

Structural and electron properties of the highest epoxygenated fullerene C₆₀O₃₀, a DFT study

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Abstract

Ab initio Hartree–Fock (HF) and density functional theory (DFT) calculations were carried out to determine the structural and electronic properties of the highest epoxygenated fullerenes C₆₀O₃₀. For comparison, other fullerene oxides C₆₀O₂₉, C₆₀O₃, C₆₀O₂ and C₆₀O were also studied. The highly symmetrical I_h structure of the parent C₆₀ is reserved in C₆₀O₃₀ and C₆₀O₃₀ was calculated to be a nonpolar molecule. It was demonstrated that C₆₀O₃₀ should be more stable than other C₆₀ oxides such as C₆₀O₂₉, C₆₀O₃, C₆₀O₂ and C₆₀O. Compared with C₆₀, it is less possible for C₆₀O₃₀ to accept or donate electrons from the reduced EAs and enhanced IPs. The IR active modes and harmonic vibrational frequencies of C₆₀O₃₀ were also discussed.

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1. Introduction

The isolation of fullerenes in macroscopic quantities [1] has stimulated intensive efforts to investigate their derivation reactions. Realization of the anticipated technical potential of fullerenes will depend to a great extent on the availability of well-characterized derivatives. Among the numerous compounds created by fullerene's versatile chemistry, oxygenated fullerenes have been of particular interest in regard to its applications in various fields such as cluster science [2] or medicine and photoelectronic devices [3]. For instance, electrochemically active films can be grown on electrode surfaces upon reduction of C₆₀O [4]. Fullerene dimer oxides have also caught the attentions, being the precursors for odd numbered all carbon fullerene dimers such as C₁₁₉ [5] or methylene-bridged C₆₀ dimers [6]. Since the fullerene oxides were first found in the carbon soot generated by graphite vaporization during the bulk preparation of fullerenes [7,8], C₆₀O_n had been synthesized by various techniques such as

photooxygenation, electrochemical oxidation, ozonization, epoxidation and other experimental methods [9–16]. Detailed experimental works [9,12] on the synthesis and characterization of C₆₀O suggested that it had two stable isomers; i.e., an epoxide structure with C_{2v} symmetry (the closed [6,6] pattern) and an ether structure with Cs ([5,6]-open oxidoannulene) symmetry, respectively. Systematic researches including isolation, ultraviolet visible UV–vis spectra, ¹³C-nuclear magnetic resonance NMR spectra characterization and single-crystal analysis on C₆₀O₂ revealed that this dioxide was a fullerene diepoxide with both oxygen atoms positioned over [6,6] ring junctions on a common six-membered face of the carbon cage [14]. Besides the fullerene ozonide [15] with C_{2v} symmetry, another isomer of C₆₀O₃ [16] with C_{3v} symmetry in which three oxygen atoms are added onto one benzenoid ring of C₆₀ was also experimentally isolated and characterized. Parallel to the experimental studies, theoretical works have been playing an important role in investigating the structural and electronic properties of the fullerene oxides. Some of the theoretical studies had good accordance with experimental results. Raghavachari [17] presented semi-empirical (MNDO) and ab initio Hartree–Fock (HF) (3–21G) calculations on the structures and stabilities of C₆₀O and found that the isomer with a bridging oxygen across the bond between a five- and a

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six-membered ring was the ground state of $C_{60}O$. Tight-binding molecular dynamics technique had also been used to optimize the structures of $C_{60}O$ and $C_{60}O_2$ [18]. Quantum-chemical model evaluations of thermodynamics and kinetics of oxygen atom additions to narrow nanotubes found that the enthalpically favored structures are produced by oxygen additions to the nanotube tips and the lowest energy isomer had the lowest kinetic activation barrier [19]. Xu et al [20] had investigated the rearrangement between the closed [6,6] and open [5,6] isomers of $C_{60}O$ using semiempirical AM1 and MNDO methods. Their results revealed that the interconversion of the two isomers followed a two-step pathway involving an intermediate and two transition states. Feng et al [21] had studied the possible isomers of $C_{60}O_2$ and $C_{60}O_3$ with the semiempirical quantum mechanical INDO method and found that the $C_{60}O_2$ isomer of Cs symmetry and the $C_{60}O_3$ isomer of C_{3v} symmetry with a single epoxy chain connecting both carbons of a [6,6] bond were the most stable. The calculated electronic spectra of $C_{60}O_2$, and the ^{13}C NMR analysis of both $C_{60}O_2$ and $C_{60}O_3$ agreed well with experiment.

As to the fullerene oxides with more than three oxygen atoms, however, to the best of our knowledge, there is limited information about their experimental and theoretical studies. Under several circumstances, oxidation of C_{60} has been shown to give $C_{60}O$ in association with other higher oxides ($C_{60}O_n$, $n = 2-50$) in different oxidations [3,11–14]. It was proposed [14] that there are indeed 8 possible regioisomers of $C_{60}O_2$ and 43 isomers of $C_{60}O_3$. The extreme difficulties in isolating and obtaining pure samples resulted from the great similarity between these isomers thus have impeded the structural and electronic properties elucidation for those higher fullerene oxides. Subsequently, theoretical studies on derivatives containing more oxygen atoms should be forthcoming in keeping abreast of current experimental development. Recently, the highest epoxidated fullerenes $C_{60}O_{30}$ as well as other highly oxygenated fullerene were synthesized by corona discharge ionization in gas phase [22] in the presence of a trace amount of oxygen and were detected by in situ mass analysis. But their separation and electronic and structural characterization remain unresolved. In this study, we report ab initio and density functional theory (DFT) studies on the structural and electronic properties of the highest epoxygenated fullerene $C_{60}O_{30}$, for comparison, $C_{60}O_{29}$, $C_{60}O_3$, $C_{60}O_2$ and $C_{60}O$ are also studied. We hope the present study will encourage further theoretical and experimental analysis of the system.

2. Computational details

Full geometry optimizations and total energy calculations were performed at the Hartree–Fock and DFT/B3LYP levels of theory with the STO-3G and 6-31G(d) basis sets. Three models HF/STO-3G, HF/6-31G(d) and B3LYP/6-31G(d) were used in this sequence for geometry optimizations to obtain results at different theory levels as well as to minimize the computational cost. To ensure true stationary points had been found, harmonic vibrational frequencies were also calculated by analytic evaluation of the second derivative of the energy with respect

to nuclear displacement. All calculations were carried out with the GAUSSIAN 03 program package [23] executed on a SGI Onyx3900 workstation and the results were calculated to machine precision.

The hybrid density functional method B3LYP was chosen because the inclusion of electron correlation was important for accurate geometry prediction. The free molecule C_{60} was firstly calculated at HF/STO-3G (the lowest frequency 302.22 cm^{-1}) and the final B3LYP/6-31G(d) gave bond lengths 1.395 and 1.454 Å, respectively, for the [6,6] and [5,6] bonds, which agrees satisfactorily with the measured values [24] as well as the results of the previous highest level calculations, MP2 with triple ξ plus polarization basis set [25]. Our experience of theoretical calculations on C_{60} related derivatives [26–30] also indicate that DFT is a very successful method for studying fullerene compounds.

3. Results and discussions

Energy minima were found by full geometry optimizations without symmetry limitation. The optimized structures were confirmed as the local minima by frequency analyses at the HF/STO-3G level of theory, and the lowest frequencies are 224.97, 223.11, 281.19, 285.72, 293.02 and 272.58 cm^{-1} for $C_{60}O_{30}$, $C_{60}O_{29}$, $C_{60}O_3$, $C_{60}O_2$, [6,6] $C_{60}O$ and [5,6] $C_{60}O$, respectively. According to previous works, our results showed that the $C_{60}O_2$ isomer of Cs symmetry and the $C_{60}O_3$ isomer of C_{3v} symmetry [20,21] were the most stable. As was displayed in Fig. 1, the highly symmetrical I_h structure of the parent C_{60} is reserved in $C_{60}O_{30}$.

Table 1 listed the main parameters of $C_{60}O_{30}$ and some other epoxygenated fullerenes optimized at B3LYP/6-31G(d) level of theory. Compare with the intact C_{60} cage, all the cages of epoxygenated fullerenes are stretched by around 0.3 Å, which is attributed to the changes of the bond lengths, the bond angles and the twist angles of neighboring carbon atoms. However, the cages of highly epoxygenated fullerenes like $C_{60}O_3$ and $C_{60}O_{29}$ are more enlarged. Furthermore, as the number of O atom increases, the new formed bond angle C–O–C become smaller. Both the [6,6] and [5,6] C–C bonds of $C_{60}O_{30}$ are longer than that of C_{60} due to the oxygenation.

Mulliken population analysis showed that substantial electronic charge transfers had occurred from the C sites to the O sites in all epoxygenated fullerenes, owing to the higher electronegativity of O than C. High-performance liquid chromatography experiments suggested that the more oxygen atoms that are added, the larger is the dipole of a fullerene oxide [15]. As summarized in Table 2, our computational results are consistent with the experimental work. However, when the number of added O atoms increases to some degree, the dipole of the fullerene oxide may decrease. The dipole of $C_{60}O_{29}$ is almost equal to that of $C_{60}O$, and $C_{60}O_{30}$ is calculated to be a nonpolar molecule. Thus make the separation of $C_{60}O_{30}$ from other fullerene oxides possible.

It was well known that the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO play a predominant role in chemical reactions [31,32].

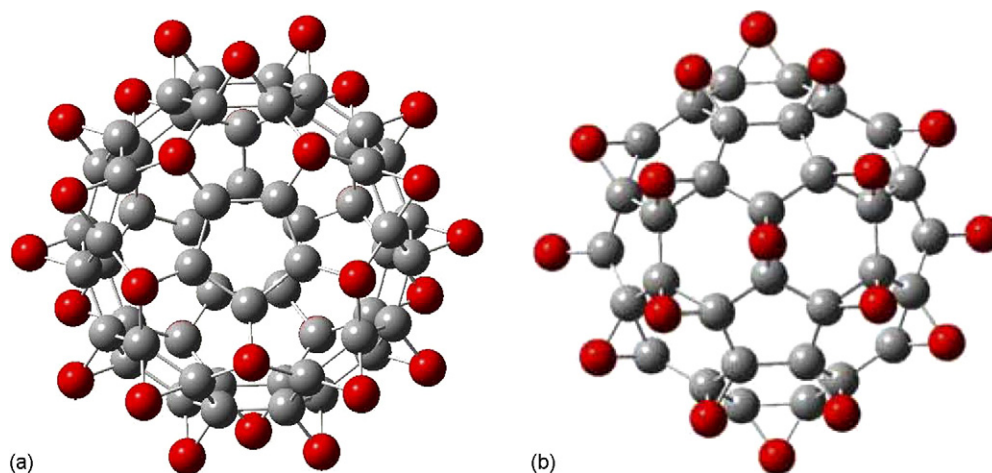


Fig. 1. B3LYP/6-31G(d) optimized geometries of $C_{60}O_{30}$, top view (a) and side view (b).

HOMO–LUMO energy separation has been used as a conventional measure of kinetic stability for various π -electron systems [33–39]. A large HOMO–LUMO gap can be associated with high kinetic stability because it is energetically unfavorable to add electrons to a high-lying LUMO, and to extract electrons from a low-lying HOMO, and so to form the activated complexes of any potential reaction [33]. Our calculations showed that $C_{60}O_n$ ($n = 1–3$) had a smaller HOMO–LUMO gap than C_{60} , which indicates that the addition of oxygen atoms can make the fullerene cage reactive, and $C_{60}O$ had been used to prepare larger fullerenes and carbon clusters [5,6,40,41]. But when the C_{60} electron-deficient system is nearly saturated by O addition, the resulted oxides become inactive, as shown in Table 2, $C_{60}O_{30}$ and $C_{60}O_{29}$ have far larger HOMO–LUMO gap than C_{60} .

Binding energies (BE) were calculated according to the gas phase reaction: $nX + mY = X_nY_m$. This means that $BE(X_nY_m) = E(X_nY_m) - nE(X) - mE(Y)$, and a more thermodynamic

stable species should have a more negative BE. It can be seen from Table 2 that as the number of O atom increases, the binding energies of the fullerene oxides become more negative. Meanwhile, our results agree with those of previous works [17,20] that [5,6] $C_{60}O$ is more stable than [6,6] $C_{60}O$ from the total energy and binding energy. $C_{60}O$ had represented a long-standing case of experiment-theory disagreement, and there has been a similar problem with $C_{60}O_2$. The disagreement has been explained by kinetic rather than thermodynamic control [19]. In the end, kinetics rather than thermodynamics controls stabilities here as already discussed in literature [19]. It can be inferred that $C_{60}O_{30}$ should be more stable than other C_{60} oxides such as $C_{60}O_{29}$, $C_{60}O_3$, $C_{60}O_2$ and $C_{60}O$, once the energy barrier is surmounted, $C_{60}O_{30}$ would be produced and exist as a stable molecule with quite a long lifetime [22].

Relative to C_{60} , the HOMOs and LUMOs of the oxides are perturbed by the oxygenation and the degenerate energy levels are split. Fig. 2 displays the electronic levels of related

Table 1
The B3LYP/6-31G(d) optimized equilibrium geometries

	R_{C-O} (Å)	$R_{6/5\ C-C}$ (Å)	$R_{6/6\ C-C}$ (Å)	Cage stretch (Å)	θ_{C-O-C} (degree)
$C_{60}O_{30}$	1.4162	1.5112	1.4982	0.366	63.87
$C_{60}O_{29}$	1.4129–1.4248	1.4867–1.5139	1.4975–1.5041	0.386	63.82–64.02
$C_{60}O_3$	1.4203	1.4409–1.5193	1.3871–1.5250	0.183	64.94
$C_{60}O_2$	1.4166–1.4280	1.4394–1.5141	1.3841–1.5262	0.186	64.89
[6,6] $C_{60}O$	1.4223	1.4411–1.4924	1.3871–1.5366	0.156	65.39
[5,6] $C_{60}O$	1.3857	1.4352–1.4891	1.3828–1.4099	0.337	101.85
C_{60}		1.4540	1.3950		

Table 2
Results of B3LYP/6-31G(d)//B3LYP/6-31G(d) Calculations

	Charge on O	Total dipole moment (debye)	Binding energies (kcal/mol)	$\Delta E_{LUMO-HOMO}$ (eV)	Total energies (a.u.)
$C_{60}O_{30}$	−0.442	0	−13954.05	−6.73	−4541.73592499
$C_{60}O_{29}$	−0.442 to −0.446	0.905	−13805.73	−5.08	−4466.54216060
$C_{60}O_3$	−0.480	3.508	−10095.61	−2.56	−2511.73738119
$C_{60}O_2$	−0.479	2.429	−9948.42	−2.62	−2436.54542490
[6,6] $C_{60}O$	−0.476	1.283	−9802.89	−2.62	−2361.35610298
[5,6] $C_{60}O$	−0.509	0.839	−9804.99	−2.60	−2361.35946565
C_{60}		0	−9661.30	−2.77	−2286.17306739

Table 3

The EAs and IPs of the oxides with respect to C_{60} at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level

	EA (eV)	IP (eV)
$C_{60}O_{30}$	−0.92	3.05
$C_{60}O_{29}$	0.38	2.69
$C_{60}O_3$	0.31	0.10
$C_{60}O_2$	0.20	0.06
[6,6] $C_{60}O$	0.11	−0.05
[5,6] $C_{60}O$	0.08	−0.09

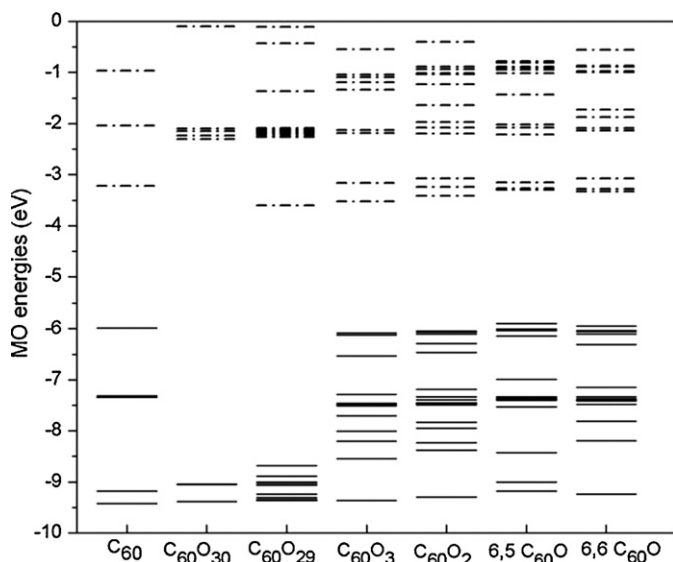


Fig. 2. Electronic energy levels of C_{60} , $C_{60}O_{30}$ and other oxides near the HOMO–LUMO gap obtained at B3LYP/6-31G(d) level of theory, solid and dashed lines refer to the occupied and unoccupied states, respectively.

complexes near the HOMO and LUMO energy gap obtained from the B3LYP/6-31G(d) level calculations. The reduction of the degeneration of electronic levels is obvious for $C_{60}O_{29}$, $C_{60}O_3$, $C_{60}O_2$ and $C_{60}O$, while in $C_{60}O_{30}$, the degeneration degree of HOMO and LUMO is the same as that of C_{60} . HOMOs are five (nearly) degenerated orbitals and LUMOs also consists of three (nearly) degenerated orbitals.

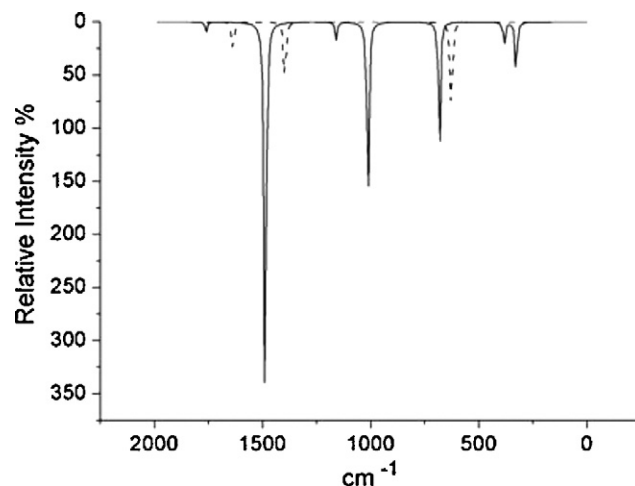


Fig. 4. Calculated IR spectra of $C_{60}O_{30}$ and C_{60} , the latter was indicated by dashed line.

In order to gain insight into the HOMO and LUMO properties of $C_{60}O_{30}$, we plot the probability density contours of the two levels. As was shown in Fig. 3, electron distribution away from the C site is clearly seen and HOMO and LUMO are found to be strongly localized on the dopant O site.

According to the Koopmans theorem, the ionization potential (IP) and electron affinity (EA) of the system is immediately obtained from the HOMO and LUMO eigenvalues. Table 3 listed the EAs, IPs of the oxides with respect to C_{60} at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. Compare with C_{60} , it is less possible for $C_{60}O_{30}$ to accept or donate electrons from the reduced EAs and enhanced IPs. Then, $C_{60}O_{30}$ is more chemically inactive than C_{60} and other oxides, as suggested by the above-mentioned HOMO–LUMO gap.

Our calculation on HF/STO-3G theory of level indicated that there are four infrared active modes in $C_{60}O_{30}$ with the triply degenerate T_{1u} symmetry. Their harmonic vibrational frequencies and intensities are 576 (7), 782 (1), 1435 (9) and 1743 cm^{-1} (50); IR intensities (in km/mol) of active modes are in parenthesis. The strongest band with intensity of 50 km/mol is associated with highest frequency mode at 1743 cm^{-1} . This normal mode is identified to correspond mainly with a C–C asymmetric stretch for the carbon atoms along the equator. A

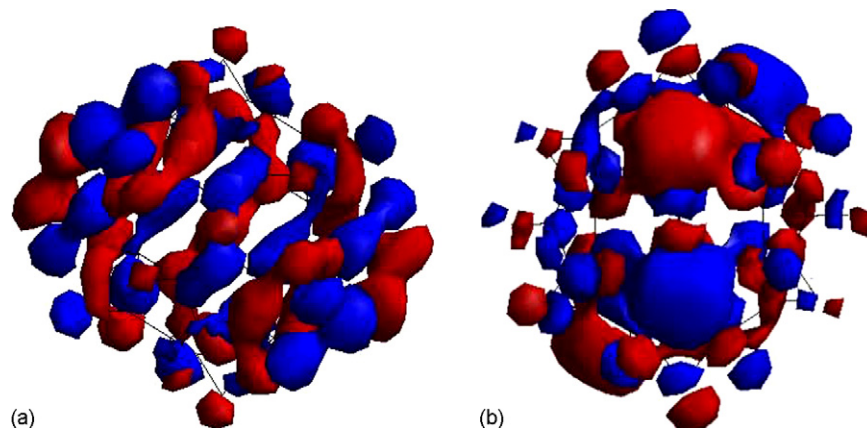


Fig. 3. Isodensity surface (0.015 e/a.u.³) associated with $C_{60}O_{30}$ Hartree-Fock: (a) LUMO and (b) HOMO.

complete list of all vibrational modes (a total of 264) is available upon request from the corresponding author. The calculated spectra of $C_{60}O_{30}$ was shown in Fig. 4, for comparison, the spectra of C_{60} calculated at the same theory level was also given. The most intensive vibration of $C_{60}O_{30}$ is ca. five times more intense than that of C_{60} .

4. Summary

We have studied the structural and electronic properties of the highest epoxygenated fullerenes $C_{60}O_{30}$ and some other fullerene oxides. The highly symmetrical I_h structure of the parent C_{60} is reserved in $C_{60}O_{30}$ and $C_{60}O_{30}$ was calculated to be a nonpolar molecule. $C_{60}O_{30}$ should be more stable than other C_{60} oxides. Compare with C_{60} , it is less possible for $C_{60}O_{30}$ to accept or donate electrons. There are four infrared active modes in $C_{60}O_{30}$ with the triply degenerate T_{1u} symmetry and the most intensive vibration of $C_{60}O_{30}$ is nearly five times more intense than that of C_{60} . The molecular properties calculated for this compound may serve as valuable predictions for future experimental research.

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