Nonfragmenting charge transfer in slow peripheral C_{60}^{q+}-C_{60} collisions

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We have investigated electron transfer and fragmentation of C_{60} molecules in slow ($1q-2q$ keV) collisions with C_{60}^{q+} projectiles ($q=2-5$) and atomic C^{q+} projectiles at somewhat higher velocities. While the latter give the characteristic fragment distributions the former only yield intact C_{60}^{r+} target molecules. Further, the atomic carbon projectiles ionize the target C_{60} up to their incident charges, $r_{max}=q$, while the maximum target charges are limited to $r_{max}=\mathrm{Int}[(q+1)/2]$ for C_{60}^{q+} projectiles. The latter results are explained by considering the energy minima for q charges distributed on the equipotential surfaces of two touching spheres.

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There are currently strong research efforts aiming at technological developments of nanoelectronic devices based on fullerene materials [1]. A recent breakthrough on the way towards this goal is the demonstration of molecular-sized rectifying diodes using intramolecular junctions between semiconducting and conducting nanotubes [2]. However, the problem of controlling the wiring between devices of this kind remains, even though the growing of Y junctions between carbon nanotubes has been reported [3]. Further, the archetype fullerene, C_{60}, has been used as a tip in scanning tunneling microscopy [4] and there are several more examples in which a detailed understanding of the electronic properties of fullerenes is needed [5]. The electronic response of the free C_{60} molecule and its ions has been studied by means of their interactions with photons [6,7], electrons [8], and atomic ions [9–11] and through the radiative cooling of hot C_{60}^{-} [12]. It has also been demonstrated that the interactions between highly charged *atomic* ions and C_{60} could be accounted for in some detail by modeling the molecule as an infinitely conducting sphere (ICS) [9,11,13,14] or as a sphere with point charges moving on its surface [11,15–17]. In the present paper, we have investigated the conditions for electrical contact between two isolated, positively charged, C_{60} molecules, which relate to the problem of making contact between fullerene-based nanoelectronic devices and wires. Based on a simple model to account for the relation between the maximum target ionization stages and q in slow *peripheral* C_{60}^{q+}-C_{60} collisions, we conclude that such contacts may be established at rather large C_{60}-C_{60} distances.

We present experimental results on target-C_{60} ionization and fragmentation in

$$C_{60}^{q+}+C_{60}\rightarrow C_{60}^{(q-s)+}+C_{60}^{r+}+(r-s)e^{-}\rightarrow\cdots \qquad (1)$$

collisions at 2 keV for $q=2$ and $2q$ keV for $q=3$-5. These results are compared with similar ones for atomic C^{q+} projectiles of the same charge states colliding with C_{60}:

$$C^{q+}+C_{60}\rightarrow C^{(q-s)+}+C_{60}^{r+}+(r-s)e^{-}\rightarrow\cdots \qquad (2)$$

at $1q$ keV. We record the mass-to-charge distributions of the collision products at 90° to the incoming C_{60}^{q+} and C^{q+} beams using weak extraction fields. The time-of-flight spectra are dramatically different for C_{60}^{q+} and C^{q+} projectiles in two ways. First, with C_{60}^{q+} projectiles ($v=0.01-0.02$ a.u.) we only observe *intact* recoiling C_{60}^{r+} ions whereas the atomic projectiles ($v=0.1-0.2$ a.u.) induce the typical fragmentation modes (which are also observed when the C_{60} is excited by electron or photon impact [18]). Second, while the atomic projectile ions ionize C_{60} up to the incident charge q, the maximum target charge is lower for C_{60}^{q+}. The first observation demonstrates that the experiment selects only peripheral, or distant, C_{60}-C_{60} collisions and that the internal excitations for the corresponding impact parameters then are too small to give significant fragmentation. We have used the Monte Carlo method (for details see Ref. [11]) to calculate elastic (nuclear) energy loss with atomic C-C Moliere potentials [19] and electronic energy loss with the Firsov formula [20]. These calculations indicate that the experiment discriminates strongly against C_{60}^{q+}-C_{60} collisions with impact parameters smaller than about $20\,a_0$. The observed maximum target charge for the more peripheral collisions will be discussed in terms of the analogy with two isolated spheres which, after contact, separate with the same surface charge densities.

Fusion of two C_{60} molecules has been observed by Rohmund *et al.* [21,22] for singly charged (C_{60}^{+}) projectiles at lower energies, about 200 eV, as weak channels on the sides of much stronger fragmentation processes. Shen *et al.* [17] found that nonfragmenting electron capture was dominant in 100-keV C_{60}^{q+}-C_{60} collisions and that the most important (C_{60} projectile) fragmentation modes were sequential C_2 emission, fission, and catastrophic breakup leading to the characteristic bimodal distributions [23]. An additional mode in which the molecules are strongly deformed leading to ejection of small-fragment jets close to 90° in the center-of-mass system is expected for near-frontal collisions around 200 eV [24]. A key feature of the present experiment is that it is only

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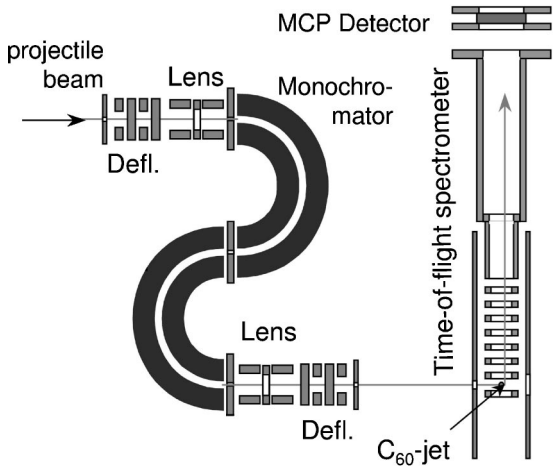

FIG. 1. A schematic of the experimental setup (cf. the text).

sensitive to fragments or recoiling intact molecules with small velocities along the projectile beam direction. This means that processes that transfer significant amounts of momenta to the target are strongly discriminated against.

Beams of C_{60}^{q+} and C^{q+} $(q=2-5)$ were delivered by the AIM facility at CEA-Grenoble. The multiply charged fullerene beams were extracted from a 14-GHz electron cyclotron resonance source with a low-power plasma supported by He and sublimated C_{60}. We used a plasma power of only 3–4 W to produce the C_{60}^{2+}, C_{60}^{3+}, and C_{60}^{4+} beams, while 6–7 W were used for the C_{60}^{5+} beam. Beams of fragmented and ionized C_{60} were separated according to their mass-to-charge ratios m/q, by a bending magnet and, thus, different ions of the same m/q were not resolved. This is not a problem for the C_{60}^{2+} beam since C_{30}^{+} is known to be very weak in the bimodal, collisionally induced, C_{60} fragment distribution [8,23]. For C_{60}^{3+}, C_{60}^{4+}, and C_{60}^{5+} there are overlaps with C_{20}^{+}, C_{15}^{+}, and C_{12}^{+} respectively. The contaminations were estimated from the energy spreads for the various m/q beams after the magnet. The fragment-beam components have wider energy distributions due to the kinetic-energy releases and the intact fullerene beams appear as narrow peaks on top of broader distributions. In addition, we measured the recoil-ion distributions due to 2-keV C_n^+-C_{60} collisions with $n=3$, 5, 7, 9, and 11. These spectra indeed showed fragmentation in much the same way as for the atomic projectiles. Thus, since the C_{60}^{5+}/C_{12}^{+}-C_{60} spectra showed very little fragmentation we concluded that the C_{12}^{+} contribution was rather weak. The atomic carbon beams were produced with a hotter plasma burning on CH_4.

The energy spreads in the m/q-analyzed beams were defined to $\pm 0.7q$ eV ($E=1q$ keV) and $\pm 1.5q$ eV ($E=2q$ keV) by means of a monochromator (cf. Fig. 1). The C_{60}^{q+} and C^{q+} beams were crossed with a perpendicular effusive C_{60} jet from an oven operated at about 500 °C. The axis of the time-of-flight spectrometer, of total length 30 cm, was oriented at 90° to the ion beam and the C_{60} jet. Slowly recoiling molecular ions were extracted from the interaction region by means of a weak, pulsed, electric field (50 V over 7 mm). These ions were accelerated to energies of 5.5 keV

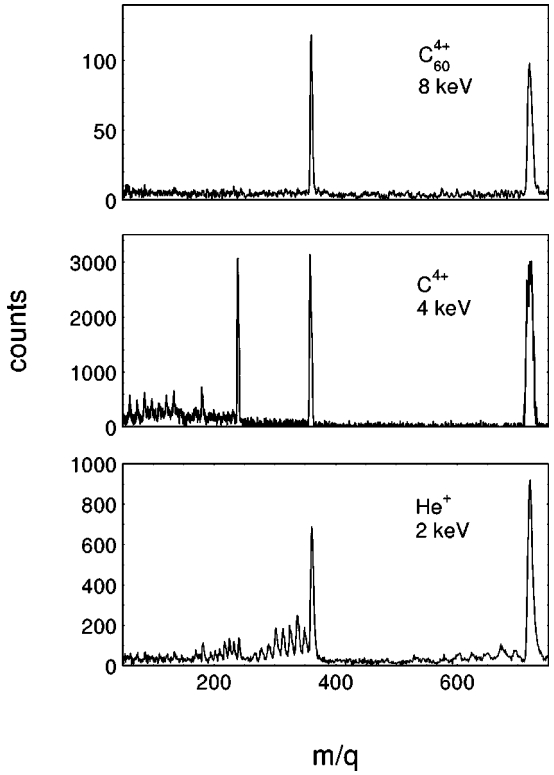

FIG. 2. Mass-to-charge spectra of ionized, intact or fragmented C_{60}-target molecules measured at 90° to the projectile beam direction for 8 keV C_{60}^{4+} (top), 4 keV C^{4+} (middle), and 2 keV He^{+} projectiles (bottom).

times their charge before they hit the microchannel plate detector. The beam was continuous and typical values of the extraction pulse lengths and repetition frequencies were 35 μs and 10 kHz, respectively. The lengths and amplitudes of these pulses were varied in order to verify full extraction efficencies for slow fragments and intact, ionized, target molecules.

In Fig. 2, we show a comparison between the time-of-flight spectra measured with 8 keV C_{60}^{4+}, 4 keV C^{4+}, and 2 keV He^{+} projectiles. The carbon atomic-projectile spectrum is dominated by intact C_{60}^{r+} ions with r ranging up to $r_{max}=4$. There is a little bit of evaporative C_2 emission associated with C_{60}^{2+}, barely visible at the left side of this peak. For C_{60}^{3+}, the characteristic C_2 emission series is clearly seen and is probably present also to the left of C_{60}^{4+} although there it is partly overlapping with smaller singly charged fragments from catastrophic breakups of the molecular cage.

In contrast, there are no indications above background of any fragments in the fullerene-projectile spectrum. Thus, there is no evaporative emission of C_2 units, no fission or any catastrophic breakup registered at 90° extraction relative to the C_{60}^{4+} beam. Such processes do of course occur for closer collisions but here they are suppressed due to large longitudinal momentum transfers, which are associated with large energy losses for the elastic (nuclear) scattering. In our model Monte Carlo calculations for one of the carbon atoms in the C_{60}^{4+} projectile colliding with the target C_{60} at $v=0.02$ a.u. we find a nuclear energy loss of 50 eV when the

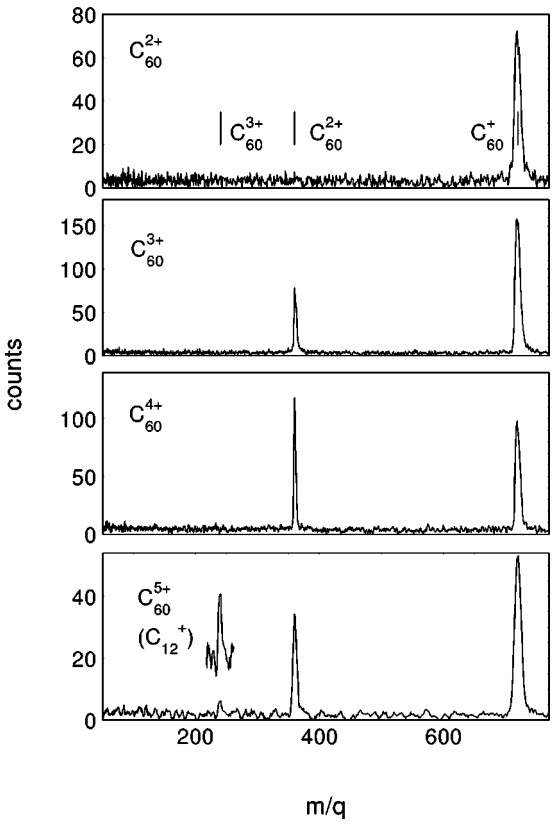

FIG. 3. Mass-to-charge spectra of ionized, intact, or fragmented C_{60} target molecules measured at 90° to the projectile beam for C_{60}^{q+}-C_{60} collisions. The C_{60} projectile charge states are ranging from $q=2$ (top) to $q=5$ (bottom). The collision energies are 2, 6, 8, and 10 keV for $q=2$, 3, 4, and 5, respectively. The C_{60}^{5+} beam is slightly contaminated by C_{12}^{+} (about 10%).

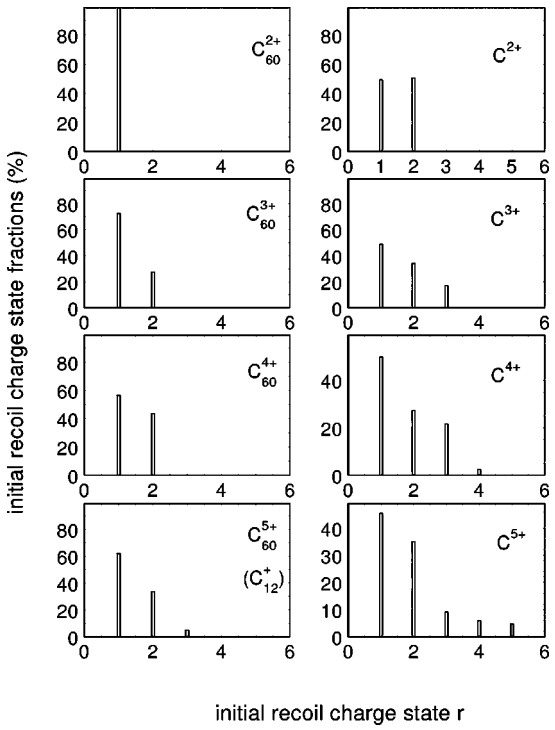

FIG. 4. The initial recoil ion charge-state distributions for C_{60}^{q+}-C_{60} and C^{q+}-C_{60} collisions. The initial distributions are the measured ones (corrected for detection efficiency variations) for the fullerene projectiles (no fragmentation has been detected), while the initial charge-state distributions for the atomic projectiles have been obtained by sorting the fragment peaks according to well-known fragmentation pathways (i.e., C_{60}^{r+} with $r \leqslant 3$ fragment predominantly through neutral C_2 emission while those of higher charges may also emit charged fragments or undergo fission).

atom passes at a distance of 8 a_0 from the center of the target. Several more of the carbon atoms in C_{60}^{q+} will, in such a collision, come close enough to transfer substantial amounts of additional energy (due to elastic scattering) and thus increase the probability for fragmentation even further. We find that it is only for C_{60} center-center distances larger than $20\,a_0$ that we can expect nuclear energy transfers well below 100 eV and, thus, $20\,a_0$ appears as a lower impact parameter limit for detection of ionized intact target molecules under the present experimental conditions. At this distance and velocity, electronic excitations are negligibly small. In contrast, the fragmentation for the C^{4+} projectiles with $v=0.12$ a.u. are dominated by electronic excitations. According to the Monte Carlo calculations the spectrum for C^{4+} projectiles is due to distant, peripheral *and penetrating* collisions of which the latter two types contribute to the fragmentation. The spectrum for C_{60}^{4+}, on the other hand, is only due to peripheral and distant collisions, since the large nuclear stopping power prohibits slow carbon atoms to pass through the target. At the bottom of Fig. 2 we show the recoil-ion spectrum for He^{+} at $v=0.14$ a.u., which has a strong C_2 evaporation series already for C_{60}^{2+}. This is due to the smaller distances required for multiple-electron removal by a singly charged, as compared to a multiply charged, projectile. The He^{+} spectrum, for which $r_{max}>q$ due to strong internal heating [25], is in essence identical to the one measured with a different extraction technique by Schlathölter *et al* [25]. For the C_{60}^{4+} beam, the maximum recoil charge is $r_{max}=2$ and there is no trace of C_{60}^{3+} (cf. Fig. 2).

In Fig. 3, we show the charge-state distributions due to C_{60}^{q+} projectiles in charge states $q=2-5$. The results are qualitatively in accordance with those for C_{60}^{4+}; only intact recoil molecules C_{60}^{r+} in narrow ranges of charge states, $r+$, are observed. One and only one electron is transferred in C_{60}^{2+}-C_{60} collisions. At the most two electrons are transferred to C_{60}^{3+} or C_{60}^{4+} projectiles. For C_{60}^{5+} there is, except for the peaks at C_{60}^{+} and C_{60}^{2+}, a small peak also for C_{60}^{3+}.

In Fig. 4, we compare the relative, initial (before fragmentation), recoil charge-state distributions for atomic and fullerene projectiles. For the former, we have sorted the corresponding fragment intensities according to well-established fragmentation modes (e.g., emission of neutral and/or charged C_2 fragments) giving information on the parent C_{60} charge before fragmentation [23].

For C_{60}^{q+}-C_{60} collisions, the maximum recoil charge states are given by $r_{max}=\mathrm{Int}[(q+1)/2]$. This can be understood from very simple considerations if we assume that the colliding C_{60} molecules may be modeled as contacting spheres

of the same radius. When the spheres are in contact, a common equipotential surface on which the active charge carriers move freely is formed. These active (positive) charges repel each other and they move in order to minimize the total repulsive energy. This means that q positive charges will be distributed equally on the two spheres for even q while the target may or may not carry away the last charge, after even partition, for odd q. This reasoning leads to the predictions that the maximum target charge states should be $r_{max}=1,1,2,2$, and 3 for $q=1,2,3,4$, and 5, respectively, which is in perfect agreement with the observation. In addition, the intensities of the C_{60}^{r+} peaks at $r=r_{max}$ should be lower for odd than for even q since there is a probability of 1/2 for the last charge to end up on the target, which is in qualitative agreement with Fig. 4. Note, however, that a more detailed and quantitative discussion of the relative intensities of the C_{60}^{r+} peaks requires a treatment of electron transfer also at larger distances. Simple estimates using the ICS [11] model yield first critical over-the-barrier distances around $23\,a_0$, which only depend weakly on q. The results in Fig. 4 show that there are regions of impact parameters for which one but not two electrons may be transferred from the target indicating that the electrical contact is established for C_{60} center-center distances of at least $20\,a_0$ (detection limit) and substantially less than $30\,a_0$.

The maximum target-C_{60} charge states for the *atomic* C^{q+} projectiles are $r_{max}=q$. This result follows directly from a consideration of sequential over-the-barrier charge transfer along projectile trajectories a few atomic units outside the radius of a metal sphere even when full screening of the projectile charge is assumed [11].

In this paper we have studied *peripheral* C_{60}^{q+}-C_{60} ($q=2-5$) collisions at low velocities. The closer collisions in which the projectile and the target may exchange large amounts of momenta are strongly suppressed by the extraction method. Our Monte Carlo calculations show that collisions with impact parameters in excess of $20\,a_0$ are required in order for the nuclear energy loss to be small enough to be compatible with the observed nonfragmenting ionization of the target C_{60}. The charge-state distributions of the intact target molecules created extend up to maximum values $r_{max}=\mathrm{Int}[(q+1)/2]$, which we readily account for by modeling the molecules as two spheres which, for short times during the collisions, have been in electrical contact. The electrical contact between two isolated charged C_{60} molecules is thus established already at center-center distances in excess of $20\,a_0$ and the charges redistribute on a time scale shorter than 10^{-14}–10^{-15} s (the contact time).

Finally, we note that highly efficient electrical contacts between fullerene materials may be created without actually forming molecular bonds as has been demonstrated by the rapid flow of charge between isolated C_{60} molecules with their cage surfaces separated by several atomic units. Similar *intermolecular* junctions may perhaps be of use in the nanoelectronic technology.

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