Photoelectron Spectroscopy and Electronic Structures of Fullerene Oxides: C\textsubscript{60}O\textsubscript{x}\textsuperscript{−} (x = 1–3)

Xue-Bin Wang, Hin-Koon Woo, Boggavarapu Kiran, and Lai-Sheng Wang*

Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99354, and W. R. Wiley Environmental Molecular Sciences Laboratory and Chemical Sciences Division, Pacific Northwest National Laboratory, MS 8-88, P.O. Box 999, Richland, Washington 99352

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We report a photoelectron spectroscopy (PES) study on a series of fullerene oxides, C\textsubscript{60}O\textsubscript{x}\textsuperscript{−} (x = 1–3). The PES spectra reveal one isomer for C\textsubscript{60}O\textsuperscript{−}, two isomers for C\textsubscript{60}O\textsubscript{2}−, and multiple isomers for C\textsubscript{60}O\textsubscript{3}−. Compared to C\textsubscript{60}, the electronic structures of C\textsubscript{60}O\textsubscript{x} are only slightly perturbed, resulting in similar anion photoelectron spectra. The electron affinity of C\textsubscript{60}O\textsubscript{x} was observed to increase only marginally with the number of oxygen atoms, x, from 2.683 eV for C\textsubscript{60}, to 2.745 eV for C\textsubscript{60}O, and 2.785 eV/2.820 eV for C\textsubscript{60}O\textsubscript{2} (two isomers). We also carried out theoretical calculations, which confirmed the observed isomers and showed that all the fullerene oxides are in the form of epoxide. The PES and theoretical calculations, as well as molecular orbital analysis, indicate that addition of oxygen atoms to the C\textsubscript{60} cage only modifies the local carbon network and leave the rest of the fullerene cage largely intact geometrically and electronically.

Introduction

Fullerene oxides (C\textsubscript{60}O\textsubscript{x}), common residues in fullerene bulk synthesis as a result of oxidation, are a class of important functionalized fullerene derivatives. First detected in mass spectrometry and electrochemical oxidation of C\textsubscript{60},\textsuperscript{1,2} the oxides were reported to be the starting materials to form large odd-numbered carbon clusters, such as C\textsubscript{119}\textsuperscript{3–5} Theoretical calculations suggested that for the fullerene monoxide (C\textsubscript{60}O) there were two isomers, i.e., [6,6]-closed epoxide (1) and [5,6]-open oxidoannulene (an ether structure) with comparable stabilities,\textsuperscript{6–11} but only the epoxide was initially synthesized\textsuperscript{12–14} with the latter missing until more recently.\textsuperscript{15} Oxidation of C\textsubscript{60} with m-chloroperbenzoic acid produced bulk quantities of C\textsubscript{60}O\textsubscript{2} and X-ray diffraction showed it was a fullerene diepoxide with both oxygen atoms positioned over [6,6] ring junctions on a common six-member face of the carbon cage (2).\textsuperscript{16} HPLC chromatogram analyses of the reaction products of C\textsubscript{60} with O\textsubscript{3} indicated two isomers for C\textsubscript{60}O\textsubscript{2} one with the proposed structure of 2 and the other one similar to that for 2, but with the two oxygen atoms bridging the neighboring six-member ring (3).\textsuperscript{17} The electronic structures and electron affinities (EAs) of C\textsubscript{60}O\textsubscript{x} are expected to play an important role in any of its applications, and extensive electrochemical studies have been pursued as such.\textsuperscript{1,18–20} Unlike C\textsubscript{60} and C\textsubscript{60}O\textsuperscript{−}, which have been intensively investigated using gas phase photoelectron spectroscopy (PES) since the early stage of its discovery\textsuperscript{21–24} and recently revisited with vibrational resolution,\textsuperscript{25–27} no gas-phase PES study is available for C\textsubscript{60}O\textsubscript{x} and their anions.

In this Letter, we report the first PES study of C\textsubscript{60}O\textsubscript{x}− in the gas phase. The PES spectra were taken at 70 K with three different photon energies using a recently constructed low-temperature electrospray PES apparatus. Our PES spectra show that all oxides have electronic structures similar to that for C\textsubscript{60}, with only a slight increase of EA as the number of oxygen atoms increases. We observe one isomer for C\textsubscript{60}O, two isomers for C\textsubscript{60}O\textsubscript{2}, and multiple isomers for C\textsubscript{60}O\textsubscript{3}. Theoretical calculations were carried out to provide further insight into the electronic and structural properties of the fullerene oxides.

Experimental Details

The experiments were carried out using a newly developed low-temperature PES apparatus, which consists of an electrospray ionization source (ESI), a cryogenically cooled ion trap time-of-flight mass spectrometry, and a magnetic bottle time-of-flight photoelectron analyzer.\textsuperscript{27} The ESI source and the magnetic-bottle photoelectron spectrometer are similar to that described previously.\textsuperscript{20} C\textsubscript{60}O\textsuperscript{−} anions were produced as byproducts from a solution intended to generate C\textsubscript{60}− anions in an acetonitrile solution.\textsuperscript{29} After guided by a RF-only octopole and a quadrupole mass filter (operated in the RF-only mode), all anions were turned 90° via a quadrupole ion bender and entered into a three-dimensional Paul trap for ion accumulation and collision cooling. The ion trap was attached to a cold head of a cryostat and its temperature can be controlled from 10 to 400 K. For the current experiment, the trap was kept at 70 K and the collision background gas used was 10\textsuperscript{−4} Torr N\textsubscript{2}. The cooled ions were pulsed out of the trap at a 10 Hz repetition rate and separated in a linear TOF mass spectrometer according to their respective mass-to-charge ratios. The C\textsubscript{60}O\textsubscript{x}− (x = 0–3) anions of interest were selected by a pulsed mass-gate, and decelerated before being intercepted by a detachment laser beam in the interaction zone of the magnetic-bottle electron analyzer. In the current experiment, three detachment photon energies were used: 355 nm (3.496 eV) and 266 nm (4.661 eV) from a Nd: YAG laser, and 193 nm (6.424 eV) from an excimer laser. The detachment laser was operated at 20 Hz with the ion beam off...
on alternate shots for background subtraction. The photodetached electrons were collected with nearly 100% efficiency by the magnetic-bottle and analyzed in a 5.2 m long electron flight tube. The electron energy resolution of the apparatus is $\Delta E/E \sim 2\%$, i.e., 20 meV for 1 eV electrons. Photoelectron time-of-flight spectra were collected and then converted to kinetic energy spectra, calibrated by the known spectra of $\text{I}^-$ and $\text{ClO}_2^-$. The electron binding energy spectra presented here were obtained by subtracting the kinetic energy spectra from the detachment photon energies.

Theoretical Methods

All calculations were done at the level of generalized gradient approximation using the Perdew–Wang exchange-correlation functional. The standard Slater-type-orbital (STO) basis set with quality of triple-$\zeta$ plus with two sets of polarization functions (TZ2P) were used for the valence orbitals of all the atoms, with frozen core approximation. The geometries of all molecules (both anions and neutrals) were fully optimized with default convergence criteria. The adiabatic detachment energies (ADEs) were obtained by taking the energy difference between the anions and the neutrals in their optimized geometries. All the calculations were accomplished using the Amsterdam density functional (ADF 2004.01) program.

Experimental Results

Figure 1 shows the PES spectra of $\text{C}_6\text{O}_x^- (x = 1–3)$ at 266 nm (left) and 193 nm (right). The low-temperature spectra of $\text{C}_6\text{O}_x^-$, which have been recently reported, are shown for comparison. Major spectral features are labeled A, B, and C in the order of increasing electron binding energies. Surprisingly, the spectra of the $\text{C}_6\text{O}_x^-$ anions are very similar to that of $\text{C}_{60}^-$. In particular, the spectra of $\text{C}_6\text{O}^-$ are almost identical to those of $\text{C}_{60}^-$ with only a slight increase of electron binding energies. The HOMO–LUMO gap of $\text{C}_6\text{O}^-$, defined by the X–A separation, is 1.52 eV, which is only slightly lower than that of $\text{C}_{60}^-$ (1.62 eV). The quality of the spectra for $\text{C}_6\text{O}_2^-$ and $\text{C}_6\text{O}_3^-$ was poorer due to their weak mass intensities, but their similarity to the $\text{C}_{60}^-$ spectra is obvious. Even the autodetachment features, labeled “AD” in the 266 nm spectrum of $\text{C}_{60}^-$, are also present in the oxide spectra as weak signals in the HOMO–LUMO band gap region. Vibrational structures were also discernible in the X band of the oxide spectra at both 193 and 266 nm, and they also appeared to be similar to that of the $\text{C}_{60}^-$ spectra. The HOMO–LUMO gaps of $\text{C}_6\text{O}_2^-$ and $\text{C}_6\text{O}_3^-$ are estimated to be 1.5 eV, similar to that of $\text{C}_{60}^-$. Due to existence of multiple isomers for the higher oxides (as discussed below) and poorer resolution, the 1.5 eV HOMO–LUMO gap should be regarded as the average of the different isomers. The HOMO–LUMO gaps for all species are summarized in Table 1.

The details of the vibrational structures in the first PES band of $\text{C}_6\text{O}_x^-$, were revealed more clearly at 355 nm (Figure 2). Vibrational structures of $\text{C}_6\text{O}^-$ are seen to be identical to that of $\text{C}_{60}^-$, even though the resolution of the $\text{C}_6\text{O}^-$ spectrum was slightly poorer. This observation suggests that the vibrational modes and their frequencies excited in the ground-state transition in $\text{C}_6\text{O}^-$ and $\text{C}_{60}^-$ are identical; i.e., the O atom has very little perturbation to the electronic and geometrical structures of the C$_6$O cage in C$_6$O, indicating the electronic and structural robustness of the C$_6$O cage structure. The EA of $\text{C}_6\text{O}$ is measured accordingly from the 0–0 transition to be 2.745 eV, compared to 2.683 eV for $\text{C}_{60}^-$ in Table 1.

The vibrational structures in the 355 nm spectrum of $\text{C}_6\text{O}_x^-$ were poorly resolved. However, two peaks (X$_1$ and X$_2$) were resolved for what appeared to be the 0–0 transition. These two peaks could be due to a vibrational progression of a low frequency mode. But they are most likely due to the 0–0 transitions for two isomers of $\text{C}_6\text{O}_2^-$, as verified below by the theoretical calculations. From the peak positions of X$_1$ and X$_2$, we obtained the ADEs for these two isomers of $\text{C}_6\text{O}_2^-$ as 2.785 eV (X$_2$) and 2.820 eV (X$_1$). The 355 nm spectrum of $\text{C}_6\text{O}_3^-$ was even less resolved, partly due to the poorer resolution and partly due to the fact that multiple isomers were expected to be present for $\text{C}_6\text{O}_3^-$. Thus, we could not obtain the ADE for $\text{C}_6\text{O}_3^-$. An estimate of 2.8 eV is listed in Table 1, which should be viewed as an average of the different isomers.

Theoretical Results

We carried out theoretical calculations using density functional theory with the TZ2P basis set. For $\text{C}_6\text{O}^-$, the lowest

Table 1: Experimental and Theoretical Adiabatic Detachment Energies (ADEs) of $\text{C}_{60}^-$ and $\text{C}_6\text{O}_x^-$ ($x = 1–3$) and the Measured HOMO–LUMO Gaps for the Neutral Species (All Energies in eV)

<table>
<thead>
<tr>
<th>Species</th>
<th>ADE (expt)$^{ab}$</th>
<th>ADE (cal)</th>
<th>HOMO–LUMO gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_{60}^-$</td>
<td>2.683(8)</td>
<td>2.86</td>
<td>1.62 ± 0.01</td>
</tr>
<tr>
<td>$\text{C}_6\text{O}^-$</td>
<td>2.745(8)</td>
<td>2.95</td>
<td>1.52 ± 0.01</td>
</tr>
<tr>
<td>$\text{C}_6\text{O}_2^-$ (isomer 1)</td>
<td>2.820(10)</td>
<td>3.02</td>
<td>~1.5</td>
</tr>
<tr>
<td>$\text{C}_6\text{O}_2^-$ (isomer 2)</td>
<td>2.785(10)</td>
<td>3.00</td>
<td>~1.5</td>
</tr>
<tr>
<td>$\text{C}_6\text{O}_3^-$</td>
<td></td>
<td>~2.8</td>
<td>~1.5</td>
</tr>
</tbody>
</table>

$^a$ The ADEs were determined from the 0–0 transitions in the 355 nm spectra (Figure 2) except for $\text{C}_6\text{O}_2^-$, for which only a rough estimate from the detachment threshold was obtained. The ADEs also represent the EA of the corresponding neutral species. $^b$ Numbers in parentheses are uncertainties in the last digits. $^c$ From ref 27.
energy structure is the epoxide structure with the oxygen bridging one [6,6] C—C bond (1) (Figure 3). We identified two low-lying diepoxide isomers for C$_{60}$O$_2$ separated by only 0.33 eV in energy. For the more stable isomer 1 (2), the two oxygen atoms position over [6,6] ring junctions on one six-member ring, whereas for isomer 2 (3) they bridge the [6,6] C—C bond over neighboring six-member rings (Figure 3). The energetics of C$_{60}$O$_2$ neutrals are similar to that of the anions, and isomer 2 is 0.31 eV higher in energy. The calculated ADEs for C$_{60}$O and C$_{60}$O$_2$ are compared with the experimental values in Table 1. The calculated values are ~0.2 eV higher than the experimental ones but reproduce the experimental trend well. Particularly, the calculation predicts that the more stable isomer 1 of C$_{60}$O$_2$ has a slightly higher ADE compared to that of isomer 2, consistent with the experimental observation (Figure 2).

Discussions

The PES spectra of C$_{60}$O$_x$ (x = 1–3) at 355 nm (3.496 eV), compared with that of C$_{60}^-$ from ref 27 with assignments of the main vibrational features.

Figure 2. Photoelectron spectra of C$_{60}$O$_x$ (x = 1–3) at 355 nm (3.496 eV), compared with that of C$_{60}^-$ from ref 27 with assignments of the main vibrational features.

Figure 3. Optimized structures of C$_{60}$O$^-$ (1) and C$_{60}$O$_2^-$ (2, 3). The numbers are the relative energies in electronvolts for the anions and the neutrals (in parentheses).

The apparent similarity between the C$_{60}$O$^-$ and C$_{60}$O$_2^-$ spectra indicates the oxides have electronic and geometrical structures essentially similar to that of C$_{60}$ although the overall symmetries are lower for the oxides. This is born out from the calculations. As shown in Figure 3, each oxygen atom breaks one C=C double bond to form two epoxide bonds locally and does not seem to induce global changes to the cage. The valence MOs of the oxides are still expected to be composed of the p orbitals from the cage (C=C π orbital), very much like the bare C$_{60}^-$. These are shown clearly in Figure 4. We note that the O atoms...
have very little contribution to the valence MOs of the oxides and they only affect the proximal carbons. Thus the C₆₀Oₓ oxides can be viewed as O atoms chemisorbed to the C₆₀ surface.

According to geometric structure analyses, there can be two isomers for the fullerene monoxide C₆₀O ([5,6]-open oxidoanulene and [6,6]-closed epoxide) and eight isomers for the fullerene dioxide C₆₀O₂. Although the two isomers of C₆₀O are predicted to have similar stabilities with a high conversion barrier between them, experimentally only the epoxide was found initially.[12–14] The [5,6]-open isomer has been discovered more recently with photolysis of a C₆₀ ozonation solution.[15] We study on a series of fullerene oxides, C₆₀Oₓ. For C₆₀O₂, we observed two dominant isomers (2, 3) among eight possible ones, also consistent with the previous studies.[16,17]

The broadness of our PES spectra of C₆₀Oₓ indicates the presence of multiple isomers. This observation agrees with two previous reports showing three isomers existed for the trioxides C₆₀O₃.[18,19] In conclusion, we report a combined PES and theoretical study on a series of fullerene oxides, C₆₀Oₓ (x = 1–3). Our spectra reveal similar electronic structures for the oxides compared to that of C₆₀. This similarity is confirmed via MO analyses. The EAs of C₆₀Oₓ are found to increase slightly with the oxygen content, x. We observed one isomer for C₆₀O−, two dominant isomers for C₆₀O₂−, and multiple isomers for C₆₀O₃−. Our results showed that O atoms only perturb the C₆₀ cage locally and have very little global effect on the C₆₀ cage. This finding demonstrates the electronic and structural stability of the C₆₀ cage.

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References and Notes