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Photoelectron spectroscopy and electronic structure of $Ca@C_{60}$

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Abstract. The electronic structure of an isolated $Ca@C_{60}$ molecule was probed by photoelectron spectroscopy (PES) of $Ca@C_{60}^-$, generated by laser desorption of a preformed $Ca@C_{60}$/fullerene thin film. The PES spectrum of $Ca@C_{60}$ was found to be similar to that of C_{60}^-, except that $Ca@C_{60}$ has an electron affinity of 3.0 eV, about 0.3 eV higher than that of C_{60}. The spectrum suggests that Ca atom donates its two 4*s* electrons to the C_{60} t_{1u} lowest unoccupied molecular orbital. Thus, the interaction between the central Ca atom and C_{60} is quite ionic, and $Ca@C_{60}$ can essentially be expressed as $Ca^{2+}@C_{60}^{2-}$.

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1. Introduction

After the discovery of a simple way of producing bulk amounts of fullerenes by Kratschmer *et al.*[1], the next challenge was to make fullerenes with metals inside. With their unusual cage-like structures, fullerenes have a unique type of inner empty space, where a wide variety of atoms may reside with little perturbation of the fullerene cage structure. Thus, a whole new series of materials may be created with tailored physical and chemical properties by tuning the inside atom. An important question concerns the nature of the interaction between the inside atom and the fullerene cage, which governs the physical and chemical properties of these endohedral materials. In this paper, we probe this interaction in $Ca@C_{60}$ with photoelectron spectroscopy. It is shown that the interaction is quite ionic, that is, Ca donates its two 4*s* electrons to the C_{60} t_{1u} LUMO (lowest unoccupied molecular orbital). Thus, C_{60} maintains its molecular integrity in this endohedral complex.

Macroscopic quantities of fullerenes with a metal atom inside were first produced for lanthanum by laser vaporization of a La_2O_3/graphite composite rod in a high temperature tube furnace [2]. In the sublimed film, $La@C_{60}$, $La@C_{70}$, $La@C_{74}$, and $La@C_{82}$ were all present, while $La@C_{82}$ was the most abundant and was found to be uniquely stable when dissolved in toluene and exposed to air. This finding has since been confirmed by EPR (electron paramagnetic resonance) [3] and XPS (x-ray photoelectron spectroscopy) [4] probes. In fact, many rare earth elements have been found to be readily trapped inside fullerenes with one or more than one atoms both by the laser vaporization/high temperature furnace technique and by the carbon arc technique.

2. Experimental

By using a CaO/graphite composite rod, we have successfully produced calcium-containing fullerenes with the laser vaporization/high temperature furnace technique, which has been described in detail earlier [2]. The CaO concentration in the starting composite graphite rod was very crucial to the yield. A CaO/C ratio of about 0.3% by atom was found to be optimum for making $Ca@C_{60}$. More importantly, the abundances of Ca-fullerenes were found to be similar to those of the empty fullerenes, and they are all soluble. This is very different from the La- and other rare earth-fullerenes, as mentioned above. Figure 1 shows a mass spectrum of a dried toluene solution on a Cu substrate probed by a laser-desorption (0.6 mj, 532nm) FT-ICR (Fourier Transform Ion Cyclotron Resonance) mass spectrometer with ArF excimer laser ionization. Note that besides the C_{60}^+ and C_{70}^+ signals, there is a prominent peak at the mass of CaC_{60}^+. Small amount of CaC_{70} and CaC_{84} are present, but there is very little CaC_{82}. XeCl excimer laser photofragmentation showed that this CaC_{60}^+ ion dissociates