



Electron tunneling through the repulsive Coulomb barrier in photodetachment of multiply charged anions

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Abstract

There exists a repulsive Coulomb barrier for electrons in multiply charged anions. Tunneling through this barrier is expected to be important in photodetachment of MCAs. Photodetachment spectra were found to shift to lower binding energies in the tunneling regime. We present a systematic study of the tunneling effect in photodetachment experiments on a series of dianions, $^-\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^-$ ($n = 3-6$). The observed tunneling effect and spectral shift are explained using WKB approximation based on a model potential with a square well at short range and a repulsive Coulomb potential at long range. © 1999 Elsevier Science B.V. All rights reserved.

Ionization of a neutral atom or molecule results in an outgoing electron and a positive ion, whose long-range interaction is the Coulomb attraction. Photodetachment of a singly charged anion will produce an outgoing electron and a neutral particle, whose long-range interactions are also attractive in nature. However, photodetachment of a multiply charged anion (MCA) leads to two negatively charged particles (a free electron and a negative ion with one less charge than the parent MCA), whose long range interactions are mainly the Coulomb repulsion. The short range binding of the electron and the long range Coulomb repulsion result in a potential barrier

for the outgoing electron. This repulsive Coulomb barrier (RCB) was inferred by Compton et al. and others in studies of multiply charged fullerene anions [1–6]. As pointed out previously [1,2], the RCB in MCAs is analogous to the potential barrier binding the α particles in a radioactive atomic nucleus, see for example [7], even though the length and energy scales are quite different in the two cases. Therefore, analogous to the α -decay phenomenon, interesting quantum tunneling effects are expected to occur in the photodetachment of MCAs at appropriate detachment laser energies. Quantum mechanical tunneling is an important and interesting process in chemistry and physics. Important examples include chemical reactions involving the H atom [8,9], electron transfer reactions [10], scanning tunneling microscopy [11], molecular electronic devices [12], nuclear fusion [13], and nuclear decays [7]. Here we present

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another example of the tunneling phenomenon – tunneling through RCB in photodetachment of MCAs, in very close analogy to the α -decay [7].

MCAs are common in solution and act as building blocks for many inorganic solid materials [2,14]. To study the physics and chemistry of MCAs in the gas phase, we have recently developed a new experimental apparatus that combines a magnetic-bottle time-of-flight (TOF) photoelectron analyzer with an electro-spray ionization (ESI) source. We have performed the first photoelectron spectroscopy (PES) experiments on a variety of doubly charged anions, including organic [15,16], inorganic [17,18], and solvated species [19], and obtained quantitative information about the RCBs and the electrostatic interactions in the doubly charged anions. In the current Letter, we want to address the issue of electron tunneling through the RCB when detachment photon energy is below the top of the RCB. In particular, we observed that the PES spectra tend to shift to lower binding energies in the tunneling regime. In fact, the shift of the PES spectra is universal and has become a hallmark for photodetachment of MCAs [17,18]. We will understand quantitatively the tunneling phenomenon using a model potential and the WKB approximation [7] and explain the shift of the PES spectra in the tunneling regime.

We carried out a systematic study of the tunneling effect on a series of dicarboxylate (DC^{2-}) dianions, $-O_2C-(CH_2)_n-CO_2-$ ($n = 3-6$), photodetached at 266, 355 and 532 nm, as a prototype of this common phenomenon observed generally in PES studies of MCAs. The DC^{2-} anions were chosen here because we could systematically change the separation between the two charges in the dianions, thus allowing us to systematically study the tunneling probabilities through RCBs with different heights and widths. The experiments were performed with the newly developed magnetic-bottle TOF photoelectron facility. Details of the apparatus have been published elsewhere [20]. To produce the desired anions, we electro-sprayed a 10^{-4} molar solution of the corresponding linear dicarboxylic acids $HO_2C(CH_2)_nCO_2H$ at pH ~ 10 in a water/methanol mixed solvent (2/98 ratio). For the PES experiments, the dianions of interest were mass-selected and detached by a laser beam from a Q-switched Nd:YAG laser [266 (4.66 eV), 355 (3.496 eV), and 532 nm (2.331 eV)]. 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 I^- and O^- [21]. Binding energy spectra were obtained by subtracting the ki-

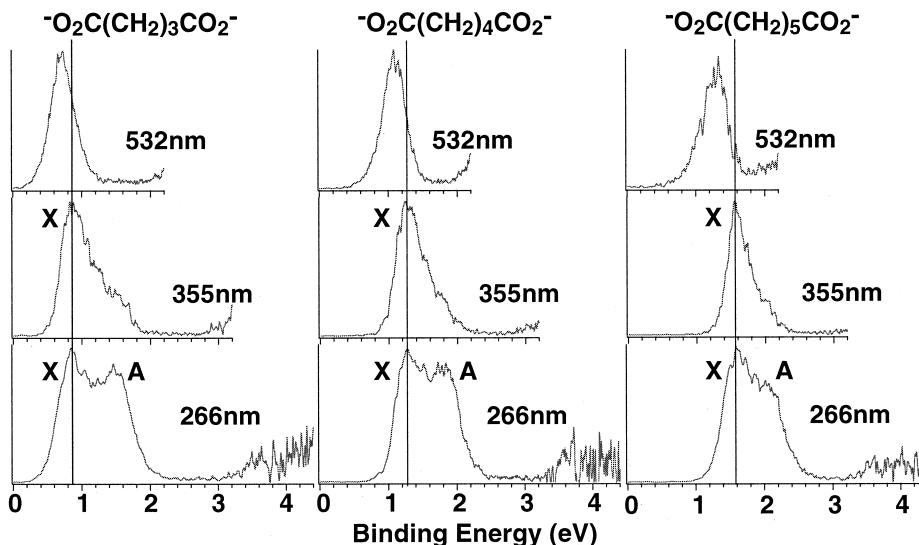


Fig. 1. Photoelectron spectra of DC^{2-} anions ($n = 3-5$) at 266, 355, and 532 nm. Note the shift to lower binding energies of the 532 nm spectra relative to that of the 266 and 355 nm spectra. The vertical lines are drawn to guide the eyes.

netic energy spectra from the photon energies. The energy resolution of the current spectrometer is about 11 meV for 0.4 eV electrons as calibrated from the 355 nm spectrum of I^- .

The PES spectra of DC^{2-} ($n = 3-5$) at 266, 355 and 532 nm are shown in Fig. 1. The PES features are quite broad, indicating that there are substantial vibrational excitations upon photodetachment from DC^{2-} to DC^- . We have previously reported the PES results at 266 and 355 nm for the DC^{2-} with $n = 3-10$ [16]. The spectral features were well understood. In particular, the disappearance of the A state in the 355 nm spectra were due to the RCBs, as shown schematically in Fig. 2a. The obtained binding energies and RCBs for the DC^{2-} ($n = 3-6$) are given in Table 1. We observed a surprising shift to lower binding energies for all the 532 nm spectra. The magnitude of the shift increases for the larger anions. We also found that the photoelectron signals were very weak at 532 nm relative to those at 355 and 266 nm and decreased for the larger DC^{2-} . Eventually, we could not observe PES spectra for DC^{2-} with $n \geq 6$ at 532 nm. The relative signals at 532 nm compared to those at 355 nm are also listed in Table 1, decreasing from 12% for the $n = 3$ case to a merely 3% for the $n = 5$ case, (total signals were normalized to the photon fluxes, ion intensities, and laser shots). The PES signals were negligible for the larger DC^{2-} species.

Even though the 532 nm photon energy (2.33 eV) is higher than the binding energies of the X state for all the DC^{2-} species (Fig. 1), the electron kinetic energies in all cases are lower than the corresponding RCB (Table 1). Therefore, the observed photoelectron signals at 532 nm were in fact entirely due to electron tunneling. The potential energy between the outgoing electron and the singly charged anion, DC^- , is determined by their Coulomb repulsion at long range and the electron binding energy to DC^- at short range. The exact shape of the short-range potential is not known and would require a rigorous quantum treatment. Since our purpose here is to understand the tunneling phenomenon well below the barrier top, we choose to use a very simple model potential:

$$\begin{aligned} V(r) &= -V_0, & r < R, \\ V(r) &= \alpha/r, & r > R, \end{aligned} \quad (1)$$

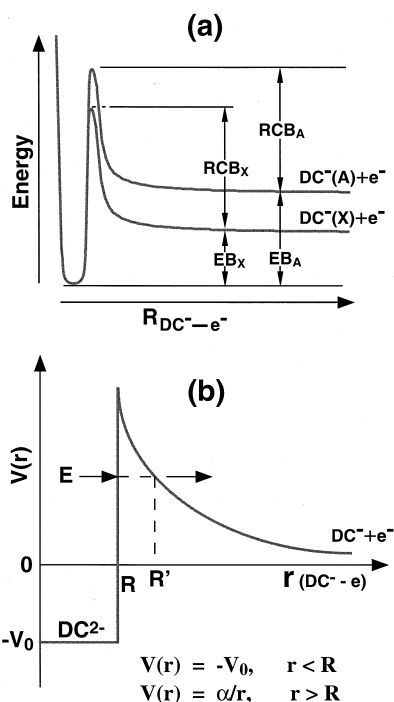


Fig. 2. (a) Schematic potential curves explaining the two transitions in the PES spectra of DC^{2-} and the repulsive Coulomb barriers [15]. (b) The potential used to model the interaction of an excess electron with the singly charged anion, DC^- . Here the short range potential is modeled as a square well. V_0 is the binding energy of the outgoing electron, as measured from the PES spectra. R is the equilibrium distance between the two charges in DC^{2-} . α is a constant taken as 16.8 eV-Å [15]. E is the kinetic energy of the outgoing photoelectron.

as shown in Fig. 2b. This potential is entirely analogous to the nuclear potential used in the α -decay theory [7]. Here the short range potential is modeled as a square well; V_0 is the binding energy of the outgoing electron, which is measured experimentally; R is the equilibrium distance between the two charges in DC^{2-} , as given in Table 1. The value of α should be $14.4 (e^2/4\pi\epsilon_0 R)$, if we use the unit of eV for energy and Å for distance. However, we take the α value as 16.8, as derived previously [16]. The larger α value is due to the fact that the two charges are not point charges, but rather slightly delocalized. According to WKB theory [7], the tunneling probability can be calculated as:

$$T = \exp \left[-\frac{2}{\hbar} \left| \int_R^{R'} \sqrt{2m(E - V(r))} dr \right| \right], \quad (2)$$

Table 1

The equilibrium charge separation (R), adiabatic binding energies (EB_X), electron kinetic energies at 532 nm (E), repulsive Coulomb barrier heights (RCB), calculated and experimental tunneling probabilities for DC^{2-} ($n = 3-6$)

n	$R(\text{\AA})^a$	EB_X (eV) ^b	E (eV)	RCB (eV) ^c	T (cal.)	T (exp.) ^d
3	6.37	0.60	1.73	2.60(0.3)	0.144	0.12
4	7.66	1.01	1.32	2.23(0.3)	0.059	0.08
5	8.85	1.34	0.99	1.91(0.24)	0.011	0.04
6	10.0	1.52	0.81	1.74(0.23)	0.003	0.00

^a R is estimated using standard bond angles and bond lengths. We also performed ab initio calculations on the DC^{2-} systems and obtained R values very close to the value used here [15].

^bThe EB_X , measured from the threshold of the 355 nm spectra [16], is equal in magnitude to V_0 in Eq. (1).

^cThe RCBs were estimated by assuming that they have the same magnitude for the X and A states [16] and are equal in magnitude to the Coulomb repulsion energy of the two charges in each DC^{2-} dianion.

^dThe T (exp.) was derived by normalizing the intensity of the 532 nm spectra relative to that of the corresponding 355 nm spectra, (total signals were normalized to the photon fluxes, ion intensities, and laser shots).

where R and R' define the width of the RCB at energy E , as shown in Fig. 2b, m is the mass of the electron and \hbar is the Planck constant. Using our model potential (1), Eq. (2) is reduced to [7]:

$$T = \exp \left[-\frac{2}{\hbar} \alpha \sqrt{\frac{2m}{E}} \left(a \cos \sqrt{\frac{E \cdot R}{\alpha}} - \sqrt{\frac{E \cdot R}{\alpha}} \left(1 - \frac{E \cdot R}{\alpha} \right) \right) \right]. \quad (3)$$

The kinetic energy of the outgoing electron, E , is the difference between the detaching photon energy (532 nm, 2.331 eV) and the electron binding energy.

Clearly the tunneling probability decreases exponentially as the outgoing electron kinetic energy (E) decreases. Using the values of EB_X and E given in Table 1, we calculated the tunneling probabilities for DC^{2-} ($n = 3-6$), as listed in Table 1 (note that EB_X is equal in magnitude to V_0 , which is different for n). The tunneling probabilities decrease rapidly for the larger DC^{2-} dianions, in excellent agreement with the experimental observation.

The calculated tunneling probabilities given in Table 1 are essentially for a single quantum state of DC^- , i.e. for the detachment transition to the vibrational ground state of DC^- . In reality, the PES spectra represent a distribution of vibrational levels, due to the Franck–Condon factors pertaining to a given photodetachment transition and sequence bands (hot bands) as a result of vibrationally excited states of the parent dianions. Transitions to the higher

vibrational levels of DC^- result in photoelectrons with lower kinetic energies (higher binding energies) and thus will have much lower tunneling probabilities. Therefore, the PES spectra at 532 nm do not reflect the true Franck–Condon envelopes of the DC^- vibrational states. They are biased by the tunneling probabilities, which diminish rapidly for the higher vibrational levels. This can be seen more clearly in Fig. 3, where the 532 nm spectra are normalized and compared to the 355 nm spectra. Thus the shift of PES spectra at 532 nm in Fig. 1 is explained based on this tunneling mechanism.

Furthermore, substantial hot band transitions existed in the PES spectra because the temperatures of the dianions were at or above room temperature. The hot band transitions have lower binding energies, corresponding to photoelectrons with higher kinetic energies. Therefore, they tend to have higher tunneling probabilities, further contributing to the shift of the 532 nm spectra to lower binding energies. Since the tunneling probabilities for the dianions with $n = 4$ and 5 are very small, only transitions with very low binding energies have observable tunneling probabilities. Therefore, the 532 nm spectra appeared to shift even more toward the low binding energy side for the larger dianions. The majority of the 532 nm spectrum of the $n = 5$ DC^{2-} dianion was actually due to the hot bands, i.e. transitions from the highly vibrationally excited dianions or the Boltzman tail of the parent dianions.

Therefore, the adiabatic detachment energies for MCAs cannot be accurately determined from PES

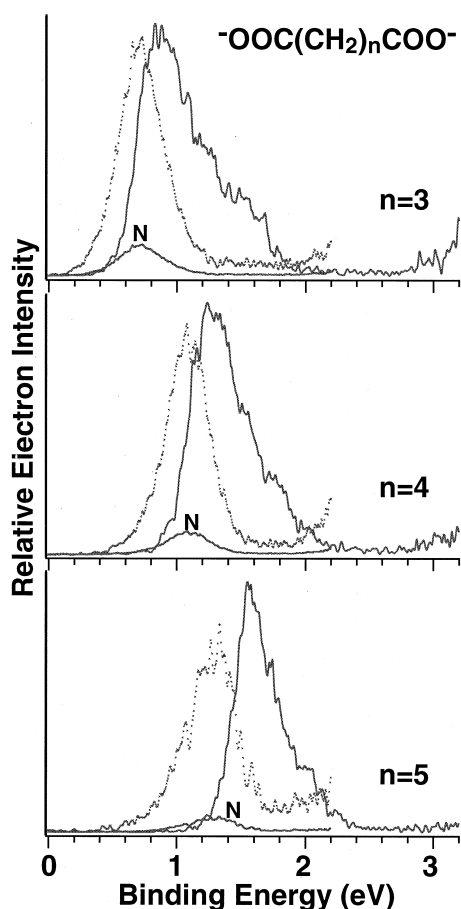


Fig. 3. Comparison of the unnormalized (dotted) and normalized (N) 532 nm spectra to the 355 nm spectra, showing that the spectral shift at 532 nm was really due to the dependence of the tunneling probabilities on the kinetic energies.

spectra taken in the tunneling regime due to the bias in tunneling probabilities that appear to shift the spectra toward lower binding energies. In the present experiments, the 355 nm spectra yielded unbiased adiabatic binding energies for all the DC^{2-} dianions because the photon energy is above the RCB for transitions to the ground state (X) of DC^- . However, the 355 nm photon is below the barrier to the A state of DC^- and only weak intensities due to tunneling were observed for the A state in the 355 nm spectra for $n = 3-5$ (Fig. 1). The intensity of the A state decreased rapidly and completely disappeared in the 355 nm spectra for the larger DC^{2-} dianions [16].

In conclusion, we examined systematically the tunneling effect in photodetachment of MCAs using

a series of dicarboxylate dianions as prototypes. Using a simple Coulomb potential and WKB approximation, we successfully explained the PES spectral shift in the tunneling regime as a result of the strong dependence of tunneling probabilities on electron kinetic energies. The RCB is an important feature of MCAs and the spectral shift is a unique characteristic in photodetachment spectra of MCAs in the tunneling regime. It is also interesting to emphasize that the tunneling phenomenon in MCAs is quite analogous to the α -decay. In fact, the simple Coulomb potential and the WKB formulation are directly borrowed from the α -decay theory [7]. Our experimental time scale limits us to observe only fast tunneling effect, i.e. high tunneling probabilities whereas many α -decays are rather slow because the kinetic energies of the α particles are very low relative to the RCB in those cases. A distinct advantage in studying tunneling in MCAs is that we can continuously tune the detachment photon energies across the RCB top and study the quantum tunneling and reflection near the barrier top. Finally, we emphasize the generality of the PES spectral shift in MCAs due to the electron tunneling effect: we have observed such spectral shift in every MCA that we have investigated, including both simple and large complicated species.

Acknowledgements

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