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Photoelectron and threshold photoelectron valence spectra of pyridine[⋆]

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Abstract. The pyridine molecule has been examined by the means of photoelectron and threshold photoelectron spectroscopies. Ionization energies were determined for both outer and inner valence orbitals and new adiabatic values were also resolved. Vibronic structure associated with several states was assigned mainly to be due to C–C stretches and ring bends. Additionally a Rydberg state converging to $7b_2$ state was ascribed. The data shown here are in a good agreement with previous results and brings some new insights into the electronic structure of this biologically and astrochemically relevant and important molecule.

1 Introduction

Pyridine molecule, shown in Figure 1, was chosen as the subject of this study. This molecule is often used as a precursor to agrochemicals (bacteri- and herbicides) and medicines (sulfapyridine or tripelennamine) [1] and also utilized as a solvent or chemical reagent [2]. Many chemicals contain pyridine ring structure, like B-group vitamins or nicotine [3]. Investigations of this molecule are thus not only important due to its industrial or biological implications but are also valid for astrochemistry, since it has been shown that B-group vitamins [4] can be found on the surface of meteorites [5].

This simple aromatic azabenzene has been extensively studied in the past with respect to both its vibrational [6–8] and electronic structure [9] by experimental [10–14] and computational [15–18] approaches. Moreover, low-lying Rydberg states have also been examined for this molecule [19,20]. From the abovementioned studies it was concluded that the HOMO in pyridine is of n-type. Introducing the nitrogen atom into the benzene ring causes perturbation in the energy levels and thus some new transitions are available in pyridine that are due to the lone-pair electrons [13,21].

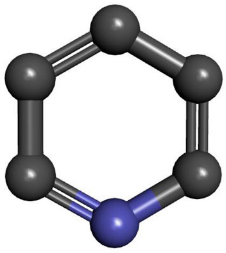

Fig. 1. Pyridine molecule; gray indicates carbon atoms, blue indicates nitrogen substituting one of the methine groups of benzene ring.

Also, photoionization and fragmentation of this molecule have been studied in the 8–30 eV range indicating that there is a significant bond rearrangement and nuclear motion during dissociation, since relative fragment yields formed upon varying excitation energy differ significantly [22]. Recently, it was found that dissociation of pyridine may occur via ring opening and isomerization mechanisms [23].

In this work we focused on photoelectron (PES) and threshold photoelectron (TPES) spectroscopic studies of the pyridine molecule. Using a high resolution photoelectron spectrometer, described later, it was possible not only to resolve the inner and outer valence ionization energies, but also, throughout the threshold electron measurements, confirm the vibronic structure associated with most of the bands in the spectrum.

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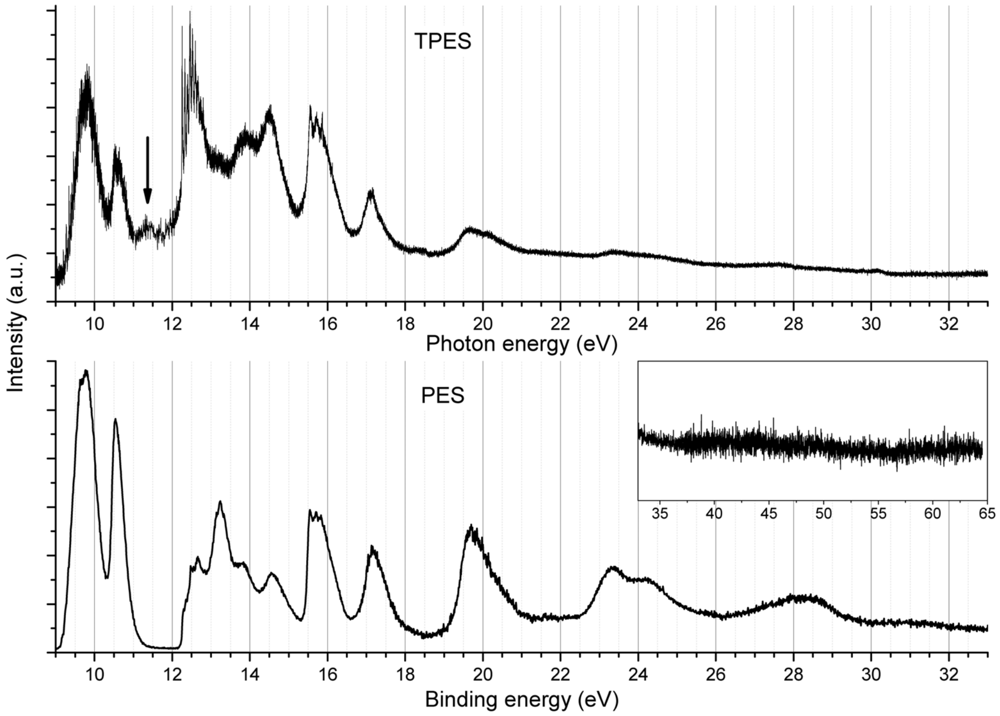

Fig. 2. Complete valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy; the insert in PES shows 33–65 eV binding energy range, obtained at 100 eV incident photon energy; see text for further details.

2 Materials and methods

2.1 Pyridine sample

Pyridine sample of purity higher than 99.9% was purchased from Sigma-Aldrich, Canada, and used with no further processing. In order to introduce the sample into the UHV system, pyridine (liquid) was transferred into a stainless steel container and degassed in four freeze-thaw-pump cycles.

2.2 Threshold and photoelectron spectra

Both the threshold photoelectron and photoelectron spectra of pyridine (Fig. 2) were recorded at the VLS-PGM beamline [24], at the Canadian Light Source facility in Saskatoon, Canada, using a Double Toroidal Coincidence Spectrometer. The apparatus was described previously in detail [25] and a specific description of the operation in the threshold mode was also provided [26]. Although it was primarily designed to be used for measurements of noble gases and small, diatomic molecules, it was recently proven that it may also be used for measurements on more complicated systems, such as pyrimidine and of its heavier derivatives [27] or esters [28,29].

Briefly, a photoelectron-photoelectron coincidence spectrometer allows for the two electrons, of specified energies, to be detected over a wide range of emission angles. The spectrometer is based on a toroidal geometry and has properties ideally suited for measuring electron angle distributions, since toroidal analysers can be made to energy-select the photoelectrons while preserving the initial angle of emission. The spectrometer consists of two toroidal analyzers, each focused on the interaction region. One collects electrons over an azimuthal range of 180°, the other over 120°. These electrostatic analyzers are independent, i.e., they are able to detect dissimilar electron energies, with different resolutions.

For photoelectron spectra measurements, both analyzers were set to a pass energy of 4 eV. The analysis was performed for the data collected by the 180° toroidal detector. Spectra shown here were calibrated against the $X^2\Sigma_g^+$, $\nu' = 0$ and $A^2\Pi_u$, $\nu' = 0$ peaks of N_2^+, rounded to three decimal places [30,31], introduced to the chamber together with the pyridine sample. The measured resolution from the nitrogen calibration spectra was 60 meV. The photoexcitation energy for the photoelectron spectrum presented here was 80 eV in the 0–33 eV region and 100 eV for 33–65 eV photoelectrons, recorded with the entrance and exit slits of the VLS-PGM beamline set at 50 μm.

For the threshold photoelectron spectra measurements only the 120° toroidal detector was used. The detector was set to collect near-zero-eV electrons and the resolution was determined against the Ar $^2P_{3/2}$ and $^2P_{1/2}$ lines to yield 7 meV. Spectra were normalized to the incident photon flux. No evidence of significant higher order contamination in the TPES spectra was seen. Specifically, there is no vibrationally-resolved structure above 20 eV, which would be reflected in the nominal PES around 10 eV.

3 Results and discussion

From the photoelectron spectrum shown in Figure 2 it was possible to assign all the ionization energies for the inner and outer valence orbitals of the pyridine molecule. The adiabatic and vertical values were obtained through the Gaussian function fitting procedure and are summarized in Table 1, together with the values obtained from the literature. The fitting was performed using Origin Pro 2015 software and the obtained results were at the level of 10% with respect to the values of residuals. Vertical values are marked with lines on the PES spectra in Figures 3–7, bottom panels. The nomenclature for labelling the states followed that proposed by Clementi [9], although various authors have different recommendations for the order of the molecular orbitals (see for example Moghaddam et al. [17]). The data presented here is not only in an excellent agreement with the previous results, but also, due to high resolution of present experiment, it was possible to assign some new adiabatic ionization energies and resolve bands that previously appeared as one feature.

This was achieved with assistance of measured TPES, shown in Figures 2–7 in the top panels. TPES measurements allowed resolving the vibronic structure associated with most of the ionization energies as well as to assign a possible Rydberg state. These assignments are shown in Figures 3–7 and summarised in Tables 2–4.

A very thorough review by Innes et al. [32] on azabenzenes gives a summary of 27 fundamental vibrational frequencies that can be assigned in pyridine spectrum. From there, Reineck et al. concluded that in the photoelectron spectrum, only the fully symmetric vibrational modes are expected to be strongly excited, and thus only ten of them are of potential interest. In our spectra we also found the series that could not have been assigned to those ten modes due to discrepancies in energy values, therefore, we also used assignments proposed by Partal Urena et al. [7]. In their work additional combinations of vibrational modes were assigned. Table 2 shows the vibrational modes assigned in the spectra presented here (marked in bold in the text).

Over the first band, that consists of the $11a_1$ and $1a_2$ states it was possible to ascribe a rich vibronic structure associated with the first IE to a combination of modes: **1** (C–C stretch) and **6a** (in-plane ring bend). It should be noted that the obtained values of electron binding energy for all higher electronic states are in an excellent agreement with values given by Reineck et al. [12] and those of Liu et al. [14] that were obtained by a sophisticated photoelectron imaging spectrometer. Also, the value of adiabatic ionization energy, 9.197 eV, is in an excellent agreement with values reported by Liu et al. [14] (9.199 eV), Reineck et al. [12] (9.197 eV) and Riese et al. [33] (9.198 eV). The latter obtained this value through mass-ionized threshold ionization spectroscopy studies.

The position of the vertical ionization energy of the second electronic state of the ion was assigned to be 9.855 eV and also one quantum of the **1** mode can be distinguished on the shoulder of the band.

Table 1. Assignment of bands and their experimental vertical energies obtained from PES of pyridine together with calculated ionization energies (all in eV); second row – adiabatic values.

Orbital	$11a_1$	$1a_2$	$2b_1$	$7b_2$	$1b_1$	$10a_1$	$6b_2$	$5b_2$	$9a_1$	$8a_1$	$7a_1$	$4b_2$	$6a_1$	$3b_2$	$5a_1$
Calculated															
von Niessen et al. [15]	9.57	9.59	10.24	12.87	13.43	14.18	15.11	16.32	16.33	18.00	21.17	21.15			
Case et al. [16]	9.36	10.28	9.91	12.14	12.37	13.25	13.73	14.56	15.85	15.88	19.25	19.09	22.37	23.31	26.41
Moghaddam et al. [17]	9.44	9.78	10.15	12.73	13.18	13.92	14.65	16.02	16.18	17.60	20.08	20.44	25.30	25.94	16.02
Wan et al. [18]	9.23	9.36	10.12	12.48	13.06	13.56	14.41	15.60	15.70	17.10	20.05	20.43	23.27	24.35	
Experimental															
Gleiter et al. [10]	9.8	9.7	10.5	12.5	12.6										
Åsbrink et al. [15]	9.7	9.7	10.5	12.5	13.2	13.7	14.4	15.7	15.7	17.1	19.6	20.0			
Utsunomiya et al. [11]	9.66	9.8	10.54	12.48	13.27										
Reineck et al. [12]	9.66	9.85	10.51	12.454	13.2	13.8	14.5	15.838	15.838	17.1					
	9.197		10.51	12.257				15.544	15.544						
Walker et al. [13]	8.843	9.526	10.127	12.908	13.044	13.696	14.636	15.947	16.048						
Moghaddam et al. [17]	9.60	9.75	10.51	12.61	13.10	13.80	14.5	15.9	15.9	17.4	19.8	20.6	23.4	24.5	28.0
Liu et al. [14]	9.58		10.56	12.51	13.23	13.70	14.26	15.22	15.22	16.66	19.54				
This work	9.550±0.007	9.855±0.013	10.583±0.003	12.608±0.004	13.219±0.004	13.796±0.012	14.561±0.006	15.584±0.003	15.881±0.009	17.108±0.004	19.684±0.005	20.247±0.057	23.264±0.004	24.118±0.017	28.122±0.008
	9.197		10.315	12.262	12.999			15.247		16.703	18.789				

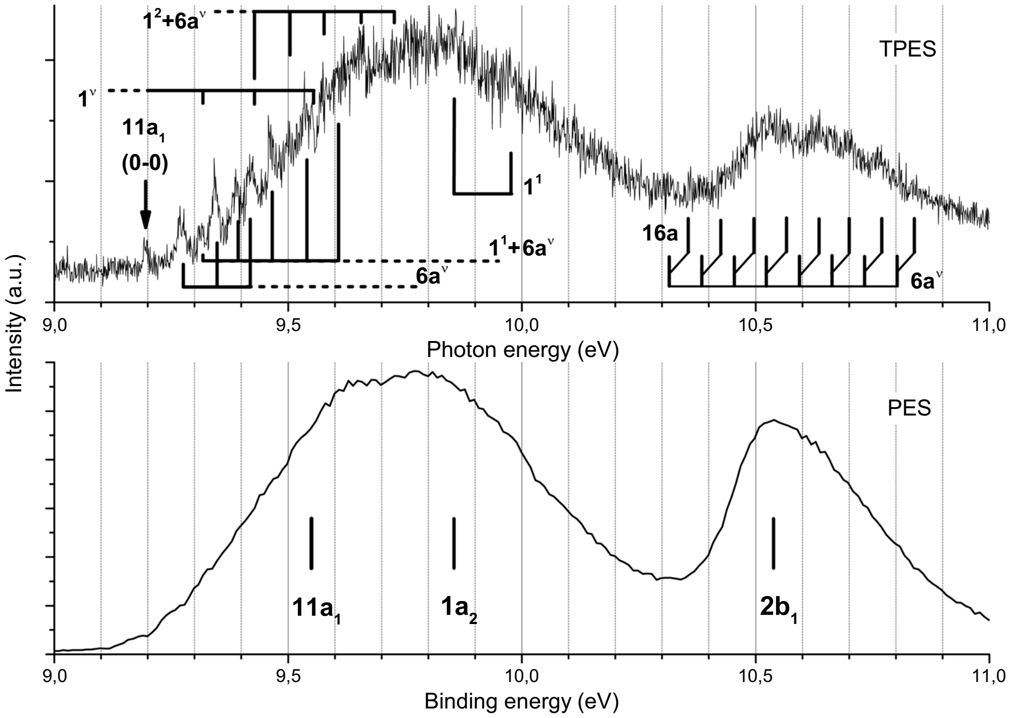

Fig. 3. Valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy in the energy range of 9–11 eV.

Table 2. Vibrational modes (Wilson's notation) [7,32] and their energies found in the pyridine spectrum.

Mode	Desctiption	Energy (meV)
16b	out-of-plane ring bend	31
16a	out-of-plane ring bend	41
6a	in-plane ring bend	70
1	carbon-carbon stretch	116
18a	in-plane C–H bend	152
14	carbon-carbon stretch	161
8a	carbon-carbon stretch	204
(16a+3)	out-of-plane ring bend with in-plane C–H bend	214
(8a+12)	C–C stretch with in-plane ring bend	240

On the third electronic state of the ion, $2b_1$, a combination of **16a** (both out-of-plane ring bend) and **6a** modes was resolved, with the adiabatic value found at 10.315 eV.

The feature visible only in the TPES, centred at the 11.325 eV, marked in Figure 2 (top) with an arrow, can be assigned to a 4*s* Rydberg state, converging to the $7b_2$ ionization energy. The quantum defect, $\delta = 0.74$, is within the same range with the value obtained by others for the *ns* transitions converging to the $11a_1$ state ($\delta = 0.85$) [20].

In Figure 4 the band consisting of four ionization energies: $7b_2$, $1b_1$, $10a_1$ and $6b_2$, is presented. Additionally, in the band of $7b_2$ state, a vibronic structure consisting of combination of mode **8** (C–C stretch) with modes **18a** (in-plane CH bend) and **6a** can be resolved. These results are also in a good agreement with the ones shown previously [12]. Over the $1b_1$ band, three quanta of mode **1** can be seen in both the PES and TPES spectra. The adiabatic ionization energies found for these two states yielded 12.262 eV and 12.999 eV, respectively. For the $10a_1$ and

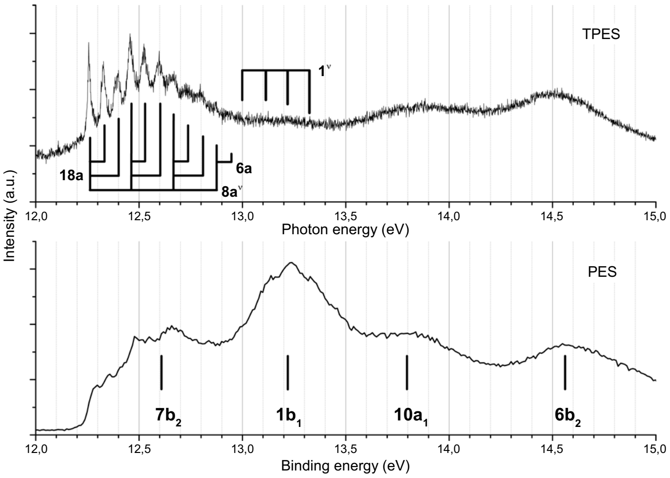

Fig. 4. Valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy in an energy range of 12–15 eV.

Table 3. Binding energies of Rydberg and vibrational assignments of bands in pyridine spectrum.

Binding energy (eV)	Assignment	Utsunomiya et al. [11]	Reineck et al. [12]	Liu et al. [14]
$11a_1$ (Fig. 3)				
9.199	0–0	–	9.197	9.199
9.276	6a	9.26	9.271	9.273
9.318	1	–	9.319	9.318
9.348	$6a^2$	9.36	9.346	9.348
9.393	1+6a	–	9.391	9.3925
9.419	$6a^3$	–	9.421	9.419
9.428	1^2	9.46	–	9.428
9.466	$1+6a^2$	–	9.465	9.467
9.504	1^2+6a	–	–	9.504
9.540	$1+6a^3$	–	9.536	9.541
9.555	1^3	9.56	–	9.555
9.577	1^2+6a^2	–	9.580	9.579
9.608	$1+6a^4$	–	9.608	9.610
9.656	1^2+6a^3	9.66	9.657	9.644
$1a_2$ (Fig. 3)				
9.855	Vertical IE	9.80	9.85	–
9.977	1	9.90	9.97	–
$2b_1$ (Fig. 3)				
10.351	0–0	–	–	–
10.356	16a	–	–	–
10.385	6a	–	–	–
10.425	6a+16a	–	–	–
10.455	$6a^2$	–	–	–
10.496	$6a^2+16a$	–	–	–
10.522	$6a^3$	–	–	–
10.566	$6a^3+16a$	–	–	–
10.594	$6a^4$	–	–	–
10.636	$6a^4+16a$	–	–	–
10.663	$6a^5$	–	–	–
10.699	$6a^5+16a$	–	–	–
10.733	$6a^6$	–	–	–
10.770	$6a^6+16a$	–	–	–
10.801	$6a^7$	–	–	–
10.841	$6a^7+16a$	–	–	–
$7b_2$ (Fig. 4)				
11.325 (Fig. 2)	$4s(7b_2)$, $\delta = 0.74$	–	–	–
12.262	0–0	–	12.285	–
12.332	6a	–	12.349	–
12.401	18a	–	12.392	–
12.463	8a	–	12.478	–
12.529	8a+6a	–	12.549	–
12.602	8a+18a	–	12.580	–
12.667	$8a^2$	–	–	–
12.736	$8a^2+6a$	–	–	–
12.802	$8a^2+18a$	–	–	–
12.875	$8a^3$	–	–	–
12.946	$8a^3+6a$	–	–	–
$1b_1$ (Fig. 4)				
12.999	0–0	–	13.081	–
13.114	1	–	13.207	–
13.219	1^2	–	13.317	–
13.324	1^3	–	–	–

Table 4. Binding energies of vibrational assignments of bands in pyridine spectrum; asterisks marks tentative assignments, star marks a combined mode from reference [7].

Binding energy (eV)	Assignment
$5b_2$ (Fig. 5)	
15.247	0–0
15.410	16b
15.563	$16b^2$
15.601	$16b^2 + 14$
15.726	$16b^3$
15.762	$16b^3 + 14$
$9a_1$ (Fig. 5)	
15.871	Vertical IE
16.122	(8a + 12) (⋆)
$8a_1$ (Fig. 5)	
16.703	0–0
16.938	(8a + 12) (⋆)
17.062	(8a + 12) + 1 (⋆)
17.168	$(8a + 12)^2$ (⋆)
17.403	$(8a + 12)^3$ (⋆)
$7a_1$ (Fig. 6)	
18.789	0–0
19.043*	(16a + 3) (⋆)
19.257*	$(16a + 3)^2$ (⋆)
19.468	$(16a + 3)^3$ (⋆)
19.684	$(16a + 3)^4$ (⋆)
19.896	$(16a + 3)^5$ (⋆)
20.109	$(16a + 3)^6$ (⋆)

$6b_2$ states it was only possible to obtain the vertical values of 13.796 eV and 14.561 eV, respectively.

There are two bands shown in Figure 5. In the first one, two ionization energies from orbitals $5b_2$ and $9a_1$ can be distinguished. Further, a mode **16b** (out-of-plane ring bend) combined with one quantum of mode **14** (C–C stretch) was resolved over $5b_2$ state. This structure was not resolved previously and provided an adiabatic value for ionization of 15.247 eV. The ionization from the $9a_1$ state can be associated with one mode of **(8a + 12)** that is an in-plane ring bend associated with a C–C stretch, according to the findings of Partal Urena et al. [7]. The second band is due to ionization from $8a_1$ orbital. The ionization energy in this band is accompanied by three quanta of the combined **(8a + 12)** mode and one quantum of mode **1**. Here, it was also possible for the first time to assign the adiabatic value for ionization from the $8a_1$ orbital of 16.703 eV.

In Figure 6 there is only one band that is due to two ionization energies from the orbitals $7a_1$ and $4b_2$. There is also a vibronic progression associated with the former that can be attributed to six quanta of a combined mode **(16a + 3)**, which is an out-of-plane ring bend mixed with in-plane CH bend. Thus, it was possible to assign an adiabatic value of 18.789 eV for the $7a_1$ state, whereas for the $4b_2$ only the vertical value of 20.247 eV could be established.

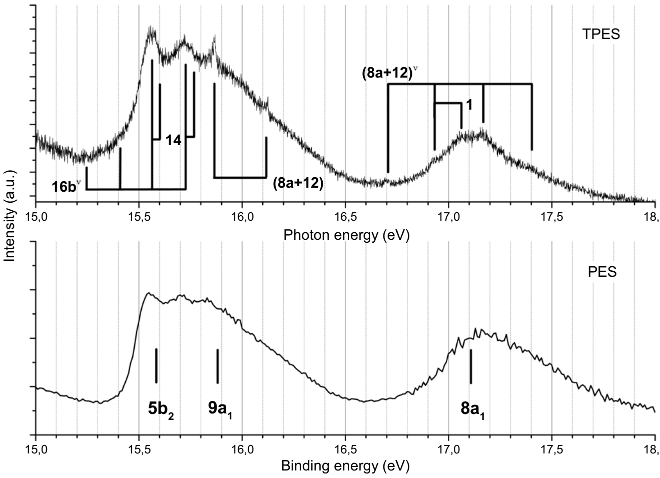

Fig. 5. Valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy in an energy range of 15–18 eV.

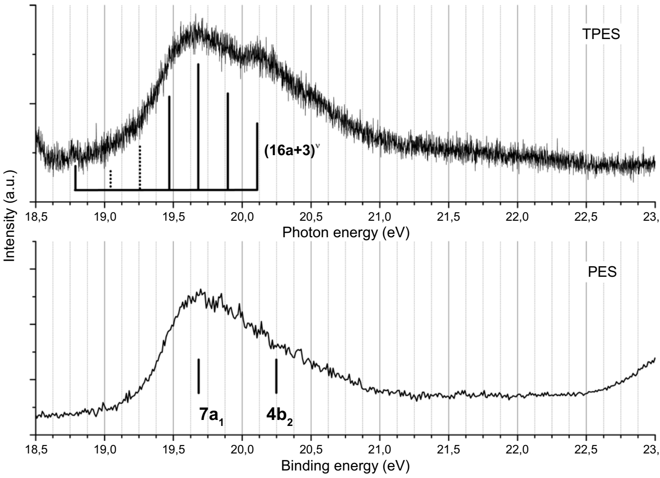

Fig. 6. Valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy in an energy range of 18.5–23 eV; dotted lines mark a tentative assignment.

A broad double peak, seen in Figure 7, was determined to be a result of ionization from the $6a_1$ and $3b_2$ orbitals with vertical values of 23.264 eV and 24.118 eV, respectively. There are also additional two peaks visible in the PES in Figure 7. The first one is due to ionization from the $5a_1$ orbital at 28.122 eV. As it was shown through computational methods [18], the features observed in the PES above the binding energy of 25 eV are strongly influenced by multielectron processes (MEP) and thus we ascribed the band centered around 31.2 eV to be due to such interactions. A slight increase in the photoionization efficiency at this energy was also observed by others [34]. In the TPES there are other distinguished features in the range of 29–31 eV that were attributed to the pressure fluctuations during this measurement.

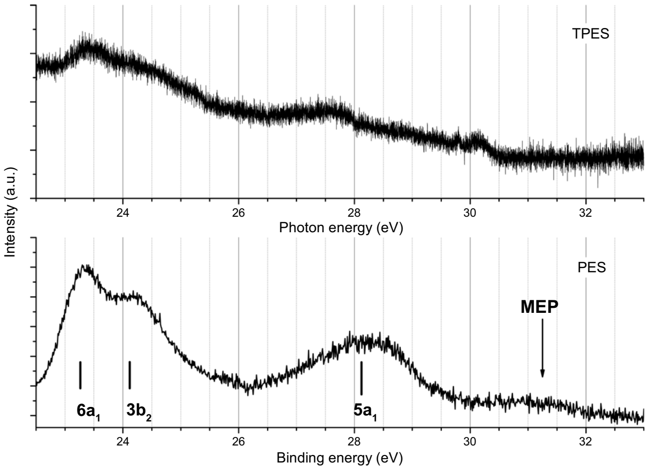

Fig. 7. The valence shell photoelectron spectra of pyridine recorded at (top) thresholds and (bottom) 80 eV incident photon energy in an energy range of 22.5–33 eV.

4 Conclusions

In this work we revisited on the subject of photoelectron spectroscopy investigations of the pyridine molecule. Using a high resolution photoelectron spectrometer, it was possible not only to resolve the inner and outer valence ionization energies, but also, throughout the threshold electron measurements, confirm the vibronic structure associated with most of the bands in the spectrum. This vibronic structure associated with several states was assigned mainly to be due to C–C stretches and ring bends. Additionally, a possible Rydberg state, converging to $7b_2$ state, was ascribed. The data shown here are in an excellent agreement with previous results and brings some new insights into the electronic structure of pyridine molecule.

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