Dynamical Fragmentation of C_{60} Ions

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The distribution of fragments resulting from collisions between 50–200-keV C_{60}^+ ions and H_2 and He is found to follow approximately a simple power law $I(m)=cp^m$, where p is a constant depending on both energy and target gas, and m is the number of missing "pairs" of carbon atoms. Based on this observation, a new dynamical fragmentation model involving the ratio of two characteristic times is proposed. In collisions by 300-keV C_{60}^{2+} ions, the singly charged products are distributed quite differently, which implies the first evidence of the presence of charge-separation reactions.

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The discovery [1] of the exceptional stability of C_{60} (Buckminsterfullerene) and its ions has prompted a large number of experimental and theoretical investigations concerning this soccerball-shaped molecule (see, e.g., Ref. [2], and references therein). After the discovery of a method [3] by which macroscopic quantities of C_{60} are available, this molecule has become an obvious candidate for structural and dynamic investigations by atomic collision experiments.

Several collision studies utilizing mass spectrometry have been reported [4–6]. Typical laboratory collision energies of C_{60}^+ have been less than 10 keV. Collisionally induced dissociation studies are reported by Young, Cousins, and Harrison [4]. They found, in agreement with photodissociation studies, that fragmentation occurs by the loss of an even number of carbon atoms. In collisions involving C_{60}^{2+} and C_{60}^{3+}, they also found that fragmentation occurs by the loss of an even number of neutral carbon atoms. Singly charged fragment ions resulting from collisions between C_{60}^{2+} and O_2 were later reported by Doyle and Ross [5] but were attributed to the formation of excited C_{60}^+ resulting from electron capture and subsequent dissociation. Both electron capture and loss without fragmentation have been observed [5], but no absolute values of cross sections are reported. Campbell *et al.* [6] have measured mass spectra resulting from collisions between 0.2–6-keV C_{60}^+ and various target gases. They conclude that the distribution with peaks around C_{15}^+ and C_{50}^+ originates from collision-induced fission of C_{60}^+. Another interesting collision aspect of C_{60} is its ability to form endohedral cluster compounds. Inclusion of rare gases and D_2 has been reported [7–10]. A more detailed explanation of the fragmentation pattern resulting from various interactions with C_{60} ions is still lacking. In the present work, we found a "simple" distribution of fragment ions as a result of collisions between high-energy C_{60} ions and light target gases. These systems were chosen as test cases for a better understanding of collision dynamics in the limit where the energy transfer absorbed from a light particle is much larger than the dissociation energy.

We report on fragmentation of 50–300-keV C_{60}^+ and C_{60}^{2+} ions in collisions with H_2 and He. We also discuss an observed exponential behavior of the fragment-ion intensities versus the number of lost pairs of carbon atoms. Such a dependence has not been reported earlier and may be specific for collisions between high-energy fullerenes and light target gases. A model, which assumes that the fullerene sphere is open as a result of a collision, and that pairs of C atoms can evaporate before it closes again, is found to explain the observations. We also report on strong evidence for observation of decomposition into two singly charged components when high-energy C_{60}^{2+} collides with He.

The C_{60} ions were prepared in a standard plasma ion source [11] by heating a C_{60}-C_{70} mixture [12] to $\sim 300\,^\circ$C in an insertion oven and subsequent electron bombardment with ~ 50-eV electrons. The ions extracted from the ion source were then accelerated to an energy of 50–300 keV by an electrostatic accelerator of the isotope-separator type. This accelerator is equipped with a magnetic analyzer with a dispersion of $1364\Delta M/M$ mm in the focal plane. By this arrangement, we can obtain a beam of isotopically pure C_{60}^+ or C_{60}^{2+}. The maximum current obtained is 40 nA C_{60}^+ and ~ 1 nA C_{60}^{2+}. However, the present measurements were conducted with a particle current of only 10^{-14} A. The beam exiting the accelerator was then passed through a 3-cm-long differentially pumped gas cell with 1-mm and 3-mm entrance and exit apertures, respectively. At a distance of 35 cm after the gas cell, the fragments were analyzed by an electrostatic analyzer, and finally the ions were counted by a Ceratron electron multiplier. The obtained spectra show intensity versus energy divided by charge, but, since the energy is essentially proportional to mass, a change to M/q (mass divided by charge) is straightforward. Fragment mass spectra were obtained by stepping the analyzer voltage proportionally with the channel advance of a multichannel analyzer. Single-collision conditions were ensured by varying the target

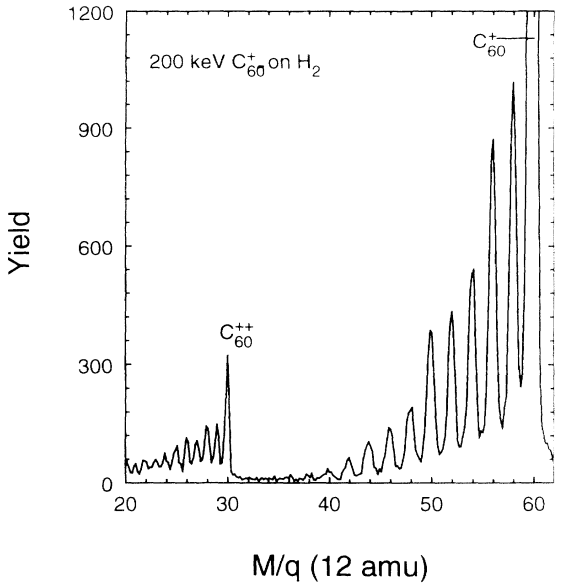

FIG. 1. M/q (mass divided by charge) spectrum resulting from fragmentation of 200-keV C_{60}^+ colliding with H_2. The right- and left-hand parts reflect singly and doubly charged fragments, respectively.

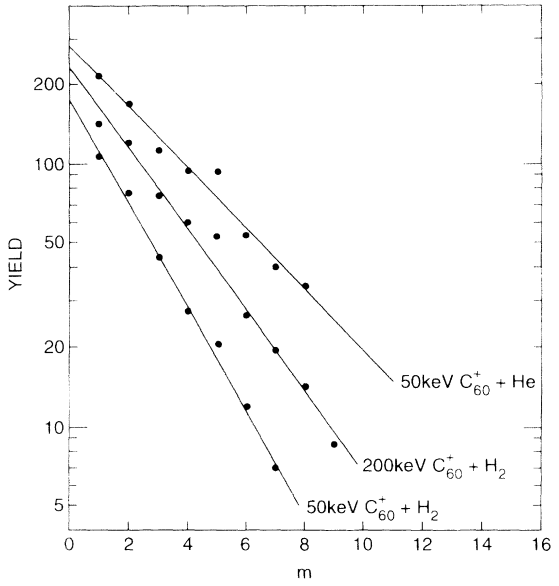

FIG. 2. Fragment-peak intensities as a function of lost number of C_2's.

pressure, and most spectra were recorded at pressures around 1 mtorr.

Figure 1 shows a mass spectrum obtained by colliding 200-keV C_{60}^+ with H_2. The dominating process is the loss of an even number of carbon atoms, resulting in even-numbered peaks ranging from C_{36}^+ to C_{58}^+. The intensity of odd-numbered peaks relative to even-numbered peaks in this mass range is less than 0.01. It should also be noted that electron loss and electron loss accompanied by fragmentation are quite probable. Also, in this process, only even-numbered fragments are observed. The absolute cross sections for attenuation of the primary beams are found to be around $(3\text{-}3.5)\times10^{-15}$ cm^2, which is almost of geometrical size ($\sim4\times10^{-15}$ cm^2) and in agreement with qualitative calculations of atom-atom scattering based on a screened Coulomb potential. At the velocities in question, "elastic" collisions between gas atoms and a carbon atom have large cross sections, $\sim\pi a_0^2$, where a_0 is the Bohr radius, for substantial energy transfer [13]. Accordingly, a gas atom which encounters C_{60} will suffer a number of collisions with individual carbon atoms. It seems reasonable to suppose that a large rift in C_{60} will then be produced.

Spectra of the same type as that shown in Fig. 1 have been obtained both as a result of collisions with various atoms at low energies [4] and as a result of photofragmentation [14] and electron-impact fragmentation [15]. The present spectrum, however, is different in the respect that it shows an almost exponential behavior with the number of lost pairs of carbon atoms.

In Fig. 2, the fragment intensities versus lost C pairs are plotted on a semilogarithmic plot for various energies and target gases. The intensities are seen to follow an exponential behavior rather well, with C_{50}^+ and sometimes C_{58}^+ as exceptions. The extra stability of C_{50}^+ compared to its neighbors has been observed also in several other fragmentation experiments. The general shape of the fragmentation patterns can now be given in the simple form $I(m)=\text{const}\times p^m$, where m is the number of lost pairs of C atoms and p is an experimentally determined number. In Table I, we list the experimentally determined p values for different collision energies in collisions of C_{60}^+ with H_2 and He.

The spectrum shown in Fig. 1 suggests that the C_{60} ions break up either by successive losses of pairs of C or by single-step loss of a larger even number of neutral carbon atoms. Note that nothing can be concluded about the actual structure of the lost carbon-atom groups, i.e., whether they actually stay together either in pairs or in larger groups of an even number of atoms. In the collision experiments reported by Young, Cousins, and Harrison [4], the available center-of-mass collision energy is as low as 28 eV, and it is argued that sequential loss of C_2 is impossible when a larger number of carbon atoms are missing, simply from energy-conservation considerations.

TABLE I. $I=cp^m$.

E (keV)	Target	Projectile	Product	p	t_1/t_2
50	H_2	C_{60}^+	C_n^+	0.63	0.59
100	H_2	C_{60}^+	C_n^+	0.66	0.52
200	H_2	C_{60}^+	C_n^+	0.70	0.43
50	He	C_{60}^+	C_n^+	0.76	0.32
100	He	C_{60}^+	C_n^+	0.74	0.35
200	He	C_{60}^+	C_n^+	0.76	0.32

In our experiments, where the available center-of-mass collision energy is between 150 and 1000 eV, such energy-conservation arguments are not essential. In fact, the fragment distributions shown in Fig. 2 suggest a mechanism where fragmentation occurs by sequential loss of "pairs" of C atoms.

If we accept the exponential behavior of ions evaporated as a basic general phenomenon for a wide interval of energy and for light background gases, there is only little choice as to the mechanism of decay. We have been able to account for it only in terms of the following competition between an evaporation lifetime t_1 and a closure lifetime t_2. Suppose that the C_{60}^+ ion has got a large "rift" as a result of a collision with the target atom and that C pairs can evaporate with a characteristic time t_1 while the system is open. Since the available energy is large, we can assume that the losses of C pairs are independent events, all with the same characteristic time. The probability for m evaporations in the time interval $(0,t)$ is then

$$P_t(m)=\frac{1}{m!}\left(\frac{t}{t_1}\right)^m e^{-t/t_1}. \quad (1)$$

Suppose further that the remaining fullerene closes in $(t,t+\delta t)$ with a probability $e^{-t/t_2}\delta t/t_2$, where t_2 is a characteristic lifetime of the rift. Then the total probability for m evaporations is

$$P(m)=\frac{t_1}{t_2}\left(\frac{t_2}{t_1+t_2}\right)^{m+1}. \quad (2)$$

The distribution described by this formula is equivalent to the experimental exponential behavior if we make the following substitution:

$$p=t_2/(t_1+t_2). \quad (3)$$

In Table I, values for t_1/t_2 are also listed, and it is found that the times for which the molecule is open in collisions with H_2 are approximately twice the characteristic evaporation time, whereas the ratio is around three for He.

It should be noted from (3) that the constancy of p for successive evaporations requires that the ratio t_1/t_2 remains constant during the evaporation. The result that C_{50} lies slightly higher will then correspond to slightly smaller closure time. As to the magnitudes of t_1 and t_2, they must of course be long compared with the collision time $\sim(1-3)\times10^{-15}$ sec. They must further be short compared to the passage time from the target to the analyzer, $\sim3\times10^{-6}$ sec. Finally, it is implied that the evaporation time of the system after closure of the rift should be longer than the passage time. On the basis of the above discussion, we propose that the dominant fragmentation mechanism in collisions between fast C_{60} ions and light targets is independent sequential loss of neutral pairs of C atoms.

Figure 3 shows the fragmentation spectra obtained for C_{60}^{2+} colliding with H_2 and He. Once again, the dominant structure is due to loss of an even number of carbon atoms, and the structure of the spectra of heavy, doubly charged fragments is in qualitative agreement with the model proposed above. Singly charged product ions are also observed with C_{15}^+ as the dominating cluster ion in the lower-mass group. The distribution of singly charged, higher-mass fragments is markedly different in the two spectra. In collisions with H_2, a relatively strong electron-capture (C_{60}^+) peak is observed, whereas no observable capture occurs in He. This marked difference can be related to the large difference in ionization potential in the two cases. For He, the ionization potential is 24.6 eV and, for H_2, it is 15.8 eV. These values should be compared to the second ionization potential of C_{60} which is measured to be around 10–12 eV [16,17]. Charge transfer for C_{60}^{2+} collisions with H_2 has an energy defect of only ~5 eV but, with He, it is strongly endothermic. These differences are known to lead to large differences in electron-capture cross sections for low-energy ion-atom collisions [18].

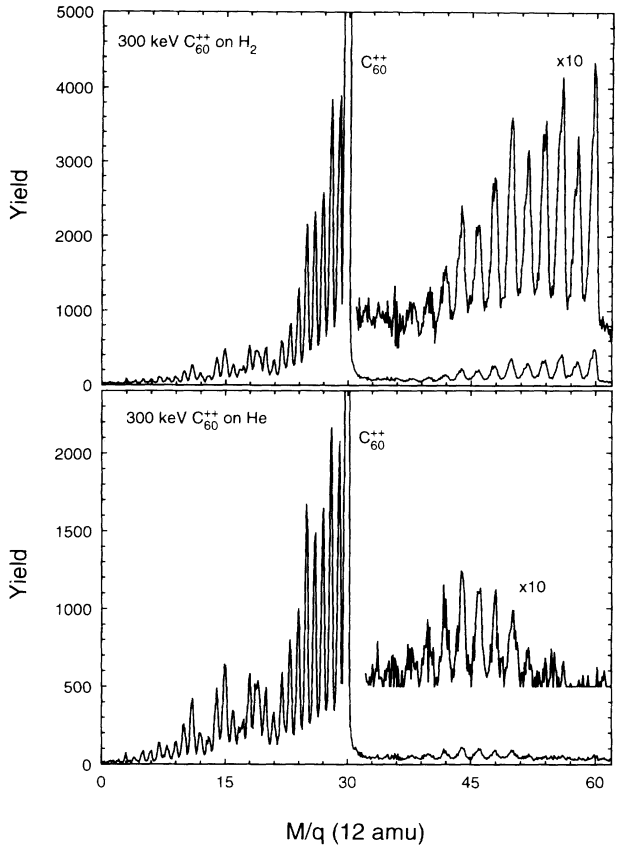

FIG. 3. Mass-over-charge spectra resulting from fragmentation of 300-keV C_{60}^{2+} colliding with H_2 and He.

The singly charged heavy fragments resulting from collisions with H_2 basically follow the pattern for singly charged ions. We believe that they originate from fragmentation of a singly charged C_{60}^+ ion formed by electron capture. This process was also suggested by Doyle

and Ross [5] as the dominating mechanism for production of singly charged fragments in low-energy collisions with O_2. For He, no electron capture is observed. The distribution of singly charged, heavy-product fragments is different from the "normal" behavior, and stronger signals corresponding to singly charged, low-mass fragments are observed. These observations indicate that we have observed a new fragmentation mechanism where the doubly charged C_{60}^{2+} ions separate into two charged components. It is interesting to note that a distribution of singly charged fragments with a maximum around 44 has also been observed, as a result of low-energy collisions [5].

In analogy with compound-nuclear processes leading to neutron evaporation and fission [19] and multiple ionization of atoms [20], the aim of the reported investigation has been to gain insight into the structure and dynamics of the new compound system C_{60}. Based on the measured exponential behavior of the product ions, we have proposed a fragmentation model which is applicable in the limit where the available energy transfer is much larger than typical fragmentation energies. Further investigations at collision energies in the energy interval (50–300 keV) are under way, and new channels, such as charge separation, are likely to occur. Such investigations are also of importance for experiments involving storage of C_{60} ions in heavy-ion storage rings [21]. Long-time storage of C_{60} ions offers some unique prospects for looking at instabilities in the system, and the first experiments have recently been initiated [22].

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