of Bolovinos *et al.*⁵ and

attributed to vibronic coupling with the lowest ($\pi^* \leftarrow \pi$) state, with a small vibrational progression with a separation of 0.095 eV (~ 770 cm⁻¹). However, we have not been able to detect such a transition in the present experiments, which we would also expect for the symmetry reasons reported. Moreover, due to the decreasing trends of the cross section in this energy region, we suspect that the early work of Bolovinos may have had a contamination from other nitrogen-containing molecules studied in that contribution.

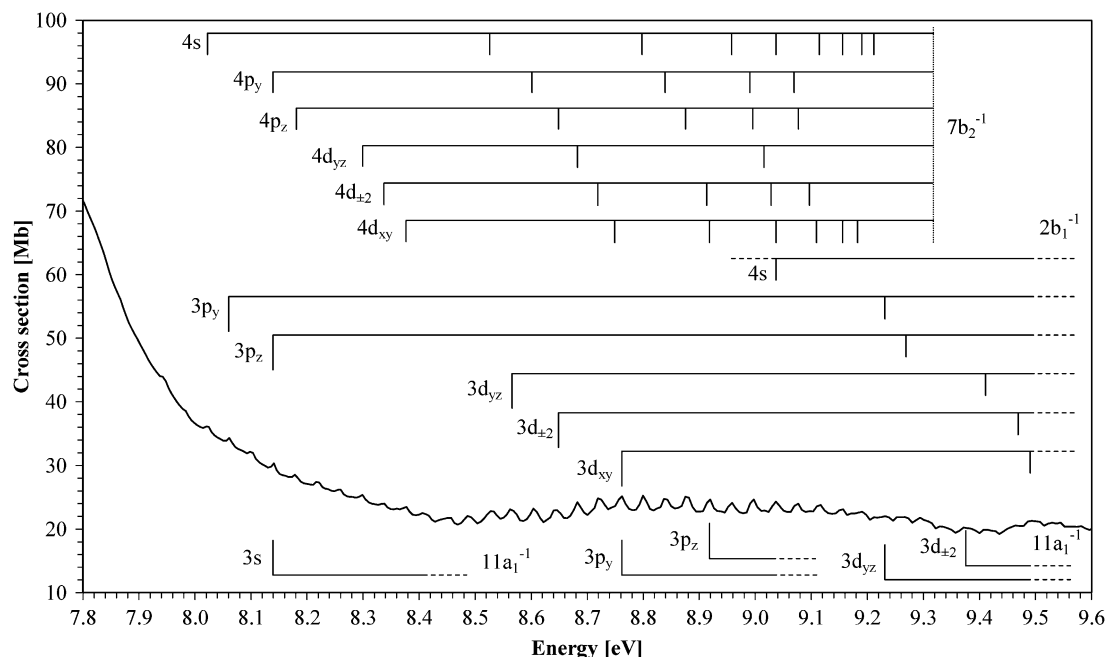


Fig. 6 Vibrational progressions in the 7.8–9.6 eV absorption band of pyrimidine.

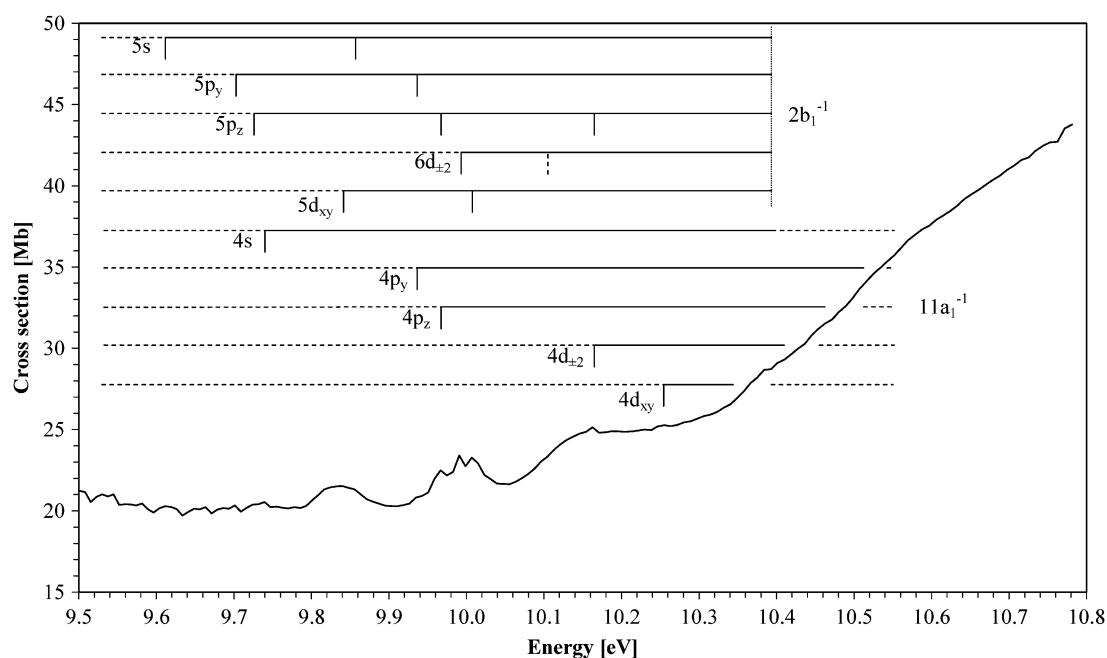


Fig. 7 Vibrational progressions in the 9.5–10.8 eV absorption band of pyrimidine.

4.1 Valence excitation of pyrimidine, C₄H₄N₂

Fig. 2 shows the structure between 3.8 and 4.3 eV. The energy of the band maximum agrees with both the calculated and experimental values of 4.183 eV. Vertical excitation and 0–0 transition energies of pyrimidine are shown in Table 1 and compared with other experiments and results of calculations. Notwithstanding the low intensity signal below 4.3 eV, the data provides the first high resolution photoabsorption evidence for features extending from 3.8 to 4.3 eV. The low

cross section and rich structure of this band has been identified as the first singlet-singlet absorption and assigned to the allowed ($\pi^*(2a_2) \leftarrow n_N(7b_2)$, $1^1B_1 \leftarrow 1^1A_1$) transition.⁵ Accordingly, the associated vibronic series are proposed to be mainly due to (C–H) in-plane bending and out-of-plane deformation, ring in-plane bending and have been assigned to combinations of $\nu'_1(a_1)$, $\nu'_4(b_1)$, $\nu'_{6a}(a_1)$, $\nu'_{6b}(b_2)$, $\nu'_9(a_1)$, although the nature of the features suggests that further modes and combinations may also contribute to the observed structure.

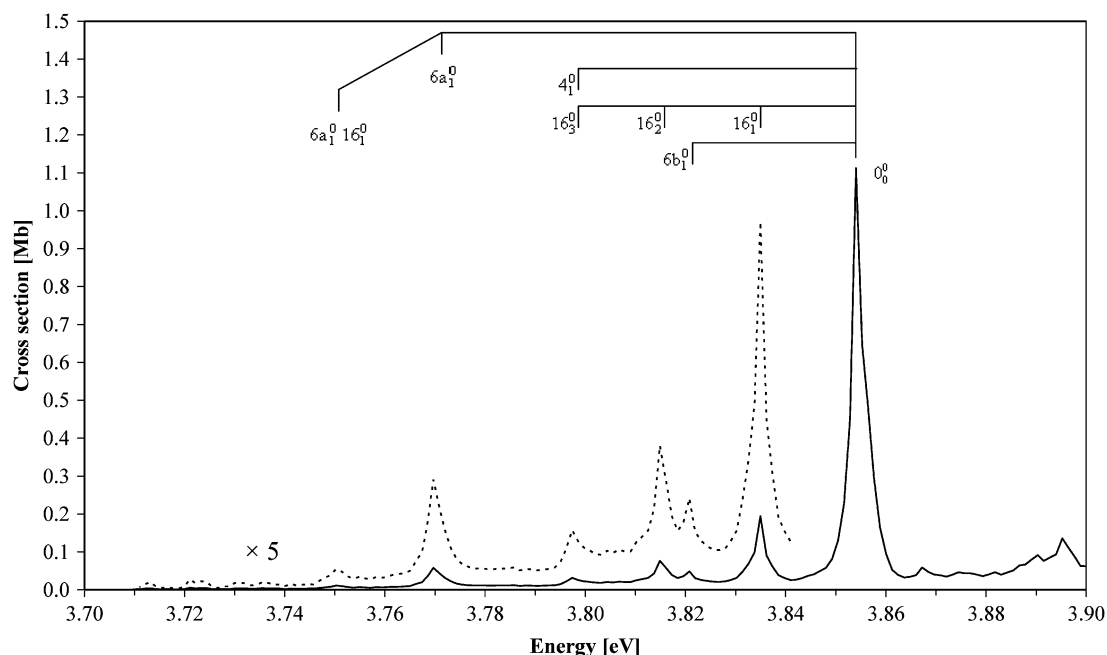


Fig. 8 Vibrational progressions in the 3.7–3.9 eV absorption band of pyrimidine, identifying hot bands.

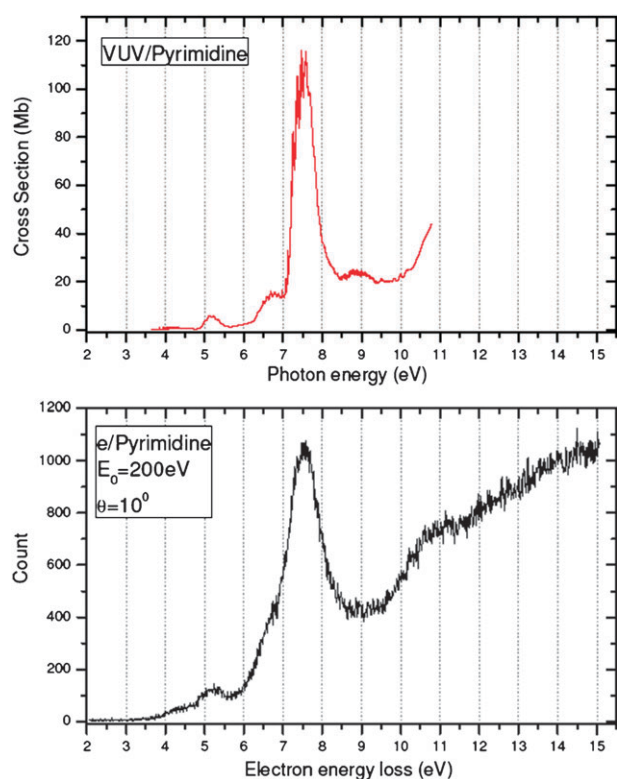


Fig. 9 Absolute photoabsorption cross section for the pyrimidine molecule as determined by optical (3.7–10.8 eV) method and corresponding electron energy loss (2–15 eV) spectrum.

None of the totally symmetric modes are vibronically active so that the excited states potential energy surfaces having shallow double-minimum structures, give rise to symmetry breaking effects.¹² The upper electronic states relax within the C_{2v} point group and the theoretical calculations of Fischer *et al.*¹² support the existence of a double-well potential in one or more asymmetric modes. The normal mode configuration may lead to Fermi resonances (Table 2), such as $2\nu'_4(b_1)$ in respect to $\nu'_1(a_1)$. The observed mean vibrational frequencies for the excited states of pyrimidine are compared with previous experimental and theoretical calculations in Table 3.

The absorption structure shown in Fig. 3 between 4.5 and 6.0 eV, has been assigned to $(\pi^* \leftarrow \pi(7b_2), 1^1B_2 \leftarrow 1^1A_1)$ with a maximum at 5.22(5) eV (Table 1). This band shows vibrational structure (Table 3 and 4) with tentative position of (0–0) at 5.01(6) eV where only one active mode assigned to the totally symmetric $\nu'_1(a_1)$. The mean energy is 0.102 eV and the ground state frequency is reported to be 0.119 eV.¹⁴

The broad features extending from 6.0 to 7.0 eV have been attributed to 2^1B_1 and 2^1A_1 , the former with no structure and centred at ~ 6.0 eV, the latter with its origin at 6.342 eV, in good agreement with most of the experimental and theoretical predictions (Table 1). The 6.0 eV feature is attributed principally to excitation from a nonbonding orbital localized on the N atom, $(\pi^*(3b_1) \leftarrow n_N(11a_1), 2^1B_1 \leftarrow 1^1A_1)^{5,6}$ (see inset in Fig. 4), while the second transition is due to $(\pi^* \leftarrow \pi(2b_1), 2^1A_1 \leftarrow 1^1A_1)$. This band maximum (6.695 eV)

agrees very well with the vertical energies calculated by Fischer *et al.*¹² (6.69 eV) and the experimental values reported by Bolovinos *et al.*⁵ and Palmer *et al.*⁶ Moreover, clear vibrational structure is observed at 6.342 eV and at higher energies, in good agreement with a theoretical prediction at 6.26 eV.¹² $\nu'_1(a_1)$, $\nu'_{6a}(a_1)$, $\nu'_{6b}(b_2)$ and $\nu'_9(a_1)$ modes are being excited (Table 5), with mean energies of 0.117, 0.078, 0.039 and 0.157 eV, respectively (Table 3). This band is also complicated by the presence of a 3s Rydberg state excitation (see section 4.3.1) in the low-energy region with the dominant vibrational mode appearing to be $\nu'_{6a}(a_1)$ coupled with $\nu'_{6b}(b_2)$ (Table 5), with mean energies of 0.078 and 0.039 eV, respectively.

The most intense band, extending from 6.9 to 7.8 eV has been assigned to the $1^1\pi\pi^*(3^1A_1 + 2^1B_2)$ transition, with a maximum at 7.478 eV (Table 1 and Fig. 5). Likewise the 6.0–7.0 eV band, the $(3^1A_1 + 2^1B_1)$ shows an excitation to a Rydberg states ($3p_y$ and $3p_z$) (section 4.3.1). The 0–0 position is observed at 7.134 eV, in agreement with ref. 6, and the observed well-developed vibrational structures have been assigned to excitation of $\nu'_1(a_1)$, $\nu'_{6a}(a_1)$ and $\nu'_9(a_1)$ (Table 6) together with $\nu'_{16}(a_2/b_1)$ (0.035 eV, 0.043/0.049 eV in the ground state¹⁴) (Table 6).

The differential cross section (DCS) for inelastic scattering upon excitation of the most intense band $1^1\pi\pi^*(3^1A_1 + 2^1B_2)$ peaking at about 7.5 eV is shown in Fig. 10. The recently reported, both measured and calculated, absolute DCSs for elastic scattering of electrons from pyrimidine¹⁸ are also presented. Since the elastic DCS is about two orders of magnitude higher than the inelastic cross section, it is scaled by a factor of 0.01 in Fig. 10, in order to facilitate visual comparison. The present inelastic DCS shows a similar angular behaviour to the elastic DCS, with pronounced forward-peaking which is characteristic of optically allowed excitations. Fig. 11 shows the angular dependencies of the intensity ratios of the EEL bands peaking at about 5.3 eV, assigned to $(\pi^* \leftarrow \pi(7b_2), 1^1B_2 \leftarrow 1^1A_1)$, and at about 6.55 eV, attributed to 2^1B_1 and 2^1A_1 , relative to the most intensive band at 7.5 eV, at an electron impact energy of 100 eV. These results indicate that the DCS of the corresponding excited states behave very similarly to the $1^1\pi\pi^*(3^1A_1 + 2^1B_2)$. A strong decrease in the inelastic DCSs with scattering angle limits the angular range where DCS ratios can be deduced with acceptable accuracy. The $(3^1A_1 + 2^1B_2)$ states have never been experimentally resolved which could be due to the lack of resolution in the experimental data of.^{5,6} However, a closer look in this energy region (Fig. 6), especially between 7.8–8.4 eV shows evidence of vibrational excitation, which has been suggested to be due to the ring and CH out-of-plane deformation ν'_{16} mode (Table 7). Therefore, the tentative assignment of 7.90(2) eV for the 'origin' of the 2^1B_2 band seems reasonable, which is in good agreement with the vertical theoretical prediction of Öhrn and Christiansen¹¹ placing it at 8.01 eV.

The $1^1\pi\pi^*4^1A_1$ state was not assigned experimentally despite the VUV spectra of Bolovinos *et al.*⁵ and Palmer *et al.*⁶ having shown a broad structure band centred at 8.8 eV with a width of 1 eV. Both authors have considered Rydberg transitions in this region only. This energy region is also extremely rich in

Table 1 Vertical excitation and 0–0 transition energies of pyrimidine (energies in eV)

Symmetry	This work	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]					
$n \rightarrow \pi^*$																
0 – 0	max.	max.	0 – 0	max.	0 – 0	max.	max.	max.	0 – 0	max.	0 – 0	max.	max.			
1^1B_1	3.854	4.183	3.853	—	—	—	—	3.853	4.32	4.24	4.40	3.91	4.55	3.74	4.26	3.82
1^1A_2	—	—	4.073	—	4.62	—	4.7	—	4.74	4.74	4.72	3.93	4.91	4.19	4.49	4.22
2^1B_1	—	~6.0	—	—	6.05	—	6.0	—	6.35	6.11	6.18	—	6.39	6.21	6.60	—
1^1A_2	—	—	—	—	6.05	—	5.7	—	5.98	5.84	5.94	—	6.00	5.56	6.31	—
$\pi \rightarrow \pi^*$																
1^1B_2	5.01(6)	5.22(5)	4.998	5.00	5.12	—	5.12	—	5.29	5.01	5.04	5.02	5.44	5.29	5.52	5.33
2^1A	6.34	6.69(1)	6.49	—	—	—	6.70	—	6.86	6.5	6.87	6.31	6.95	6.69	7.10	6.96
1^1B_{1c}	—	—	5.902	6.49	6.70	—	—	—	—	—	—	—	—	6.21	6.60	—
$3^1A_1 + 2^1B_2$	7.134	7.478	7.254	—	7.57	7.14	7.59	—	7.74	7.35	7.44	—	7.65	7.80/8.10	8.10/8.33	7.67
1^1B_2	—	—	7.254	—	—	—	—	—	8.03	7.69	7.77	—	8.01	—	—	8.21
4^1A_1	8.486	8.800	—	—	—	—	—	—	—	—	—	—	—	—	—	8.80
A_1																
$3p_y \leftarrow b_2$	6.977	—	6.978	—	6.97	—	6.984	—	—	—	—	6.94	7.43	—	—	—
$3d_{yz} \leftarrow b_2$	7.367	—	—	—	—	—	7.983 ^a	—	—	—	—	7.59	8.08	—	—	—
$3s \leftarrow a_1$	8.141	—	—	—	—	—	8.077 ^a	—	—	—	—	8.10	8.20	—	—	—
$4p_y \leftarrow b_2$	8.141	—	—	—	8.14, 8.29	—	8.182	—	—	—	—	8.15	8.64	—	—	—
$4d_{yz} \leftarrow b_2$	8.299	—	—	—	8.36	—	8.335, 8.378	—	—	—	—	8.32	8.81	—	—	—
B_2																
$3s \leftarrow b_2$	6.421	—	6.339	—	6.42	—	6.423	—	—	—	—	6.25	6.74	—	—	—
$3p_z \leftarrow b_2$	7.056	—	—	—	6.97	—	6.984	—	—	—	—	6.93	7.42	—	—	—
$3d_{\pm 2} \leftarrow b_2$	7.55(5)	—	—	—	—	—	7.556 ^a	—	—	—	—	7.55	8.04	—	—	—
$4s \leftarrow b_2$	8.020	—	—	—	7.97	—	8.024	—	—	—	—	7.87	8.36	—	—	—
$4p_z \leftarrow b_2$	8.178	—	—	—	8.14, 8.29	—	8.182	—	—	—	—	8.10	8.59	—	—	—
$4d_{\pm 2} \leftarrow b_2$	8.338	—	—	—	8.36	—	8.335, 8.378	—	—	—	—	8.34	8.83	—	—	—
B_1																
$3s \leftarrow b_1$	7.442	—	—	—	—	—	7.293 ^a	—	—	—	—	7.25	7.51	—	—	—
$3p_z \leftarrow b_1$	8.141	—	—	—	—	—	8.062	—	—	—	—	8.00	8.26	—	—	—
$3d_{xy} \leftarrow b_2$	7.578	—	—	—	—	—	8.141 ^a	—	—	—	—	7.79	8.28	—	—	—
$3d_{\pm 2} \leftarrow b_1$	8.640	—	—	—	—	—	8.092 ^a	—	—	—	—	8.61	8.87	—	—	—
$4d_{xy} \leftarrow b_2$	8.377	—	—	—	8.36	—	8.335, 8.378	—	—	—	—	8.38	8.87	—	—	—
A_2																
$3p_y \leftarrow b_1$	8.061	—	—	—	—	—	8.062	—	—	—	—	8.03	8.29	—	—	—
2^1B_2	—	—	9.325 ^b	—	—	—	9.32 ^b	—	—	—	9.48	—	—	—	—	—
2^1B_1	—	—	—	—	—	—	10.41 ^b	—	—	—	10.96	—	—	—	—	—
$2^1A_1 + 2^1A_2$	—	—	—	—	—	—	11.10 ^b	—	—	—	10.44/11.34	—	—	—	—	—
The last decimal of the energy value is given in brackets for these less-resolved features. ^a Calculated value. ^b Means adiabatic.																

The last decimal of the energy value is given in brackets for these less-resolved features.^a Calculated value. ^b Means adiabatic.

Rydberg states converging to the three lowest ionisation energies, ($7b_2^{-1}$), ($2b_1^{-1}$), ($11a_1^{-1}$) (Fig. 6). However, comparing the oscillator strengths calculated for the 2^1A_1 and 4^1A_1 states,¹³ and the experimental intensities of the corresponding bands (Fig. 1), our VUV data supports the theoretical prediction of Malmqvist *et al.*¹³ Therefore, we place the maximum at 8.800 eV and tentatively assigned the origin of this band at 8.486 eV, which also coincides with the excitation of several quanta of out-of-plane ring and CH deformation $v'_{16b}(b_1)$ mode (Table 7).

4.2 1^1B_1 singlet-singlet hot-band of pyrimidine, $C_4H_4N_2$

The 1^1B_1 singlet-singlet hot-band description has been recently discussed by Fischer *et al.*¹² However, due to the high resolution achieved in the VUV experiments (~ 1 meV), a new analysis is proposed (Fig. 8) and we have also slightly extended it to lower energies (Table 13). However, such an assignment is still a difficult task, owing to vibronic interactions associated with closely spaced singlet excited state and to the presence of strong Fermi resonances. We assign the feature at 3.770 eV as $6a_1^0$ in good agreement with the 3.769 eV value reported by

Knight *et al.*⁷ The other active modes have been assigned to v'_{6b} and v'_{16} and the energy values are listed in Table 13.

4.3 Rydberg transitions

The VUV spectrum above 6.0 eV consists of structures superimposed on a diffuse absorption feature extending to the lowest ionisation energy (IE). The proposed Rydberg structures are labelled in Fig. 4–7 and presented in Tables 10–15. The peak positions, E_n , have been compared using the Rydberg formula:

$$E_n = E_i - R/(n - \delta)^2 \quad (3)$$

where E_i is the ionisation energy (adiabatic values), n is the principal quantum number of the Rydberg orbital of energy E_n , R is the Rydberg constant (13.61 eV), and δ the quantum defect resulting from the penetration of the Rydberg orbital into the core. Quantum defects in the range 0.7–1.0, 0.4–0.6 and less than 0.3 are observed for ns, np, and nd transitions, respectively. The experimental values for the lowest terms of the ns(a_1), np(b_1) and nd(a_2) ($n = 3, 4$) Rydberg series are in good agreement with the calculations of ref. 6 and 11.

Table 2 Vibrational assignments in the 3.8–4.3 eV absorption band of pyrimidine

Energy/eV	Vibrational modes	$\Delta\nu'_1$ (eV)	$\Delta\nu'_4$ (eV)	$\Delta\nu'_{6a}$ (eV)	$\Delta\nu'_{6b}$ (eV)	$\Delta\nu'_{9a}$ (eV)
3.854	ν_{00}	—	—	—	—	—
3.895	$1\nu_{6b}$	—	—	—	0.041	—
3.911	$1\nu_4$	—	0.057	—	—	—
3.931	$1\nu_{6a}$	—	—	0.077	—	—
3.937	$2\nu_{6b}$	—	—	—	0.042	—
3.971	$2\nu_4/1\nu_1$	0.117	0.060	—	—	—
3.980	$3\nu_{6b}$	—	—	—	0.043	—
3.955	$1\nu_{6b} + 1\nu_4$	—	0.060	—	—	—
3.992	$2\nu_{6b} + 1\nu_4$	—	0.055	—	—	—
4.00(7) (s)	$2\nu_{6a}$	—	—	0.076	—	—
4.010	$1\nu_{6b} + 2\nu_4$	—	0.055	—	—	—
4.014	$1\nu_{9a}$	—	—	—	—	0.160
4.02(2) (s)	$4\nu_{6b}$	—	—	—	0.042	—
4.032	$3\nu_4$	—	0.061	—	—	—
4.038	$3\nu_{6b} + 1\nu_4$	—	0.058	—	—	—
4.05(0) (s)	$2\nu_{6b} + 2\nu_4$	—	0.058	—	—	—
4.057	$2\nu_{6a} + 1\nu_4$	—	0.050	—	—	—
4.062	$5\nu_{6b}$	—	—	—	0.040	—
4.068	$1\nu_{6b} + 3\nu_4$	—	0.058	—	—	—
4.080	$4\nu_{6b} + 1\nu_4$	—	0.058	—	—	—
4.08(5) (s)	$3\nu_{6a}$	—	—	0.078	—	—
4.091	$4\nu_4/2\nu_1$	0.120	0.062	—	—	—
4.096	$3\nu_{6b} + 2\nu_4$	—	0.058	—	—	—
4.105	$6\nu_{6b}/2\nu_{6b} + 3\nu_4$	—	0.055	—	0.043	—
4.116	$5\nu_{6b} + 1\nu_4$	—	0.054	—	—	—
4.125	$1\nu_{6b} + 4\nu_4$	—	0.057	—	—	—
4.134	$4\nu_{6b} + 2\nu_4$	—	0.054	—	—	—
4.140	$5\nu_{6b} + 1\nu_{6a}$	—	—	0.078	—	—
4.149	$7\nu_{6b}/5\nu_4$	—	0.058	—	0.044	—
4.155	$3\nu_{6b} + 3\nu_4$	—	0.059	—	—	—
4.165	$2\nu_{6b} + 4\nu_4/4\nu_{6a}$	—	0.060	0.080	—	—
4.17(3) (b)	$5\nu_{6b} + 2\nu_4/2\nu_{9a}$	—	0.057	—	—	0.159
4.183	$1\nu_{6b} + 5\nu_4$	—	0.058	—	—	—
4.188	$4\nu_{6b} + 3\nu_4$	—	0.054	—	—	—
4.194	$8\nu_{6b}$	—	—	—	0.045	—
4.206	$6\nu_4/3\nu_1$	0.115	0.057	—	—	—
4.216	$5\nu_{6b} + 2\nu_{6a}$	—	—	0.076	—	—
4.221	$2\nu_{6b} + 5\nu_4$	—	0.056	—	—	—
4.231	$5\nu_{6b} + 3\nu_4$	—	0.058	—	—	—
4.239	$9\nu_{6b}/1\nu_{6b} + 6\nu_4/5\nu_{6a}$	—	0.056	0.074	0.046	—
4.243	$4\nu_{6b} + 4\nu_4$	—	0.055	—	—	—
4.255	$8\nu_{6b} + 1\nu_4$	—	0.061	—	—	—
4.265	$7\nu_4$	—	0.059	—	—	—
4.281	$10\nu_{6b}/2\nu_{6b} + 6\nu_4$	—	0.060	—	0.042	—
4.290	$5\nu_{6b} + 4\nu_4$	—	0.059	—	—	—
4.299	$1\nu_{6b} + 7\nu_4$	—	0.060	—	—	—

(s) means shoulder; (b) broad feature (the last decimal of the energy value is given in brackets for these less-resolved features).

4.3.1 Rydberg series converging to the ionic ground state, $\tilde{X}^2B_2(7b_2^{-1})$. The lowest energy Rydberg band, 1B_2 , (Table 1) in the present spectrum is assigned to the $n_N(7b_2) \rightarrow 3s$ transition (Fig. 4). Innes *et al.*,⁴ have proposed this transition at 6.339 eV which is not in agreement with the present result due to the shape of the observed structure. Though, in agreement with Bolovinos *et al.*,⁵ Palmer *et al.*,⁶ and with Öhrn and Christiansen,¹¹ the structure at 6.421 eV is identified as the origin of this band (the adiabatic transition), corresponding to a plausible quantum defect of $\delta = 0.85$ (Table 8).

Assignments in the spectrum above 8.0 eV for higher members of the ns Rydberg series, where $n \geq 4$ members are expected to lie, is rather complex due to the presence of several other Rydberg series and the fine structure observed. The vibrational structure observed in this low member of the ns Rydberg series has been assigned to $\nu'_{6a}(a_1)$ coupled with

$\nu'_{6b}(b_2)$ (Table 5), with mean energies of 0.078 and 0.039 eV, respectively, the former in clear agreement with the observations of Palmer and co-workers.⁶ Moreover, the average $\nu'_{6a}(a_1)$ excitation energy in the $n_N \rightarrow 3s$ band is essentially the same as observed in the neutral electronic ground state (0.084 eV), reinforcing the fact that the HOMO is merely non-bonding and also the fact that the lowest ionic band shows an energy spacing of 0.081 eV for this mode.¹⁶

The second member $n = 4$, is located at 8.020 eV with a quantum defect $\delta = 0.81$. The peak at 9.036 eV is interpreted as $n = 8$, with a calculated quantum defects $\delta = 1.08$, slightly high for an ns Rydberg series. This is probably due to the broadness of the peak which also accommodates vibrational structure.

Palmer *et al.*⁶ reported that a $n_N(7b_2) \rightarrow np$ excitation may contribute to three Rydberg excitations, two optically allowed (p_y , 1A_1 and p_z , 1B_2) and a third (p_x , 1A_2) symmetry-forbidden.

Table 3 Observed mean vibrational frequencies for excited states of pyrimidine (energies in eV)

State	This work		[4]		[11]		[12]		[14]	
$n \rightarrow \pi^*$	assignment	ν'	assignment	ν'	assignment	ν'	assignment	ν'	assignment	ν'
1^1B_1	1	0.117	1	0.117	a_1	0.118	—	—	1	0.117
	4	0.057	—	—	b_2	0.079	—	—	—	—
	6a	0.077	6a	0.076	a_1	0.080	—	—	6a	0.076
	6b	0.043	—	—	b_1	0.046	—	—	6b	0.042
	9a	0.160	—	—	a_1	0.179	—	—	9a	0.138
$\pi \rightarrow \pi^*$	assignment	ν'	assignment	ν'	assignment	ν'	assignment	ν'	assignment	ν'
1^1B_2	1	0.102	1	0.118	—	—	1	0.118	1	0.124
2^1A_1	1	0.117	?	0.095	—	—	1	0.112	—	—
	6a	0.078	—	—	—	—	6a	0.070	—	—
	6b	0.039	—	—	—	—	—	—	—	—
	9a	0.157	—	—	—	—	9a	0.118	—	—
$3^1A_1 + 2^1B_2$	1	0.114	?	0.113	—	—	1	0.127	—	—
	6a	0.076	—	—	—	—	6a	0.085	—	—
	9a	0.153	—	—	—	—	9a	0.140	—	—
	16	0.035	—	—	—	—	—	—	—	—
$3p_y \leftarrow b_2$	6a	0.079	1	0.077	—	—	—	—	—	—
	6b	0.032	—	—	—	—	—	—	—	—
$3p_z \leftarrow b_2$	6a	0.076	—	—	—	—	—	—	—	—
	6b	0.041	—	—	—	—	—	—	—	—

Table 4 Vibrational assignments in the 4.5–6.0 eV absorption band of pyrimidine

Energy/eV	Vibrational modes	$\Delta\nu'_1$ (eV)
5.016	ν_{00}	—
5.119	$1\nu_1$	0.103
5.225	$2\nu_1$	0.106
5.319	$3\nu_1$	0.094
5.42(6) (b)	$4\nu_1$	0.107

(b) Means broad (the last decimal of the energy value is given in brackets for this less-resolved feature).

The np_y series has its first member at 6.977 eV, with a quantum defect of 0.59, in good agreement with most of the reported data (see Table 1). This series is accompanied by vibrational excitation of modes $\nu'_{6a}(a_1)$ and $\nu'_{6b}(b_2)$ (Table 3 and 9). The peaks at 8.99(1) and 9.07(0) eV with quantum defects $\delta = 0.57$ and $\delta = 0.62$, respectively, appear as shoulders.

The first member of the $n_N(7b_2) \rightarrow np_z$ series (Table 1) appears at 7.056 eV with a quantum defect $\delta = 0.55$, and the next at 8.178 eV with a quantum defect $\delta = 0.55$ (Table 9). We have been able to identify up to eight members for this

Table 5 Vibrational and sequential vibrational assignments in the 6.0–7.0 eV absorption band of pyrimidine

Energy/eV	Vibrational modes	$\Delta\nu'_1$ (eV)	$\Delta\nu'_{6a}$ (eV)	$\Delta\nu'_{6b}$ (eV)	$\Delta\nu'_{9a}$ (eV)
6.342	ν_{00}	—	—	—	—
6.37(8) (b)	$1\nu_{6b}$	—	—	0.036	—
6.421	$2\nu_{6b}/1\nu_{6a}$	—	0.079	0.043	—
6.45(8) (b)	$3\nu_{6b}/1\nu_1$	0.116	—	0.037	—
6.498	$4\nu_{6b}/2\nu_{6a}/1\nu_{9a}$	—	0.077	0.040	0.156
6.536	$5\nu_{6b}$	—	—	0.038	—
6.577	$6\nu_{6b}/3\nu_{6a}/2\nu_1$	0.119	0.079	0.041	—
6.616	$7\nu_{6b}$	—	—	0.039	—
6.655	$8\nu_{6b}/4\nu_{6a}/2\nu_{9a}$	—	0.078	0.039	0.157
6.695	$9\nu_{6b}/3\nu_1$	0.118	—	0.040	—
6.731	$10\nu_{6b}/5\nu_{6a}$	—	0.076	0.036	—
6.77(5) (b)	$11\nu_{6b}$	—	—	0.044	—
6.809	$12\nu_{6b}/6\nu_{6a}/4\nu_1/3\nu_{9a}$	0.114	0.078	0.034	0.154
6.858	$13\nu_{6b}$	—	—	0.049	—
6.892	$14\nu_{6b}/7\nu_{6a}$	—	0.083	0.034	—
6.927	$15\nu_{6b}/5\nu_1$	0.118	—	0.035	—
6.96(9) (s)	$16\nu_{6b}/8\nu_{6a}/4\nu_{9a}$	—	0.077	0.042	0.160
6.488	$1\nu_{6a}$	—	—	—	—
6.56(0) (b)	$2\nu_{6a}$	—	0.072	—	—
6.59(5) (s)	$2\nu_{6a} + 1\nu_{6b}$	—	—	0.035	—
6.637	$3\nu_{6a}$	—	0.077	—	—
6.67(7) (s)	$3\nu_{6a} + 1\nu_{6b}$	—	—	0.040	—
6.71(3) (s)	$4\nu_{6a}$	—	0.076	—	—
6.75(2) (s)	$4\nu_{6a} + 1\nu_{6b}$	—	—	0.039	—
6.79(0) (b)	$5\nu_{6a}$	—	0.077	—	—
6.82(7) (b)	$5\nu_{6a} + 1\nu_{6b}$	—	—	0.030	—
6.869	$6\nu_{6a}$	—	0.079	—	—

(b) means broad; (s) means shoulder (the last decimal of the energy value is given in brackets for this less-resolved feature).

Table 6 Vibrational and sequential vibrational assignments in the 6.9–7.8 eV absorption band of pyrimidine

Energy/eV	Vibrational modes	$\Delta\nu'_1$ (eV)	$\Delta\nu'_{6a}$ (eV)	$\Delta\nu'_{9a}$ (eV)	$\Delta\nu'_{16}$ (eV)
7.134	ν_{00}	—	—	—	—
7.208	$1\nu_{6a}$	—	0.074	—	—
7.251	$1\nu_1$	0.117	—	—	—
7.289	$2\nu_{6a}/1\nu_{9a}$	—	0.081	0.155	—
7.367	$3\nu_{6a}/2\nu_1$	0.116	0.078	—	—
7.442	$4\nu_{6a}/2\nu_{9a}$	—	0.075	0.153	—
7.478	$3\nu_1$	0.111	—	—	—
7.519	$5\nu_{6a}$	—	0.077	—	—
7.59(2) (s)	$6\nu_{6a}/4\nu_1/3\nu_{9a}$	0.114	0.073	0.150	—
7.668	$7\nu_{6a}$	—	0.076	—	—
7.70(6) (s)	$5\nu_1$	0.114	—	—	—
7.74(4) (s)	$4\nu_{9a}$	—	—	0.152	—
7.23(4) (s)	$1\nu_{16}$	—	—	—	—
7.272	$2\nu_{16}$	—	—	—	0.038
7.31(4) (s)	$3\nu_{16}$	—	—	—	0.042
7.349	$4\nu_{16}$	—	—	—	0.035
7.38(9) (w)	$5\nu_{16}$	—	—	—	0.040
7.42(9) (s)	$6\nu_{16}$	—	—	—	0.040
7.46(8) (s)	$7\nu_{16}$	—	—	—	0.039
7.50(5) (w)	$8\nu_{16}$	—	—	—	0.037
7.54(6) (s)	$9\nu_{16}$	—	—	—	0.041
7.578	$10\nu_{16}$	—	—	—	0.032
7.61(1) (s)	$11\nu_{16}$	—	—	—	0.033
7.64(9) (w)	$12\nu_{16}$	—	—	—	0.038
7.686	$13\nu_{16}$	—	—	—	0.037

(s) means shoulder; (w) weak feature (the last decimal of the energy value is given in brackets for this less-resolved feature).

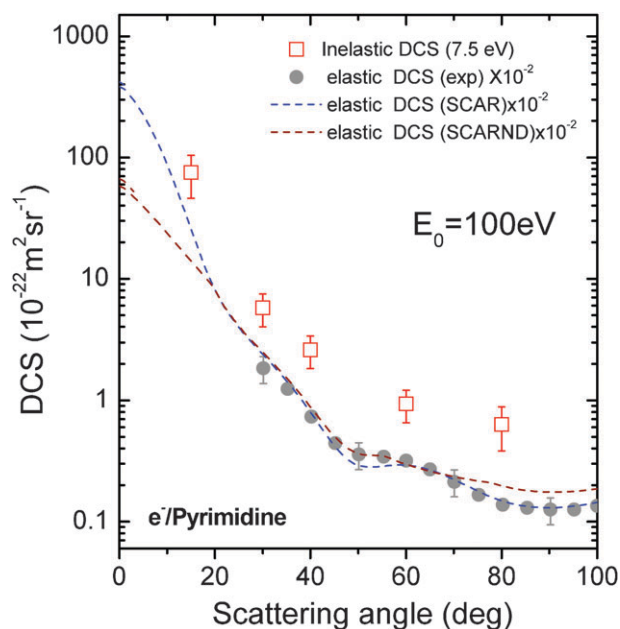


Fig. 10 Differential Cross Sections (DCS) for the $1\pi\pi^*$ ($3^1A_1 + 2^1B_2$) band peaking at about 7.5 eV at an electron impact energy of 100 eV. The experimental (full circles) and theoretical (lines) elastic DCS¹⁸ are presented as well, scaled by a factor 0.01.

series. Vibrational excitation of modes $\nu'_{6a}(a_1)$ and $\nu'_{6b}(b_2)$ are particularly active.

The $n_N(7b_2) \rightarrow 3d_{yz}$ transition, $1A_1$, (Table 1) in the present spectrum is assigned to 7.367 eV (Fig. 5), which is in reasonable agreement with Palmer *et al.*⁶ and with Öhrn and Christiansen,¹¹ corresponding to a quantum defect of

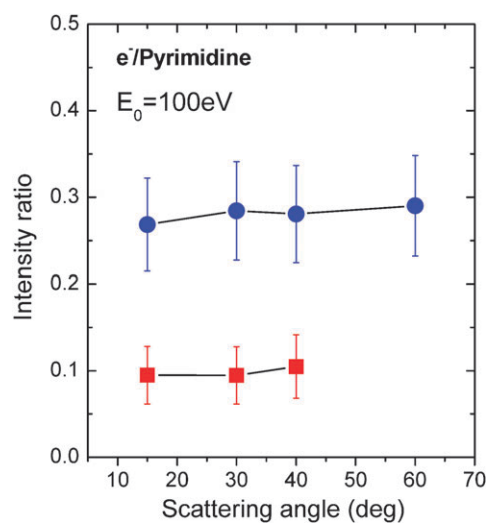


Fig. 11 Angular dependencies of the intensity ratios of EEL bands peaking at about 5.3 eV (circles) and 6.55 eV (squares) relative to the most intensive band at 7.5 eV at an electron impact energy of 100 eV.

$\delta = 0.36$ (Table 10). As far as $n = 6$ member is concerned, we were not able to assign it due to several Rydberg series coupled with vibrational excitation. For the 9.01(7) eV we propose $n = 7$, with a $\delta = 0.30$, although its intensity is particularly low.

The $n_N(7b_2) \rightarrow 3d_{\pm 2}$ transition, $1B_2$, (Table 1) appears at 7.55(5) eV with a quantum defect $\delta = 0.22$. This value is in good agreement with the calculated values 7.556 eV of Palmer *et al.*⁶ and 7.55 eV of Öhrn and Christiansen.¹¹ The features at 8.91(3) and 9.03(0) eV with quantum defects

Table 7 Vibrational assignments in the 7.8–9.6 eV absorption band of pyrimidine

Energy/eV	Vibrational modes	$\Delta\nu'_{16}$ (eV)
7.90(2) (w)	—	—
7.943	1v ₁₆	0.041
7.984	2v ₁₆	0.041
8.020	3v ₁₆	0.036
8.061	4v ₁₆	0.041
8.09(8) (b)	5v ₁₆	0.037
8.141	6v ₁₆	0.043
8.178	7v ₁₆	0.037
8.21(6) (b)	8v ₁₆	0.038
8.26(0) (b)	9v ₁₆	0.044
8.299	10v ₁₆	0.039
8.338	11v ₁₆	0.039
8.377	12v ₁₆	0.039
8.41(1) (b)	13v ₁₆	0.034
8.486	—	—
8.527	1v ₁₆	0.041
8.562	2v ₁₆	0.035
8.604	3v ₁₆	0.042
8.646	4v ₁₆	0.042
8.682	5v ₁₆	0.036
8.719	6v ₁₆	0.037
8.762	7v ₁₆	0.043
8.800	8v ₁₆	0.038
8.837	9v ₁₆	0.037
8.875	10v ₁₆	0.038
8.920	11v ₁₆	0.045
8.958	12v ₁₆	0.039
8.997	13v ₁₆	0.039
9.037	14v ₁₆	0.040
9.076	15v ₁₆	0.039
9.116	16v ₁₆	0.040
9.157	17v ₁₆	0.041
9.19(1) (b)	18v ₁₆	0.034

(w) means weak feature; (b) means peak broad (the last decimal of the energy value is given in brackets for this less-resolved feature).

Table 8 Energy values, quantum defect assignments of the ns Rydberg series converging to the ionic electronic ground state $\tilde{X}^2B_2(7b_2^{-1})$ of pyrimidine (energies in eV)

Energy/eV			
Present work	6	Quantum defect	Assignment
6.421	6.423	0.85	3s
8.020	8.024	0.81	4s
8.527	8.576	0.86	5s
8.800	8.809	0.89	6s
8.958	8.965	0.87	7s
9.036	9.047	1.08	8s
9.116	9.123	0.84	9s
9.157	9.164	0.86	10s
9.190	—	0.77	11s
9.21(1) (w)	—	0.83	12s

(w) means weak feature (the last decimal of the energy value is given in brackets for this less-resolved feature).

$\delta = 0.22$ and $\delta = 0.15$, respectively, appear as shoulder structures (Table 10).

The first member of the last nd series (7.578 eV) converging to the ionic ground state of pyrimidine, has been assigned to $n_N(7b_2) \rightarrow 3d_{xy}$ transition, 1B_1 , (Table 10), in good agreement with ref. 11 (Table 1) and with a quantum defect $\delta = 0.20$. The second feature is assigned at 8.377 eV (with the same value

for the quantum defect) and in agreement with ref. 6 and 11. There is a strong evidence of vibronic coupling with the ν'_{16} mode for $n = 3$ (see Table 7). The quantum defects for the peaks at 9.11(0) and 9.15(6) eV, $\delta = -0.05$ and $\delta = -0.11$, respectively, may suggest contributions from other members of Rydberg series converging to the ionic ground state and also vibrational excitation.

4.3.2 Rydberg series converging to the ionic electronic first excited state, $\tilde{A}^2B_1(2b_1^{-1})$. Rydberg series converging to ionic electronic first excited state are associated with the vacation of $\pi(b_1)$ orbitals. Accordingly, Åsbrink *et al.*¹⁶ reported a 3sa₁ Rydberg transition at 7.5 eV in good agreement with the present value of 7.442 eV (Table 1). Moreover, Palmer *et al.*⁶ assigned the peaks observed at 8.062 and 9.234 eV to b₁3p ($\delta = 0.59$) and b₁4p ($\delta = 0.58$) whereas in the present work we observe these features at 8.061 (3p_y) and 9.232 eV (4p_y), respectively (Table 11). The $\pi(b_1) \rightarrow 3p_y$ transition, 1B_1 , (Table 1) in the present spectrum is assigned to 8.141 eV, which is in reasonable agreement with Palmer *et al.*⁶ and with Öhrn and Christiansen,¹¹ corresponding to a quantum defect of $\delta = 0.55$ (Table 10). Three other nd series are proposed (Table 11), where $\pi(b_1) \rightarrow 3d_{\pm 2}$ is in good agreement with the theoretical calculation of Öhrn and Christiansen¹¹ (Table 1).

4.3.3 Rydberg series converging to the ionic electronic second excited state, $\tilde{B}^2A_1(11a_1^{-1})$. Several low members of ns, np_y, np_z, nd_{yz}, nd_{±2} and nd_{xy} Rydberg series converging to the ionic electronic second excited state of pyrimidine have been assigned in Table 12. Öhrn and Christiansen¹¹ have calculated the $b_1 \rightarrow 3s$ transition, 1A_1 , at 8.10 eV which is found to be in agreement with our experimental value of 8.141 eV (Table 1). To the authors' knowledge, no other calculations are available for higher members of Rydberg series converging to the ionic excited states of pyrimidine. Therefore, with quantum defect calculations as our only guide, we cannot propose assignments for these bands with confidence, so Table 12 is just a tentative assignment.

4.4 Absolute photoabsorption cross sections

Previous absolute VUV photoabsorption cross sections of pyrimidine are only available in the energy ranges 3.85–9.00 eV⁵ and 5.0–11.8 eV.⁶ Bolovinos *et al.*⁵ and Palmer *et al.*⁶ reported cross section values at ~ 7.5 eV of ~ 53.2 and 95.0 Mb†, respectively, which is not in agreement with the present value of 116.1 Mb. Bolovinos reported a much smaller cross section than Palmer and the present measurements. Normally, if a contaminant is present in the sample, a low cross section is due to the partial pressure from the contaminant and we believe this may be the explanation for Bolovinos' low cross section. Moreover, they report some structure in the 4.5–4.9 eV (Fig. 3b in ref. 5), which is not present in our experiments, reinforcing our suspicions that it should be due to the presence of pyridine, which has also been investigated in their studies on gaseous azabenzenes. For the newly reported bands 2^1B_2 at 7.902 eV and the $^1\pi\pi^* 4^1A_1$ at 8.800 eV, we obtain local cross sectional values of 49.09 and 25.26 Mb, respectively. The 1B_1 singlet-singlet hot-band with its origin at

† 1 Mb = 1×10^{-18} cm² = 1×10^{-22} m²

Table 9 Energy values, quantum defects and vibrational assignments of the np_y , np_z Rydberg series converging to the ionic electronic ground state $\tilde{X}^2B_2(7b_2^{-1})$ of pyrimidine (energies in eV)

Energy/eV		Quantum defect	$\Delta v'_{6a}$ (eV)	$\Delta v'_{6b}$ (eV)	Assignment
Present work	6				
6.977	6.984	0.59	—	—	$3p_y$
7.009	—	—	—	0.032	$3p_y + 1v'_{6b}$
7.056	—	—	0.079	—	$3p_y + 1v'_{6a}$
8.141	8.182	0.60	—	—	$4p_y$
8.604	8.649	0.64	—	—	$5p_y$
8.837	8.884	0.69	—	—	$6p_y$
8.99(1) (s)	9.006	0.57	—	—	$7p_y$
9.07(0) (s)	—	0.62	—	—	$8p_y$
7.056	—	0.55	—	—	$3p_z$
7.097	—	—	—	0.041	$3p_z + 1v'_{6b}$
7.171	—	—	0.074	—	$3p_z + 1v'_{6b} + 1v'_{6a}$
7.251	—	—	0.080	—	$3p_z + 1v'_{6b} + 2v'_{6a}$
7.328	—	—	0.077	—	$3p_z + 1v'_{6b} + 3v'_{6a}$
7.402	—	—	0.074	—	$3p_z + 1v'_{6b} + 4v'_{6a}$
7.478	—	—	0.076	—	$3p_z + 1v'_{6b} + 5v'_{6a}$
7.555	—	—	0.077	—	$3p_z + 1v'_{6b} + 6v'_{6a}$
7.630	—	—	0.075	—	$3p_z + 1v'_{6b} + 7v'_{6a}$
7.70(6) (s)	—	—	0.076	—	$3p_z + 1v'_{6b} + 8v'_{6a}$
8.178	—	0.55	—	—	$4p_z$
8.646	—	0.51	—	—	$5p_z$
8.875	—	0.47	—	—	$6p_z$
8.997	—	0.51	—	—	$7p_z$
9.076	—	0.53	—	—	$8p_z$

(s) means peak shoulder (the last decimal of the energy value is given in brackets for this less-resolved feature).

Table 10 Energy values and quantum defects of the nd_{yz} , $nd_{\pm 2}$, nd_{xy} Rydberg series converging to the ionic electronic ground state $\tilde{X}^2B_2(7b_2^{-1})$ of pyrimidine (energies in eV)

Energy/eV		Quantum defect	Assignment
Present work	6		
7.367	—	0.36	$3d_{yz}$
8.299	—	0.35	$4d_{yz}$
8.682	—	0.38	$5d_{yz}$
—	—	—	$6d_{yz}$
9.01(7) (w)	—	0.30	$7d_{yz}$
7.55(5) (s)	—	0.22	$3d_{\pm 2}$
8.338	8.335	0.28	$4d_{\pm 2}$
8.719	8.731	0.24	$5d_{\pm 2}$
8.91(3) (s)	8.928	0.22	$6d_{\pm 2}$
9.03(0) (s)	—	0.15	$7d_{\pm 2}$
9.09(6) (w)	—	0.21	$8d_{\pm 2}$
7.578	—	0.20	$3d_{xy}$
8.377	—	0.20	$4d_{xy}$
8.75(0) (s)	—	0.11	$5d_{xy}$
8.920	—	0.16	$6d_{xy}$
9.037	—	0.07	$7d_{xy}$
9.11(0) (s)	—	−0.05	$8d_{xy}$
9.15(6) (b)	—	−0.11	$9d_{xy}$

(w) means weak feature; (s) means peak shoulder; (b) means broad feature (the last decimal of the energy value is given in brackets for this less-resolved feature).

3.854 eV has a cross section value of 1.112 Mb. Finally, we report the maximum local cross section value at 4.183 eV to 1.222 Mb. The agreement of previous cross sections measured

at the ASTRID beamline with the most precise data available in the literature (see Eden *et al.*²² and Limão-Vieira *et al.*²³ and references therein, for example), suggests that the present pyrimidine cross sections can be relied upon across the range studied.

5. Conclusions

The present work provides the first complete optical electronic spectra of pyrimidine and the most reliable set of absolute photoabsorption cross sections available from 3.7 to 10.8 eV. Within the uncertainty of 5% for the optical case and approximately 10% for the electron impact method, the agreement between the two sets of data is very good. Fine structure in the 4.0 eV energy region is reported here for the first time, the 2^1B_1 state is proposed to have its origin at 7.026 eV according to the vibrational excitation reported in this energy region (7.8–8.4 eV) and new experimental evidence for the 4^1A_1 state with a maximum at 8.800 eV is supported by previous *ab initio* quantum chemical calculations.

The observed photoabsorption structure has been assigned to a combination of valence and Rydberg transitions on the basis of comparison with available calculations of vertical excitation energies and oscillator strengths for this molecule. Fine structures have been assigned to vibrational series, involving excitation of the $v'_1(a_1)$, $v'_4(b_1)$, $v'_{6a}(a_1)$, $v'_{6b}(b_2)$, $v'_9(a_1)$ (C–H) in-plane bending and out-of-plane deformation and ring in-plane bending modes. The available theoretical results are in good agreement with the experimental data and predict significant mixing of Rydberg and π^* states.

Table 11 Energy values and quantum defects of the ns, np_y, np_z, nd_{yz}, nd_{±2}, nd_{xy} Rydberg series converging to the ionic electronic first excited state $\tilde{A}^2B_1(2b_1^{-1})$ of pyrimidine (energies in eV)

Energy/eV	Quantum defect	Assignment
7.442	0.86	3s
9.037	0.84	4s
9.611	0.85	5s
9.85(6) (s)	1.00	6s
8.061	0.59	3p _y
9.232	0.58	4p _y
9.701	0.59	5p _y
9.93(5) (s)	0.59	6p _y
8.141	0.55	3p _z
9.26(6) (b)	0.54	4p _z
9.72(4) (b)	0.52	5p _z
9.966	0.40	6p _z
—	—	7p _z
10.163	0.43	8p _z
8.562	0.28	3d _{yz}
9.41(4) (b)	0.29	4d _{yz}
8.640	0.22	3d _{±2}
9.45(0) (b)	0.22	4d _{±2}
—	—	5d _{±2}
9.991	0.23	6d _{±2}
10.10(5) (s)	0.21	7d _{±2}
8.762	0.12	3d _{xy}
9.49(3) (b)	0.13	4d _{xy}
9.840	0.07	5d _{xy}
10.007	0.12	6d _{xy}

(s) means peak shoulder; (b) means broad structure (the last decimal of the energy value is given in brackets for this less-resolved feature).

Table 12 Energy values and quantum defects of the ns, np_y, np_z, nd_{yz}, nd_{±2}, nd_{xy} Rydberg series converging to the ionic electronic second excited state $\tilde{B}^2A_1(11a_1^{-1})$ of pyrimidine (energies in eV)

Energy/eV	Quantum defect	Assignment
8.141	0.86	3s
9.740	0.84	4s
8.762	0.59	3p _y
9.93(5) (s)	0.58	4p _y
8.920	0.50	3p _z
9.966	0.54	4p _z
9.232	0.30	3d _{yz}
9.371	0.20	3d _{±2}
10.163	0.19	4d _{±2}
9.49(3) (b)	0.09	3d _{xy}
10.25(5) (b)	−0.01	4d _{xy}

(s) means peak shoulder; (b) means broad structure (the last decimal of the energy value is given in brackets for this less-resolved feature).

Acknowledgements

DA acknowledges the Portuguese Foundation for Science and Technology (FCT-MCTES) for a post-graduate scholarship SFRH/BD/61645/2009. ARM and BPM acknowledge the

Table 13 Vibrational assignments in the region of the 1B_1 singlet–singlet hot bands of pyrimidine

Energy/eV	Assignment	$\Delta v'_4$ (eV)	$\Delta v'_{6a}$ (eV)	$\Delta v'_{6b}$ (eV)	$\Delta v'_{16}$ (eV)
3.750	6a ₁ ⁰ 16a ₁ ⁰	—	—	—	0.020
3.770	6a ₁ ⁰	—	0.084	—	—
3.797	16 ₃ ⁰ /14 ₁ ⁰	0.057	—	—	0.018
3.815	16 ₂ ⁰	—	—	—	0.020
3.821	6b ₁ ⁰	—	—	0.033	—
3.835	16 ₁ ⁰	—	—	—	0.019
3.854	0 ₀ ⁰	—	—	—	—

support from the Ministry of Science and Technological Development of Republic of Serbia under project 141011. PLV acknowledges the visiting research fellow position in the Department of Physics and Astronomy, The Open University, UK, together with NJM the support from the British Council for the Portuguese-English joint collaboration and together with GG from CSIC, Madrid for the Spanish-Portuguese Project No. HP2006-0042; Ministerio de Ciencia e Innovación (project FIS2009-10245), Spain is also acknowledge. The authors wish to acknowledge the beam time at the ISA synchrotron facility, Aarhus University, Denmark, I3 Integrated Activity on Synchrotron and Free Electron Laser Science (IA-SFS), contract number RII3-CT-2004-506008, under the Research Infrastructure Action of the FP6 EC programme Structuring the European Research Area. The I3 programme European Light Sources Activities (ELISA), grant agreement number 226716, is also acknowledged. Some of this work forms part of the EU/ESF RADAM COST Action-P9, the Electron Controlled Chemical Lithography (ECCL) CM0601, Astrochemistry CM0805 COST Action and the ESF RADAM programme.

References

- 1 L. Sanche, *Eur. Phys. J. D*, 2005, **35**, 367.
- 2 B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels and L. Sanche, *Science*, 2000, **287**, 1658.
- 3 C. von Sonntag, in *The Chemical Basis for Radiation Biology*, Francis, London, 1987.
- 4 K. K. Innes, I. G. Ross and W. R. Moomaw, *J. Mol. Spectrosc.*, 1988, **132**, 492.
- 5 A. Bolovinos, P. Tsekeris, J. Philis, E. Pantos and G. Andritsopoulos, *J. Mol. Spectrosc.*, 1984, **103**, 240.
- 6 M. H. Palmer, I. C. Walker, M. F. Guest and A. Hopkirk, *Chem. Phys.*, 1990, **147**, 19.
- 7 A. E. W. Knight, C. M. Lawburgh and C. S. Parmenter, *J. Chem. Phys.*, 1975, **63**, 4336.
- 8 Y. Li, J. Wan and X. Xu, *J. Comp. Chem.*, 2007, **28**, 1658.
- 9 J. E. Del Bene, J. D. Watts and R. J. Bartlett, *J. Chem. Phys.*, 1997, **106**, 6051.
- 10 M. Nooijen, *Spectrochim. Acta Part A*, 1999, **55**, 539.
- 11 A. Öhrn and O. Christiansen, *Phys. Chem. Chem. Phys.*, 2001, **3**, 730.
- 12 G. Fischer, Z.-L. Cai, J. R. Reimers and P. Wormell, *J. Phys. Chem. A*, 2003, **107**, 3093.
- 13 P.-Å. Malmqvist, B. O. Roos, M. P. Fülscher and A. P. Rendell, *Chem. Phys.*, 1992, **162**, 359.
- 14 F. Billes, H. Mikosch and S. Holly, *J. Mol. Struct. (Theochem)*, 1998, **423**, 225.
- 15 Y. Luo, H. Ågren, S. Knuts and P. Jørgensen, *Chem. Phys. Lett.*, 1993, **213**, 356.

-
- 16 L. Åsbrink, C. Fridh, B. Ö. Jonsson and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, 1972, **8**, 215.
- 17 O. Plekan, M. Coreno, V. Feyer, A. Moise, R. Richter, M. de Simone, R. Sankari and K. C. Prince, *Phys. Scr.*, 2008, **78**, 058105.
- 18 S. Eden, P. Limão-Vieira, S. V. Hoffmann and N. J. Mason, *Chem. Phys.*, 2006, **323**, 313.
- 19 A. R. Milosavljević, S. Madžunkov, D. Šević, I. Čadež and B. P. Marinković, *J. Phys. B: At. Mol. Opt. Phys.*, 2006, **39**, 609.
- 20 J. B. Maljković, A. R. Milosavljević, F. Blanco, D. Šević, G. García and B. P. Marinković, *Phys. Rev. A*, 2009, **79**, 052706.
- 21 J. A. Davies, N. J. Mason, G. Marston and R. P. Wayne, *J. Phys. B*, 1995, **28**, 4179.
- 22 S. Eden, P. Limão-Vieira, S. V. Hoffmann and N. J. Mason, *Chem. Phys.*, 2007, **331**, 232.
- 23 P. Limão-Vieira, S. Eden, P. A. Kendall, N. J. Mason, A. Giuliani, J. Heinesch, M.-J. Hubin-Franskin, J. Delwiche and S. V. Hoffmann, *Int. J. Mass Spectrom.*, 2004, **233**, 335.