

Electronic Structure of Metallofullerene LaC₈₂: Electron Transfer from Lanthanum to C₈₂

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Ultraviolet photoelectron spectra (UPS) of LaC₈₂ questioning whether the La atom is inside the C cage or not are measured for the first time. The UPS of LaC₈₂ is analogous to those of C₈₂, but there is a critical difference in the region just below the Fermi level. It is an appearance of two new peak components at 0.9 and 1.6 eV with the intensity ratio of 1:2 in the UPS of LaC₈₂. Their origin is the transfer of three electrons from La to C₈₂ to form the electronic structure of La⁺³C₈₂⁻³. Present results combined with theoretical calculations on the position of the La atom in the molecule assert an encapsulation of the La atom inside the C cage.

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Chai *et al.* [1] indicated that there is an air stable and solvent extractable metallofullerene, LaC₈₂, in the laser vaporized soot of a composite rod of La₂O₃ and graphite. They suggested that the metal atom of the metallofullerene was entrapped inside the C cage (endohedral form, to be described as La@C₈₂). Since then, many attempts have been made to obtain metallofullerenes [2-8]. An ESR measurement [2] indicates the +3 oxidation state for the La atom of LaC₈₂. An x-ray photoelectron spectroscopy (XPS) [9] result on the mixture of metallofullerene LaC_n also indicates that the La atom is in a formal charge state close to +3 and is effectively protected from water and oxygen. These experiments strongly suggest that the La atom is inside the cage. However, there still remains an ambiguity whether the metal atom is actually inside the C cage. The basis of an encapsulation of the metal atom inside the cage is the +3 oxidation state which is obtained by the measurements of the mixture of empty fullerenes, metallofullerenes, and a carbon soot. There is a possibility that the +3 oxidation state of the metal atom is the result of the formation of La carbides. Further, an extended x-ray absorption fine structure study [10] on the mixture of fullerenes and YC_n (containing a small amount of YC₈₂) is inconsistent with the endohedral form of the metallofullerene; it claims that the Y atom is outside the cage. A settlement of the controversy on the position of the metal atom requires a precise electronic structure of pure LaC₈₂ itself.

Recently a sufficient amount of LaC₈₂ was separated and purified [11] and its optical absorption property ranging from ir to the visible/uv region strongly suggests that the metal atom is inside the cage. Here we report the first measurement of ultraviolet photoelectron spectra

(UPS) of LaC₈₂. Comparison between the UPS of LaC₈₂ and pristine C₈₂ [12] together with *ab initio* calculations of La@C₈₂ and empty C₈₂ [13] reveal whether the molecular geometry of LaC₈₂ is the same as that of C₈₂ and how the La atom affects the electronic structure of C₈₂.

LaC₈₂ was separated and purified from the extract of the solution of the carbon soot produced by an arc heating of the La₂O₃ and graphite composite rods by means of a preparative high performance liquid chromatography (HPLC) [11]. Details of the preparation are described elsewhere [1-9]. A film for the photoelectron measurement was prepared by a deposition of LaC₈₂ onto a gold-coated molybdenum disk in a vacuum of less than 3×10^{-9} Torr from a resistive heating quartz crucible. Before deposition, heavy degassing was observed during the preheating period of the crucible, which was due to the evaporation of the solvent used in the HPLC separation. Though the temperature of the crucible was not monitored, the sublimation temperature of LaC₈₂ was much higher than that of C₈₂ since we had to apply about twice as much wattage as was used for the C₈₂ deposition to sublime the LaC₈₂ powder. The thickness of the film was about 7 nm, which was thick enough to prevent the photoemission from the gold-coated substrate. Photoelectron spectra were measured at BL8B2 of UVSOR, Institute for Molecular Science. Resolution of the spectrometer was 150 meV, and the energy calibration of the spectrometer was carried out using the Fermi level of gold deposited onto the sample disk before and after the measurement.

Figure 1 shows the incidence photon energy dependence of photoelectron spectra of LaC₈₂. A spectral onset is located at 0.2 eV below the Fermi level, while that of

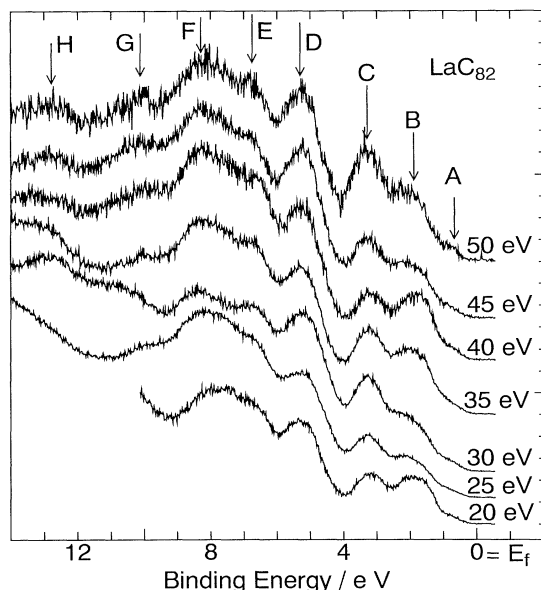


FIG. 1. The incident photon energy dependence of the ultraviolet photoelectron spectra of LaC_{82} . Eight distinct structures $A-H$ are indicated by arrows.

empty fullerenes is much deeper than 1 eV [12,14-17]. The difference observed in the onset energies relates to the ionization energies of both empty and metal containing fullerenes. A theoretical calculation using an *ab initio* method [13] on both empty and La atom entrapped fullerenes assuming C_2 symmetry gives 1.7 eV ionization energy difference (7.1 eV for empty C_{82} and 5.4 eV for La@C_{82}), which principally agrees with the large difference in the onset energies. The small onset energy corresponds with the optical absorption observed in the 1500 nm wavelength region [11].

There are eight distinct structures down to 14 eV labeled $A-H$. They are all observed in every spectrum, although their relative intensity differs from one to the other. This phenomenon is clearly observed in bands B and C . While the intensity of these two bands is about the same at 20 and 40 eV excitation, the intensity of band C is about $1.5\times$ stronger than that of band B in other spectra. Band E also clearly exhibits the intensity dependence on the incident photon energy. This kind of intensity oscillation seems to be typical in the fullerene compounds [12,14-17].

The spectra below 4 eV are analogous to that of other fullerenes [12,14-17]. The spectra of this region are mainly due to the σ electrons that are responsible for composing the skeletal structure of the fullerenes. This means that the electronic structure of the σ electrons of LaC_{82} resembles that of other fullerenes.

There is a suggestion that the chemical shift of La $5s$ and La $5p$ levels is indicative to determine whether the La atom is inside the cage [18]. The bands due to La $5s$

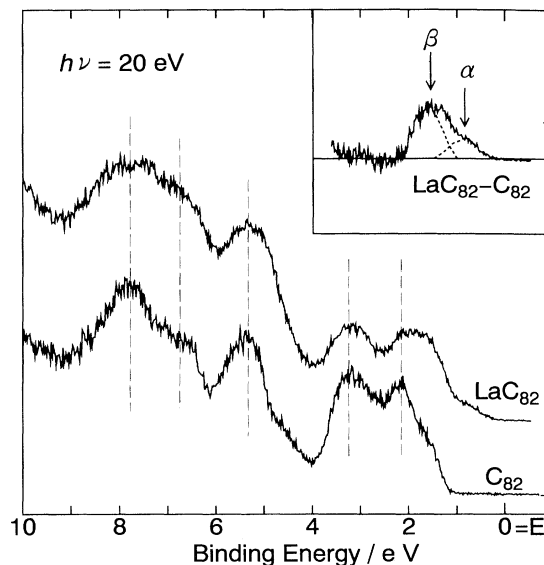


FIG. 2. The ultraviolet photoelectron spectra of LaC_{82} and C_{82} . The inset is the difference spectrum between them. The difference spectrum is obtained by subtraction of normalized spectra at the 3.3 eV peak and exhibits two peak components α and β of 1:2 intensity ratio.

and La $5p$ levels are sought with the 50 eV incident photon energy, but they are not detected. The ratio of the number of La atoms to the C atoms is so small that the signal derived from the La atoms must be covered.

Figure 2 shows a comparison of the spectra of LaC_{82} and C_{82} [12]. The incident photon energy is 20 eV. The peaks or structures observed in the spectrum of C_{82} are observed at almost the same position in the spectrum of LaC_{82} , which means that the electronic structures of C_{82} and LaC_{82} are essentially identical. This also suggests that the molecular geometries of C_{82} (a main product of C_{82} isomers) and LaC_{82} are in the same C_2 symmetry [19]. A distinct difference is observed only at the onset region of these spectra. The spectral edge of the LaC_{82} spectrum extends toward the E_f and is located at 0.2 eV, while that of C_{82} remains at 1.15 eV. To have a more accurate view a difference spectrum is shown in the inset of Fig. 2. The difference spectrum is obtained by normalizing both spectra at 3.3 eV (the peak top of the second peak) and subtracting the normalized UPS of C_{82} from that of LaC_{82} .

The difference spectrum of $\text{LaC}_{82}-C_{82}$ shows a structure that can be divided into two components as indicated by dotted lines. These two components α and β are located at 0.9 and 1.6 eV and their intensity ratio is 1:2. The formation of the α and β components is the result of the electron transfer from the La atom to the C_{82} molecules. As the intensity ratio is 1:2, the number of the electrons transferred to the β component must be twice those transferred to the α component. Therefore, three (or

multiples of three, but this case cannot take place because of the ionization energy difference) electrons must be transferred from the La atoms to the lowest unoccupied molecular orbital (LUMO) and second LUMO of C_{82} . The LUMO is filled by two electrons to form the β component, but the second LUMO is filled by only one electron to form the α component. That is, the oxidation state of the La atom is +3 and that of C_{82} is -3. Our result is in good agreement with the theoretical calculations of the $La@C_{82}$ molecule [13,18], the ESR measurement [2], and the XPS measurement [9] of LaC_{82} and supports that the La atom is inside the C cage.

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- [1] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford, and R. E. Smalley, *J. Phys. Chem.* **95**, 7564 (1991).
- [2] R. D. Johnson, M. S. de Vries, J. Salem, D. S. Bethune, and C. S. Yannoni, *Nature (London)* **355**, 239 (1992).
- [3] M. M. Alvarez, E. G. Gillan, K. Holczer, R. B. Kaner, K. S. Min, and R. L. Whetten, *J. Phys. Chem.* **95**, 10561 (1991).
- [4] H. Shinohara, H. Sato, Y. Saito, M. Ohkouchi, and Y. Ando, *J. Phys. Chem.* **96**, 3571 (1992).
- [5] M. M. Ross, H. H. Nelson, J. H. Callahan, and S. W. McElvany, *J. Phys. Chem.* **96**, 5231 (1992).
- [6] H. Shinohara, H. Sato, M. Ohkouchi, Y. Ando, T. Komeda, T. Shida, T. Kato, and Y. Saito, *Nature (London)* **357**, 52 (1992).
- [7] C. S. Yannoni, M. Hoinkis, M. S. de Vries, D. S. Bethune, J. R. Salem, M. S. Crowder, and R. D. Johnson, *Science* **256**, 1191 (1992).
- [8] S. Suzuki, S. Kawata, H. Shiromaru, K. Yamauchi, K. Kikuchi, T. Kato, and Y. Achiba, *J. Phys. Chem.* **96**, 7159 (1992).
- [9] J. H. Weaver, Y. Chai, G. H. Kroll, C. Jin, T. R. Ohno, R. E. Haufler, T. Guo, J. M. Alford, J. Conceicao, L. P. F. Chibante, A. Jain, G. Palmer, and R. E. Smalley, *Chem. Phys. Lett.* **190**, 460 (1992).
- [10] L. Soderholm, P. Wurz, K. R. Lykke, D. H. Parker, and F. W. Lytle, *J. Phys. Chem.* **96**, 7153 (1992).
- [11] K. Kikuchi *et al.* (unpublished).
- [12] S. Hino, K. Matsumoto, S. Hasegawa, K. Iwasaki, K. Yakushi, T. Morikawa, T. Takahashi, K. Seki, K. Kikuchi, S. Suzuki, I. Ikemoto, and Y. Achiba, *Phys. Rev. B* **48**, 8418 (1993).
- [13] S. Nagase, K. Kobayashi, T. Kato, and Y. Achiba, *Chem. Phys. Lett.* **201**, 475 (1993); S. Nagase (private communication).
- [14] J. H. Weaver, J. L. Martins, T. Komeda, Y. Chen, T. R. Ohno, G. H. Knoll, N. Troullier, R. E. Haufler, and R. E. Smalley, *Phys. Rev. Lett.* **66**, 1741 (1991).
- [15] M. B. Jost, P. J. Benning, D. M. Poirier, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, *Chem. Phys. Lett.* **184**, 423 (1991).
- [16] S. Hino, K. Matsumoto, S. Hasegawa, H. Inokuchi, T. Morikawa, T. Takahashi, K. Seki, K. Kikuchi, S. Suzuki, I. Ikemoto, and Y. Achiba, *Chem. Phys. Lett.* **197**, 38 (1992).
- [17] S. Hino, K. Matsumoto, S. Hasegawa, K. Kamiya, H. Inokuchi, T. Morikawa, T. Takahashi, K. Seki, K. Kikuchi, S. Suzuki, I. Ikemoto, and Y. Achiba, *Chem. Phys. Lett.* **190**, 169 (1992).
- [18] K. Laasonen, W. Andreoni, and M. Parrinello, *Science* **258**, 1916 (1992).
- [19] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, *Nature (London)* **357**, 142 (1992).