Probing the Potential Barriers and Intramolecular Electrostatic Interactions in Free Doubly Charged Anions

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Multiply charged anions, though ubiquitous in nature, have been difficult to produce and study in the gas phase. Photoelectron spectroscopy has been combined with an electrospray ion source to probe the repulsive Coulomb barriers, excess electron binding, and intramolecular electron-electron interactions in a series of dicarboxylate dianions, $^{-}O_2C(CH_2)_nCO_2^{-}$ ($n = 3-10$). These experiments provide quantitative information about the repulsive Coulomb barriers and how the excess electron binding energy and the barrier height depend on the intramolecular Coulomb repulsion. [S0031-9007(98)07243-3]

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Multiply charged anions are ubiquitous in nature and play important roles in chemistry, biochemistry, and solid materials. In contrast, they are seldom observed in the gas phase, where the interactions with surrounding media that are needed to stabilize the charges are absent. Experimental evidence for long-lived multiply charged anions in the gas phase has so far come only from mass spectrometric techniques [1,2] and their intrinsic properties are essentially unexplored [3]. Analogous to the binding of α particles in heavy atomic nuclei [4], the excess electrons in multiply charged anions are bound by a repulsive Coulomb barrier (RCB) [1]. The existence of the RCB has been inferred by Compton and others in studies of multiply charged fullerene anions [1,5–8]. However, there has been no direct experimental measurement of the RCB, nor of the excess electron binding energy, of any multiply charged anion. Using a newly developed photodetachment photoelectron spectroscopy (PES) apparatus, we have recently reported the first direct measurement of the RCB in citrate dianions [9]. In the present Letter, we report a PES study of a series of linear dicarboxylate dianions (DC^{2-}),$^{-}O_2C(CH_2)_nCO_2^{-}$ ($n = 3-10$), revealing how the RCB and the excess electron binding energy in the dianions depend on the equilibrium charge separation.

Recently, the electrospray ionization (ESI) technique [10] has been shown to be a powerful means of generating multiply charged anions in the gas phase [11–14]. Our experimental apparatus couples an ESI source with a magnetic-bottle time-of-flight (TOF) photoelectron analyzer [15]. We chose the dicarboxylate dianions because they were known to be stable in the gas phase when n is greater than 2 [16], and the charges are largely localized on the two carboxylate groups, allowing their separation to be systematically varied. For each dianion, we used a 10^{-4} molar solution at pH ~ 10 in a water/methanol mixed solvent ($\frac{2}{98}$ 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 [17], 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. In each experiment, the dianions were mass selected and decelerated before being intercepted by a laser beam in the detachment zone of the magnetic-bottle photoelectron analyzer. The photoelectron spectra, plotted in electron binding energies, are shown in Fig. 1 for $n = 3-10$ at 266 nm (4.66 eV) and 355 nm (3.49 eV). The energy resolution was about 20 meV at 0.4 eV kinetic energy and deteriorated at higher kinetic energies.

Our initial spectroscopic investigations of the dianions were done at 266 nm. These photoelectron spectra [Fig. 1(a)] show two broad and overlapping features, representing transitions from the ground state of DC^{2-} to the ground (X) and first excited (A) states of the singly charged radical anion (DC^{-}). The binding energy increasing with the chain length. The energy separation between the X and A bands also varies with chain length, decreasing from $\sim$0.60 eV for $n = 3$ to $\sim$0.42 eV for $n = 8$. Further increases in chain length result in no measurable change in the X-A separation. To enhance the spectral resolution, we next measured the photoelectron spectra of the dianions at a lower photon energy of 355 nm [Fig. 1(b)]. Surprisingly, except for a small shoulder for the $n = 3$ case, only the lower binding energy feature (X) was observed, even though the 3.49 eV photon energy was higher than the binding energy of the A state in all cases. The data in Fig. 1(b) suggest that there is a potential energy barrier for the A state [9].

The 355 nm spectra were better resolved and thus provided more accurate measures of the electron binding energies for the X state. We found that the X bandwidth decreases with increasing n. Above $n = 8$ the spectral width shows no appreciable change. We performed

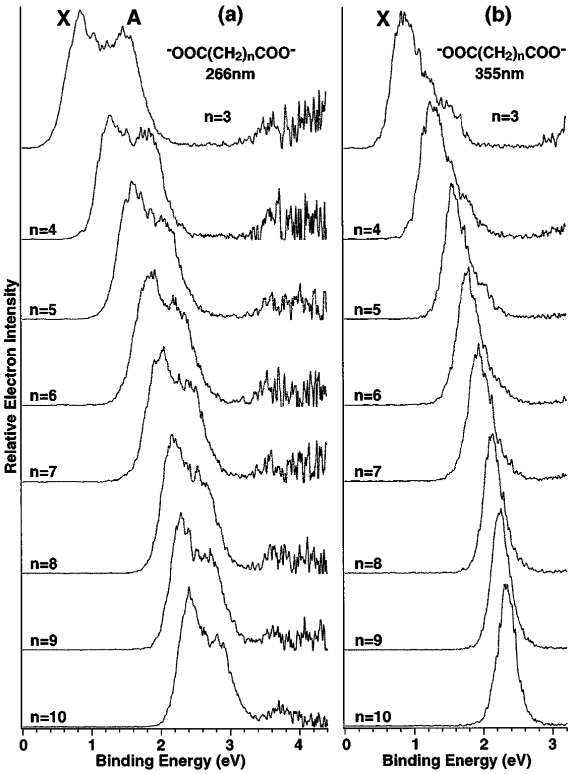

FIG. 1. Photoelectron spectra of $^{-}$OOC-$(CH_2)_n$-COO^{-} (DC^{2-}) dianions ($n = 3-10$) at (a) 266 nm (4.66 eV) and (b) 355 nm (3.49 eV).

further experiments at 532 nm (2.33 eV) and only observed very weak signals for $n = 3-5$. We could not obtain spectra for $n = 6$ and above, thus providing further evidence for the potential energy barrier, in this case for the X state.

Figure 2 schematically illustrates the potential energy barriers suggested experimentally [9]. RCB_X and RCB_A are the repulsive Coulomb barriers for the X and A states, respectively. Because of the potential barriers, photon energies substantially higher than the binding energies are required to reach the X or A state. EB_X, which also is the electron affinity of DC^-, can be measured directly from the detachment threshold, and is expected to increase as the Coulomb repulsion between the two charges is reduced by increasing the chain length, as shown by the data in Fig. 1. The measured EB_X values are plotted in Fig. 3 for $n = 3-10$ as a function of $1/r_n$, r_n being the average distance between the oxygen atoms of the two carboxylate groups [18], and reveal a linear relationship. A least squares fit yielded $EB_X = 3.21(4) - 16.7(3)/r_n$, where the numbers in parentheses give the uncertainties in the last digits. Extrapolating the curve to $EB_X = 0$ eV, we obtained a critical r_n value of ~5.2 Å, below which EB_X becomes negative. Our estimated value of r_n when $n = 2$ is ~5.3 Å [18], very close to the critical r_n value. Hence, this dianion is expected to be very weakly bound or metastable (bound only by the Coulomb barrier), consistent with the fact that it was not observed in the previous mass spectrometric study [16]. Only a very weak $^{-}O_2C(CH_2)_2CO_2^{-}$ mass signal was detectable under our experimental conditions and time scale (~0.1 s) [19].

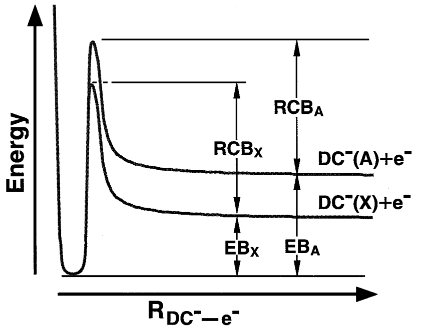

FIG. 2. Schematic potential energy curves explaining the observed photoelectron spectra of DC^{2-}. X and A represent the ground and excited states of the DC^- singly charged radical anion, accessed from the detachment of DC^{2-}. EB_X, EB_A, RCB_X, and RCB_A are the adiabatic binding energies and the repulsive Coulomb barriers for the X and A states, respectively. Note that RCB_X and RCB_A are assumed to have similar magnitudes for DC^{2-} (see text).

We next consider the nature of two photodetachment transitions leading to the X and A states in each dianion. One possibility is that the two bands are due to the presence of two inequivalent carboxylate groups. This possibility can be tested by comparing the dianion spectra to that of a singly charged monocarboxylate anion.

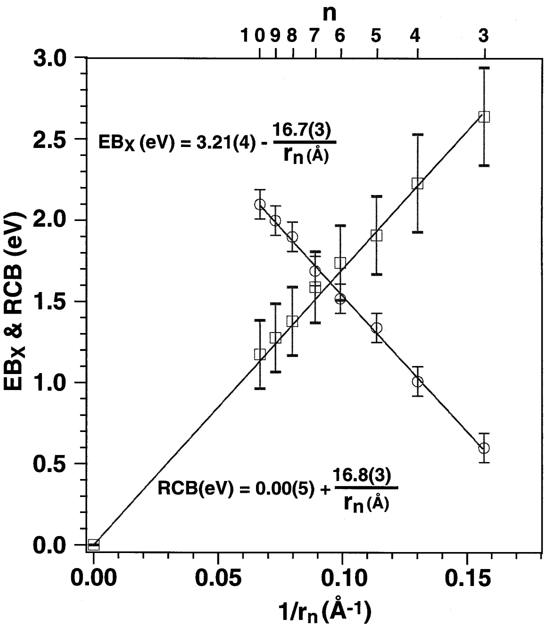

FIG. 3. The measured adiabatic electron binding energies (EB_X) and the estimated repulsive Coulomb barrier heights (RCB) for DC^{2-} as a function of $1/r_n$, where r_n is the average equilibrium distance (Å) between the two charge centers in DC^{2-}, assumed to be localized on the O atoms of the carboxylate groups [18]. Circles—EB_X; squares—RCB; lines—least squares fits.

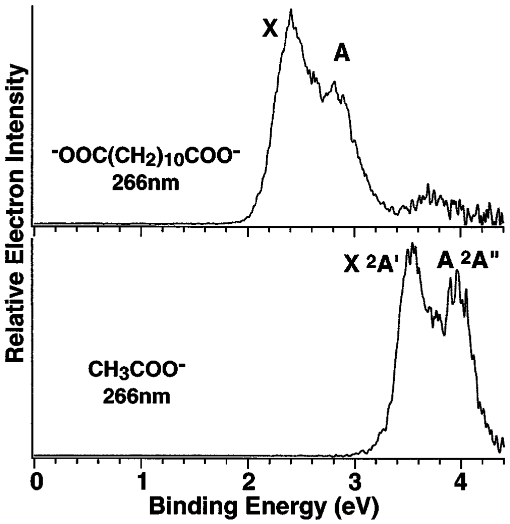

FIG. 4. Comparison of the photoelectron spectrum of $^-$OOC-(CH$_2$)$_{10}$-COO$^-$ to that of CH$_3$COO$^-$ at 266 nm (4.66 eV). Note the high binding energy of the acetate anion due to the absence of the Coulomb repulsion. The X ($^2A'$) state was due to the removal of a p_y lone pair electron and the A ($^2A''$) state was due to the removal of a p_z electron from the carboxylate group of acetate [20].

Figure 4 shows the spectrum of $CH_3CO_2{}^-$ compared to that of DC^{2-} at $n = 10$. The spectrum of acetate exhibits two spectral features very similar to those of the dianion, with an identical separation between the two peaks (~0.42 eV). As expected, acetate has a much higher electron binding energy due to the absence of the Coulomb repulsion present in the dianions. The *ab initio* molecular orbital calculations indicate that the X band is due to the removal of one of the O p_y electrons of acetate, giving a $^2A'$ state [20]. The A band results from the removal of one of the O p_z electrons of the anion, giving a $^2A''$ species in which the unpaired electron is shared between the two O atoms.

The similar spectral features in both the singly and doubly charged carboxylates suggests that they result from similar detachment transitions and are not due to the presence of inequivalent carboxylate groups in the dianions. However, the Coulomb repulsion present in the dianions should result in a perturbation of the electronic structure relative to that of the monoanion, and the perturbation should depend on the chain length. As noted earlier, both the bandwidth and the A-X separation decrease with the chain length and show no measurable changes for $n \geq 8$ (Fig. 1). We attribute these spectral variations to a decreased perturbation between the two carboxylate groups with increasing chain length.

The repulsive Coulomb barrier and the stability of a multiply charged anion are determined by the balance between the short-range attraction and long-range Coulomb repulsion of the excess charges. In the DC^{2-} dianions the short-range attraction can be characterized by the binding of an electron to a carboxyl group (approximately the EB of acetate), whereas the Coulomb repulsion depends on the equilibrium distance between the two charge centers (r_n). We assume that the RCB for both the X and A states are the same, because in both cases the electron is detached from the carboxylate group. We can therefore estimate the barrier heights, using the measured binding energies for the X and A states and the fact that at 355 nm (3.49 eV) only the X state was observed. For example, for the $n = 10$ case, we know the barrier has to be smaller than 1.39 eV ($3.49\text{ eV} - \text{EB}_X$) and larger than 0.97 eV ($3.49\text{ eV} - \text{EB}_A$). The estimated barrier heights, taken as the average of the upper and lower bounds, for $n = 3$–10 are plotted against $1/r_n$ in Fig. 3. Despite the approximations made in evaluating the RCB, a linear relationship is clear. The repulsive Coulomb barrier decreases as the distance between the two charge centers increases, consistent with the Coulombic nature of the potential barrier. As r_n approaches infinity, RCB approaches zero. Thus, the RCB curve should pass through the origin. A least squares fit including the origin yielded $\text{RCB} = 0.00(5) + 16.8(3)/r_n$, where the numbers in parentheses give the uncertainties in the last digits [21].

Combining the two fitted equations for RCB and EB_X, we obtain the following result: $\text{RCB} + \text{EB}_X \approx 3.21$ eV for all values of r_n. As seen from Fig. 2, $\text{RCB} + \text{EB}_X$ is equal to the potential well depth that binds the excess electron relative to the ground state (X) of DC^-. Therefore, the well depth for all DC^{2-} appears to be independent of the chain length and is close to the binding energy of the singly charged monocarboxylate (3.4 eV). This observation is reasonable because the excess charges are mainly localized on the two carboxyl groups in the dianions. The lower binding energy in the dianions relative to the monocarboxylate is due purely to the Coulomb repulsion between the excess charges, which in turn is the cause of the potential barrier. The coefficient of the Coulomb term is larger than predicted by Coulomb's law, 14.4 eV ($e^2/4\pi\varepsilon_0 r$), consistent with the fact that the charges are not strictly localized on the O atoms, but rather delocalized over the carboxylate groups in the DC^{2-} dianions [22].

For $n = 3$ and, to a lesser degree, for $n = 4$ and 5, a hint of the A band was also observed in the 355 nm spectra [Fig. 1(b)]. We estimate that the well depth for the A state is about 3.7 eV ($\text{RCB} + \text{EB}_A$), which is higher than the 3.49 eV energy of the 355 nm photons. Therefore, the weak intensity of the A state in the 355 nm spectra for $n = 3$–5 must be due to tunneling through the Coulomb barrier. The considerable decrease of the intensity of the A state with increasing chain length, and its eventual disappearance for large n in the 355 nm spectra, indicates that the tunneling probability decreases rapidly as the kinetic energies of the emitted electrons decrease (i.e., as the electron binding energy increases).

The dependence of the tunneling probability on kinetic energy is a well-known phenomena in the α decay of atomic nuclei [4]. The α particles are bound by an analogous Coulomb barrier, though with much different energy and length scales.

Multiply charged anions provide ideal systems to probe the Coulomb barriers. Using tunable lasers, one can obtain even more quantitative information about the barrier height, tunneling, and barrier reflection in multiply charged anions. The combination of the electrospray ionization technique and photodetachment spectroscopy will make it possible to investigate the chemistry and physics of a broad range of isolated multiply charged anions, including simple inorganic and organic species, as well as biomolecules. Using solvated clusters, one can study how solvation influences the stability and energetics of multiply charged anions. In addition, photodetachment is analogous to an oxidation reaction. By preparing and studying solvated and/or ligated clusters in different charge states, one should also be able to obtain microscopic information about redox processes and the factors influencing electron transfer.

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[19] We found that $^{-}OOC\text{-}(CH_2)_2\text{-}COO^{-}$ can be stabilized by one water. We measured a binding energy of $\sim$0.3 eV for $^{-}OOC\text{-}(CH_2)_2\text{-}COO^{-}(H_2O)$.

[20] Optimizations at the $MP2/6-311+G^*$ level of theory, followed by single point calculations at the $CCSD(T)/6-311+G^*$ level, predict vertical detachment energies (VDEs) of 3.36 eV to the $^2A'$ state of the neutral and 3.72 eV to the $^2A''$ states of CH_3COO. The theoretical VDEs are $\sim$0.1 eV less than the corresponding experimental values. The theoretical difference in energy between the two transitions (0.36 eV) is also very close to the experimentally observed separation (0.42 eV). We used GAUSSIAN 94 (Revision D.4, M. J. Frisch *et al.*, Gaussian, Inc., Pittsburgh, PA, 1995) for all of the calculations.

[21] The origin was taken as a data point in the fit because the RCB is zero at infinitive r_n, i.e., at $1/r_n = 0$. A fit excluding the origin crosses the RCB axis at 0.03 eV, which is negligible and within the $\pm$0.05 eV uncertainty.

[22] When the aliphatic chain was replaced by one and two phenyl groups, $^{-}OOC\text{-}(C_6H_4)_n\text{-}COO^{-}$ $(n = 1,2)$, an even larger coefficient ($\sim$19) was obtained in the Coulomb term, signifying more extended charge delocalization over the conjugated phenyl groups.