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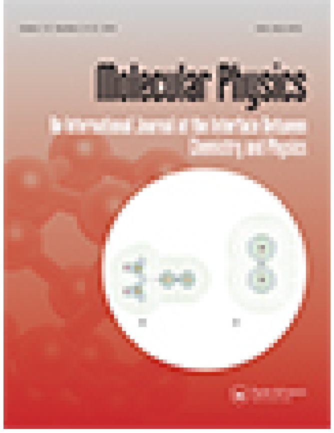

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Publication details, including instructions for authors and subscription information:
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Photoelectron spectrum of a polycyclic aromatic nitrogen heterocyclic anion: quinoline$^-$

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Published online: 22 Jan 2015.

To cite this article: Allyson M. Buytendyk, Yi Wang, Jacob D. Graham, Anil K. Kandalam, Boggavarapu Kiran & Kit H. Bowen (2015): Photoelectron spectrum of a polycyclic aromatic nitrogen heterocyclic anion: quinoline$^-$, Molecular Physics: An International Journal at the Interface Between Chemistry and Physics, DOI: 10.1080/00268976.2014.1003261

To link to this article: http://dx.doi.org/10.1080/00268976.2014.1003261

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Molecular Physics, 2015
http://dx.doi.org/10.1080/00268976.2014.1003261

RESEARCH ARTICLE

Photoelectron spectrum of a polycyclic aromatic nitrogen heterocyclic anion: quinoline$^-$

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(*Received 24 November 2014; accepted 23 December 2014*)

We report a joint photoelectron spectroscopic and theoretical study on the molecular anion, quinoline$^-$. Analysis of the vibrationally resolved photoelectron spectrum found the adiabatic electron affinity, $EA_a(C_9H_7N)$, to be 0.16 ± 0.05 eV. These findings were supported by density functional theory calculations. Our experimental and computational results demonstrate the unusual electrophilicity for a polycyclic aromatic heterocycle.

Keywords: molecular anion; electron affinity; photoelectron spectroscopy; gas phase; density functional theory

1. Introduction

Typically, cyclic aromatic hydrocarbons, such as benzene and naphthalene as well as their heteroaromatic analogue structures, do not support a valence bound anion. Quinoline is a polycyclic aromatic nitrogen heterocycle that is structurally equivalent and π-isoelectronic to naphthalene, where a nitrogen atom replaces the position 1 CH group on the hydrocarbon. Semi-empirical calculations predicted a small *positive* electron affinity for quinoline almost 50 years ago [1]. The neutral quinoline molecule has been extensively studied computationally [2–9] and experimentally in the gas phase by measuring the dielectric constant to determine the dipole moment [10], photoionisation [11–13], UV–Vis absorbance [14–16], microwave [17] and infrared [18] spectroscopy. Quinoline has also general astrophysical interest [19–21]. Nevertheless, few experimental negative ion gas-phase studies exist. The compound negative ion resonance [22] of quinoline was reported and the gas-phase lifetime [23] of the negative parent ion was determined; however, no experimentally measured electron affinity value for quinoline has been reported in the literature.

Here, we present the vibrationally resolved anion photoelectron spectrum of quinoline$^-$ anion. From the spectrum, we determined the adiabatic electron affinity to be 0.16 ± 0.05 eV. This assignment is supported by our theoretical calculations and computationally simulated spectrum. The active vibrational frequencies observed compare favourably with previous experimentally measured vibrational modes of quinoline.

2. Methods

2.1. Experimental

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy analysing the resultant photodetached electrons. The photodetachment process is governed by the relationship $h\nu = EBE + EKE$, where $h\nu$ is the photon energy, EBE is the electron binding energy, i.e., the transition energy between the anion and a particular vibronic state of its neutral counterpart, and EKE is the electron kinetic energy. Negative ions of quinoline were formed in a biased (−500 V) supersonic expansion nozzle-ion source, where the quinoline sample was placed in a stagnation chamber, heated to 70 °C, and coexpanded with ~30 psig of argon gas through a 23 μm orifice into $\sim 10^{-4}$ Torr vacuum. Negative ions were formed by injecting low-energy electrons from a more negatively biased, thoriated-iridium filament into the expanding jet, where a microplasma was formed in the presence of a weak external magnetic field. These anions were then extracted, collimated and transferred into the flight tube of a 90° magnetic sector mass spectrometer with a mass resolution of ~400. The mass-selected anions of interest were then crossed with the intracavity laser beam of an argon ion laser, and the photodetached electrons were energy-analysed in a hemispherical electron energy analyser having a resolution of ~20 meV. The photoelectron spectrum reported here was recorded with 2.540 eV photons (488 nm), and it was calibrated against the photoelectron spectrum of the O$^-$ anion

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[24]. It was also measured at lower resolution using our pulsed photoelectron magnetic bottle instrument.

2.2. Computational

Density functional theory (DFT) calculations of quinoline neutral and anion were performed with the Gaussian09 [25] software package. Geometry optimisations, energy calculations and frequency analysis were all performed with the unrestricted wb97xd [26] functional and aug-cc-pVTZ [27,28] basis set. The highest occupied molecular orbital (HOMO) of the relaxed anion was generated in GaussView [29]. A simulated photoelectron spectrum was generated using the Franck–Condon method as implemented [30] in Gaussian09 using the default parameters which includes a convolution of the spectrum with Gaussian distributions with a 135 cm^{-1} half-width at half-maximum.

3. Results and discussion

The photoelectron spectrum of quinoline anion, presented in Figure 1(a), exhibits a vibrationally resolved profile. The observed transitions are centred at EBE 0.16 eV (peak A), 0.23 eV (peak B), 0.33 eV (peak C) and 0.52 eV (peak D). The lowest EBE transition in the spectrum is its origin-containing transition, i.e., the $\nu' = 0 \leftarrow \nu'' = 0$ transition, and it defines the adiabatic electron affinity. Thus, $\text{EA}_\text{a}(\text{C}_9\text{H}_7\text{N})$ was determined to be 0.16 eV ± 0.05 eV (Peak A). Our electronic structure calculations, including the zero-point energy, found quinoline to support a bound valence anion with an EA of 0.19 eV, which is in very good agreement with our experimentally measured value and the previous calculated semi-empirical value of 0.2 eV [2]. Since the electron is added to a closed shell molecule, the electron affinity is expected to be small. There is scant evidence of vibrational hot bands in the spectrum, possibly because of anion autodetachment. The optimised geometries for both anion and neutral quinoline were calculated and found to be planar with very similar bond lengths between the structures (Figure 2(a)). The HOMO structure for the quinoline anion is shown in Figure 2(b), where the excess electron is delocalised in the π^* anti-bonding orbital. A computationally simulated photoelectron spectrum was generated and is also shown in Figure 1(b). The profile of the calculated spectrum matches well compared with the experimentally measured photoelectron spectrum.

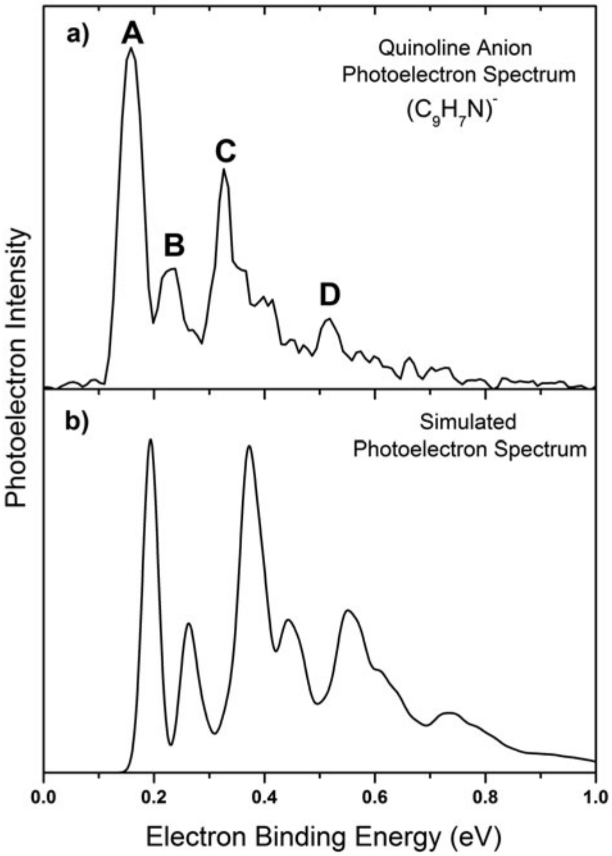

Figure 1. (a) The measured photoelectron spectrum of the quinoline− anion recorded using 2.540 eV photons. (b) The calculated Franck–Condon simulated photoelectron spectrum. 190 × 262 mm (300 × 300 DPI).

Since quinoline is a planar species belonging to the C_s point group, there are 45 vibrational modes that can be classified as even or odd, $31\text{A}'$ and $14\text{A}''$, respectively. The A' modes will have the greatest Franck–Condon overlap and be active in a photoelectron spectrum. The vibrational frequencies from Figure 1(a) were measured as the energy spacing between peak centres in the spectrum and are presented in Table 1. Previous IR studies were considered to identify and assign the vibrational modes [18]. The vibrational frequency 565 cm^{-1} (spacing between A and B) is assigned as vibrational mode ν_{29}, an in-plane ring distortion. The adjacent vibrational frequency (between A and C) at 1371 cm^{-1} is assigned as the vibrational modes ν_{14} and ν_{15} a C–C bond stretch. The spacing between A and D is 2904 cm^{-1} which corresponds to the C–H vibrational modes $\nu_{1\text{–}7}$. The calculated vibrational frequencies are close to the experimentally measured vibrational modes which is expected since the calculated simulated spectrum of quinoline is very similar to the experimentally measured spectrum (Table 1).

4. Summary

The molecule quinoline, displays a greater electrophilicty than its analogue, naphthalene. Quinoline anion was formed by injecting low-energy electrons into a supersonic expansion of the molecule seeded in argon and the anion photoelectron spectrum was recorded. A small but positive electron affinity of 0.16 eV was experimentally measured, indicating that quinoline supports a valence bound anion. DFT calculations at the wb97xd /aug-cc-pVTZ level of

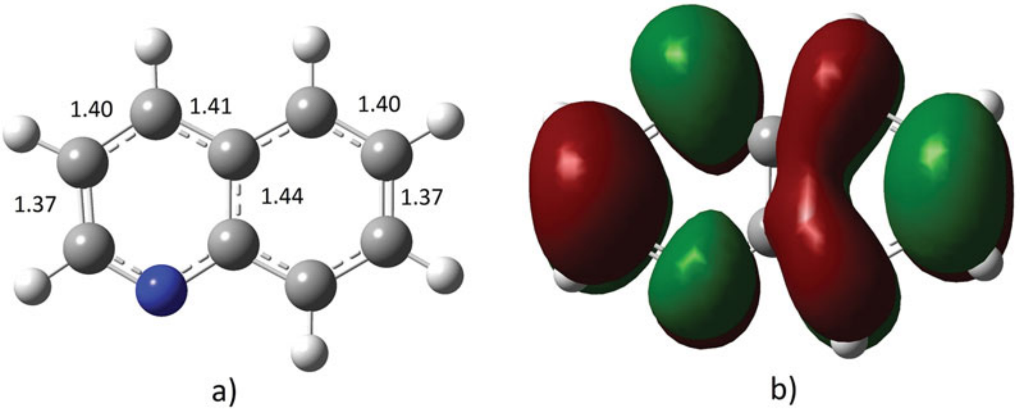

Figure 2. (a) Optimised (wb97xd/aug-cc-pVTZ) structure of the quinoline− anion along with the critical bond lengths (Å). (b) The highest occupied molecular orbital (HOMO) of the ground state of the anion. 564 × 231 mm (96 × 96 DPI).

Table 1. Transition assignments for the photoelectron spectrum of quinoline compared with calculations from this study[a] and previously reported literature values.

Experimental (this work)					Calculated (this work)		Reported values (from the literature)	
Peak location		Vibrational spacing			Peak location	Vibrational mode	Experimental vibrational spacing[b]	Calculated peak location[c]
	(eV)	Δ	(eV)	(cm^{-1})	(eV)	(cm^{-1})	(cm^{-1})	(eV)
A	0.16				0.19			0.20
B	0.23	B-A	0.07	565	0.26	532, 535	522 (ν_{29})	
C	0.33	C-A	0.17	1371	0.37	1371	1392 (ν_{14}), 1371(ν_{15})	
D	0.52	D-A	0.36	2904	0.55	3161	3086(ν_1), 3056(ν_2), 3036(ν_3), 3014(ν_4), 3004(ν_5), 2979(ν_7)	

[a] Uncertainties are ± 0.05 eV or less.
[b] From Ref. [18].
[c] From Ref. [2].

theory found the electron affinity to be 0.19 eV. Both our experimental and theoretical results were in good agreement with those from previous studies.

Acknowledgements

We acknowledge a helpful discussion with G. B. Ellison. This contribution is in honour of Prof. Dr. John P. Maier.

Funding

This work was supported by the US National Science Foundation [Grant No. CHE-1360692 (KHB)].

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