Ultraviolet photoelectron spectra of Ce₂@C₈₀ and La₂@C₈₀

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1. Introduction

Fullerene cages often encapsulate metal atoms and C₈₂ cage seems to be the most favorable cage in which metal atoms are entrapped [1]. However, other cages also encapsulate metal atoms although their production yield from direct current arc discharge of metal oxide/carbon composite rods is not so high compared with that of C₈₀ endohedral fullerenes. Among other cage endohedral fullerenes, C₈₀ endohedral fullerenes attract attention because of the reasons such as (a) empty Iₚ-C₈₀ is not stable and cannot be isolated [2] but it becomes stable upon encapsulation of metal atoms [3], (b) Iₚ-C₈₀ has the same symmetry as C₈₀ [4] which exhibits many interesting solid state properties like superconductivity [5] and ferromagnetism [6]. Although early stage X-ray diffraction analysis combined with maximum entropy method (MEM) [7] suggested Iₚ-La₂@C₈₀ cage, theoretical calculations [4,8–12] revealed that metal atoms entrapped Iₚ-C₈₀ did not retain the original symmetry and encapsulation of metal atoms induced the degradation of symmetry. Crystallographic structure of a La₂@C₈₀ adduct also supported this conclusion that the encapsulation of metal atoms is favorable for the stability of the fullerene cage [13].

Early theoretical calculation on La₂@C₈₀ suggested that entrapped two La atoms rotated in the D₃h-C₈₀ cage [8]. X-ray crystallographic analysis of its adduct, La₂@C₈₀ (CH₂(CH₃)₂)₃N, revealed that the rotation was frozen [4]. [The oxidation state of entrapped La in both La₂@C₈₀ [8] and the adduct [13] was calculated by DFT calculation to be +3.] On the other hand, vibrational mode analysis using DFT calculation of La₂@C₈₀ suggested D₃h symmetry that is the global minimum in total energy [10]. This proposal was questioned by recent DFT calculations [11,12] that supported D₃d geometry; using relativistic basis sets could be a crucial factor to a favor of D₃d.

The argument on the geometry of Iₚ-C₈₀ endohedral fullerenes did not stop at this point. Another Iₚ-cage endohedral fullerene, Ce₂@C₈₀, was isolated [14] and its predicted geometry was not D₃h but D₃d [12]. The reason of Ce₂@C₈₀ having D₃d geometry was attributed to specific bonding condition of Ce atoms to the cage; they bonded to C atoms on the opposite side of Ce axis of C₈₀.

We have been measuring ultraviolet photoelectron spectra (UPS) of endohedral fullerenes and reported the most plausible cage geometry by a comparison of the UPS [15–17]. There is an empirical rule for endohedral C₈₂ fullerenes that their electronic structure is essentially governed by the cage structure (symmetry) and the amounts of electrons transferred from the entrapped species. Thus, if one obtains analogous UPS from different endohedral fullerenes, both their cage structure (symmetry) and the amounts of transferred electrons should be almost identical. Furthermore, we have compared the UPS of endohedral fullerenes with theoretically obtained simulated spectra [18–22]. There is no theoretical reasoning that Kohn–Sham orbital energies obtained from DFT calculation is compatible with Koopmans’ theorem, but Janak’s theorem is analog to Koopmans’ theorem in DFT calculation; that...
Kohn–Sham orbital energies correspond the highest occupied and the lowest unoccupied molecular orbitals energy levels. Further, it has been found that simulated spectra generated from Kohn–Sham orbital energies reproduce the UPS very well and the comparison was helpful to estimate the cage geometry. The UPS of La2@C80 was tried to measure but any specific structure which was produced by direct-current arc heating were calculated with and the simulated spectra was impossible. It is reported in Ref. [7].

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Sublimation was conducted using a resistive heating quartz crucible in a preparation vacuum chamber directly attached to a photoelectron measurement chamber. The temperature of the crucible during La2@C80 and Ce2@C80 sublimation was about 850–870 K. The pressure of the chamber during the deposition increased to 2 × 10−6 Pa (base pressure before the deposition was less than 4.0 × 10−7 Pa). The thickness of deposited endohedral fullerenes was tried to monitor by a quartz thickness monitor located beside the disk, but because of the collimation of the crucible the reading of the monitor indicated several nm thickness. However, the actual thickness of the film might be several tens of nm, since the gold Fermi edge was not observed after repeated sample deposition.

The UPS were measured using a photoelectron spectrometer at BL18B2 of UVSOR (Ultraviolet Synchrotron Orbital Radiation Facility) at the Institute for Molecular Science. The resolution of the spectrometer was 110 meV. Energy calibration of the spectra was carried out using the Fermi edge of a gold-deposited sample disk before the UPS measurements of La2@C80 and Ce2@C80. The spectra were referenced against the Fermi level. The base pressure of the measurement chamber was <9.0 × 10−8 Pa, and the pressure during the measurement was about 6.0 × 10−8 Pa.

Molecular orbitals of La2@C80 and Ce2@C80 were calculated with a Gaussian 03 program module. Their geometry was optimized at the Hartree–Fock level using the CEP-31G basis set. Poor correlation was observed between the UPS and simulated spectra generated by broadening the calculated Eigen values at the Hartree–Fock level with Gaussian functions of 0.2 eV full width at half maximum. The DFT calculation was performed on the optimized structures of La2@C80 and Ce2@C80 using the B3LYP hybrid functional to obtain the Kohn–Sham orbital energies with basis sets Sapporo-DZP for C atoms and TK/NOSeC–V–TZP function for La and Ce atoms [25,26]. Simulated spectra obtained by the same procedure describe above using Kohn–Sham orbital energies reproduced the UPS far better than those obtained from the Hartree–Fock calculation. The simulated spectra in the following text are the result of the DFT calculation.

3. Results and discussion

Figs. 1 and 2 show the UPS of La2@C80 and Ce2@C80 obtained with the incident photon energy indicated beside each spectrum.

The spectral onset of La2@C80 and Ce2@C80 was 0.77 and 0.89 eV below the Fermi level, respectively. Except for the onset energy, their UPS are almost identical. There are 12 structures labeled A to L in their UPS. Among them, structure E appears as a shoulder not explicit and structure H appears as a distinct peak in the spectra obtained with the incident photon energy larger than 30 eV. Approximate peak positions of their structures are indicated with dotted lines. As were observed in the UPS of other fullerenes [18–23,27], the relative intensity of these structures oscillates...
when the energy of the incident photon is tuned. Because of this intensity oscillation, peak positions deviate slightly in accordance with the incident photon energy change.

Fig. 3 shows the photoelectron spectra of La2@C80 and Ce2@C80 obtained by 40 eV incident photon energy together with the UPS of empty C80 obtained by 60 eV energy [28]. There is a very poor correspondence between the UPS of La2@C80 and Ce2@C80, and the UPS of C80. Only distinct resemblance among these spectra might be a structure appeared at about 5.5 eV which is a typical structure in the UPS of fullerenes [15–17,19–23] and a broad band between 6.0 and 9.5 eV which is due to $\sigma$-electrons constituting fullerene backbone. The UPS of La2@C80 and Ce2@C80 are almost identical and hard to distinguish them. Structures labeled A–H of Ce2@C80 appear at deeper binding energy side by about 0.2 eV than corresponding ones of La2@C80. Their relative intensity is almost the same. On the other hand, structures labeled I–L appear at the same binding energy and there is a slight change in the relative intensity of structures I and J. Resemblance of the UPS means that these two endohedral fullerenes have analogous electronic structure. Since the electronic structure of endohedral fullerenes strongly depends on the geometry of fullerenes, both cage and entrapped atoms, it is highly plausible that they have the same cage structure. In order to examine the validity of this deduction, their electronic structure was calculated by the DFT method and Gaussian functions.

Two possible geometries of $M_2@C_{80}$ ($M = \text{La, Ce}$), $D_{2h}$ and $D_{3d}$ have been proposed [4,8–14]. Three initial conformations of metal atoms in $D_{3d}$-$C_{80}$ were adapted: (a) $D_{3d}$ symmetry, two metal atoms were in the $C_3$ axis of $I_h$-$C_{80}$, (b) $D_{2h}$ symmetry, they were in the $C_2$ axis penetrating the center of hexagon rings perpendicular to the mirror plane of $I_h$-$C_{80}$ and (c) $D_{3d}$ symmetry, in the $C_3$ axis penetrating the center of phenalene rings. Optimized structures retained the same symmetry adapted as the initial geometry. Kohn–Sham orbital energies were obtained using the optimized geometry. Kohn–Sham orbital energies and simulated spectra generated by broadening them by Gaussian functions are shown in Fig. 4 (La2@C80) and Fig. 5 (Ce2@C80). The UPS of La2@C80 and Ce2@C80 obtained with 30 eV excitation energy are also shown for comparison. The bars in Figs. 4 and 5 indicate the calculated ionization energies (Eigenvalues of occupied states). Scale of the simulated spectra and Kohn–Sham orbital energies is shifted by 4.4 eV for an easy comparison. Since the similarity between the UPS and the simulated spectra generated from $D_{3d}$ geometry of $M_2@C_{80}$ ($M = \text{La and Ce}$) was very poor, the structure of these endohedral fullerenes should not be $D_{3d}$ geometry. Further, the formation energy of this geometry is much larger than that of the most stable one. Therefore, we do not treat this geometry any farther in this text. The simulated spectra generated from $D_{3d}$ and $D_{2h}$ geometry seem to reproduce the UPS very well; the first four structures A–D are well reproduced and deeper structures F–J are also reproduced reasonably well. There are slight difference in Kohn–sham orbital energies (indicated by bars) of $D_{2h}$-$\text{La}_2@C_{80}$ and $D_{2h}$-$\text{Ce}_2@C_{80}$, but it is so small that the simulated spectra obtained by their convolution do not show any significant difference. Only attractive difference in the simulated spectra might be associated with the position of the HOMO; the HOMO of Ce2@C80 appears at slightly shallower than the HOMO-1 or -2, whereas that of La2@C80 locates rather close to the HOMO-1. From these data, present findings suggest that the simulated spectra obtained from $D_{3d}$ geometry reproduced the UPS of Ce2@C80 and La2@C80 very well. Hence the actual geometry of La2@C80 and Ce2@C80 might be $D_{3d}$.

Fig. 6 shows calculated energy diagrams of Ce2@C80, C80 of the same cage symmetry and the entrapped Ce atoms. Fig. 7 shows calculated energy diagrams of La2@C80, C80 of the same cage symmetry and the entrapped La atoms. Wave functions of some frontier orbitals of Ce2@C80, La2@C80 and C80 are also depicted in the figures. The HOMO-3 and HOMO-2 wave functions of Ce2@C80 are almost identical with the LUMO and LUMO + 1 of C80, and similar resemblance is observed in the HOMO-4 of Ce2@C80 and the LUMO + 2 of C80. That is, the upper three levels of Ce2@C80 are derived from the unoccupied molecular orbitals of C80 and electrons of the entrapped Ce atoms are transferred to these levels. Thus, the formal oxidation state of the fullerene can be described...
On the other hand, the HOMO-2 and HOMO-3 wave functions of La$_2$@C$_{80}$ are almost identical with the LUMO and LUMO + 1 of C$_{80}$, and similar resemblance is observed in the HOMO-1 of La$_2$@C$_{80}$ and the LUMO + 2 of C$_{80}$. That is, the upper three levels of La$_2$@C$_{80}$ are derived from the unoccupied molecular orbitals of C$_{80}$ and electrons of the entrapped La atoms are transferred to these levels. Thus, the formal oxidation state of the fullerene can be described as La$_2$$^{6+}$@C$_{80}$$^6$/C$_0$. Calculated charges of entrapped atoms are estimated by the natural population analysis (NPA). Presently obtained NPA charge of Ce atom in Ce$_2$@C$_{80}$ is +2.21 and that of La atom in La$_2$@C$_{80}$ is +2.31. The formal oxidation state of Ce and La atoms might be +3 and two atoms donates six electrons to the cage. The fullerene cage accepts the same amounts of the electrons from the entrapped atoms, Ce$_2$$^{6+}$@C$_{80}$ and La$_2$$^{6+}$@C$_{80}$.

The empirical rule that the electronic structure of endohedral fullerenes depends on the cage structure and the amounts of transferred electrons holds in La or Ce atoms entrapped fullerenes.

4. Conclusions

The intensity of the structures appearing in the UPS of Ce$_2$@C$_{80}$ and La$_2$@C$_{80}$ oscillates in accordance with the incident photon energy change, which means that this molecule has analogous geometry to other fullerenes. The UPS of La$_2$@C$_{80}$ are the same as those of Ce$_2$@C$_{80}$, both have the same electronic structure. The UPS of Ce$_2$@C$_{80}$ and La$_2$@C$_{80}$ is well reproduced by the simulated spectrum obtained from the geometry optimized structure using DFT calculations, which indicates the validity of the geometry optimized structure. Comparison of the UPS with theoretically generated simulation spectra indicates that the most plausible structure of Ce$_2$@C$_{80}$ and La$_2$@C$_{80}$ has $D_3$d symmetry. Charge population analysis suggest Ce$_2$$^{6+}$@C$_{80}$ and La$_2$$^{6+}$@C$_{80}$ oxidation state.

Conflict of interest

There is no conflict of interest among authors.

Acknowledgments

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