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Mass analyzed threshold ionization spectroscopy of 4-aminobenzonitrile cation

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Abstract

Mass analyzed threshold ionization (MATI) and two-color resonant two-photon ionization (R2PI) methods were used to investigate the ionic properties of 4-aminobenzonitrile (4-ABN). The adiabatic ionization energy of this molecule was determined to be $66493 \pm 4 \text{ cm}^{-1}$ by the MATI spectroscopy and $66494 \pm 7 \text{ cm}^{-1}$ by the two-color R2PI spectroscopy. The active vibrations of the 4-ABN cation include the in-plane ring deformation, CC stretching, C–CN stretching, and CH bending motions. The present experimental results are well supported by our *ab initio* and density functional theory calculations. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Over the past few decades, many experimental [1–6] and theoretical [7–9] studies on 4-aminobenzonitrile (4-ABN) have been conducted. In the S_0 state 4-ABN is nonplanar and belongs to the point group of C_s . Upon absorption of UV photons of wavelength near 299 nm, it is subject to a $\pi^* \leftarrow \pi$ electronic transition. Strong interaction between the π electrons of the ring and the lone-paired electrons of the amino group causes this molecule to become planar in the S_1 state. Previous investigations have helped us gain information on the structures, vibrations, spectroscopy, and charge transfer dynamics of 4-ABN in the ground and electronically excited states. To the best of our knowledge, spectroscopy and other properties of

the 4-ABN ion are not rich in the literature and need to be explored.

Zero kinetic energy photoelectron spectroscopy has proved to be a powerful means to probe the ionization threshold and vibrations of molecular ions in high precision [10,11]. The later developed mass analyzed threshold ionization (MATI) method involves detection of ions rather than electrons and thus can provide an unambiguous mass resolved spectral information [11,12]. This method is particularly useful if one needs to select a desired species in a mixture for some spectroscopic experiments.

In this paper we report the determination of the adiabatic ionization energy (IE) of 4-ABN and vibrational levels of the 4-ABN cation by using two-color resonant two-photon ionization (R2PI) and MATI spectroscopy. We have also performed *ab initio* and density functional theory (DFT) calculations for obtaining structures, total energies, and vibrational frequencies of this molecule in the S_0 , S_1 , and ionic states. It is found that the

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calculated results well support the experimental findings.

2. Experimental and computational details

2.1. Experimental method

The experiments reported in this paper were performed with a laser-based TOF mass spectrometer as described in our previous publication [13]. 4-ABN (98% purity) was purchased from Sigma-Aldrich Corporation and used without further purification. The sample was heated to about 90°C to obtain sufficient vapor pressure, seeded into 2 bar of helium and expanded into the vacuum through a pulsed valve with a 0.15 mm diameter orifice. The molecular beam was collimated by a skimmer located 15 mm downstream from the nozzle orifice.

The two-color resonant two-photon excitation/ionization process was initiated by utilizing two independent tunable UV laser systems controlled by a pulse delay generator (Stanford Research Systems, DG 535). The excitation source is a Nd:YAG pumped dye laser (Quanta-Ray GCR-3/PDL-3) with bandwidth $\leq 0.3 \text{ cm}^{-1}$. The visible radiation is frequency doubled to produce UV radiation. The ionization UV laser (Lambda-Physik, ScanmateUV with BBO-III crystal) was pumped by a frequency-doubled Nd:YAG laser (Quantel, Brilliant B). A Fizeau-type wavemeter (New Focus 7711) was used to calibrate the wavelengths of both dye lasers. The respective UV laser outputs were monitored with two separated photodiodes (Hamamatsu 1722S) and fed into a transient digitizer (LeCroy 9450). The two counter-propagating laser beams were focused and intersected perpendicularly with the skimmed molecular beam at 50 mm downstream from the nozzle orifice.

In the MATI experiments, a pulsed electric field of -1.0 V cm^{-1} (duration = 10 μs) was switched on $\approx 0.7 \mu\text{s}$ after the occurrence of the laser pulses to reject the prompt ions. After a time delay of $\approx 9.60 \mu\text{s}$, a second pulsed electric field of $+525 \text{ V cm}^{-1}$ (duration = 10 μs) was applied to field-ionize the Rydberg neutrals. These threshold ions

were then accelerated and passed a 1.0 m field-free region before being detected by a dual-stacked microchannel plate particle detector. The ion signal from the detector was collected and analyzed by a multichannel scaler (Stanford Research Systems, SR430). The multichannel scaler and the transient digitizer were interfaced to a personal computer. Mass spectra were accumulated at 1.2 cm^{-1} spacing for 300 laser shots. Composite optical spectra of intensity versus wavelength were then constructed from the individual mass spectra. As the detected ion signal is proportional to the photon intensities of the excitation and ionization lasers for a two-color resonant two-photon process, the obtained optical spectra were normalized to the laser power in order to avoid spurious signals due to shot-to-shot laser fluctuation.

2.2. Computational method

Ab initio and DFT calculations were performed using the GAUSSIAN 98 program package [14]. The labeling of the carbon atoms is 1–6 around the ring and the substituent portions are numbered as $>\text{C}_1\text{--NH}_2$ and $>\text{C}_4\text{--CN}$. The IE was obtained as the difference in the zero-point energies of the cation and the corresponding neutral. All quoted vibrational frequencies were scaled by a factor of 0.92 for the S_1 state and 0.95 for the ionic state calculations to approximately correct for the combined errors stemming from basis set incompleteness and negligence of electron correlation and vibrational anharmonicity.

3. Results

3.1. One-color R2PI spectrum

Fig. 1 display the one-color R2PI spectrum of jet-cooled 4-ABN in the energy range near its lowest electronic transition. The intense band at 33481 cm^{-1} is identified as the band origin of the $\text{S}_1 \leftarrow \text{S}_0$ electronic transition. The frequencies of the observed bands resulting from various vibronic transitions are listed in Table 1, together with the calculated values. Within the experimental error the observed transitions are in very good agree-

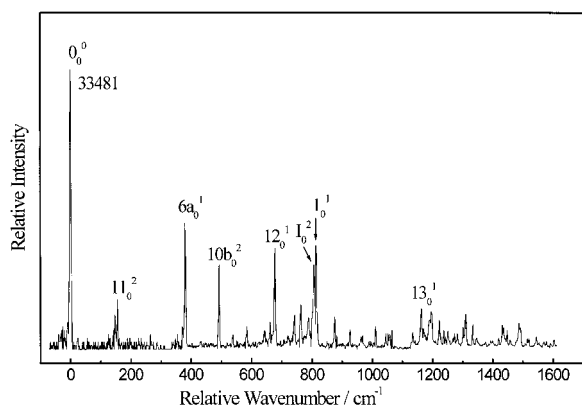


Fig. 1. One-color R2PI spectrum of 4-ABN.

ment with those reported previously [1,3,7]. When a scaling factor of 0.92 is applied, the predicted vibrational frequencies from the CIS/cc-pVDZ

calculations are very close to the measured values. The assignments are based on Varsanyi's nomenclature [15] for approximately describing the benzene-like vibrational modes. Detailed spectroscopic investigations on the electronic transition as well as analysis on the normal vibrations of 4-ABN in the S_0 and S_1 states have been covered by Phillips and coworkers [3,9]. Here, we focus on the ionic properties of this molecule.

3.2. Two-color R2PI spectrum

Fig. 2 shows the two-color R2PI spectrum of 4-ABN. It was recorded via the $S_1 0^0$ intermediate level when a static electric field of 350 V cm^{-1} was applied in the laser and molecular beam interaction region. A rising step in the spectrum clearly appears at two-photon energy of $\approx 66380 \text{ cm}^{-1}$.

Table 1

Assignment of the observed bands (cm^{-1}) in the one-color R2PI spectrum of 4-ABN

Ref. [3]		This work ^a		Assignment and approximate description ^b
Experimental	Assignment	Experimental	Calculated	
224	15_0^2	155		11_0^2 , $\gamma\text{C-NH}_2$
382	$6a_0^1$	380	383	15_0^2 , $\beta\text{C-NH}_2$
494	$10b_0^2$	492		$6a_0^1$, βCCC
		585	605	$10b_0^2$, $\gamma\text{C-NH}_2$, $\gamma\text{C-CN}$
		643	607	4_0^1 , γCCC
		662	667	$6b_0^1$, βCCC
678	12_0^1	677	680	$17a_0^1$, γCH
742		742	738	12_0^1 , βCCC
761	$6a_0^2$	762		5_0^1 , γCH
781	$17b_0^1$	787	688	$6a_0^2$, βCCC
807	I_0^2	806		$17b_0^1$, γCH
815	1_0^1	813	815	I_0^2 , γNH_2 (wag)
877	$6a_0^1 10b_0^2$	875		1_0^1 , ring breathing
		925		$6a_0^1 10b_0^2$
		967	980	$9b_0^2$, $\beta\text{C-CN}$
1012	$6a_0^1 6b_0^1$	1010		$18a_0^1$, βCH
1045		1045	1036	$6a_0^1 6b_0^1$
1059	$6a_0^1 12_0^1$	1058		$18b_0^1$, βCH
1165	13_0^1	1162	1177	$6a_0^1 12_0^1$
1068	$15_0^1 18a_0^1$	1065		13_0^1 , $\nu\text{C-CN}$
1174	$12_0^1 10b_0^2$	1169		$16b_0^2$, γCCC
1191	$I_0^2 6a_0^1$	1191		$12_0^1 10b_0^2$
1199	$1_0^1 6a_0^1$	1197		$I_0^2 6a_0^1$
				$1_0^1 6a_0^1$

^a The experimental values are shifts from 33481 cm^{-1} , whereas the calculated ones are obtained from the CIS/cc-pVDZ calculations.

^b Assignments are based on Varsanyi's nomenclature. ν , β , and γ represent stretching, in-plane bending, and out-of-plane bending vibrations, respectively.

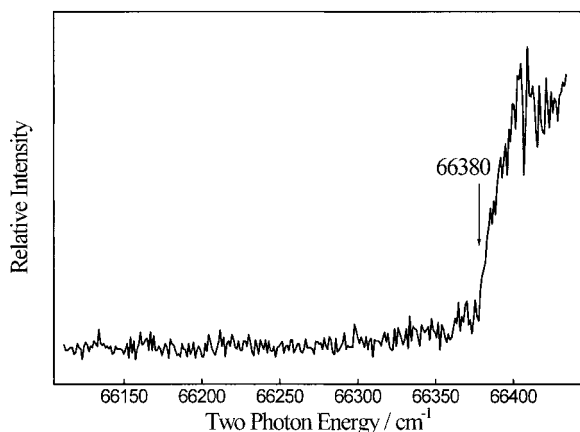


Fig. 2. Two-color R2PI spectrum of 4-ABN obtained when a static electric field of 350 V cm^{-1} was applied in the ionization region.

The classical theory states that the external static electric field can cause the measured value to be lower than the true IE by $\approx 6.1 F^{1/2}$, where F is the field strength in the unit of V cm^{-1} [16]. Thus, the field-corrected adiabatic IE of 4-ABN is determined to be $66494 \pm 7 \text{ cm}^{-1}$, as listed in Table 2.

3.3. MATI spectra

Fig. 3a and b depicts the MATI spectra of 4-ABN recorded via the vibrationless $S_1 0^0$ (33481 cm^{-1}) and the vibronic $S_1 6a^1$ (33861 cm^{-1}) levels. Since this technique involves ionization of molecules in high Rydberg states by a delayed pulsed

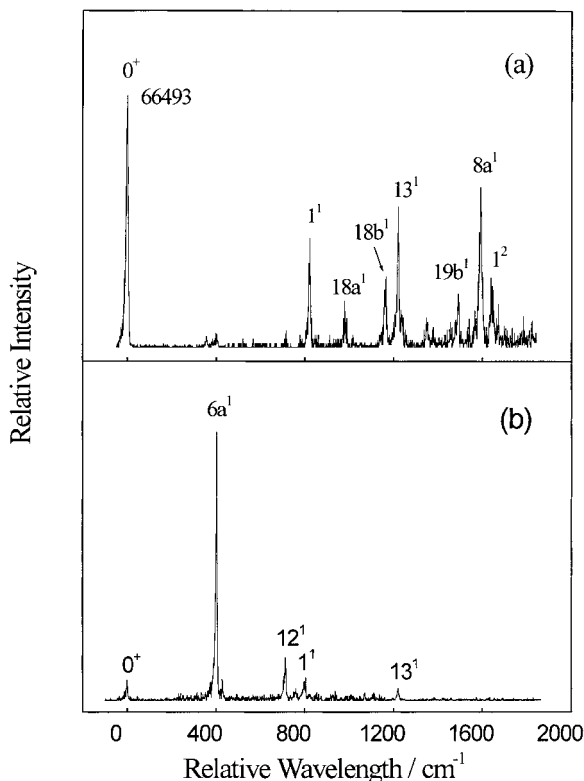


Fig. 3. Threshold ion spectra of 4-ABN recorded by MATI method via the (a) $S_1 0^0$ and (b) $S_1 6a^1$ intermediate states.

electric field of -1 V cm^{-1} , the ions occur at energy slightly below the true ionization threshold. The magnitude of the resulting Stark shift may be approximated by $4.0 F^{1/2}$ [16]. Thus, the adiabatic IE of 4-ABN determined by this method is $66493 \pm 4 \text{ cm}^{-1}$, which is in very good agreement with that by the two-color R2PI spectroscopy.

The MATI bands shifted from the 0^0 band are related to the vibrations of the ion. The frequencies of the observed bands are listed in Table 3, along with the calculated frequencies and possible assignments. When the vibrationless $S_1 0^0$ state is used as the intermediate level for ionization, many active vibrations of the ion are observed, as shown in Fig. 3(a). The moderately intense bands at 823 and 1639 cm^{-1} are assigned to the ring breathing vibration 1^1 and the corresponding overtone 1^2 . Modes related to the ring CC stretching vibrations $19b^1$ and $8a^1$ occur at 1492 and 1593 cm^{-1} , res-

Table 2

Experimental and calculated IE of 4-ABN

Method	IE (cm^{-1})	
<i>Experimental</i>		
Two-color R2PI via $S_1 0^0$	66492 ± 7	
MATI via $S_1 0^0$	66493 ± 4	
MATI via $S_1 6a$	66493 ± 4	
		Dev. (%)
<i>Computational</i>		
HF/6-31+G*	54257	-18.2
HF/cc-pVDZ	52942	-20.4
B3LYP/6-31+G*	64302	-3.3
B3LYP/6-311+G**	65012	-2.2
B3PW91/6-31+G*	64587	-2.9
B3PW91/6-311+G**	65071	-2.1

Table 3

Assignment of the observed bands (in cm^{-1}) in the MATI spectra of 4-ABN

Intermediate level		Calculated ^a	Assignment and approximate description ^b
$S_1 0^0$	$S_1 6a^1$		
356		354	$16a^1$, γCCC
403	403	408	$6a^1$, βCCC
	430		$10b^2$, $\gamma\text{C-NH}_2$
709	712	706	12^1 , βCCC
823	820	817	1^1 , ring breathing
979		998	$18a^1$, βCH
1167		1153	$18b^1$, βCH
1221	1219	1228	13^1 , $\nu\text{C-CN}$
1348		1399	3^1 , βCH
1492		1467	$19b^1$, νCC
1593		1594	$8a^1$, νCC
1639			1^2 , ring breathing

^a The experimental values are shifts from $66\,493\text{ cm}^{-1}$, whereas the calculated ones are obtained from the UHF/cc-pVDZ calculations.

^b Assignments are based on Varsanyi's nomenclature. ν , β , and γ represent stretching, in-plane bending, and out-of-plane bending vibrations, respectively.

pectively. The intense band at 1221 cm^{-1} results from the substituent-sensitive in-plane C–CN stretching vibration 13^1 . In addition, the in-plane CH bending vibrations $18a^1$, $18b^1$, and 3^1 are seen at 979, 1167, and 1348 cm^{-1} , respectively. The weak band at 356 cm^{-1} is related to the out-of-plane ring bending vibration $16a^1$. If the vibronic state, $S_1 6a^1$, were used as the intermediate level only a few active MATI bands are observed. Fig. 3(b) shows that the most intense band in the spectrum represents the $6a$ normal vibration of the ion. The weak bands at 709, 823, and 1221 cm^{-1} result from the in-plane ring vibrations 12^1 , 1^1 , and 13^1 , respectively.

4. Discussion

The geometry parameters of 4-ABN in the solid phase have been determined by crystallography [2], as listed in Table 4. Recently, it has been reported that the predicted values from the RHF/cc-pVDZ calculations are in good agreement with the measured ones [7]. In addition, the computed frequencies at the CIS/cc-pVDZ level were used to

Table 4

Calculated^a geometry parameters of 4-ABN

	S ₀	RHF	S ₁	Ionic
	Experi- mental ^b		CIS	UHF

<i>Bond length (Å)</i>				
C ₁ –C ₂	1.405	1.399	1.425	1.443
C ₂ –C ₃	1.369	1.380	1.411	1.372
C ₃ –C ₄	1.398	1.394	1.413	1.427
C ₁ –NH ₂	1.370	1.383	1.338	1.305
C ₄ –CN	1.431	1.442	1.437	1.421
C≡N	1.148	1.139	1.140	1.150
C–H		1.081	1.079	1.080
N–H	0.900	1.000	0.997	1.005
C ₁ ⋯C ₄		2.800	2.787	2.802

<i>Bond angles (deg)</i>				
∠C ₆ C ₁ C ₂		118.7	121.7	120.1
∠C ₁ C ₂ C ₃		120.5	118.9	119.4
∠C ₂ C ₃ C ₄		120.6	119.1	120.3
∠C ₃ C ₄ C ₅		119.0	122.3	120.5
∠HN ₇ C ₁	115	115.1	121.0	121.5
∠HNNH	114	111.6	118.1	116.4

^a The respective restricted Hartree–Fock (RHF), configuration singles (CIS), and unrestricted Hartree–Fock (URF) calculations with the cc-pVDZ basis set are performed for the S_0 , S_1 , and ionic states.

^b Ref. [2].

successfully assign the vibronic bands in the R2PI spectrum. Therefore, we have performed the RHF, CIS, and UHF calculations with the cc-pVDZ basis set for predicting various molecular properties in the S_0 , S_1 , and cationic ground states, respectively. In the S_0 state, 4-ABN has a nonplanar geometry with the two hydrogen atoms of the NH_2 group bent out of the aromatic ring plane by 39° . It belongs to the point group C_s . When it undergoes a $\pi^* \leftarrow \pi$ electronic excitation to the S_1 state, this bending angle vanishes as the two hydrogen atoms move to the plane of the ring. The delocalization of the lone-paired electrons of the amino group over the aromatic ring causes the molecule in the S_1 state to become planar with C_s (nearly C_{2v}) symmetry.

Mulliken population analysis on the total atomic charges of 4-ABN indicates that the transition from the neutral to the cationic ground state corresponds to the removal of one of the lone-paired electrons of the nitrogen of the amino group. The remaining nonbonded electron on the

nitrogen conjugates with one of the π electrons on the ring forming a C=N double bond and causing this ion to be planar. Similar findings have been reported for aniline [17,18] and *p*-fluoroaniline [13]. The intensity of the ion signal in a photoionization spectrum is closely related to the Franck–Condon overlaps. In case that the equilibrium geometries of an ion and its corresponding neutral species are alike, the energy dependence of the onset of ionization will give rise to a sharp step function. As shown in Fig. 2, an abrupt step in the two-color R2PI spectrum is an indication that the geometry of the 4-ABN ion is quite similar to that of the neutral species in the S_1 state.

The adiabatic IE of 4-ABN was determined to be $66493 \pm 4 \text{ cm}^{-1}$ ($8.2436 \pm 0.0005 \text{ eV}$) by the MATI spectroscopy and $66494 \pm 7 \text{ cm}^{-1}$ by the two-color R2PI spectroscopy. This value is in good agreement with that of 8.17 eV estimated from the onset of a photoelectron spectrum [19], $8.64 \pm 0.04 \text{ eV}$ measured using the retarding potential difference technique [20], and 8.51 eV calculated by the linear combination bond orbital treatment [21]. It is worth mentioning that the B3PW91/6-311+G** calculation yields a value of 65071 cm^{-1} (8.067 eV), which only underestimates the IE of 4-ABN by about 2.1%, as shown in Table 2.

The observed band intensity in the MATI spectra is related to (1) the oscillator strength corresponding to the $S_1 \leftarrow S_0$ transition, (2) the transition cross-section from the S_1 state to the Rydberg state, and (3) the pulsed field ionization efficiency. When the vibrationless $S_1 0^0$ state is used as the intermediate level, most of the observed vibrations of the ion are related to the in-plane ring vibrations, as seen in Fig. 3(a). These vibrations include the breathing (1), the ring CC stretching (8a and 19b), the substituent-sensitive C–CN stretching (13), and the CH bending (18a and 18b) modes. It is interesting to note that all these vibrations appear to be active in S_1 state, as seen in Fig. 1. When the vibronic state, $S_1 6a^1$, is used as the intermediate level only one intense band corresponding to the 6a vibration of the ion is observed, as shown in Fig. 3(b). Other bands appear to be weak and are related to the in-plane ring deformation, which is somewhat similar to the

pattern of 6a. These findings prove that the geometry and symmetry of the ion closely resemble those of the neutral species in the S_1 state. The present experimental and theoretical investigations have helped us gain more insights into the ionization threshold and ionic properties of 4-ABN.

Acknowledgements

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