

## LETTERS

### Photoelectron Spectroscopy of Doubly Charged Anions: Intramolecular Coulomb Repulsion and Solvent Stabilization

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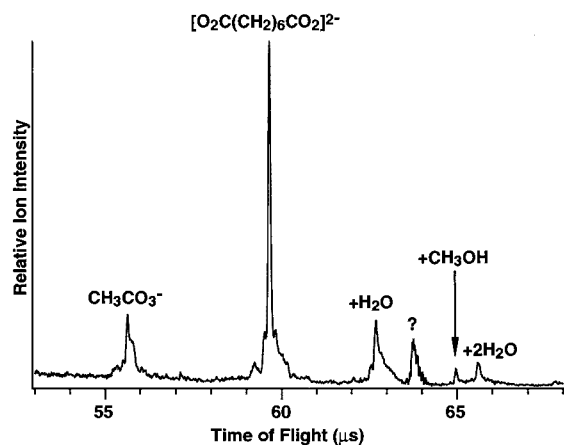
Photoelectron spectroscopy has been combined with an electrospray ionization technique to study gas-phase multiply charged anions and their intramolecular Coulomb repulsion and solvation stabilization. We report an initial study on a series of linear dicarboxylate dianions ( $\text{DC}^{2-}$ ),  $^{-}\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^{-}$  ( $n = 3-6$ ), solvated by one and two waters. The second electron binding energy of  $\text{DC}^{2-}$  decreases with decreasing aliphatic chain length owing to the increasing Coulomb repulsion between the two charges; the dianion with  $n = 2$  has a binding energy close to zero and is not stable in the gas phase. We found that this dianion can be stabilized by one water, and in general the first water stabilizes the electron binding energy of  $\text{DC}^{2-}$  by  $\sim 0.3$  eV. The second water, however, was observed to show a much stronger stabilization effect ( $\sim 0.6$  eV), suggesting that the two waters solvate the two carboxylate groups separately.

#### Introduction

Multiply charged anions (MCAs) are ubiquitous in nature and play important roles in chemistry, biochemistry, and solid materials. Although the existence of MCAs has been taken for granted, free MCAs are not widely observed, largely owing to their instability and difficulties in their formation in the gas phase. Considerable theoretical efforts have been directed at understanding the properties of free MCAs and have been reviewed recently.<sup>1-3</sup> Comparatively, experimental progress on MCAs has been slow.<sup>2,4</sup> Recent experimental efforts have been concentrated on MCAs of fullerenes and related species.<sup>5-10</sup> Notably, Kebarle and co-workers<sup>11-13</sup> have shown that the electrospray ionization (ESI) technique<sup>14-16</sup> provides a convenient means to generate gas-phase MCAs besides its capability as a soft ionization technique of proteins and DNAs for biomedical mass spectrometry.<sup>17</sup>

We have been developing a photoelectron spectroscopy (PES) technique, coupled with an ESI source, to study gas-phase

MCAs. The stability and energetics of isolated MCAs, free from interactions with the condensed media, are dominated by the intramolecular Coulomb repulsion and sensitive to solvation effects.<sup>1,3,18,19</sup> PES, capable of measuring directly the excess electron binding energies of MCAs, is an ideal technique to investigate the intrinsic properties of free MCAs. We have performed a series of experiments designed to probe the stability and solvation effect of gas-phase MCAs. In a recent work,<sup>20</sup> we reported the first PES spectra of a doubly charged anion, citrate dianion, and provided the first direct experimental measurement of the repulsive Coulomb barrier that binds excess electrons in MCAs. In another study,<sup>21</sup> we demonstrated how the binding energies and the Coulomb barrier heights depend on the distances between the two charges in a series of dicarboxylate dianions ( $\text{DC}^{2-}$ ),  $^{-}\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^{-}$  ( $n = 3-10$ ), where the charge separations can be well-controlled. In the present investigation, we report our initial results on the solvent stabilization of the dicarboxylate dianions by one and two waters



**Figure 1.** Time-of-flight mass spectrum of  $^{-}\text{O}_2\text{C}(\text{CH}_2)_6\text{CO}_2^{-}$  dianion using a  $10^{-4}$  M electrospray solution of  $\text{NaO}_2\text{C}(\text{CH}_2)_6\text{CO}_2\text{Na}$  salt at pH  $\sim 10$  in a water/methanol mixed solvent (2/98 ratio). Note the solvated species by one  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and two  $\text{H}_2\text{O}$ .

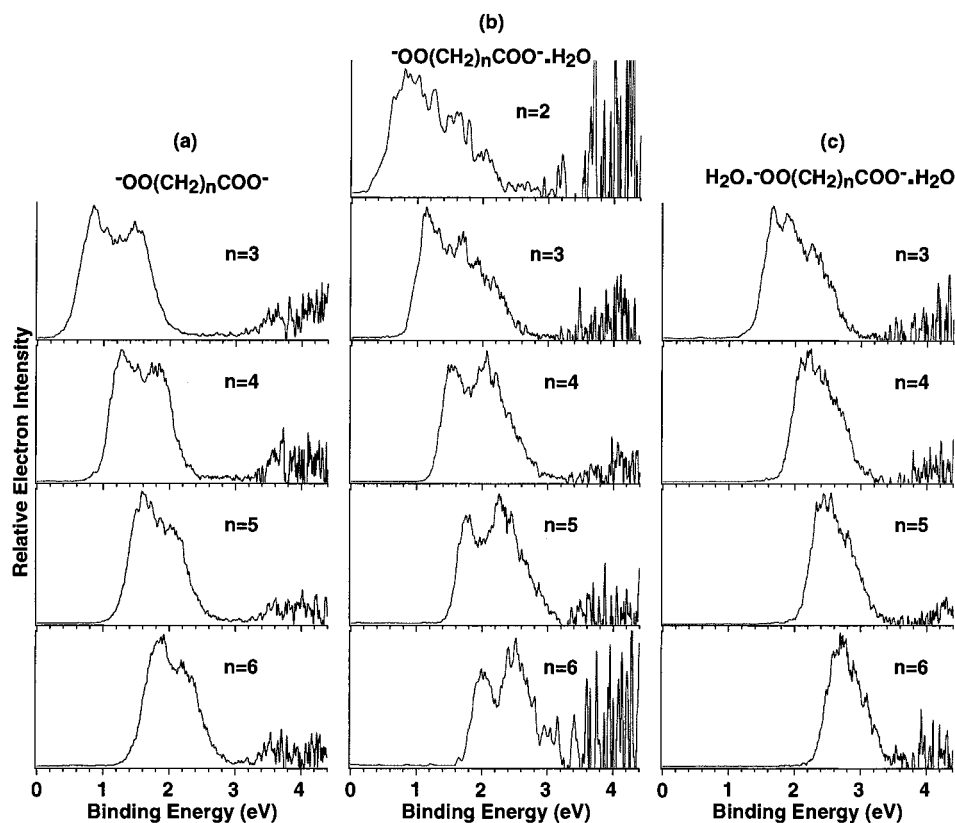
for  $n = 2-6$ . We show that the  $n = 2$  dianion, whose PES spectrum could not be obtained in our previous study owing to its instability in the gas phase, can be stabilized by one water. We found that the first water enhances the binding energies of  $\text{DC}^{2-}$  by  $\sim 0.3$  eV, whereas the second water stabilizes the dianions by almost twice as much,  $\sim 0.6$  eV.

### Experimental Section

The experimental apparatus involves a magnetic bottle time-of-flight (TOF) photoelectron analyzer<sup>22</sup> and an ESI source. To produce the desired dianions, we used a  $10^{-4}$  M solution of the corresponding dicarboxylate salts at pH  $\sim 10$  in a water/methanol mixed solvent (2/98 ratio), spraying it through a 0.01 mm diameter syringe needle at ambient atmosphere. Negatively

charged molecular ions emerging from a desolvation capillary were guided by a radio-frequency-only quadrupole mass filter into an ion trap,<sup>23</sup> where the ions were accumulated for 0.1 s before being pushed into the extraction zone of a TOF mass spectrometer. The anions produced from each solution contained dicarboxylate dianions and monoanions as the dominant masses and weaker signals of solvated species. Figure 1 shows a typical mass spectrum of  $\text{DC}^{2-}$  ( $n = 6$ ) around the dianion mass range. The  $\text{CH}_3\text{CO}_3^{-}$  anion is a typical contamination resulting from reactions between  $\text{CH}_3\text{OH}$  and desolved  $\text{CO}_2$  in the solution and can become the dominating anion depending on the pH of the spraying solution. The mass resolution of our TOF mass spectrometer is mass-dependent and can be tuned for a given mass to about  $700 (M/\Delta M)$ .

In each PES experiment, the dianions of interest were mass-selected and decelerated before being intercepted by a laser beam in the detachment zone of the magnetic bottle photoelectron analyzer. For the current study, primarily the 266 nm (4.66 eV) photons from a Nd:YAG laser were used. The photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 4 m long TOF tube. The photoelectron TOF spectra were then converted to kinetic energy spectra, calibrated by the known spectra of  $\text{I}^{-}$ ,  $\text{ClO}_2^{-}$ , and  $\text{O}^{-}$ .<sup>24</sup> The binding energy spectra presented were obtained by subtracting the kinetic energy spectra from the photon energies used. The energy resolution was about 20 meV fwhm at 0.4 eV kinetic energy, as measured from the spectrum of  $\text{I}^{-}$  at 355 nm, and would deteriorate at higher kinetic energies. However, the spectra of the solvated species were taken at lower resolution because their mass abundance was quite weak and these dianions could not be fully decelerated to achieve the optimum resolution.



**Figure 2.** 266 nm (4.66 eV) photoelectron spectra of (a)  $^{-}\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^{-}$ ,  $n = 3-6$ ; (b)  $^{-}\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^{-}(\text{H}_2\text{O})$ ,  $n = 2-6$ ; (c)  $^{-}\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^{-}(\text{H}_2\text{O})_2$ ,  $n = 3-6$ .

**TABLE 1: Adiabatic Electron Binding Energies (eV) of  $^{-}\text{OOC}(\text{CH}_2)_n\text{COO}^{-}$  ( $\text{DC}^{2-}$ ) and Those Solvated by One and Two Waters<sup>a</sup>**

	<i>n</i>				
	2	3	4	5	6
$\text{DC}^{2-}$	~0	0.55	1.01	1.34	1.52
$\text{DC}^{2-}(\text{H}_2\text{O})$	0.35	0.90	1.32	1.60	1.81
$\text{DC}^{2-}(\text{H}_2\text{O})_2$		1.45	1.90	2.18	2.42

<sup>a</sup> Uncertainty:  $\pm 0.09$  eV.

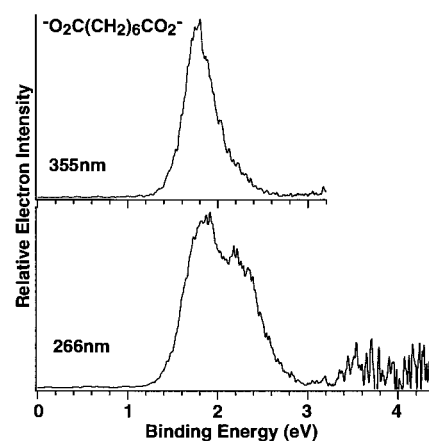
## Results and Discussion

The major results are summarized in Figure 2, where the PES spectra of  $\text{DC}^{2-}$  solvated with one and two  $\text{H}_2\text{O}$  are compared to those of the bare  $\text{DC}^{2-}$  dianions. The count rates were low for the spectra of the solvated species, particularly for the cases of  $\text{DC}^{2-}(\text{H}_2\text{O})$  ( $n = 2$  and 6) where poor statistics and strong noises were quite notable at the high binding energy side.

We first examine the PES spectra of the bare dianions (Figure 2a), which were discussed in detail in our previous investigation.<sup>21</sup> A brief recapitulation is necessary here in order to understand the solvated species. The PES spectra represent transitions from the ground states of the dianions ( $\text{DC}^{2-}$ ) to states of the radical anions ( $\text{DC}^{\cdot-}$ ). The weak signals at the high binding energy side, similar in all the spectra, were likely due to further detachment of the  $\text{DC}^{\cdot-}$  anions by a second photon.<sup>25</sup> Two major overlapping bands were observed. The lower binding energy features represent the ground state of  $\text{DC}^{\cdot-}$  whereas the second feature would represent an excited state of  $\text{DC}^{\cdot-}$ . The spacing between the two bands decreases slightly as the chain length increases. More importantly, the binding energy increases with the chain length as a result of decreasing Coulomb repulsion. The adiabatic binding energies represent the adiabatic electron affinity (AEA) of the  $\text{DC}^{\cdot-}$  singly charged radical anions and are listed in Table 1. Extrapolating the trend of the AEA to  $n = 2$ , we estimated an AEA of about 0 eV, consistent with the fact that the  $\text{DC}^{2-}$  ( $n = 2$ ) is not stable in the gas phase. We could only produce a barely observable mass signal for this dianion and were not able to measure its PES spectrum. Our attempt to obtain better resolved spectra for  $\text{DC}^{2-}$  at lower photon energies revealed that only the lower binding energy feature could be observed as a result of the repulsive Coulomb barrier.<sup>20,21</sup> Figure 3 compares the 355 and 266 nm spectra of  $\text{DC}^{2-}$  ( $n = 6$ ). Despite the fact that the 355 nm photon energy (3.49 eV) is higher than the binding energy of the second PES feature, it could not be observed at 355 nm owing to the Coulomb barrier, whose height was estimated to be about  $1.74 \pm 0.23$  eV for  $\text{DC}^{2-}$  ( $n = 6$ ).<sup>21</sup>

Figure 2b shows the PES spectra of the  $\text{DC}^{2-}$  anions solvated with one  $\text{H}_2\text{O}$ . The PES spectra of the  $\text{DC}^{2-}(\text{H}_2\text{O})$  complexes all exhibit higher binding energies by about  $\sim 0.3$  eV (Table 1) relative to that of  $\text{DC}^{2-}$ . The spectral features of the solvated complexes appear to be similar to those of the bare ones, except that the second band is broadened, indicating the complexity caused by the water solvation. Most notably, we found that  $\text{DC}^{2-}(\text{H}_2\text{O})$  ( $n = 2$ ) is stable with an AEA of  $\sim 0.35$  eV. On the basis of the stabilization effect of one  $\text{H}_2\text{O}$  on the electron binding energy of the dianions, we again can extrapolate that the bare  $\text{DC}^{2-}$  ( $n = 2$ ) dianion has an AEA of about 0 eV; i.e., one  $\text{H}_2\text{O}$  is enough to stabilize this bare dianion in the gas phase.

Figure 2c shows the PES spectra of  $\text{DC}^{2-}$  solvated with two  $\text{H}_2\text{O}$ . The mass abundance of the  $\text{DC}^{2-}(\text{H}_2\text{O})_2$  ( $n = 2$ ) was too weak for us to obtain its spectrum. The binding energies for the two-water solvated species are all increased, and the adiabatic binding energies are summarized and compared to that



**Figure 3.** Comparison of the 266 and 355 nm spectra of  $^{-}\text{O}_2\text{C}(\text{CH}_2)_6\text{CO}_2^{-}$ , showing the Coulomb barrier effect.

of the bare and the one-water solvated species in Table 1. Surprisingly, the binding energies of the  $\text{DC}^{2-}(\text{H}_2\text{O})_2$  species are all stabilized by about 0.6 eV relative to the  $\text{DC}^{2-}(\text{H}_2\text{O})$  species; i.e., the second  $\text{H}_2\text{O}$  exhibits a stabilization effect that is twice as strong as that of the first  $\text{H}_2\text{O}$ . Furthermore, the PES features of the  $\text{DC}^{2-}(\text{H}_2\text{O})_2$  species appeared to be quite different, and only one broad band was observed in each case. High binding energy features should exist for the two-water solvated species. However, they could not be observed owing to the repulsive Coulomb barrier, analogous to the spectral variations observed at different photon energies as shown in Figure 3. The 4.66 eV photon energy was not high enough to overcome the Coulomb barrier to access the higher binding energy features in the  $\text{DC}^{2-}(\text{H}_2\text{O})_2$  species.

Why does the second water stabilize the dianions twice as much as the first water? PES has been well used to study solvation of singly charged anions.<sup>26–29</sup> In particular, Markovich et al.<sup>27</sup> reported PES spectra of halogen anions solvated with water and found that the differential stabilization effect of water on the anion electron binding energy always decreases with the number of water molecules. However, the  $\text{DC}^{2-}$  dianions are different. Owing to the strong intramolecular Coulomb repulsion, the bare  $\text{DC}^{2-}$  dianions all assume linear structures so that the two charges, mainly localized on the terminal carboxyl groups, could be separated as far as possible. The single  $\text{H}_2\text{O}$  molecule is expected to solvate one  $^{-}\text{CO}_2^{-}$  group at one end of the dianions, forming strong H-bonding<sup>30</sup> to one  $^{-}\text{CO}_2^{-}$  and thus making the two  $^{-}\text{CO}_2^{-}$  groups inequivalent. The effect of the water on the other charge is indirect, thus exerting a smaller stabilization effect that comes primarily from two mechanisms: (1) charge–dipole interaction and (2) charge delocalization through the H-bonding.

When the second water is added, the most likely bonding position is on the second  $^{-}\text{CO}_2^{-}$  group, making both charges equally solvated. Thus a directly solvated electron is detached in the  $\text{DC}^{2-}(\text{H}_2\text{O})_2$  species, compared to the  $\text{DC}^{2-}(\text{H}_2\text{O})$  complexes whose AEA is determined by the detachment from the unsolvated  $^{-}\text{CO}_2^{-}$  group. The stabilization energy of the second water should be comparable to that of a water to an analogous singly charged anion. For example, Markovich et al. showed that the first water stabilizes  $\text{Br}^{-}$  by 0.55 eV and the differential stabilization energy decreases with each additional water molecule.<sup>27</sup> Therefore, we expect that an even–odd effect should be observed when  $\text{DC}^{2-}$  is solvated with more  $\text{H}_2\text{O}$ .

## Conclusions

We present a photoelectron spectroscopy study of solvated doubly charged anions of a series of linear dicarboxylates ( $\text{DC}^{2-}$ ),  $^{-}\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^{-}$  ( $n = 3-6$ ), solvated by one and two  $\text{H}_2\text{O}$ . We found that  $^{-}\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2^{-}$ , though not stable as a bare anion in the gas phase, can be stabilized by one  $\text{H}_2\text{O}$ . The stabilization of the first water on the binding energies of all the  $\text{DC}^{2-}$  dianions is about 0.3 eV. The second water was found to stabilize the binding energies by nearly twice as much,  $\sim 0.6$  eV. This was explained as evidence that the two waters solvate the two  $^{-}\text{CO}_2^{-}$  groups, respectively, in the two-water complexes, while the single water solvates only one  $^{-}\text{CO}_2^{-}$  group in the  $\text{DC}^{2-}(\text{H}_2\text{O})$  complexes.

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