

Formations of Dumbbell C_{118} and C_{119} inside Clusters of C_{60} Molecules by Collision with α Particles

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We report highly selective covalent bond modifications in collisions between keV alpha particles and van der Waals clusters of C_{60} fullerenes. Surprisingly, C_{119}^+ and C_{118}^+ are the dominant molecular fusion products. We use molecular dynamics simulations to show that C_{59}^+ and C_{58}^+ ions—effectively produced in prompt knockout processes with He^{2+} —react rapidly with C_{60} to form dumbbell C_{119}^+ and C_{118}^+ . Ion impact on molecular clusters in general is expected to lead to efficient secondary reactions of interest for astrophysics. These reactions are different from those induced by photons.

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Photodriven intracluster reactions have been observed in clusters of fullerenes [1,2] and in, e.g., clusters of methanol, water, dimethyl ether, and acetic acid molecules [3]. Clusters of fullerenes are of particular interest in this context as C_{60} and C_{70} recently have been observed in space [4,5] at temperatures indicating that they may reside on grains [4] or are in the solid phase (fullerite) [6]. The question of how fullerenes form in space and elsewhere [7–9] is still open and here we report experimental observations on specific very efficient fullerene growth processes inside small pieces of fullerite material. These ion-impact induced growth processes in which so-called dumbbell fullerene systems are formed are inherently different from the ones induced by photons [1,2] for reasons that will be discussed in the following.

The lowest energy barrier for formation of covalently bound dumbbell C_{120} from two neutral C_{60} molecules is roughly one or two electron volts [10]. Thus, two C_{60} molecules in their ground states may, in principle, form such a C_{120} system when the center-of-mass kinetic energy is larger than this barrier. However, molecular dynamics simulations by Jakowski, Irle, and Morokuma [11] have shown that, in practice, much larger kinetic energies are needed to form dumbbell C_{120} (≥ 60 eV) or single-cage C_{120} (≥ 100 eV) efficiently [11]. The reason is that at least one C_{60} cage needs to rearrange to form covalent bonds with the other cage on very short, picosecond, time scales. This is highly unlikely in a single encounter at low kinetic energy, as the transferred energy is redistributed over the fullerene molecule and a critical energy needs to be localized in a specific bond in order to break it. On the other

hand, the reverse reaction (dissociation) may proceed at much lower energies but after many vibrations and on much longer time scales. For C_{60} - C_{60} collisions at kinetic energies above 60/100 eV covalent bond formation becomes much more likely but will then also give internally hot dumbbell/single-cage C_{120} . Single-cage C_{120} will fragment through sequences of C_2 emissions yielding molecular mass distributions with an even number of carbon atoms [1] as C_2 loss is the lowest-energy dissociation channel at about 10 eV. The dumbbell $C_{120} \rightarrow C_{60} + C_{60}$ dissociation energy is only a couple of eV [10] and this will then be the dominant decay channel. In Fig. 1 we indicate

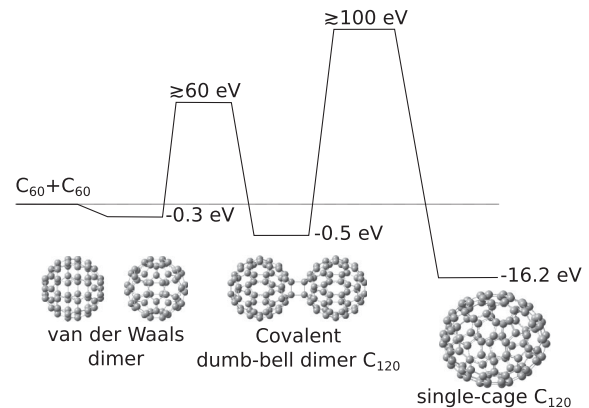


FIG. 1. Center-of-mass kinetic energies required to efficiently form the covalent C_{120} dimer (≥ 60 eV) or the fully fused C_{120} fullerene (≥ 100 eV) in $C_{60} + C_{60}$ collisions according to molecular dynamics simulations [11]. Binding energies are from the present calculations (cf. text).

binding energies of the van der Waals dimer, dumbbell C_{120} , and the C_{120} fullerene from reference molecular structure calculations [B3LYP-6-31G(d)] with basis set superposition error correction [12] and Grimme's dispersion correction [13].

In this Letter we report combined experimental and theoretical results on covalent bond modification processes following collisions between 22.5 keV He^{2+} and van der Waals clusters of C_{60} molecules. These processes are very efficient and take place during the fragmentation of the cluster—i.e., on the few picosecond time scale. Surprisingly, dumbbell C_{119}^+ and C_{118}^+ are the dominant reaction products. The He^{2+} -ion impact is key here. It leads to prompt knockout of one or two carbon atoms producing C_{59}^+ and C_{58}^+ inside the cluster. Further, these ions are very reactive in comparison with C_{60}^+ (cf. Fig. 1). There are no adjacent pentagons in C_{60}^+ while such motifs are present in C_{58}^+ . Thus, while the bonds are mainly of the unreactive sp^2 type in C_{60}^+ they have more sp^3 character in C_{58}^+ , which strongly favors covalent bonding with C_{60} . The C_{59}^+ is even more reactive as it has 8- and 9-membered rings with unsaturated carbon atoms.

The experimental part of the work was carried out at the ARIBE facility at GANIL in Caen, France. There, a 22.5 keV He^{2+} ion beam was produced in an ECR ion source and chopped into 0.5 μs long pulses at a rate of 1.9 kHz. These projectile ions interact with clusters of fullerenes from a liquid nitrogen cooled cluster aggregation source operated with a flow of He gas [14]. The cold source produces neutral van der Waals clusters following a broad lognormal size distribution [15]. When the beam pulse has left the interaction region, the extraction voltage is switched on after a delay of 0.1 μs and the mass-to-charge ratio of the positively charged collision products are measured by a linear time-of-flight mass spectrometer. Secondary electrons are emitted when the ions hit a metal plate at the end of the spectrometer and these electrons are guided to a MCP detector by a weak magnetic field. This gives high detection efficiencies, which allows for coincidence measurements of charged fragments stemming from single collision events.

In Fig. 2 we show two representations of the measured mass-to-charge state distributions. The top panel shows the total distribution, i.e., the spectrum of all detected ions, and the bottom panel shows the distribution for ions detected in coincidence with one or several intact C_{60}^+ ions. In both cases the C_{60}^+ peak dominates the intensity providing clear evidence that most collisions between He^{2+} ions and van der Waals clusters of C_{60} molecules lead to single- or multiple ionization *and* fragmentation of the clusters, but rarely to fragmentation of the individual C_{60}^+ ions. The C_{60}^+ peaks are broad in both spectra due to kinetic energy releases which become much larger when several C_{60}^+ ions are emitted due to stronger Coulomb repulsions in these cases. The typical kinetic energies [16] for emitted C_{60}^+ ions are 0.9 ± 0.1 eV as extracted from the full width

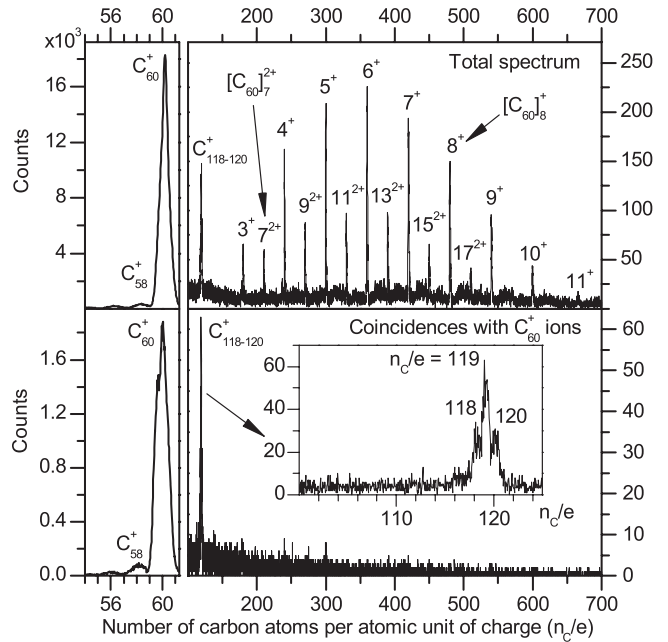


FIG. 2. The measured mass-to-charge distributions following 22.5 keV $He^{2+} + [C_{60}]_n$ collisions. The top and bottom panels show the distributions including all events (total spectrum) and for events correlated with one or several intact C_{60}^+ ions (coincidences with C_{60}^+ ions), respectively. Note the different scales for the left and right panels. The inset in the lower right panel shows a zoom-in on the mass region from 100 to 125 carbon masses per atomic unit of charge, n_C/e .

at half maximum of the C_{60}^+ peak in the lower left panel of Fig. 2. Small amounts of C_{60-2m}^+ fragments are also observed and are mainly due to evaporation of $m C_2$ units [7] from the few hotter C_{60}^+ ions emitted from the clusters.

The narrow $[C_{60}]_n^+$ and $[C_{60}]_n^{2+}$ peaks at large mass-to-charge ratios (labeled as n^+ and n^{2+} in the upper right panel in Fig. 2) are mainly due to collisions in which the clusters have been ionized but not fragmented. These peaks are observed for events in which one and only one ion is produced and are very weak in coincidence with C_{60}^+ ions as can be seen in the lower right panel of Fig. 2. The latter spectrum is instead dominated by peaks at the positions for 120, 119, and 118 carbon masses per atomic unit of charge, n_C/e , where the intensity relation is 0.44:1:0.48 in a Gaussian fit. Taking the differences in flight times into account we find that these three peaks are almost twice as broad as (a factor of 1.7 ± 0.1 broader than) the narrow $[C_{60}]_n^+$ ($[C_{60}]_6^+$) peaks in the upper panel of Fig. 2. This shows that the $n_C/e = 120, 119, 118$ peaks are due to cluster fragmentation processes. The peak at $n_C/e = 120$ may be due to (i) $[C_{60}]_2^+$ dimers remaining after emissions of C_{60}^+ ions and C_{60} molecules from larger clusters similar to what has been observed for other loosely bound cluster systems [17,18], and/or (ii) $C_{60}^+ + C_{60} \rightarrow C_{120}^+$ covalent bond formation. The peaks at $n_C/e = 119$ and $n_C/e = 118$ are, in contrast, most likely due to low energy

$C_{59}^+ + C_{60}$ and $C_{58}^+ + C_{60}$ reactions in which covalently bound C_{119}^+ and C_{118}^+ dumbbell systems are formed. The highly reactive C_{59}^+ and C_{58}^+ ions are efficiently produced in prompt single- and double knockout processes together with singly ionized C_{60} molecules along ion trajectories through the clusters. Similar knockout processes have been identified in $C_{60}^- + He$ collisions from which only C_{59}^+ and C_{58}^+ fragments but no smaller fragments like C_{56}^+ were detected [19]. For C_{60}^- collisions on Ar or Xe, C_{59}^+ fragments were not observed [20] because penetrating collisions often lead to knockouts of several carbon atoms due to larger nuclear stopping energies (see also Ref. [21]).

We have performed stopping energy calculations for 22.5 keV He^{2+} ions colliding with C_{60} monomers and $[C_{60}]_n$ clusters, in order to investigate the significance of direct knockout processes. Density functional theory (DFT) [22] is then first used to calculate the electron density distribution for the C_{60} monomer. This distribution is used to model the individual molecules in the $[C_{60}]_n$ clusters which are placed according to icosahedral cluster geometries [23]. We have verified the validity of this simplified approach by comparison with the real electron density distribution in the case of the van der Waals dimer. In the next step we employ a Monte Carlo approach to launch large numbers of He^{2+} ions at such, randomly oriented, C_{60} monomers or clusters where we use friction coefficients from Puska and Nieminen [24] (fits to their results) to determine the electronic energy loss for ions traversing the target electron clouds. We use our DFT results for the electron density distributions along each individual ion trajectory and we also calculate the related nuclear energy loss along the same trajectories using the well-established method described, for example, in Ref. [20]. We find that electronic stopping processes dominate and induce typical excitation energies in excess of 100 eV and with wide distributions and a weak dependence on cluster size, while typical nuclear stopping energies are significantly lower. In most cases the resulting excitations should lead to fragmentation of the clusters but seldom to fragmentations of the individual molecules which is consistent with the present experimental observations (cf. Fig. 2). The reason is that the electronic excitation

energy is distributed rapidly [25,26] over the whole cluster before fragmentation such that the individual molecules most often become sufficiently cold to stay intact [17].

From the Monte Carlo simulations described above, we have also extracted the absolute cross sections for transfer of at least 15.1 eV—the energy required to remove a single carbon atom in a hard He-C nuclear scattering process in C_{60} . For this we have used DFT at the B3LYP-6-31G(d) level to calculate the difference in energy between the C_{60} and the $C_{59} + C$ systems where the geometry of the C_{59} is assumed to be frozen during the very fast knockout process. We have further calculated the *adiabatic* energies at the same level of DFT for $C_{60}^+ \rightarrow C_{58}^+ + C_2$, $C_{60}^+ \rightarrow C_{59}^+ + C$, and $C_{59}^+ \rightarrow C_{58}^+ + C$ dissociation to be 10.7, 11.9, and 5.4 eV, respectively. Thus, C_{59}^+ is very fragile and a second carbon atom may be easily lost in some of the knockout processes.

Using the same Monte Carlo approach, we calculate the single knockout cross sections for 22.5 keV He^{2+} impact to be $0.4 \times 10^{-15} \text{ cm}^{-2}$ for C_{60} monomers and $5 \times 10^{-15} \text{ cm}^2$ for $[C_{60}]_{13}$ clusters. The geometrical cross section of a C_{60} molecule is about $4 \times 10^{-15} \text{ cm}^2$, and, using the calculated numbers above we conclude that substantial fractions (about 10%) of the target-penetrating collisions lead to single-atom knockout for clusters in the present size range. The registered numbers of events containing either C_{119}^+ or C_{118}^+ ions are about 4.5×10^3 for the spectrum in Fig. 2. The corresponding total number of events is 7×10^5 . We use the over-the-barrier concept [27] to estimate that only about 30% of the latter are due to penetrating collisions for typical cluster sizes. The remaining part is due to ionizing peripheral collisions which are too distant for single atom knockout. With this we estimate that $4.5 \times 10^3 / (0.3 \times 7 \times 10^5)$, roughly 2%, of the penetrating collisions yield C_{119}^+ or C_{118}^+ . That is, one out of five of the prompt single atom knockouts lead to dumbbell formation corresponding to a cross section of $\sim 1 \times 10^{-15} \text{ cm}^2$ for $[C_{60}]_{13}$.

We have performed classical molecular dynamics (MD) simulations for $C_{60}^+ + C_{60}$, $C_{59}^+ + C_{60}$, and $C_{58}^+ + C_{60}$ collisions and for C_{59}^+ and C_{58}^+ interacting with several C_{60} molecules inside fragmenting clusters in order to

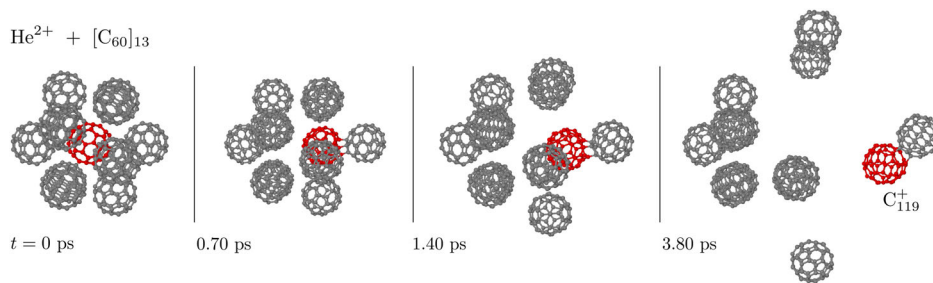


FIG. 3 (color online). Left to right: A cluster of thirteen molecules just after a prompt single carbon knockout process $He^{2+} + C_{60} \rightarrow C_{59}^+ + C + \dots$, followed by three snapshots from our molecular dynamics simulations. The C_{59}^+ molecule (in red) collides with a C_{60} molecule such that a covalently bound dumbbell C_{119}^+ system forms within a few picoseconds.

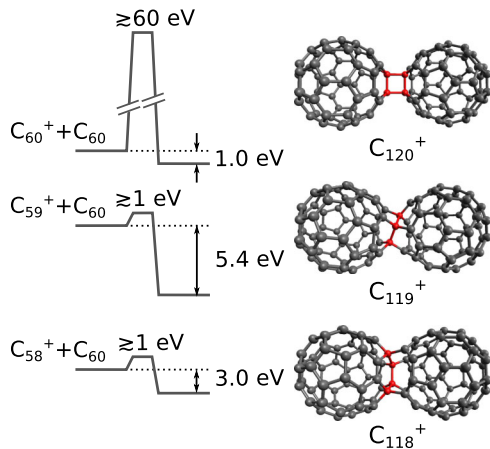


FIG. 4 (color online). Kinetic energies required for covalent bond formations in collisions between C_{58}^+ , C_{59}^+ , or C_{60}^+ and C_{60} on picosecond time scales according to the present molecular dynamics simulations. The dissociation energies are calculated for the ground states of the most stable dumbbell structures (cf. text).

investigate efficiencies of bond formation processes. We have varied the center-of-mass collision energies and used different internal temperatures of the ions and the DL_POLY package [28] in the microcanonical (NVE) ensemble. With the Tersoff potential [29] for carbon-carbon interactions we find that covalently bound dumbbell C_{119}^+ and C_{118}^+ systems are formed for collision energies all the way down to 0.9 eV, i.e., the typical kinetic energy which we measure for intact fullerenes emitted from fragmenting clusters. We have confirmed that the variation of the average Tersoff potential with the intercage distance is very similar to the variation of the density functional theory [BLYP-6-31G(d)] potential with rigid fullerene cages.

In Fig. 3, we show results from the MD simulations following prompt (femtosecond) knockout of a single carbon atom from the central C_{60} molecule in a $[C_{60}]_{13}$ cluster in the archetype icosahedral geometry [23]. The so-formed C_{59}^+ ion is given a kinetic energy of a few eV for the simulations and in the figure we see how two molecular cages link to form a covalent C_{119}^+ system within a few picoseconds. A possible C_{119}^+ structure with three intermediate atoms forming sp^3 bonds between the two cages is shown in Fig. 4. Interestingly, the C_{119}^+ and C_{118}^+ systems have adiabatic dissociation energies of 5.4 and 3.0 eV, respectively, which are significantly higher than that of C_{120}^+ at 1.0 eV—as we have calculated at the B3LYP-6-31G(d) level of theory for the ground states in all three cases. Thus, not only do the C_{119}^+ and C_{118}^+ systems form much more readily than C_{120}^+ , they are also inherently more stable and therefore more likely to remain intact once they are formed (cf. Fig. 4).

Ion-induced bond rearrangement processes have been observed before for, e.g., highly charged ions colliding on *single* molecules [30]. In this Letter we have shown that

keV ions may induce very efficient routes to molecular growth processes when such rearrangement processes involve other molecules *inside a cluster*. We have found that ion impact often leads to nonstatistical decay processes and thus to highly reactive fragments of the individual molecules while photoabsorption leads to statistical fragmentation favoring more stable and less reactive fragments. Until now it has been assumed that processing of molecules and molecular clusters in space mostly is driven by interactions with photons. Examples here are the processing of interstellar molecules, molecular clusters, grains, etc., by UV photons in the outflows from dying stars [31] and formation of fullerenes from, e.g., large polycyclic aromatic hydrocarbon (PAH) molecules in the interstellar medium [9]. The present results demonstrate that processing by ions likely opens up very different molecular growth routes. This ion processing may be particularly relevant for shocks driven by supernova explosions.

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