Two-Step Explosion Dynamics of Highly Charged Fullerene Cations C_{60}^{q+} (q = 20–60)

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Abstract: C_{60}^{q+} (q = 20-60) firstly ejects fast atomic cations C^{z+} ($z \geq 1$) *via* Coulomb explosions on a 10 fs timescale. Thermal evaporations of slow atomic and molecular fragments subsequently occur in 100-1000 fs.

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Highly charged atomic and molecular cations can be produced by various techniques such as ion impact, multiphoton ionization using intense near-infrared femtosecond (fs) lasers and X-ray free electron laser (XFEL) irradiation. The fragmentation dynamics of highly charged molecular cations have been studied toward clarification of the mechanism of radiation damage, which is the most serious problem on the single molecule XFEL diffraction imaging of biomolecules and nano-materials [1]. Understanding the fragmentation dynamics of nano-materials should lead to their precise processing by laser pulses of short wavelength [2].

Fullerene C_{60} is referred to as a prototype in the study of the fragmentation dynamics of various nanoscale molecules. S. Martin et al. succeeded in producing C_{60}^{q+} cations up to q = 60 by Xe^{25+} impact.[3] Tomita et al. also examined the fragments of C_{60}–Xe^{25+} collision by velocity map imaging and found that $q \approx 30$ can be a threshold charge around which the major fragment switches from molecular fragments to atomic ones.[4] They pointed out that the non-Coulombic fragmentation channels might contribute to the dynamics even if $q \approx 50$ [4]. Is there any unified mechanism behind the dynamics depending on its charge q and initial excess kinetic energy E_{in}?

To answer the question above, we carried out *on-the-fly* classical trajectory calculations for the fragmentation dynamics of C_{60}^{q+} (q = 20–60) at the self-consistent charge density-functional based tight-binding (SCC-DFTB) theory [5]. We assumed that C_{60}^{q+} is prepared by a vertical ionization from C_{60} and that the fragmentation dynamics proceeds in the electronic ground state of each q (i.e., electronic energy is rapidly converted to vibrational energy). We performed simulations with finite initial vibrational (kinetic) energies of E_{in} = $5q$ and $10q$ eV. These conditions may represent the case where 10 to 30 cycles of core ionization and subsequent Auger decay accumulate an internal energy of 10 or 20 eV for each ionization and Auger decay cycle [6].

For $q \geq 20$ with $E_{in} \geq 100$ eV, we found that a two-step fragmentation mechanism governs the fragmentation dynamics. In this mechanism, C_{60}^{q+} firstly ejects singly and multiply charged fast atomic cations C^{z+} ($z \geq 1$) on a timescale of 10 fs to stabilize the remaining core cluster. The core cluster breaks into slow atomic and molecular fragments on a timescale of 100 fs to 1 ps. A representative trajectory of fragmentation of C_{60}^{60+} with E_{in} = 300 ($5q$) eV at the SCC-DFTB level of theory and the time evolutions of mean numbers of distinguished daughter fragments are presented in Figs. 1 and 2, respectively. The fragmentation of C_{60}^{60+} starts with the ejection of C^{4+} by t = 12 fs, which is driven by Coulomb repulsion. The subsequent fragmentations from the remaining core cluster C_n^{z+} (n = 25 ± 5 and z = 5 ± 2) to C^{z+} (z = 1–3) and molecular fragments take place by t = 25 fs. The Coulomb repulsion energy is 69.8 eV/bond for C_{60}^{60+} at t = 0 fs, which is approximately ten times larger than the typical bond dissociation energy of the C=C double bond (6.3–6.5 eV), and the value decreases to ~0.5±0.3 eV/bond for the core cluster (~C_{25}^{5+}) at t = 25 fs. The value of 0.5 eV is roughly 10 % of the C=C double bond energy. The sum of the remaining vibrational and rotational energy in the core cluster at t = 25 fs is in total 152.3 ± 54.3 eV, which is equivalent to the bond dissociation energies of 24 ± 8 C=C double bonds. These results indicate that the subsequent fragmentation of the core cluster to molecular and atomic fragments occurs thermally.
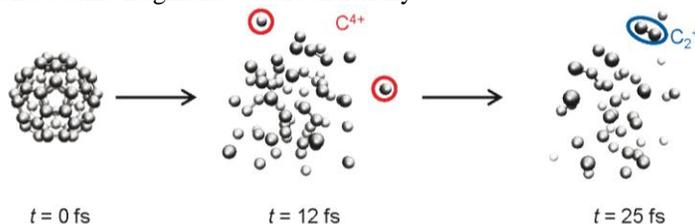

Fig.1. Representative trajectory of fragmentation of C_{60}^{60+} with E_{in} = 300 eV at the SCC-DFTB level of theory.

We also analyzed the kinetic energy distributions of fragments to investigate the fragmentation mechanism in detail. We found that the distribution functions f for any size of fragment can be fitted as a function of the fragment kinetic energy K_T by one or two Maxwell-Boltzmann energy distributions [7]

$$f(K_T) = \sum_{i=1}^{2} N_i \frac{2\sqrt{K_T}}{\sqrt{\pi}(k_B T_i)^{3/2}} \exp\left(-\frac{K_T}{k_B T_i}\right), \qquad (1)$$

where T_i and N_i are the translational temperature and number of fragments of the i-th energy distribution, respectively, and k_B is the Boltzmann constant. The values of T_i and N_i are determined by the least-square fitting method. The kinetic distributions of the resultant fragments of size n (C_n^{z+}, where $z = 0, 1, \ldots$) for C_{60}^{60+} at $E_{in} = 300$ eV are plotted in Fig. 3. The translational temperatures of the fast component $k_B T_1$ and slow component $k_B T_2$ for C^{z+} ($z = 1, 2$) are 150.9 and 14.3 eV, respectively. The values of $k_B T_1$ of atomic fragments decrease as q becomes smaller. Tomita et al. experimentally found that the mean kinetic energy for the fast component of C^+ decreases with decreasing q [4]. We confirmed that the values of $k_B T_1$ and $k_B T_2$ for molecular fragments of $n = 2$ and 3 lie in ~10 eV (and the values are almost constant even for smaller q). According to our simulation, these trends do not change qualitatively in a wide range of E_{in}. In addition, Tomita et al. also reported that the kinetic energy for the slow component of C^+ remains to be 10–20 eV (independent of q) [4]. Therefore the fast and slow components correspond to the fragments created by Coulomb explosion and thermal evaporation, respectively. The direct evidence of the two-step mechanism can be obtained by simultaneous detections of energetic C^+ and low energy C_n^+ ($n = 1$–3) or by recording momentum and/or energy correlation of two or more fragment ions produced from a single C_{60}^{q+} cation using coincidence or covariance methods. The time evolution of the number of fragment as displayed in Fig. 2 can be obtained by XFEL-pump UV-probe experiment.

Fig.2. Time evolutions of mean numbers of representative daughter fragments of C_{60}^{60+} at $E_{in} = 300$ eV calculated from 31 trajectories.

Fig.3. Kinetic energy distributions of daughter fragments at $t = 10$ ps from C_{60}^{60+} at $E_{in} = 300$ eV. The solid lines represent the kinetic energy distribution $f(K_T)$ defined in equation (1) fitted to each fragment species.

In summary, we carried out *on-the-fly* classical trajectory calculations on the fragmentation dynamics of C_{60}^{q+} ($q = 20$–60). We used the self-consistent charge density-functional based tight-binding theory. For $q \geq 20$, C_{60}^{q+} firstly ejects singly and multiply charged fast atomic cations C^{z+} ($z \geq 1$) *via* Coulomb explosions on a timescale of 10 fs to stabilize the remaining core cluster. Thermal evaporations of slow atomic and molecular fragments from the core cluster subsequently occur on a timescale of 100 fs to 1 ps. This two-step mechanism governs the fragmentation dynamics in the most likely case that the initial kinetic energy accumulated upon ionization to C_{60}^{q+} by ion impact or XFEL is larger than 100 eV. Strong interplay between experiments and simulations on reaction dynamics is essential to understand the fragmentation dynamics of highly charged molecular cations of nano- and bio-materials.

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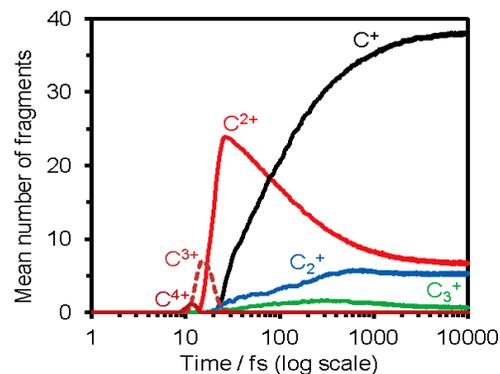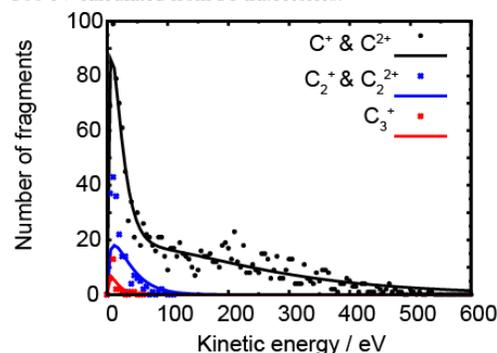[7] C. Nordling, & J. Österman, *Physics handbook for science and engineering 8th ed.*. (Studentlitteratur: Lund, Sweden, 2006.) pp 346.