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Formation of Li_mC_{60+2n} ($m = 1$–3, $n = -1$ to 4) endohedral fullerenes in the collision of Li^+ ion with C_{60}

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Abstract

The collision-induced reaction of Li^+ with neutral C_{60} vapor was investigated in the energy range of 10–100 eV using laser desorption time-of-flight mass spectrometry (TOFMS). From the positively charged TOF mass spectra, the maximum intensity of $[Li@C_{60}]^+$ was determined, which was about 60% of that for the C_{60}^+. In addition, $[Li_2@C_{60}]^+$ complex was also observable. The negatively charged lithium endohedral fullerene ions of both fragment products (C_{58}) and adductive products were observed in the negatively charged TOF mass spectra for collision energies in the range of 30–50 eV. In addition, it was found that up to three lithium atoms can be trapped into the fullerene cages and the intensity of $[Li_mC_{60+2n}]^-$ ($m = 1, 2$ and $3, n = 0, 1, 2, 3, 4$) in the mass spectra decreases with the increase of m and n. Li^+ inserts into the C_{60} cage via a "slip-through" mechanism was proposed.

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1. Introduction

Collision between C_{60} and a variety of ions or atoms is becoming a very new field of cluster research. The aim is to gain better understanding of the behavior of this novel material, not only for theoretical investigation but also for applications in the future. It is possible to form new compounds where atomic or molecular substituents are attached to the cage surface, or where carbon atoms in the C_{60} cage are replaced or displaced by ejective ions. On the other hand, the cavity in C_{60} cage with diameter of ~0.55 nm is large enough to trap an atom or small molecule inside [1], or even the cage will open a window to form an endohedral site for containing an atom, which may or may not be bound to the interior surface of the C_{60} cage [2].

Anderson's group reported systematic studies of endohedral complex formation and fragmentation in $M^+ + C_{60}/C_{70}$ (M = Li, Na and K) system [3,4]. The insertions of Li^+ and Na^+ to form the endohedral $[Li@C_{60}]^+$ and $[Na@C_{60}]^+$ species are observed for collision energies above ~6 and ~18 eV, respectively. They also published brief reports on the chemistry of Ne^+ [5], C^+ [6], O^+ [7], and N^+

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[8] ion collision with C_{60}. Recently, Tellgmann and co-wokers [9] reported that when monolayers of C_{60} film exposed to an intense beam of Li^+ ion with 30 eV kinetic energy, about 27% of the alkali-containing endohedral C_{60} were produced.

In this paper we present some of the new results on the collision of C_{60} neutral vapor with Li^+ ion beam, which was generated from a solid ion source. Mass-to-charge ratio (m/z) of the deposited film was measured with a LDTOF-MS. In addition to the expected $Li@C_{60}^+$ endohedral fullerene, we also obtained $Li_2@C_{60}^+$, $Li@C_{58}^+$ and $Li_m@C_{60+2n}^-$ $(m = 1, 2, 3;\ n = -1, 0, 1, 2, 3, 4)$ endohedral fullerene anions.

2. Experimental

Home made C_{60} powder with a purity higher than 99.5% was used in this experiment as a deposition source after baking in a vacuum of 10^{-4} Pa at 573–673 K for 10 min and then at 523 K for a few hours to remove solvent. The neutral C_{60} vapor was generated from an oven with a small hole. The substrate was set in the vacuum chamber. The ion beam was produced from thermionic emission of a special solid alkali ion source provided by SPECTRA-MAT, INC.USA. Through a simply designed accelerator and Einzel lens, the energy of ion beam can be changed continuously from 10 to 100 eV. The maximum beam current was 4 μA. By simultaneously heating both the C_{60} vapor (about 623 K) and the ion source under 10^{-4} Pa, the collision of Li^+ ions with C_{60} vapor was carried out in front of a copper substrate on which a thin film was deposited. The deposition rate monitored by a quartz-crystal thickness meter was about 1 nm/min, and the flux ratio between the C_{60} and the ion beam was about 1:3. The typical thickness of the film deposited was about 300 nm.

Mass analysis was done with a laser desorption Time-of-flight mass spectrometer (TOFMS). A Nd:YAG laser (532 nm), which had a pulse width of 7 ns and a power of 10 mJ/cm^2, was used to produce plasma over the film. Both positively charged and negatively charged ions could be generated and detected by the TOF.

3. Results and discussion

3.1. Postively charged ion spectrum

Fig. 1 shows the LDTOF-MS for the film deposited with a collision energy of 30 eV. The dominant peak is for C_{60}^+. However, the mass peak at 727 amu for $Li@C_{60}^+$ has a considerable high intensity. The spectrum also shows that there is no evidence of significant intensities for fragment products (e.g. C_{58}^+, C_{56}^+). Since only a single peak corresponding to C_{60}^+ was observed for both pure C_{60} film and conventionally doped lithium fulleride in the laser dosorption spectra, it is clear that the peaks corresponding to chemical species except C_{60} arise from the collision and subsequent film deposition processes. The conclusion was also proved by field desorption mass spectra of argon plasma polymerized C_{60} film [10].

Fig. 2(a) and (b), respectively, shows the intensities of lithium endohedral fullerenes ($Li@C_{60}^+$, $Li@C_{58}^+$, $Li@C_{56}^+$ and $Li@C_{54}^+$) and fragment ions (C_{58}^+, C_{56}^+ and C_{54}^+) relative to C_{60}^+ as a function of Li^+ energy. We can see that $Li@C_{60}^+$ appears at about 10 eV, similar to the results of Anderson et al. [4], while the $Li@C_{60-2n}^+$ appear at relatively higher energy depending on the number of C_2 units eliminated from C_{60}. The fragment ions also show the similar results. This behavior is fairly consistent with the mechanism of sequential loss

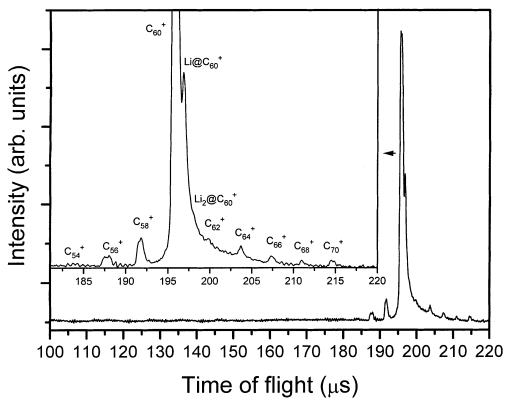

Fig. 1. Time-of-flight mass spectrum of positively charged ions for the film deposited with a collision energy of 30 eV of Li^+ ion beam.

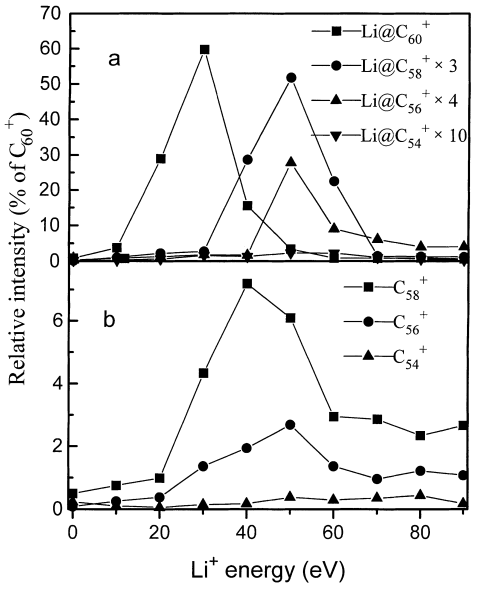

Fig. 2. Dependence of intensities of lithium endohedral fullerenes ions (a) and fragments ions (b) relative to C_{60^+} with collision energy.

of C_2 unit in the electron, ion impact experiments as well as photo-induced fragmentation of C_{60} [11,12]. Besides, the series of C_2 loss products, LiC^+_{60-2n}, terminates quickly as n increases. This is a further evidence that hot LiC^+_{60-2n} tends to relax by elimination of Li^+ rather than C_2.

Tellgmann and co-worker [9] reported that when monolayer of C_{60} film exposed to an intense ion beam of Li^+ of 30 eV kinetic energy, about 27% of the lithium-containing endohedral C_{60} were produced. We used an experimental setup similar to that of Tellgmann et al. [9], but the collision was carried out with the C_{60} vapor as well as the C_{60} film deposited on the substrate. The ion flux are three times larger than that of Tellgmann et al. [9], the collision probability was significantly enhanced. Thus besides $Li@C^+_{60}$, we also observed $Li_2@C^+_{60}$ with two lithium atom in the C_{60} cage. Moreover, about 60% of $Li@C_{60}$ relative to empty C_{60} was formed and deposited in the film with 30 eV of collision energy, which was much higher than that of Tellgmann et al. [9].

Lithium is able to insert into C_{60} with kinetic energy below 10 eV, and escape of Li^+ from LiC^+_n is easy. This points to an insertion mechanism in which Li^+ slips through the holes in the fullerene ring system. The "hole" in the six-membered rings in C_{60} is roughly 0.52 Å in radius. The ionic radius of Li^+ is 0.68 Å, slightly larger than the six-membered ring in C_{60}, so that Li^+ can pass through the ring with a relatively low activation energy. The quantum chemical calculations [13] and molecular dynamics simulations [14] supported the "slip-through" mechanism. On the other hand, the intense ion flux in our experiment makes the multiple collision between Li^+ and C_{60} possible. The energy transfered to C_{60} excites the C_{60} electronic states, thus C_{60} in the triplet excited state may open a "window" by breaking the C–C bond between 5- and 6-membered ring [2]. This makes the insertion of Li^+ easier. Moreover, the eliminated C_2 unit may be deposited on the film and react with C_{60} and other species including endohedral fullerene complexes to form adductive products as well as endohedral C_{60} adductive complexes. We see clearly that the most obvious difference between the detection of laser desorption of deposited films and the direct detection of collisional products used by Anderson et al. [3,4] is that adduct products can be observed in the former while only fragments can be observed in the latter. It is proposed that these adductive products formed in the film deposition processes.

3.2. Negatively charged ion spectra

The negatively charged time-of-flight mass spectra were obtained in the same energy range. Fig. 3 shows the negatively charged TOFMS of film deposited with Li^+ energy of 30 eV. The negatively charged ion spectrum is more complicated than the positively charged one. Since we did not observe any fragment and adductive ions in the negatively charged spectra of both pure C_{60} film and conventionally doped lithium fulleride, as well as alkali exohedral fullerenes as in the case of potassium and rubidium doped fulleride [15], these species should be formed in the collision and film deposition processes. Both fullerenes and endohedrals are neutral in the deposited films. Under laser irradiation, they were desorbed from the film, some of them were ionized and form a plasma. The electrons in the plasma can thus be captured by

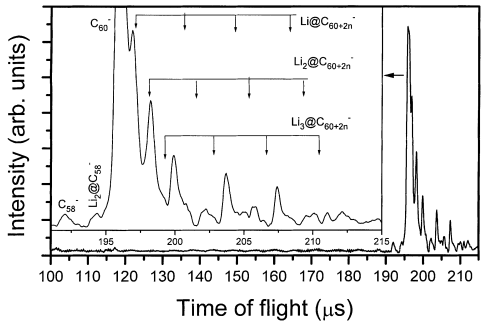

Fig. 3. Time-of-flight mass spectrum of negatively charged ions for the film deposited with a collision energy of 30 eV of Li^+ ion beam.

neutral chemical species in the time delay between the laser pulse and the electric accelerating pulse. The question is why the ion intensities of negatively charged adductive species are higher than those of positively charged ones. Perhaps it is because these species have been cooled down by emission of light or they come from the evaporation of species deep in the film only by thermal heating of laser irradiation.

From Fig. 3, we can clearly observe the $Li_mC^-_{60+2n}$ species with $m = 1, 2, 3$ and $n = -1, 0, 1, 2, 3, 4$ besides C^-_{2n} fragments and adductive products. These species are obviously observed at collision energies in the range of 30–50 eV. At lower energy (< 30 eV), the endohedrally bonded lithium atom repels the second Li^+ entering the C_{2n} cage. While at higher energy (> 50 eV), although the Li^+ has enough energy to overcome this repulsive barrier, the energy transfered to the cage may fragment the cage, thus both lithium atom and C_2 unit can be eliminated in the relaxation. The decrease in the intensity of $Li_mC^-_{60+2n}$ with the increase of m can be explained by the repulsive potential between endohedrally bonded lithium atom or atoms and the Li^+ coming later. By this explanation, we are sure that the observed Li_mC_{60+2n} species are lithium endohedral fullerenes, i.e. $Li_m@C_{60+2n}$.

For a hollow cage C_{60}, there are three possible binding arrangements for an adatom: "Exohedral", attached to the cage exterior by chemical bonds or polarization forces; "endohedral", trapped inside the cage; or "network", incorporated into the fullerene network. Our results do not allow direct determination of product structure, however, Anderson et al. [5] provided the evidence to support the endohedral binding picture. Besides, our films had fully exposed to air before we measured the mass spectra. The exohedrally bonded lithium should have been oxidized.

4. Conclusion

The reaction of neutral C_{60} vapor impacted with energetic Li^+ ion beam was investigated. Endohedral fullerenes $Li@C^+_{60}$ and $Li_2@C_{60}$ were observed obviously. The intensities of both lithium endohedral fullerenes $Li@C^+_{60-2n}$ with $n = 0, 1, 2, 3$ and fragments C^+_{60-2n} with $n = 1, 2, 3$ relative to empty C^+_{60} are fairly in agreement with the results of directly observed collisional products distribution via mass spectrometry. About 60% of $Li@C_{60}$ relative to empty C_{60} are produced and deposited in the film with a Li^+ collision energy of $\sim$30 eV due to higher flux of Li^+ ion beam. Besides the "slip-through" mechanism for the formation of lithium endohedral fullerenes, the "window" mechanism is also possible in the present high-flux collision experiment. The adductive products observed in the TOF mass spectra may be resulted from the reaction of C_2 and fullerenes in the film deposition process. In the negatively charged TOF mass spectra, we observed obviously the $Li_m@C^-_{60+2n}$ species with $m = 1, 2, 3$ and $n = -1, 0, 1, 2, 3, 4$. The intensity distribution and collision energy dependence of these species can be explained by the repulsive potential between endohedrally bonded lithium atom or atoms and the Li^+ impacted later on. Athough laser desorption can produce both fragments and adductive products, we are sure that collision and film deposition dominate this process in our observation.

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