

Negative electron binding energies observed in a triply charged anion: Photoelectron spectroscopy of 1-hydroxy-3,6,8-pyrene-trisulfonate

Jie Yang,^{1,2} Xiao-Peng Xing,^{1,2} Xue-Bin Wang,^{1,2} Lai-Sheng Wang,^{1,2,a)} Alina P. Sergeeva,³ and Alexander I. Boldyrev^{3,b)}

¹Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99354, USA

²Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, MS K8-88, P.O. Box 999, Richland, Washington 99352, USA

³Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322, USA

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We report the observation of negative electron binding energies (BEs) in a triply charged anion, 1-hydroxy-3,6,8-pyrene-trisulfonate (HPTS³⁻). Low-temperature photoelectron spectra were obtained for HPTS³⁻ at several photon energies, revealing three detachment features below 0 electron BE. The HPTS³⁻ trianion was measured to possess a negative BE of -0.66 eV. Despite the relatively high excess energy stored in HPTS³⁻, it was observed to be a long-lived anion due to its high repulsive Coulomb barrier (RCB) (~ 3.3 eV), which prevents spontaneous electron emission. Theoretical calculations were carried out, which confirmed the negative electron BEs observed. The calculations further showed that the highest occupied molecular orbital in HPTS³⁻ is an antibonding π orbital on the pyrene rings, followed by lone pair electrons in the peripheral $-\text{SO}_3^-$ groups. Negative electron BE is a unique feature of multiply charged anions due to the presence of the RCB. Such metastable species may be good models to study electron-electron and vibronic interactions in complex molecules. © 2008 American Institute of Physics. [DOI: 10.1063/1.2889001]

I. INTRODUCTION

Multiply charged anions (MCAs) are common in nature, ranging from simple inorganic anions and coordination complexes to organic anions and complex biological molecules. Multiply charged anions contain significant intramolecular Coulomb repulsions and are stabilized in the condensed phase by solvent in solution or counterions in crystals. As isolated species, MCAs are usually unstable against either electron autodetachment or charge-separation fragmentation and, therefore, are difficult to study experimentally.¹⁻⁷ The electrospray ionization technique⁸ made it possible to produce intense beams of MCAs and allowed their first spectroscopic characterization by photoelectron spectroscopy (PES).⁹⁻¹¹ One of the most interesting and unusual features of PES of multiply charged anions is the detection of the repulsive Coulomb barrier (RCB), which prevents slow electrons from being emitted. The RCB provides dynamic stability for MCAs, allowing metastable species to be observed experimentally.¹²⁻¹⁸ Metastable MCAs result in photoelectrons with kinetic energies (KEs) higher than the photodetachment photon energy ($h\nu$), leading to negative electron binding energies (BEs) on the basis of Einstein's photoelectric equation, $\text{BE} = h\nu - \text{KE}$.

Metastable MCAs are interesting molecular species because they store excess electrostatic energies, which are released upon photodetachment. Most small MCAs with negative electron BEs are too short lived to allow experimental

observation, which typically requires tens of microseconds. An interesting question concerned how much excess energy can be stored in a MCA that would still render it sufficient lifetime to allow experimental observation and interrogation. The first MCA observed with a negative electron BE was a fairly large quadruply charged anion,^{12,14} copper phthalocyanine tetrasulfonate [$\text{CuPc}(\text{SO}_3)_4^{4-}$], which was measured to possess 0.9 eV excess energy. Negative electron BEs have also been measured in a relatively small doubly charged anion, PtCl_4^{2-} , as -0.25 eV.^{13,15} The metastabilities of these MCAs have been confirmed by direct observation of autodetachment via tunneling through the RCB in a Fourier transform ion cyclotron resonance mass spectrometer.¹⁶⁻¹⁸ Their half-lives have been measured at room temperature as 2.5 s for PtCl_4^{2-} and ~ 275 s for $\text{CuPc}(\text{SO}_3)_4^{4-}$. Here, we report the observation of negative electron BEs in a triply charged anion, 1-hydroxy-3,6,8-pyrene-trisulfonate (HPTS³⁻). Stable gaseous trianions have been observed and discussed previously,^{12,14,19} but negative electron BEs have not been measured for any trianions. We have determined that HPTS³⁻ possesses a RCB of ~ 3.3 eV with a relatively high negative electron BE of -0.66 eV. *Ab initio* calculations have been carried out to help interpret the experimental PES data and to provide electronic structure information.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Photoelectron spectroscopy

1-hydroxy-3,6,8-pyrenetrisulfonic acid, commonly known as pyranine, is an important molecule for studying excited state proton transfer in solution.²⁰ It exists as a triply

^{a)}Electronic mail: ls.wang@pnl.gov.

^{b)}Electronic mail: boldyrev@cc.usu.edu.

charged anion in basic solution (HPTS^{3-}) upon deprotonation from the three sulfonic acid groups. Our experiments were done with a low-temperature magnetic-bottle PES apparatus equipped with an electrospray ion source and a cryogenically cooled ion trap.^{21,22} The HPTS^{3-} trianion was produced via electrospray of a 1 mmol solution of pyranine trisodium salt desolved in a water/methanol mixed solvent (1/3 volume ratio). Anions produced from the source were guided by a radio-frequency quadrupole and octopole into a Paul trap, which was attached to the cold head of a closed-cycle He refrigerator to allow ion temperatures to be controlled between 10 and 350 K via collisional cooling with ~ 1 mTorr He background gas containing 20% H_2 . The ion trap was operated at 18 K in the current experiment. Anions were accumulated and cooled before being pulsed out into the extraction zone of a time-of-flight mass spectrometer at 10 Hz repetition rate. The HPTS^{3-} trianion was the dominant ion from the source and it was mass selected and decelerated before being photodetached by a laser beam in the interaction zone of the magnetic-bottle PES analyzer. Four detachment photon energies were used: 193 nm (6.424 eV) from an ArF excimer laser, and 266 nm (4.661 eV), 355 nm (3.496 eV), and 532 nm (2.331 eV) from a Nd:YAG (yttrium aluminum garnet) laser. Photoelectron time-of-flight spectra were measured and converted to kinetic energy spectra, calibrated by the known spectra of I^- and ClO_2^- . The electron kinetic energy resolution ($\Delta\text{KE}/\text{KE}$) was $\sim 2\%$, i.e., 20 meV for 1 eV electrons. The electron BE spectra presented were obtained by subtracting the KE spectra from the detachment photon energies.

B. Theoretical calculations

We performed geometry optimization and frequency calculations of HPTS^{3-} using the hybrid density functional theory (DFT) method known in the literature as B3LYP (Refs. 23–25) with augmented correlation-consistent polarized double- ζ valence basis sets (aug-cc-pVDZ) for O atoms²⁶ and correlation-consistent polarized double- ζ valence basis sets (cc-pVDZ) for C, H, and S atoms.^{26,27} The first vertical detachment energy (VDE) was calculated at the B3LYP level of theory as the lowest transition from the closed-shell ground state of HPTS^{3-} to the doublet ground state of the dianion HPTS^{2-} . Higher VDEs were obtained by adding the vertical excitation energies in the HPTS^{2-} dianion (obtained using the time-dependent DFT method at B3LYP level) to the ground state VDE. The B3LYP calculations were performed using the GAUSSIAN 03 program.²⁸ Molecular orbital visualization was done using the MOLDEN 3.4 program.²⁹

III. RESULTS AND DISCUSSION

Figure 1 displays the PES spectra of HPTS^{3-} at four photon energies. The most striking observation is the appearance of detachment features with high negative electron BEs. The 532 nm spectrum [Fig. 1(a)] shows one relatively sharp ground state band (X) with a VDE of -0.62 eV. The cold ion allowed the elimination of vibrational hot bands, resulting in a sharp onset for the ground state transition. An adiabatic

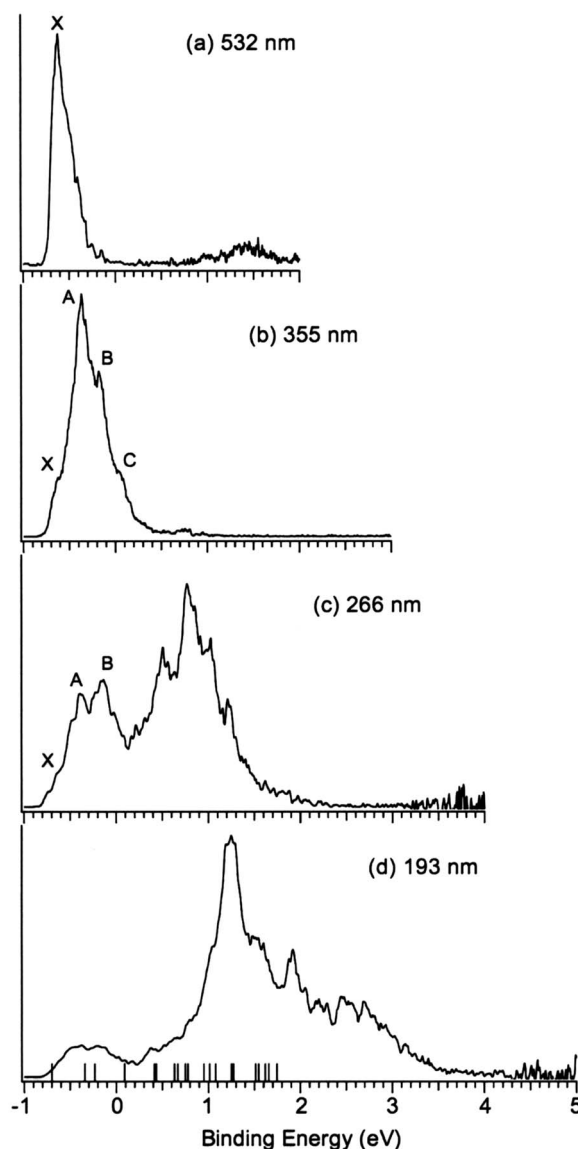


FIG. 1. Photoelectron spectra of HPTS^{3-} at (a) 532 nm (2.331 eV), (b) 355 nm (3.496 eV), (c) 266 nm (4.661 eV), and (d) 193 nm (6.424 eV). The vertical bars in (d) are the calculated vertical electron detachment energies up to 1.74 eV.

detachment energy (ADE) of -0.66 eV was measured from the onset of the X band, representing the negative electron affinity of the HPTS^{2-} radical dianion or the amount of excess electrostatic energy stored in the HPTS^{3-} trianion. At 355 nm, three more detachment bands are observed [Fig. 1(b)], among which two possess negative electron BEs, band A with a VDE of -0.37 eV and band B with a VDE of -0.18 eV. Band C is barely positive with a VDE of ~ 0.05 eV. Following a small energy gap after band C, there appeared a high density of unresolved detachment transitions between 0.3 and 3.2 eV, as revealed in the 266 and 193 nm spectra [Figs. 1(c) and 1(d)].

Another interesting feature of the PES spectra is the cutoff at the higher BE side due to the RCB, a unique characteristic of PES of MCAs.^{9–11} For example, all the higher BE features above 0.2 eV were missing in the 355 nm spectrum [Fig. 1(b)], whereas all the features above 1.4 eV were missing in the 266 nm spectrum [Fig. 1(c)]. These spectral cut-

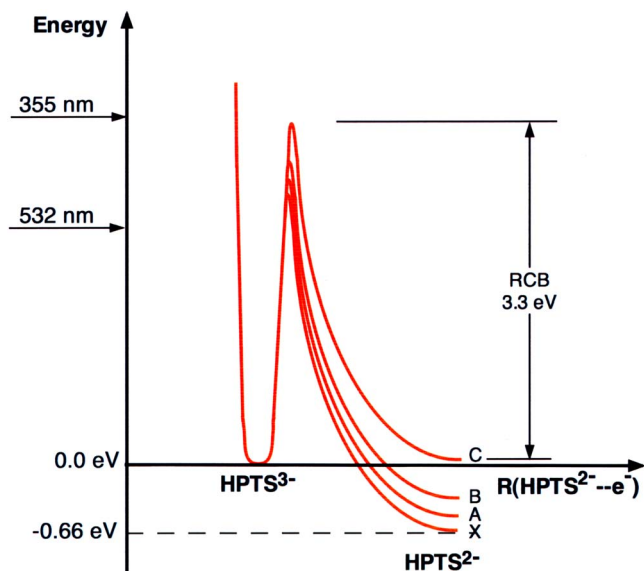


FIG. 2. (Color online) Schematic showing the repulsive Coulomb barrier (RCB) for the first four detachment channels of HPTS^{3-} . Note the negative electron binding energies for the first three detachment channels. The positions of the 532 and 355 nm photon energies are indicated in relation to the triply charged anion and the RCB.

offs yielded a RCB of about 3.3 eV, i.e., (3.496–0.2 eV) from the 355 nm spectrum or (4.661–1.4 eV) from the 266 nm spectrum. The spectral cutoff at ~ 3.2 eV in the 193 nm spectrum yielded a similar value for the RCB. The 3.3 eV RCB is quite high due to the expected large intramolecular Coulomb repulsion within the HPTS^{3-} trianion. Clearly, the photon energy at 532 nm (2.331 eV) is lower than the RCB and could not induce direct photoemission from HPTS^{3-} . Thus, the entire signals observed in the 532 nm spectrum should be due to electron tunneling through the RCB,³⁰ as schematically shown in Fig. 2.

We computed the VDEs up to ~ 1.7 eV in electron BEs. As shown in Fig. 1(d), the computed VDEs are in good agreement with the observed PES spectra. The VDEs of the first four detachment channels are also given in Table I, where they are compared with the experimental data. The first VDE was calculated to be -0.70 eV, slightly higher in magnitude than the observed value at -0.62 eV. As shown in Fig. 3, the highest occupied molecular orbital (HOMO) is an antibonding π orbital belonging to the pyrene rings. This is similar to $\text{CuPc}(\text{SO}_3)_4^{4-}$, whose (HOMO) was also found to be at the central part of the molecule because of the enormous Coulomb repulsions from the peripheral negative charges.^{12,14} The next three detachment channels come from

TABLE I. Experimental adiabatic (ADE) and vertical (VDE) detachment energies of the first four detachment channels for HPTS^{3-} triply charged anion compared to the calculated values [VDE(theor)]. All energies are in eV.

Observed features	ADE	VDE (expt.)	VDE (theor)
X	-0.66 ± 0.05	-0.62 ± 0.05	-0.70
A		-0.37 ± 0.05	-0.34
B		-0.18 ± 0.05	-0.23
C		~ 0.05	0.09

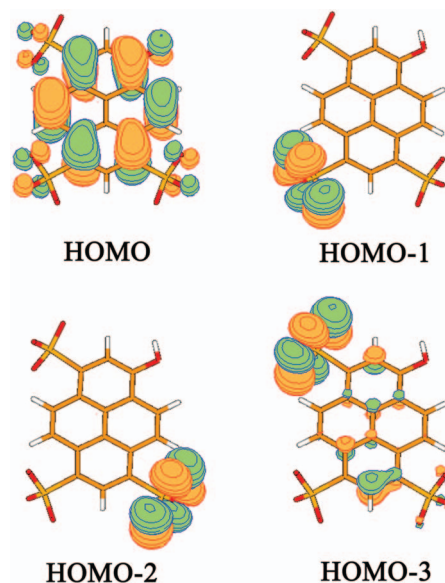


FIG. 3. (Color) Pictures of the top four molecular orbitals of HPTS^{3-} .

oxygen lone pairs on the three peripheral $-\text{SO}_3^-$ groups, respectively, ordered according to the expected Coulomb repulsion experienced by each group. For example, HOMO-1 with a calculated VDE of -0.34 eV (versus the experimental value of -0.37 eV) is the lone pair on the $-\text{SO}_3^-$ group at position 8 because it experiences the largest Coulomb repulsion from the other two negative charges due to their proximity, whereas HOMO-3, which possesses a relatively high VDE of 0.09 eV, is on the $-\text{SO}_3^-$ group at position 3 because it experiences the least Coulomb repulsions from the other two charges.

The 0.66 eV excess energy stored in the HPTS^{3-} triply charged anion is quite high, and yet, it is fairly long lived and no observable decay was detected on our experimental time scale. This is due to the high RCB, which renders the dynamic stability for this trianion. Similar to the $\text{CuPc}(\text{SO}_3)_4^{4-}$, which has an even higher negative electron BE of -0.9 eV, the peripheral negative charges provide a “coral” for the HOMO electron, preventing it from autodetachment. An interesting question is how high excess energy can be stored in a MCA within a given charge state that would still have sufficient lifetime to allow experimental observation and manipulation. Given the long lifetimes of HPTS^{3-} and $\text{CuPc}(\text{SO}_3)_4^{4-}$, it is conceivable that even higher negative BEs can be observed in suitably designed triply or quadruply charged anions or still more highly charged anions. Such metastable MCAs may be good model systems to study electron correlation effects and electron dynamics. They may also be good systems to study vibronic interactions in collision-induced electron detachments or as reagent for studying electron transfer in well-defined gaseous molecules.

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