Abstract. In this work, we show that keV-ions are able to remove single carbon atoms from individual fullerenes in clusters of C$_{60}$ molecules. This very efficiently leads to the formation of exotic C$_{39}^+$ dumbbell molecules through secondary C$_{59}^+$ + C$_{60}$ collisions within the fragmenting cluster. Such molecular fusion processes are inherently different from those induced by photons where only products with even numbers of carbon atoms are observed. Thus, ion collisions ignite unique and hitherto overlooked secondary reactions in small aggregates of matter. This relates to the question on how complex molecules may form in e.g. space.

1. Introduction

Fullerenes are hollow all-carbon molecules with the soccer-ball like C$_{60}$ as the most famous family member [1]. When they are hot, C$_{60}$ and other fullerenes may get rid of their excess energy by emission of photons, electrons and/or by fragmentation. The latter normally proceeds through the emission of C$_2$ molecules - regardless of excitation agent (photons, electrons, or ions). This is well understood based on a statistical picture where the excitation energy is redistributed among all degrees of freedom before decay, such that the lowest energy dissociation pathway is dominant. Indeed, about 10 eV is needed for C$_2$-emission from C$_{60}$ [2], while about 15 eV is required for single carbon loss [3]. Interestingly, non-statistical fullerene decay has been observed in collisions between C$_{60}$ and He/Ne atoms [4, 5], but only at low center-of-mass collision energies where single carbon atoms may be promptly knocked-out in nuclear stopping processes. Under such conditions the electronic stopping is low and C$_{59}^+$ may therefore be formed sufficiently cold to survive long enough for experimental detection.

In this work, we show that it is also possible to knock-out single carbon atoms from fullerenes inside weakly bound clusters at high (keV) center-of-mass collisions energies. Here, the key is the rapid distribution of excess energy over the whole cluster such that the so formed C$_{59}^+$ ions may
stay intact on the picosecond timescale. We demonstrate that these highly reactive fragments then have time to react with neighboring intact C\(_{60}\) molecules, efficiently forming covalently bound dumbbell shaped C\(_{119}\) molecules.

The paper is organized as follows. In Sec. 2 we give a brief description of the experimental techniques used to analyze the positively charged collision products. The experimental results are analyzed in Sec. 3. In Sec. 4 we present Monte Carlo simulations of nuclear stopping processes for He\(^{2+}/\)Ar\(^{2+}\)-ions interacting with C\(_{60}\) and Molecular Dynamics simulations of bond formations in C\(_{59}^{-}\) - C\(_{60}\) collisions. The summary and conclusions are presented in Sec. 5.

2. Experimental techniques

![Figure 1. Schematic of the time-of-flight mass spectrometer used to analyze the positively charged products from collisions between keV-ions and clusters of fullerenes.](image)

The experiments were performed at the ARIBE facility at GANIL in Caen, France. The experimental procedure has been discussed in detail elsewhere [6] and only a brief description is given here. 22.5 keV He\(^{2+}\) and 12 keV Ar\(^{2+}\) ion beams are produced in an Electron Cyclotron Resonance (ECR) ion source and then chopped at a repetition rate of a few kHz into microsecond long beam pulses. These projectile ions interact with neutral van der Waals clusters of fullerenes from a liquid nitrogen cooled cluster aggregation source. The source produces a broad distribution of cluster sizes which most likely follows a log-normal distribution [7]. After the beam pulse has left the interaction region the positively charged collision products are analyzed with the aid of a linear time-of-flight mass spectrometer (cf. Fig. 1) [8]. Secondary electrons are emitted when the ions hit a gold coated steel plate at the end of the spectrometer and are guided to a microchannel (MCP) detector by a weak magnetic field. This gives a high detection efficiency, and thus allows for coincidence measurements of charged fragment from single collision events.

3. Experimental results

In Fig. 2 we show the mass spectra for 22.5 keV He\(^{2+}\)+[C\(_{60}\)]\(_n\) collisions. All charged collision products are displayed in the upper panel. The most prominent peak corresponds to C\(_{60}^+\)-ions, which shows that the clusters most often completely disintegrate into their individual molecular building blocks similar to other loosely bound cluster systems [9, 10]. On the left hand side of this peak, there are much less intense peaks due to the emission of one and two C\(_2\) molecules from statistically driven fragmentation processes. Thus, the energy is rapidly redistributed over the whole cluster such that the emitted fullerene ions in most cases are sufficiently cold to survive until they are detected. On the right hand side of the monomer peak, there is a broad distribution of rather weak peaks corresponding to singly and doubly charged intact clusters.
Figure 2. Mass-to-charge spectra for collisions between 22.5 keV He$^{2+}$ ions and clusters of fullerenes. From top to bottom: Total spectrum, single stop spectrum - only one ion detected per collision event, and coincidence spectrum - events recorded in coincidence with one or several C$_{60}^+$ ions. Note the differences in intensity scales for the monomer region (left panels) and the cluster region (right panels). The narrow [C$_{60}$]$^+$ and [C$_{60}$]$^{2+}$ peaks in the cluster region are labelled $n^+$ and $n^{2+}$, respectively.
Figure 3. Parts of the mass-to-charge spectra due to 22.5 keV He$^{2+}$+[C$_{60}$]$_n$ (left panel) and 12 keV Ar$^{2+}$+[C$_{60}$]$_n$ collisions (right panel). The curves show events recorded in coincidence with one or several C$^+_1$ ions. As shown in the middle panel of Fig. 2, these are predominantly single stop events - i.e. not correlated with other charged products. We thus attribute these peaks to the most distant electron transfer collisions where the clusters are singly and doubly ionized and for which low amounts of energy are deposited in nuclear and electronic stopping processes. In the lower panel of Fig. 2 we show events recorded in coincidence with one or several C$^+_1$ ions. These stem from closer collisions leading to multiple ionization and high energy deposition such that there is only what appears to be one single broad peak left in the cluster region.

A zoom-in of this broad peak is shown in left panel of Fig. 3, which reveals that it has three components corresponding to 118, 119, and 120 carbon atoms. The peak at $n_C/e=120$ is most likely due to weakly bound [C$_{60}$]$^+_2$ dimers remaining after decay of larger clusters [9, 10] and possibly also due to C$^+_1$+C$_{60}$+C$_{60}$ → C$^+_1$120 covalent bond formation [11, 12]. The peaks at $n_C/e=119$ and $n_C/e=118$ are, as we will show below, due to low energy C$^+_1$59 + C$_{60}$ and C$^+_1$58 + C$_{60}$ reactions in which covalently bound C$^+_1$119 and C$^+_1$118 dumb-bell systems are formed. In the right panel of Fig. 3, we show the corresponding region of the mass spectrum due to 12 keV Ar$^{2+}$+[C$_{60}$]$_n$ collisions. In this case there are also peaks from $n_C/e=116$ and down to $n_C/e=106$.

4. Computational and modeling results
We have performed electronic and nuclear stopping energy calculations for 22.5 keV He$^{2+}$ and 12 keV Ar$^{2+}$ colliding with C$_{60}$ monomers and clusters to guide the interpretations of the experimental results [3]. We find that the electronic stopping is the dominant mechanism for dissipation of the projectile kinetic energy along the ion trajectories, but this leads to rather low internal fullerene heating since the excess energy may be rapidly redistributed among all the cluster constituents. Thus, highly reactive products (e.g. C$^+_1$59) may survive on the
Figure 4. Results from Monte Carlo calculations of nuclear stopping energies for 22.5 keV He\textsuperscript{2+} and 12 keV Ar\textsuperscript{2+} colliding with C\textsubscript{60} monomers. The upper and lower left panels show the 22.5 keV He\textsuperscript{2+} trajectories leading to single and double carbon knock-outs, respectively. The corresponding results for 12 keV Ar\textsuperscript{2+} projectiles are shown in the middle panel. The lower right panel shows the absolute cross sections for producing C\textsubscript{m}-fullerenes in direct knock-out processes (cf. text).

picosecond timescale following prompt knock-out processes due to nuclear stopping. This allows for secondary reactions inside the clusters where the product reacts with a neighbouring C\textsubscript{60} to form covalently bound systems. The results from the present nuclear stopping calculations are shown in Fig. 4, where we have followed Larsen et al [4] and used a screened Bohr potential for the He/Ar-C interactions and the knock-out threshold energy (15.1 eV) from molecular structure calculations at the B3LYP/6-31G(d) level [13]. The left and middle panels of Fig. 4 show the He\textsuperscript{2+}- and Ar\textsuperscript{2+}-trajectories leading to single and double carbon knock-outs for a fixed C\textsubscript{60} geometry (ion trajectories perpendicular to the paper plane). In the He\textsuperscript{2+} case single knock-outs are more likely than double knock-outs, while Ar\textsuperscript{2+} projectiles display the opposite behavior as the energy transfer increases for heavier projectiles. This is further illustrated in the lower right panel of Fig. 4, which shows the absolute cross sections for producing C\textsubscript{m}-fullerenes in such prompt knock-out processes. Thus, the richer distribution of covalent bound systems for Ar\textsuperscript{2+} than for He\textsuperscript{2+} projectiles (cf. Fig. 3) reflects the stronger propensity for forming highly reactive smaller fragments in the former case.

In order to further investigate the bond formation processes, we have performed Molecular Dynamics calculations for binary C\textsubscript{59} + C\textsubscript{60} collisions and such interactions inside fragmenting
clusters. We have used the DL_POLY package [14] in the micro canonical (NVE) ensemble and the Tersoff potential [15] for carbon-carbon interactions. A snapshot from one of these simulations is shown in Fig. 5, which shows that a covalently bound dumbbell \( \text{C}^{+}_{119} \) system is rapidly formed on the picosecond timescale in a fragmenting \( [\text{C}_{60}]^{13} \) cluster. By systematically varying the center-of-mass collision energies and ion temperatures, we found that such systems are efficiently formed for collision energies down to about 1 eV. Interestingly, about 60 eV is required to form \( \text{C}^{+}_{120} \) in \( \text{C}^{+}_{60} + \text{C}_{60} \) collisions. The reason for this is that the bonds in \( \text{C}^{+}_{60} \) are mainly of the unreactive sp\(^2\) type, while \( \text{C}^{+}_{59} \) is highly reactive due to 8- and 9-membered rings with unsaturated carbon atoms. Our calculated B3LYP/6-31G(d) values of the adiabatic dissociation energies for \( \text{C}^{+}_{119} \) and \( \text{C}^{+}_{120} \) are 5.4 eV and 1.0 eV, respectively. Thus, \( \text{C}^{+}_{119} \) is more likely to survive until experimental detection since it is inherently more stable than the \( \text{C}^{+}_{120} \) dumbbell. All smaller even-numbered fragments such as e.g. \( \text{C}^{+}_{58} \) have adjacent pentagons and hence have bonds with the more reactive sp\(^3\) character. This facilitates formation of smaller dumbbell shaped systems (cf. Fig. 3).

5. Summary and conclusions

In summary, we have demonstrated that keV-ions are able to induce molecular fusion processes in collisions with weakly bound clusters of fullerenes. These processes are very different from those induced by photons [16, 17] as fusion products with an odd number of carbon atoms may be efficiently formed. The production scenario for such dumbbell shaped \( \text{C}^{+}_{119} \) molecules is:

1. Highly reactive \( \text{C}^{+}_{59} \) is produced by single carbon knock out.
2. The cluster environment effectively cools the system.
3. \( \text{C}^{+}_{59} \) is extremely reactive and forms covalent bonds with \( \text{C}_{60} \) while the cluster explodes on the time scale of a few picoseconds.
4. \( \text{C}^{+}_{119} \) is thermodynamically stable and its ground state is bound by 5.4 eV.

Collisional processing of complex molecules is common in the interstellar medium due to high velocity projectiles from interstellar shocks, hot gas and cosmic rays [18, 19]. Here we demonstrate that these processes, which have been largely overlooked in the literature, may lead to very efficient molecular growth routes.
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