Electron Capture from C_{60} by Slow Multiply Charged Ions

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Cross sections and fragmentation mass spectra have been measured for the capture of electrons from C_{60} by slow Ar^{8+} ions. Two mechanisms are identified: For large impact parameters multiply charged C_{60} (up to 6+) ions are produced, while for smaller impact parameters the C_{60} is broken into smaller fragment ions. The absolute cross sections are consistent with an over-barrier picture for long range capture, while the destruction cross sections are found to be somewhat larger than the geometrical C_{60} cross section.

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The collisional production of free multiply charged C_{60} ions and the mass spectra resulting from fragmentation of C_{60} have received much attention in recent years, largely facilitated by the ready availability of C_{60} in large quantities for use as targets and projectiles [1]. A number of studies of the photoionization and electron ionization of C_{60}, for which single electron removal is most probable, have been reported [2,3]. Heavy particle collisions between C_{60} and rare gas targets at energies high enough to provoke ionization have been found to frequently cause the emission of one or more C_2 groups accompanying the ionization [4]. Recently double photoionization was reported by Steger *et al.* [5]. Experiments that probe the multiply charged ions ${C_{60}}^{3+}$ [6–8] and ${C_{60}}^{4+}$ [9] have been performed. In this Letter we report on collisions between slow-moving multiply charged ions and C_{60} targets. We find that multiply charged C_{60} ions are produced intact, up to 6 times ionized, and that certain aspects of the collision are amenable to quantitative model-based explanations.

It is well established that a multiply charged ion passing at a large impact parameter by a neutral atomic target, at a speed well below that of the target's most loosely bound electrons, removes electrons from the target by an over-barrier ionization of the target, with the extracted electron(s) temporarily retained within the potential well of the projectile but partially lost later through autoionization [10]. A similar process, field emission, occurs when the multiply charged ion is incident upon a conducting surface; this type of collision has received much attention in recent years [11–13]. In spite of the similarity of these processes, important differences in their model treatment exist. For example, in the ion atom case electrons transferred from target to projectile are commonly assumed not to screen either the projectile or the target charge on the incoming trajectory. For collisions of highly charged ions with metallic surfaces, however, Burgdörfer and Meyer [12] find that a simple model including full screening of the projectile by the captured electrons agrees well with the experimental data of Winter [13]. One would expect that a process intermediate between these two would occur if the target were a C_{60} fullerene. The surface of such a fullerene resembles in many ways that of a conducting surface, but is finite in extent and capture from it is accompanied by the acquisition of a net charge by the target as electrons are removed. Thus studies of the interaction of highly charged ions with C_{60} may help bridge the gap between the models. The object of the present study is a first exploration of this contention. A second focus of the present experiment is to yield information on the structural stability of the charged C_{60} itself. Electron removal from the C_{60} by slow, highly charged ions can be a very gentle process. For large impact parameter collisions, which dominate the reaction cross section, the target sees the slow turning on and off of a quasi-dc but very strong electric field. This process might be expected to charge the C_{60} molecule with a minimum of excitation of electronic and vibrational degrees of freedom and to produce the highest charged C_{60} consistent with the intrinsic stability of the fullerene.

Two types of experiments are reported here for slow Ar^{8+} ions on a gaseous C_{60} target. The first, carried out at the Justus Liebig University, Giessen, involved measurements of the product ion mass spectra in coincidence with charge state analyzed projectiles. The second, carried out at Kansas State University (KSU), consisted of the measurement of absolute cross sections for projectile charge change which were used to place the data from the coincidence experiment on an absolute scale.

For the coincidence experiment, a beam of 80 keV Ar^{8+} ions from an electron cyclotron resonance ion source passed approximately 1.5 mm above the 1.5 mm diameter aperture of a resistively heated Mo oven containing a commercially available soot containing approximately 5% fullerenes. Charged fragments were extracted by a field of 470 V/cm over 1.5 cm at right angles to the projectiles. After a field-free drift region of 2.5 cm they were detected with a channel plate detector with its front plate biased at 4.2 kV. The projectiles were charge state analyzed and detected by a position-sensitive channel plate detector 20 cm farther downstream. A time-to-amplitude converter, started by the projectiles and

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stopped by the recoil ions, measured the charge to mass ratio of the recoil fragment in coincidence with the projectile charge state. Further details of the experimental apparatus are reported elsewhere [14].

Figure 1 shows the recoil-flight-time spectra, gated according to the final charge state of the Ar^{+q} ion. These spectra have had the background, measured with a cool oven, subtracted, and thus represent capture from the C_{60} (and, weakly in evidence, C_{70}) only. For projectiles which have retained one or two electrons, the recoil spectra are dominated by multiply charged $C_{60}{}^{q+}$ ions, with q up to 6+. These two spectra show little evidence for the emission of C_2 units from the C_{60} cage accompanying electron removal, or for the production of light ionic fragments. We point out that the time-of-flight technique used favors the detection of the first (lighter) fragment, should two or more daughter ions be emitted from the same capture event. The evidence for 6+ is weak, but reproducible in all of our spectra. In order to substantiate that 6+ is indeed produced in such collisions, we also ran Xe^{14+} on C_{60}, and show in the inset in Fig. 1 the relevant part of the time-of-flight spectrum for this case, in which evidence for $C_{60}{}^{6+}$ is more robust. Projectile ions which have retained three or more electrons are accompanied by the production of lighter fragment ions from C_{60}, eventually dominated by $C_n{}^+ (1 \le n \le 3)$ ions for final Ar charge states of 1+ through 3+.

We interpret the data of Fig. 1 as resulting from two mechanisms. For large impact parameters the over-barrier extraction of electrons would be expected to gently remove electrons from the C_{60}, leaving the ion intact but charged. The captured electrons are expected, on the basis of the well known extended classical barrier model [15], to populate highly excited states on the projectile which subsequently decay by autoionization, leaving the projectile with at most two captured electrons, even if six or more are initially captured. The absence of projectiles retaining more than two electrons is quite consistent with the experience of capture from atomic, multielectron targets by similar projectiles at these velocities, and the main features of this process are well understood [10,15]. At the other extreme, projectiles which exit in charge states 1 through 4 we attribute to collisions which pass through (or very near) the fullerene. These collisions result in catastrophic destruction of the fullerene cage, and charged light fragments are common, of which the fastest will be preferentially detected.

The above conjectures can be more quantitatively evaluated if the reaction cross sections are known on an absolute scale, since this gives absolute values for the impact parameters involved. To this end we have measured absolute cross sections for projectile charge change from 80 keV Ar^{8+} on C_{60}. The target for this phase of the experiments was a 1.75 cm long stainless steel cell filled with C_{60} extract and heated to temperatures of 330 to 440 °C. A beam of 80 keV Ar^{8+} from the KSU electron beam ion source was directed through the cell and charge state an-

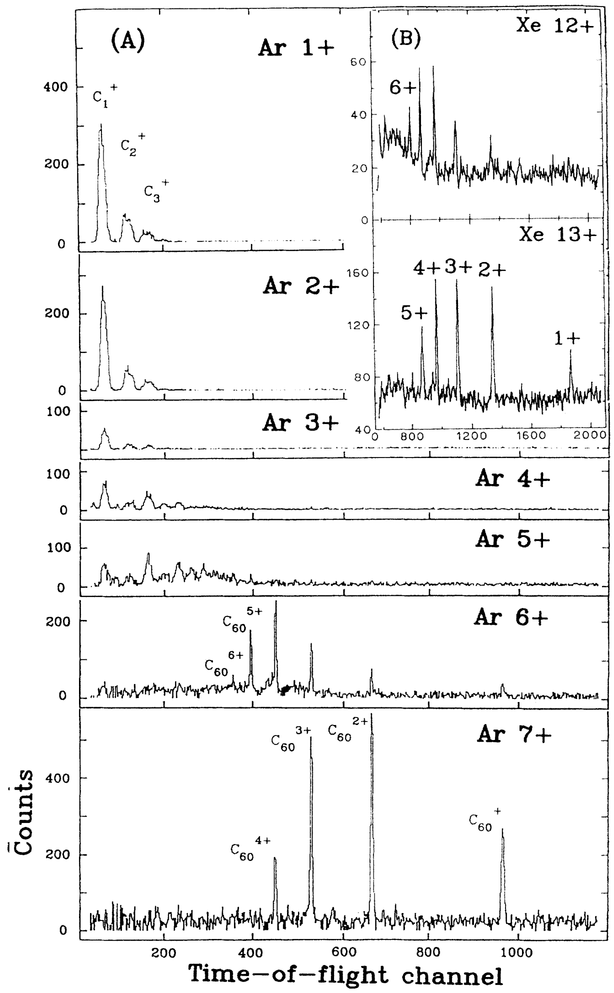

FIG. 1. (a) Time-of-flight coincidence spectra from 80 keV Ar^{8+} on C_{60}, gated on the final projectile charge state. The narrow peaks are identified as C_{60} ions, whereas the broader peaks are due to fragments. The background was subtracted, but no correction for the detection efficiency was made. (b) The inset shows the first two spectra for 140 keV Xe^{14+} on C_{60} with indication for $C_{60}{}^{6+}$.

alyzed downstream, and the projectile charge changing cross sections were deduced from the slope of the yield plotted versus target thickness. The absolute target thickness was obtained from the measured temperature of the cell using vapor pressure curves for C_{60} by Abrefah *et al.* [16].

The cross section obtained for total electron capture, summed over all final charge states of the projectile, is $(4.4 \pm 1.8) \times 10^{-14}$ cm^2, where the largest source of error is the uncertainty of the vapor pressure, which was estimated from the data of Abrefah *et al.* to be approximately 25% in our temperature range, and the uncertainty in the temperature measurement of the oven ($\pm 5°$). In Fig. 2 we show the capture cross section as a function of the final projectile charge state. We note the presence of a "hump" in the cross section for final projectile charge states 0–4 (5–8 electrons kept), which corre-

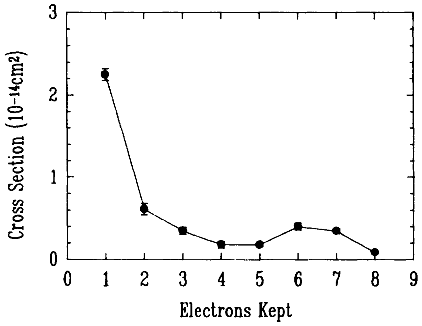

FIG. 2. Cross section for electron capture from C_{60} versus number of electrons kept by the projectile for Ar^{8+} on C_{60}. The "hump" for 5–8 electrons kept is associated with the destruction of C_{60}. The error bars represent relative errors only; the absolute uncertainty is 42%.

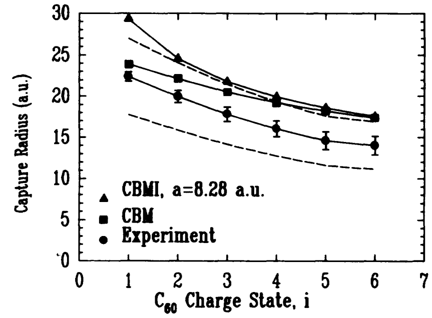

FIG. 3. Capture radii for the production of $C_{60}{}^{i+}$ for Ar^{8+} on C_{60}. The filled circles show radii deduced from experimental cross section measurements with relative error bars. The dashed lines indicate the limit which the uncertainty in the absolute cross section scale would accommodate. The squares are the classical over-barrier (CBM) model results for an atomic target (Ref. [13]), while the triangles are model results for over-barrier capture from a conducting sphere (CBMI).

sponds to the region of catastrophic C_{60} destruction seen in Fig. 1 and discussed above. We used these data in combination with those of Fig. 1, and measured relative efficiencies for the detection of $C_{60}{}^{i+}$ to obtain absolute cross sections σ_i for the production of $C_{60}{}^{i+}$. For the voltage used in this experiment, 4.2 kV, the relative detection efficiency was 36% for $C_{60}{}^{1+}$, 81% for $C_{60}{}^{2+}$, and unity for higher charge states.

We attempt to interpret the results in terms of an over-barrier model for the capture. Several versions of this model are available, depending on the form taken for the potential seen by an electron removed from the target and on the treatment of the projectile screening during subsequential capture. In the models of Bárány *et al.* and of Niehaus [15], a series of radii R_i are defined at which electrons with ionization energies I_i are able to pass over the classical potential barrier formed by the Coulomb charges of the projectile and the remaining ionic core (CBM). Successively more tightly bound electrons are thus liberated from the target at successively smaller internuclear radii. Since each electron is liberated into a less highly excited state on the projectile than the one liberated before it, the Niehaus model makes the approximation, which we adopt, that the projectile is not screened by the captured electrons. We also compare our data to a modified version of that model in which we take the target to be a conducting sphere with a radius of 8.3 a.u. (CBMI). This radius was derived from the electrical polarizability of a conducting sphere, $\alpha = R^3$, which was equated to the electrical polarizability of C_{60} [17]. The potential seen by the electron as it leaves the target includes not only the monopole Coulomb potentials of the projectile and residual target ions, but also the image potentials of the projectile and of the electron due to the conducting spherical surface:

$$V(x) = \frac{q}{r-x} + \frac{i}{x} - \frac{qa/R}{x-a^2/R} + \frac{qa/R}{x} + \frac{a/x}{x-a^2/x} - \frac{a/x}{x},$$

where q and i are the charge states of the projectile and the target, respectively, R is the internuclear distance, a is the radius of the sphere, and x is the position of the electron relative to the center of the target. The target is taken to resemble an atom with successive binding energies of 7.58 [3], 12.25 [7], and 17.0 [7] eV for the first three ionization states of C_{60}. For higher ionization potentials we have linearly extrapolated this series, giving $I_i(\mathrm{eV}) = 4.7 + 2.883q$. This procedure can be physically motivated by noting that the ionization potential can be described as the sum of a short range piece, whose size is near the work function of graphite, plus a long range piece due to the energy required to remove the electron to infinity from the residual charged C_{60} cage [18]. The radius R_i obtained for the liberation of the ith electron was calculated numerically from the over-barrier condition. We note that this particular version of the model was chosen partially because of its simplicity, and neglects not only partial projectile screening, recapture by the target of electrons on the outgoing part of the trajectory, and any time dependence of electron capture and loss or autoionization after the collision.

The resulting radii are shown in Fig. 3. The first over-barrier radius is found to be 23.9 a.u. (CBM) and 29.3 a.u. (CBMI). This should be compared with the measured radius value of $R_1 = 22.4 \pm 4.6$ a.u. which was deduced from setting πR_1^2 equal to the experimental total capture cross section. Within the absolute error bar, the experimental radius is nearly in agreement with either model, and we thus conclude that the basic interpretation of the large impact parameter capture from C_{60} in terms of over-barrier capture is correct. Experimental radii R_i for the production of specific charge states of C_{60} were extracted from the measured σ_i using $\sigma_{\mathrm{total}} = \pi R_1^2$ and $\sigma_i = \pi(R_i^2 - R_{i+1}^2)$. The results are compared with the model results in Fig. 3. The trends of experiment and theory are remarkably similar. This figure suggests that the production of $C_{60}{}^{6+}$ occurs at an impact parameter near 14 a.u., still well outside the geometrical C_{60} radius. We interpret this as meaning that collisions closer than this destroy the cage. Whether this occurs because $C_{60}{}^{i+}$ cannot survive beyond $i=6$ or because of the dynamics of this particular collision system is not answered by these data. It is noteworthy that the Xe^{14+} ion did not succeed in producing a higher charged fullerene. We point out that any metastable $C_{60}{}^{i+}$ with a lifetime longer than a few microseconds would appear as stable in our experiment.

The charge state distribution for the hump in the cross section curve of Fig. 2 for 5–8 kept electrons is similar to that which one would obtain for an 80 keV Ar ion passing through a thin C foil [19]. This hump has a summed experimental cross section of 1.5×10^{-14} cm^2. The radius extracted from this cross section is 13.3 a.u., outside the geometrical C_{60} radius of 7 a.u. This result suggests that attributing this very destructive part of the reaction to "hitting" the fullerene is probably somewhat oversimplified. Apparently, both multiple projectile capture producing projectiles which do not appreciably autoionize after the collision and catastrophic destruction of the C_{60} can occur at an impact parameter which brings the projectile near, but not directly through, the fullerene cage. We do not find the disintegration of the fullerene at this impact parameter to be entirely surprising in view of the very large charge of the projectile. However, it is remarkable that the projectile can achieve a nearly equilibrium charge state from passage so far from the surface.

In summary, we have found that long range electron capture from C_{60} by slow multiply charged ions can produce up to $C_{60}{}^{6+}$. For slow Ar^{8+} ions, this process can be attributed to a gentle over-barrier electron extraction process operating at impact parameters between about 14 and 25 a.u. For impact parameters inside about 13 a.u. the C_{60} is catastrophically destroyed and the corresponding projectile charge state resembles that of an ion passing through a thin carbon foil. The intermediate range of impact parameters produces intermediate fragmentation of the C_{60}, for which no model is yet at hand.

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