

## COMMUNICATIONS

Photodetachment photoelectron spectroscopy of doubly charged anions:  $S_2O_8^{2-}$ Chuan-Fan Ding, Xue-Bin Wang, and Lai-Sheng Wang<sup>a)</sup>*Department of Physics, Washington State University, Richland, Washington 99352  
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A photodetachment photoelectron spectroscopy study of a doubly charged anion ( $S_2O_8^{2-}$ ) in the gas phase is reported at three photon energies: 193, 266, 355 nm. Adiabatic and vertical electron binding energies of  $S_2O_8^{2-}$  were measured to be  $1.7 \pm 0.2$  and  $2.2 \pm 0.1$  eV, respectively. Several excited states were observed for the  $S_2O_8^-$  singly charged anion at 193 nm. The repulsive Coulomb barrier that binds multiply charged anions was clearly shown in the detachment spectra of  $S_2O_8^{2-}$ . The effects of the Coulomb barrier to the detachment spectra and electron tunneling through the barrier are presented. The barrier height, which is equivalent to the magnitude of the Coulomb repulsion between the two excess charges in  $S_2O_8^{2-}$  was estimated to be  $\sim 3$  eV. © 1999 American Institute of Physics. [S0021-9606(99)02208-4]

## I. INTRODUCTION

Multiply charged anions, though commonly found in solution and solid, have been scarcely studied in the gas phase.<sup>1-4</sup> The stability of free multiply charged anions, outside of the condensed phases, are dominated by the Coulomb repulsion between the excess charges.<sup>5</sup> Therefore, such common species as  $SO_4^{2-}$ ,  $PO_4^{3-}$ , and  $CO_3^{2-}$  are unstable in the gas phase,<sup>6</sup> where solvation effects or Coulomb attractions with counter ions are absent. However, free multiply charged anions are interesting gas phase species that provide opportunities to understand intramolecular electrostatic interactions and solvation effects. Increasing theoretical efforts have been focused on free multiply charged anions in the gas phase.<sup>1,5-9</sup> In contrast, experimental studies of multiply charged anions have been rather scarce, although an increasing number of stable multiply charged anions have been observed in the gas phase using mass spectrometry and electrospray ionization (ESI),<sup>10,11</sup> particularly, for fullerenes and their derivatives.<sup>12,13</sup>

Recently, we have developed an experimental technique, combining an ESI source and photodetachment photoelectron spectroscopy (PES), to investigate the chemical and physical properties of multiply charged anions in the gas phase.<sup>14</sup> PES is an ideal experimental technique to probe the intrinsic properties of multiply charged anions because it provides direct information about their stability, Coulomb repulsion, and electronic structure. We have reported the first photodetachment spectra of a multiply charged anion and observed directly the repulsive Coulomb barrier (RCB),<sup>15</sup> due to the long range Coulomb repulsion and short-range molecular binding between an anion and an excess

electron.<sup>1,2</sup> We have quantitatively determined that the barrier height in a series of doubly charged anions are exactly equal to the Coulomb repulsion present in the dianions.<sup>16</sup> We have also observed the solvent stabilization of doubly charged anions and electron tunneling effects in doubly charged anions.<sup>17,18</sup>

In the current paper, we present a photodetachment study of the first inorganic dianion,  $S_2O_8^{2-}$ . The peroxodisulfate dianion is an important inorganic chemical species in solution, and a powerful and common oxidizing agent.<sup>19</sup> It is known to be stable in the gas phase experimentally.<sup>10</sup> It has also been studied theoretically with density functional theory (DFT) and positive electron binding energies were obtained, confirming its stability as a free dianion.<sup>20</sup> We measured the PES spectra of  $S_2O_8^{2-}$  at three photon energies: 193, 266, and 355 nm and determined its electron binding energies. We show how the PES spectra are affected by the RCB and the electron tunneling effects. The RCB was estimated to be  $\sim 3$  eV, consistent with the molecular structure of  $S_2O_8^{2-}$  and the charge separation within the dianion. We also observed photodissociation of  $S_2O_8^{2-}$ .

## II. EXPERIMENT

Figure 1 shows a schematic of our experimental apparatus, which involves a magnetic-bottle time-of-flight (TOF) photoelectron spectrometer and an electrospray ionization source. Details will be published elsewhere,<sup>14</sup> and only a very brief description is given here. A  $10^{-4}$  M  $Na_2S_2O_8$  solution in a water/methanol (2/98 ratio) mixed solvent was sprayed through a 0.01 mm ID syringe needle (biased at  $-2.2$  kV) into ambient atmosphere. The resulting charged droplets were fed into a desolvation capillary heated to  $\sim 70$  °C. Molecular anions emerging from the desolvation capillary were guided by a radio-frequency quadrupole de-

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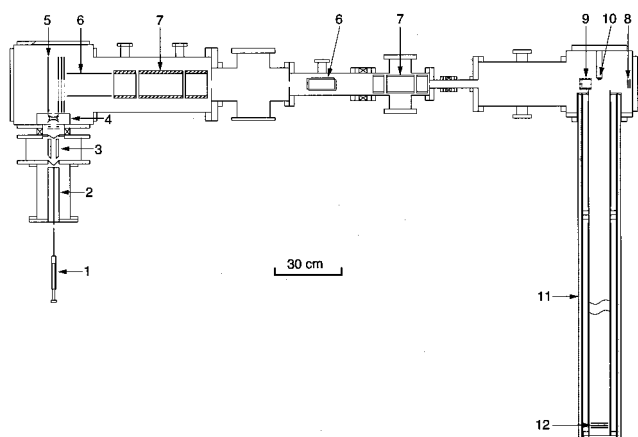


FIG. 1. Schematic of the electro spray-magnetic-bottle photoelectron apparatus. (1) Syringe; (2) Desolvation capillary; (3) Radio-frequency quadrupole ion guide; (4) 3-D ion trap; (5) Ion repeller; (6) Ion beam deflector; (7) Einzel lens; (8) In-line mass detector; (9) Mass gate and momentum deceleration assembly; (10) Permanent magnet; (11) 4 m-long electron flight tube; (12) Electron detector.

vice into a 3-D quadrupole ion trap. Ions were accumulated for 0.1 s in the ion trap before being pulsed out into the extraction zone of a TOF mass spectrometer. The ions were extracted perpendicularly with a  $-1.25$  kV high-voltage pulse for the TOF mass analyses. Figure 2 shows a typical TOF mass spectrum when the  $\text{Na}_2\text{S}_2\text{O}_8$  solution was sprayed. Besides the dominating  $\text{S}_2\text{O}_8^{2-}$  species, its water and methanol solvated species were also present. A peak at  $\sim 69.6$   $\mu\text{s}$  ( $M/Z$  28.5 higher than that of  $\text{S}_2\text{O}_8^{2-}$ ) was not identified and was probably due to a reaction product with the solvents. The  $\text{S}_2\text{O}_8^{2-}$  dianions were mass selected and decelerated before intercepted by a probe laser beam in the photodetachment zone of the magnetic-bottle photoelectron analyzer. An Nd:YAG laser (355 and 266 nm) and an ArF Excimer laser (193 nm) were used for photodetachment. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 4 m-long electron flight tube. Photoelectron TOF spectra were collected and then converted to kinetic energy spectra, calibrated by known spectra of  $\text{I}^-$  and  $\text{O}^-$ . The electron binding energy spectra presented were ob-

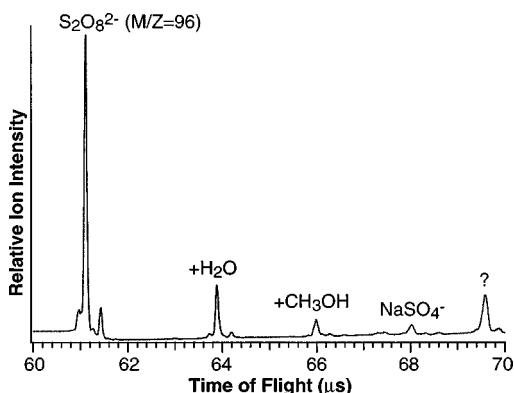


FIG. 2. Time-of-flight mass spectrum of  $\text{S}_2\text{O}_8^{2-}$  from electro spray of a  $10^{-4}$  M  $\text{Na}_2\text{S}_2\text{O}_8$  solution in methanol/water (98/2 ratio). Note the solvated species and an unidentified dianion at  $69.6$   $\mu\text{s}$ , which has an  $M/Z$  28.5 higher than  $\text{S}_2\text{O}_8^{2-}$ .

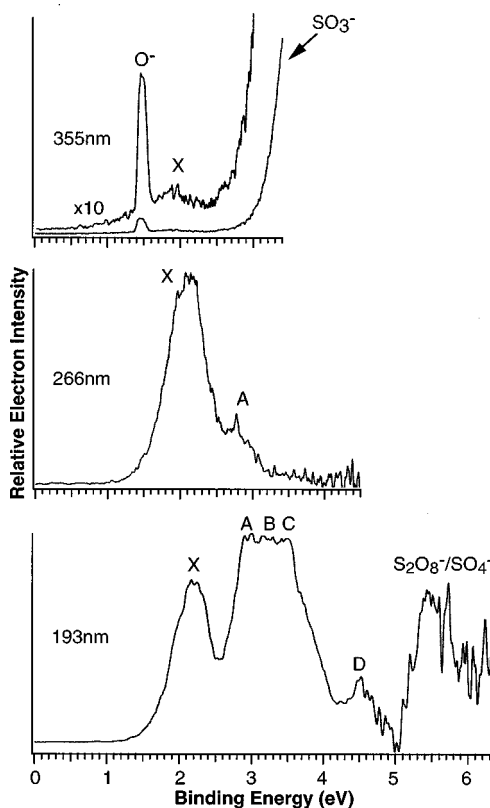


FIG. 3. Photoelectron spectra of  $\text{S}_2\text{O}_8^{2-}$  at 355 nm (3.496 eV), 266 nm (4.661 eV), and 193 nm (6.424 eV). Note the disappearance of spectral features at low photon energies and the  $\times 10$  amplification of the 355 nm spectrum.

tained by subtracting the kinetic energy spectra from the probe photon energy. The electron kinetic energy resolution was  $\Delta E/E \sim 2\%$ , i.e., 20 meV for 1 eV electrons.

### III. RESULTS AND DISCUSSION

The PES spectra of  $\text{S}_2\text{O}_8^{2-}$  are shown in Fig. 3 at the three photon energies. The 193 nm spectrum exhibits several broad features (labeled X, A, B, C, D), representing detachment transitions from the ground state of the dianion to states of the singly charged anion. There are at least three overlapping features (A, B, C) between 2.6 and 4 eV binding energies, followed by a weak feature (D) at about 4.5 eV. Features beyond 5 eV in the 193 nm spectrum cannot be due to the dianion, as will be discussed below. The 266 nm spectrum showed only the ground state (X) and a weak feature due to the A state. At 355 nm, the signals from the dianions were very weak. A sharp peak observed at about 1.46 eV was due to  $\text{O}^-$ .<sup>21</sup> The strong tail at high binding energy was shown to be due to  $\text{SO}_3^-$ .<sup>22</sup>

The photon energy dependence of the PES spectra of  $\text{S}_2\text{O}_8^{2-}$  shown in Fig. 3 demonstrates most vividly the existence of the RCB. Because of the long-range Coulomb repulsion between the outgoing photoelectron and the remaining singly charged anion, a potential barrier must exist for the outgoing electrons. These electrons must have enough kinetic energy to overcome the barrier. Therefore, even though the photon energy at 266 nm (4.661 eV) was higher than the binding energies of the transitions to the B, C, and D

states, they were not observed in the 266 nm spectrum, suggesting that this photon energy was below the respective RCB for these states. The X feature defines the adiabatic (EBa) and vertical (EBv) electron binding energies of  $S_2O_8^{2-}$ . Because of the low energy tail, due to both thermal effects and expected geometry changes between the dianion and the singly charged anion, we could only estimate the EBa to be  $1.7 \pm 0.2$  eV. The EBv was measured to be  $2.2 \pm 0.1$  eV. Apparently, the previously calculated EBa (0.35 eV) using DFT was too low.<sup>20</sup>

We noted that the X feature in the 266 nm spectrum exhibited a shift to lower binding energy relative to that at 193 nm by about 0.1 eV. As we have shown previously,<sup>18</sup> such a spectral shift was due to electron tunneling through the RCB, suggesting that even the 266 nm photon energy was below the RCB relative to the ground state. Tunneling probabilities depend exponentially on the electron kinetic energy, thus favoring low binding energy (high kinetic energy) features. This results in an apparent spectral shift in PES spectra when photon energies are below the barrier top, i.e., the Franck–Condon factors are modified by the tunneling probabilities in the tunneling regime.<sup>18</sup> Such a spectral shift in PES is characteristic of multiply charged anions and is another direct consequence of the RCB. The lower the photon energy relative to the barrier top, the smaller the tunneling probability and the larger the spectral shift. Eventually, when the photon energies are too low compared to the RCB, tunneling probabilities are negligible and no photoelectrons would be observed even if the photon energies were higher than the electron binding energies. Such was the case for the 355 nm spectrum shown in Fig. 3, where almost negligible electron signals were observed from the dianion. The significant photoelectron intensity observed at 266 nm for the X state indicated that the photon energy was close to the barrier top of the X state. Thus, the barrier height could be estimated to be  $>2.96$  eV ( $4.661 - 1.7$  eV).

Figure 4 depicts schematically the RCB for the observed detachment channels of  $S_2O_8^{2-}$  along with indications of the three photon energies. The structure of  $S_2O_8^{2-}$  obtained from the previous DFT calculations is also given.<sup>20</sup> The average distance between the terminal O atoms, where the negative charges are most likely localized, is estimated to be about 4.8 Å. Using Coulomb's law ( $e^2/4\pi\epsilon_0 r$ ) and this average charge separation distance, we estimated an intramolecular Coulomb repulsion of  $\sim 3$  eV, which is consistent with the above estimate of the RCB. We have shown previously that the RCB is equal in magnitude to the intramolecular Coulomb repulsion.<sup>16</sup> As Fig. 4 shows, the  $S_2O_8^{2-}$  dianion can be viewed as two  $O-SO_3^-$  anions linked via one of their O atoms. We have measured the electron binding energy of  $HO-SO_3^-$  to be  $4.7 \pm 0.1$  eV.<sup>22,23</sup> Thus, it should be expected that an electron bound to one of the  $O-SO_3^-$  groups in  $S_2O_8^{2-}$  would have an electron binding energy approximately equal to 4.7 eV minus the Coulomb repulsion (3 eV) due to the presence of another negative charge. The 1.7 eV binding energy from this simple estimate is in perfect agreement with the measured binding energy of  $S_2O_8^{2-}$ .

The RCB in multiply charged anions means that it would not be possible to observe very low energy electrons in their

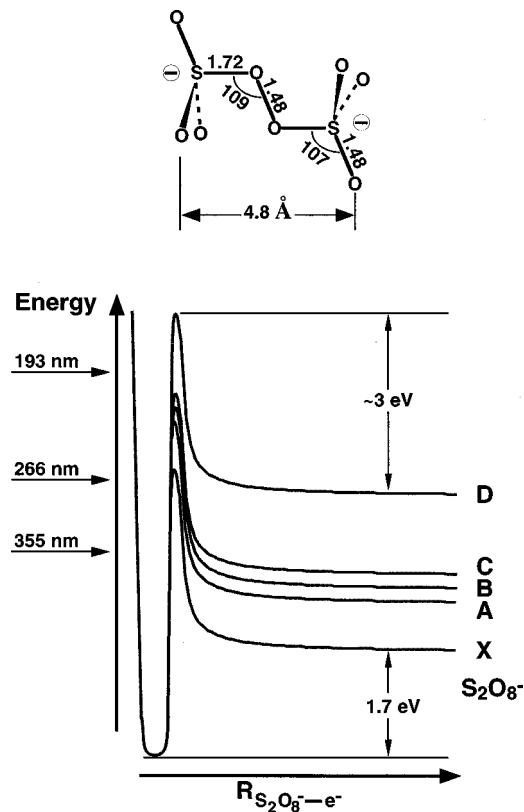


FIG. 4. Schematic structure of  $S_2O_8^{2-}$  and schematic potential energy curves showing the repulsive Coulomb barriers of  $S_2O_8^{2-}$  with respect to the different final states of  $S_2O_8^-$ . The three photon energies used are indicated.

PES. It also implies that threshold photodetachment would not be feasible for multiply charged anions since the tunneling probability at threshold would be negligible. Therefore, the high binding energy (low kinetic energy) features beyond 5 eV in the 193 nm spectrum could not be due to the dianions. These features could be either due to the singly charged  $S_2O_8^-$  or  $SO_4^-$ . We have measured the spectra of  $SO_4^-$ , which exhibits similar high binding energy features as those shown in Fig. 3.<sup>22</sup> However, we expected the  $S_2O_8^-$  species to have electronic structure and binding energies similar to that of  $SO_4^-$ . Thus, we could not definitively assign the high binding energy features.<sup>24</sup>

The  $O^-$  signal observed in the 355 nm spectrum was due to photodissociation of the parent  $S_2O_8^{2-}$  dianions, followed by photodetachment. This was possible because much higher photon fluxes had to be used at 355 nm in order to observe any signal at all. The high binding energy tail in the 355 nm spectrum coincides with the onset of the  $SO_3^-$  detachment threshold, which we have measured independently.<sup>22</sup> Several exothermic dissociation channels have been calculated in the previous DFT study.<sup>20</sup> Collisional induced dissociations of  $S_2O_8^{2-}$  have been experimentally observed.<sup>10</sup> All the dissociation processes involved formation of two singly charged anions. These processes would be interesting to investigate further theoretically because a Coulomb barrier is expected to exist against fragmentation as a result of the long-range Coulomb repulsion between the two charged fragments.

#### IV. CONCLUSIONS

We presented the photodetachment photoelectron spectra of the  $S_2O_8^{2-}$  dianion in the gas phase at 193, 266, and 355 nm. The electronic binding energies of  $S_2O_8^{2-}$  were measured and found to be quite high. We observed the repulsive Coulomb barrier in  $S_2O_8^{2-}$  against electron detachment, and showed how it affected the photodetachment spectra at different detachment energies. The barrier height was estimated to be  $\sim 3$  eV, consistent with the intramolecular Coulomb repulsion in the dianion. Several excited states of  $S_2O_8^{2-}$  were also observed nearly up to its detachment threshold, showing that photodetachment of doubly charged anions provides an experimental means to probe excited states of singly charged anions.

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<sup>24</sup>Since  $SO_4^-$  and  $S_2O_8^{2-}$  have the same M/Z, it was possible that a small amount of  $SO_4^-$  was contained in the  $S_2O_8^{2-}$  beam. There was also a possibility that  $S_2O_8^{2-}$  could undergo photodissociation into two  $SO_4^-$  in the detachment zone.