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Probing the Low-Lying Electronic States of Cyclobutanetetraone (C_4O_4) and Its Radical Anion: A Low-Temperature Anion Photoelectron Spectroscopic Approach

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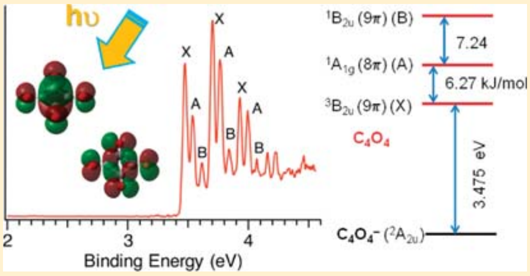
ABSTRACT: Despite a seemingly simple appearance, cyclobutanetetraone (C_4O_4) has four low-lying electronic states. Determining the energetic ordering of these states and the ground state of $C_4O_4^-$ theoretically has been proven to be considerably challenging and remains largely unresolved to date. Here, we report a low-temperature negative ion photoelectron spectroscopic approach. Well-resolved spectra were obtained at both 193 and 266 nm. Combined with recent theoretical studies and our own Franck–Condon factors simulations, the ground state of $C_4O_4^-$ and the ground and two low-lying excited states of C_4O_4 are determined to be $^2A_{2u}$, $^3B_{2u}$, $^1A_{1g}$ (8π), and $^1B_{2u}$, respectively. The frequency of the ring breathing mode (1810 ± 20 cm^{-1}), the electron affinity (3.475 ± 0.005 eV), and the term values of $^1A_{1g}$ (8π) (6.27 ± 0.5 kJ/mol) and $^1B_{2u}$ (13.50 ± 0.5 kJ/mol) are also directly obtained from the experiments.



SECTION: Dynamics, Clusters, Excited States

Recently, there has been intense theoretical interest in obtaining electronic structure information of the cyclobutanetetraone (C_4O_4) neutral and anion.[1−4] Although squarate dianion ($C_4O_4^{2-}$) was synthesized many decades ago[5] and regarded as an important extension to a new class of aromatic molecules (known as oxocarbon dianions),[6−10] the C_4O_4 neutral has not been known experimentally presumably because it is thermodynamically unstable against decomposition into four CO molecules.[4] The $C_4O_4^{2-}$ dianion is a moderately aromatic species[10] with D_{4h} symmetry and an electronic configuration of ...$(b_{1g})^2(a_{2u})^2$, where the σ b_{1g} molecular orbital (MO) (consisting of the lone-pair orbitals on the oxygen atoms of four carbonyl groups with the C−C σ bonds of the four-membered ring) and the π^* a_{2u} MO (combined from four in-phase C=O π^* orbitals) (Figure 1) are nearly degenerate.[1,2] An interesting issue arises regarding to the ground state of the singly charged radical anion ($C_4O_4^-$). Is it $^2B_{1g}$ or $^2A_{2u}$ formed by removing one electron from the doubly occupied b_{1g} or a_{2u} MOs, respectively? Further, there are four close-lying electronic states for the neutral by distributing two electrons between these two MOs, that is, the $^3B_{2u}$ and $^1B_{2u}$ states derived from the $(b_{1g})^1(a_{2u})^1$ configuration with two electron spins parallel and antiparallel, respectively, the 10π $^1A_{1g}$ state of $(b_{1g})^0(a_{2u})^2$, and the 8π $^1A_{1g}$ state of $(b_{1g})^2(a_{2u})^0$ (Figure 1). The energetic ordering of these states has proven to be a formidable challenge to date that even the most advanced theoretical methods have not provided an unambiguous answer.[1,2] In a recent theoretical paper,[1] Borden and coworkers appealed to experimentalists to join in and proposed using negative ion photoelectron spectroscopy (PES) to probe the electronic structures of C_4O_4 and its anion.

Pioneered by Lineberger and co-workers, negative ion PES has been demonstrated to be a powerful experimental technique that can be used to directly probe both ground and excited states of neutral species, in particular, for diradicals, where valuable energetic information has been obtained for a variety of interesting molecules.[11−16] We recently investigated the electronic structures of a series of benzoquinone (BQ) and related molecules using PES and experimentally confirmed that meta-BQ is a diradical with a triplet ground state.[17,18] In this Letter, we report a low-temperature PES study of $C_4O_4^-$ accompanied by ground-state theoretical calculations to probe the electronic structures of $C_4O_4^-$ and C_4O_4 and to experimentally determine the relative energies among the aforementioned low-lying states.

The experiments were conducted using a low-temperature PES instrument coupled with an electrospray ionization (ESI) source. The details of this setup were published recently.[19] The $C_4O_4^-$ anions were generated in the gas phase via ESI of a ~0.1 mM acetonitrilic aqueous solution of squaric acid ($C_4O_4H_2$) under slightly basic conditions, although the most intense ion signal generated was still $C_4O_4H^-$. The anions were

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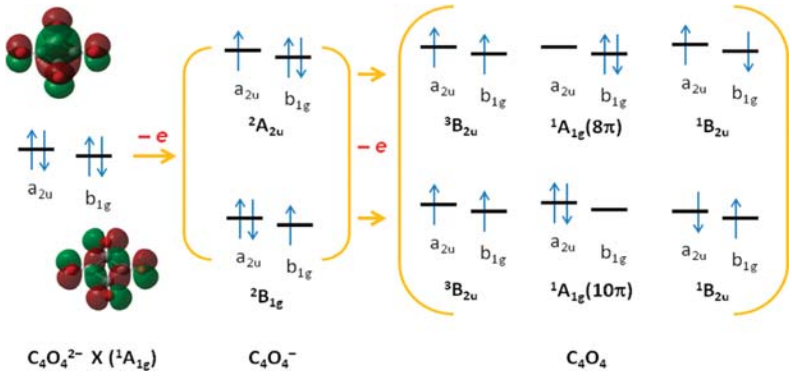

Figure 1. Two or four electronic configurations can be formed by detaching one or two electrons from the doubly occupied σ b_{1g} and π* a_{2u} MOs in $C_4O_4^{2-}$ for the singly charged anion and the neutral, respectively.

accumulated and collisionally cooled at 20 K within a cryogenically controlled ion trap to afford elimination of vibrational hot bands of the anions and to populate only the global minimum (electronically and geometrically). For each PES experiment, the desired anions of $C_4O_4^-$ were carefully mass-selected to make sure that no $C_4O_4H^-$ contamination existed in the selected ion cloud. The $C_4O_4^-$ ions were decelerated before being intercepted by a probe laser beam in the photodetachment zone of a magnetic bottle photoelectron analyzer. The laser was operated at a 20 Hz repetition rate with the ion beam off at alternating laser shots for shot-by-shot background subtraction. Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 5.2 m long electron flight tube, calibrated by the known spectra of I^- and ClO_2^-.

Figure 2 shows the 20 K spectra of $C_4O_4^-$ at 266 (4.661 eV) and 193 nm (6.424 eV). Five well-resolved spectral features with an even spacing of 1810 ± 20 cm^{-1} were observed at 193 nm in the binding energy range from 3.4 to 4.5 eV, followed by a structureless continuous slope up to the photon energy limit. Surprisingly, at 266 nm, where the intrinsic instrumental resolution was significantly improved relative to that at 193 nm, each feature observed at 193 nm further split into a three-peak (X, A, B) set. The A−X and B−A separations, measured to be 65 and 75 meV, respectively, remained the same for all observed 193 nm features. Because the experiments were conducted at 20 K, no hot bands were expected to exist. Therefore, the adiabatic detachment energy (ADE) of $C_4O_4^-$ or the electron affinity (EA) of the C_4O_4 neutral was determined from the first well-resolved peak in the 266 nm spectrum to be 3.475 ± 0.005 eV. The tight accuracy (5 meV) is warranted here because the measured EA is right between the two I^- peaks (3.059, and 4.002 eV), of which the spectrum was calibrated.

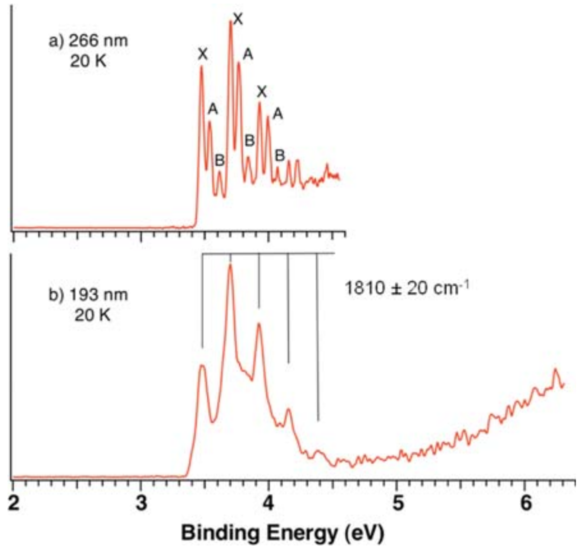

Figure 2. The 20 K photoelectron spectra of $C_4O_4^-$ at (a) 266 (4.661 eV) and (b) 193 nm (6.424 eV), showing an evenly spaced vibrational progression at 193 nm, and fine spectral manifolds rising from splitting each 193 nm feature at 266 nm.

Recently, Borden and co-workers performed theoretical studies on the electronic structures of $C_4O_4^-$ and C_4O_4 using a variety of methods, including B3LYP, CCSD(T) along with several composite methods based on CCSD(T), and CASPT2.[1,2] For the $C_4O_4^-$ anion, both DFT and CASPT2 predicted $^2B_{1g}$ as the ground state (being more stable than the $^2A_{2u}$ state by 2.7 and 4.3 kcal/mol) and the EA of C_4O_4 to be 3.525 and 3.304 eV, respectively.[1] As pointed out by the authors, the CASPT2 result was not reliable due to uneven weights of the CASSCF reference wave functions for the two electronic states.[1] However, at the CCSD(T) level of theory, the ground state switched to $^2A_{2u}$, lying 1.0 kcal/mol below the $^2B_{1g}$ state, and the predicted EA was 3.426 eV. Inconsistent results existed for the C_4O_4 neutral as well. The CCSD(T) calculation predicted that the ground state was $^3B_{2u}$, with the other three electronic states of $^1A_{1g}$ (8π) < $^1B_{2u}$ (9π) < $^1A_{1g}$ (10π) being 9.9, 22, and 24.5 kJ/mol higher in energy than the ground state, respectively; although the DFT calculations gave the same ground state of $^3B_{2u}$, the relative energies and the ordering among the other three states were quite different from that at CCSD(T), that is, $^1B_{2u}$ (9π) < $^1A_{1g}$ (10π) < $^1A_{1g}$ (8π) lying 13.0, 46.8, and 55.3 kJ/mol above the ground state[2] (a summary of the calculated results by Borden and co-workers is illustrated in Figure 3). An interesting question arises concerning which energetic scenario is closer to the truth. Is it the one predicted by DFT or that predicted by CCSD(T)?

We also conducted our own calculations focused on the ground states of $C_4O_4^-$ and C_4O_4 using the Gaussian 03 package.[20] Geometrical optimizations were performed with DFT calculations using the hybrid B3LYP exchange−correlation functional[21] and the aug-cc-pVTZ basis set.[22] The accurate energy values were obtained through single-point energy calculations at both B3LYP and CCSD(T)[23] levels of

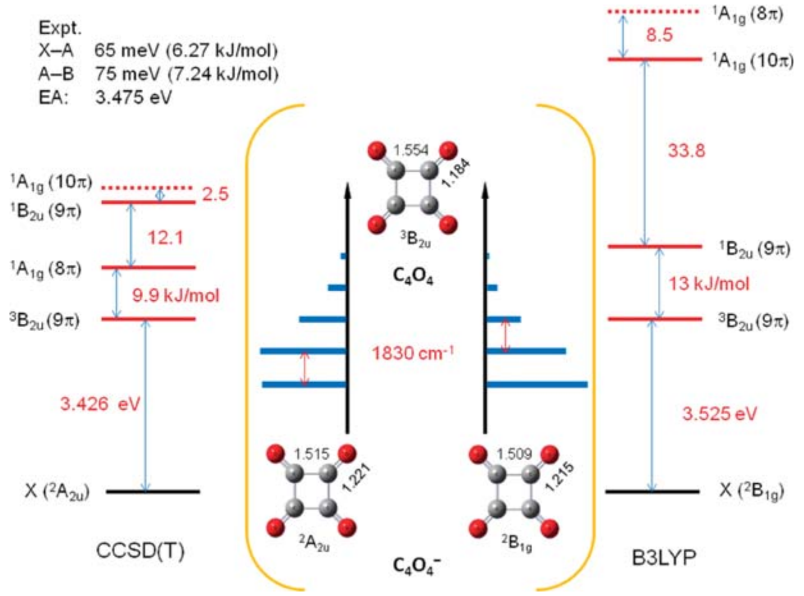

Figure 3. A summary of the ground state of $C_4O_4^-$ (solid black line) and four low-lying electronic states of C_4O_4 (red lines) calculated by Borden and co-workers (refs 1 and 2) at CCSD(T) (left) and B3LYP (right). The dashed red lines represent the electronic states of the neutral not accessible from the respective anion's electronic configuration under the single-particle approximation (Figure 1). The corresponding anion and neutral ground-state geometries from ref 1 are shown in the central column along with two simulated Franck−Condon factor stick spectra based on the respective anion−neutral structural changes.

theory including zero-point energy corrections estimated in the harmonic approximation from the B3LPY frequencies. Our calculations confirmed a triplet ground state ($^3B_{2u}$) for C_4O_4 using both theoretical methods. For two close-lying anionic states of $C_4O_4^-$, the B3LYP calculation preferred $^2B_{1g}$ as the ground state (being more stable than the $^2A_{2u}$ state by 2.7 kcal/mol), whereas the CCSD(T) calculation predicted the ground state of $^2A_{2u}$ (favored by 1.1 kcal/mol), consistent with Borden's results noted above.[1,2] Our calculated ADEs, that is, 3.485 (B3LPY) and 3.490 eV (CCSD(T)), agree excellently with the experimental value as well as those obtained by Borden and co-workers.

Both $C_4O_4^-$ and C_4O_4 were calculated and were able to maintain D_{4h} structures.[1−4] There are sizable C−C and C═O bond length changes from the anion to the neutral; the C−C bond length elongates from 1.515 ($^2A_{2u}$) and 1.509 Å ($^2B_{1g}$) to 1.554 Å ($^3B_{2u}$), and at the same time, the C═O bond length shortens from 1.221 ($^2A_{2u}$) and 1.215 ($^2B_{1g}$) to 1.184 Å (from ref 1 as well as our calculations, Figure 3). Therefore, it is expected that the symmetric ring breathing mode of the neutral with the changes of C−C and C═O bond lengths out of phase (i.e., one is increasing while the other is simultaneously decreasing) will be excited upon detaching one electron from the anion. We calculated this vibrational mode to have a frequency of 1824 cm^{-1} (after the 0.97 scaling, compared well to 1830 cm^{-1} given in the ref 8 of ref 3). Thus, it is straightforward to assign the resolved features with the even spacing of 1810 ± 20 cm^{-1} at 193 nm due to excitations of this vibrational mode. Furthermore, the observed associated vibrational progression, which shows a maximum intensity at the ($\nu'' = 0 \rightarrow \nu' = 1$) transition (Figure 2), should reflect and be sensitive to the anion−neutral geometric changes (Franck−Condon factors, FCFs). The slight intensity (I) variation observed from 193 nm, that is, $I(0\rightarrow1) > I(0\rightarrow2) > I(0\rightarrow0) > I(0\rightarrow3)$, to 266 nm, that is, $I(0\rightarrow1) > I(0\rightarrow0) > I(0\rightarrow2) > I(0\rightarrow3)$, is largely caused by the fact that the 193 nm spectral features are only partially resolved.

Under the single-particle approximation (Koopmans's theorem), PES electronic transitions can be viewed as removing electrons from each respective occupied MO of the anion. Only three neutral states are expected to be accessed by PES from either the $^2A_{2u}$ [...$(b_{1g})^2(a_{2u})^1$] or $^2B_{1g}$ [...$(b_{1g})^1(a_{2u})^2$] state of the anion, leading to $^3B_{2u}$, $^1A_{1g}$ (8π), $^1B_{2u}$; and $^3B_{2u}$, $^1B_{2u}$, $^1A_{1g}$ (10π), respectively (Figures 1 and 3). Therefore, it is evident that the three fine spectral peaks X, A, and B observed at 266 nm are due to electronic transitions from the ground state of the anion to the ground and two low-lying excited states of the neutral. As demonstrated in Figure 3, the CCSD(T) calculations preferred the $^2A_{2u}$ anionic state[1] and predicted a triplet ground state ($^3B_{2u}$) for the neutral along with the first excited state of $^1A_{1g}$ (8π) lying 9.9 kJ/mol above the ground state and the second excited state of $^1B_{2u}$ being 12.1 kJ/mol higher in energy than the first excited state.[2] On the other hand, the B3LYP calculations predicted[1] $^2B_{1g}$ as the ground state of $C_4O_4^-$ and $^3B_{2u}$ as the ground state of C_4O_4, with the first excited state of $^1B_{2u}$ lying 13.0 kJ/mol above the ground state and the second excited state of $^1A_{1g}$ (10π) being 33.8 kJ/mol higher relative to the $^1B_{2u}$ state.[2] Our measured X−A and A−B energy differences are 6.27 (65 meV) and 7.24 kJ/mol (75 meV), respectively, in much better agreement compared to the CCSD(T) calculations than to the B3LYP results, which suggests that the ground state of $C_4O_4^-$ most likely is the $^2A_{2u}$ state preferred at CCSD(T). In addition, we conducted one-dimensional FCFs simulations of the ring breathing mode for both $^2A_{2u} \rightarrow {}^3B_{2u}$ and $^2B_{1g} \rightarrow {}^3B_{2u}$ transitions (predicted by the CCSD(T) and DFT calculations, respectively) using the ezSpectrum code,[24] which are shown in the central column of Figure 3. Our simulated FCF stick spectrum based on the transition of $^2A_{2u} \rightarrow {}^3B_{2u}$ indicates that the most intense peak is the 0 → 1 vibrational excitation followed by the 0 → 0 transition, consistent with the observed 266 nm spectrum, whereas the FCFs simulation for $^2B_{1g} \rightarrow {}^3B_{2u}$ results in the 0 → 0 vibrational transition as the corresponding maximum in the whole vibrational progression, in contrast to the experimental observation. Therefore, we can assign the ground state of $C_4O_4^-$ to be $^2A_{2u}$ and the ground and two excited states of C_4O_4 to be $^3B_{2u}$, $^1A_{1g}$ (8π), and $^1B_{2u}$, respectively (see the Abstract graphic).

In summary, we report an experimental investigation on the electronic structures of C_4O_4 and its anion using the low-temperature negative ion PES technique. The ground state of $C_4O_4^-$ is determined to be $^2A_{2u}$, and the ground and excited states of the C_4O_4 neutral are $^3B_{2u}$, $^1A_{1g}(8\pi)$, and $^1B_{2u}$, with the experimentally measured term values of 6.27 ± 0.5 ($^1A_{1g}(8\pi)$) and 13.5 ± 0.5 kJ/mol ($^1B_{2u}$), respectively. Both CCSD(T) and B3LYP calculations reported by Borden et al. predicted low-lying electronic states for the C_4O_4 neutral, in good agreement with the experimental observation, in particular, for the lowest excited states. Our low-temperature PES study suggests that the CCSD(T) energetic scheme calculated by Borden and co-workers is qualitatively correct, albeit with the overestimated term values of 9.9 and 22.0 kJ/mol, whereas the B3LYP calculations predicted the energetic ordering incorrectly. The EA and the frequency of the ring breathing mode are experimentally determined to be 3.475 ± 0.005 eV and 1810 ± 20 cm^{-1}, respectively. This work demonstrates again that low-temperature PES combined with theoretical calculations is a powerful approach that is capable of unraveling detailed electronic structure information of diradical species, which often possess many extremely close-lying electronic states.

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