New highly charged fullerene ions: Production and fragmentation by slow ion impact

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Fullerene ions, C_{60}^{q+}, with q up to 9, have been observed in a study of their production by slow ($v<0.5$ au) impact of the projectiles $^{40}Ar^{4,5,8,12,16,17+}$, $^{136}Xe^{27+}$, $^{86}Kr^{28+}$, $^{209}Bi^{20,38,44,46+}$, and $^{238}U^{46+}$ on a neutral fullerene beam. The distribution of ion yields for each projectile is representable by a binomial form; variation of the biniomial fit parameters with projectile charge suggests the maximum positive charge for the fullerene ion. Correlations between the time of flight of first and second ions are shown to provide details of the fragmentation of fullerenes in close collisions.

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An outstanding property of C_{60}^{q+} ions is their high stability against Coulomb explosion; it is unusual for any molecule to remain intact while carrying more than a few units of charge, yet C_{60}^{q+} ions (with q up to 7) have been observed with lifetimes of at least many microseconds [1–3]. Among these observations, Walch *et al.* [2] produced C_{60}^{q+} ions ($q=1-6$) in single collisions of slow multiply charged Ar^{8+} or Xe^{14+} ions on C_{60} vapor targets. This process (electron transfer) is apparently a gentle removal of electrons from the fullerene with minimal excitation of its internal modes, and thus has the potential to produce fullerene ions of the highest charge. Recently, Scheier and Märk [3] have reported the production of C_{60}^{7+} by multiple electron impact. A theoretical model given by Petrie, Wang, and Bohme [4] predicted that the C_{60}^{6+} would be stable against spontaneous Coulomb explosion; and recently Märk and Scheier [5] extended their argument, using a different binding energy, to predict stability of C_{60}^{q+} up to $q=8$. Given this background, it is natural to ask: where will it end? That is, how highly may C_{60} be charged and remain stable against Coulomb decay? When decay does occur, either promptly or delayed, what is the nature of this process? In this work we report the production, by slow ion impact, of highly charged $C_{60,70}^{q+}$ ions with q up to 9, two units beyond the previously reported highest charge. The newly observed ions also remain intact for several microseconds, and a systematic study of the fullerene ion distributions indicates a limiting charge beyond which rapid dissociation occurs.

This work utilized a wide range of projectile ions from the Advanced Electron Cyclotron Resonance ion source at the Lawrence Berkeley Laboratory 88 in. cyclotron, for production of multiply charged $C_{60,70}^{q+}$ ions by impact upon fullerene vapor (the method described in [2]). The ions used were $^{40}Ar^{4,5,8,12,16,17+}$, $^{136}Xe^{27+}$, $^{86}Kr^{28+}$, $^{209}Bi^{20,38,44,46+}$, and $^{238}U^{46+}$ usually with energies of 10 keV/charge. The mass- and charge-analyzed beams, collimated to about 3 mm in diameter, intercepted a thermal fullerene molecular beam at 90°. Typical ion currents were 0.1–0.4 nA. The fullerene beam was produced by evaporating sample powder containing about 85% C_{60} and 15% C_{70} (Polygon Enterprises Inc., Waco, Texas). The oven operated usually at ≅430 °C, and the oven region, apart from a small aperture, was isolated from the main collision chamber and separately pumped; the base pressure was $<1\times10^{-8}$ Torr in the main chamber during operating conditions.

Target collision products were analyzed by an electron–recoil-ion time-of-flight (TOF) spectrometer, consisting of an ion TOF spectrometer and an electron extractor. The latter has the geometry of a first-order space-focused TOF spectrometer with a 2-cm flight tube located 1 cm from the ion beam center, followed by a channel electron multiplier. The ion spectrometer is a second-order space-focused design [6] with a first acceleration grid 0.80 cm from the ion beam center, followed by a second grid spaced 0.93 cm from the first, and a 9.27-cm free-flight tube. A channel plate multiplier assembly (first plate at -4 kV) mounted behind the flight tube detects transmitted ions. The ion time of flight is very insensitive to initial position in the beam intersection region, but is sensitive to initial velocity, and thus widths and/or shapes of time-of-flight peaks indicated initial velocity spreads. The two detectors face each other vertically, relative to the plane containing the ion and the fullerene beams. An extraction field E accelerates positive ions to the ion detector and electrons to the channel multiplier. Promptly released Auger and/or low-energy continuum electrons are often produced in collisions that remove two or more electrons from a neutral target. For a fullerene target, this was verified in the observations of Walch *et al.* [2] and recent model calculations [7,8]. Our technique uses signals from the electron and ion detectors to start and stop a time-to-amplitude converter (TAC) whose output is recorded by a microcomputer.

Figure 1(a) is an example of the ion TOF spectra produced by $^{209}Bi^{20+}$ ion impact on the fullerene beam with $E=266$ V/cm. As in all our TOF spectra, one observes two distributions which overlap slightly: (i) the fullerene ions, extending upward from $M/q\cong70$ (amu/e) and (ii) a range of broad, light-fragment peaks which appear at multiples of $M/q=12$ in the region below $M/q\cong100$. The series of narrow peaks extending to the high-mass side are the C_{60}^{q+} ions with $q=2-8$ (C_{60}^{8+} is weak) and C_{70}^{q+} with $q=3-6$ (C_{70}^{2+} is beyond the time range, C_{70}^{7+} and C_{60}^{6+} have the

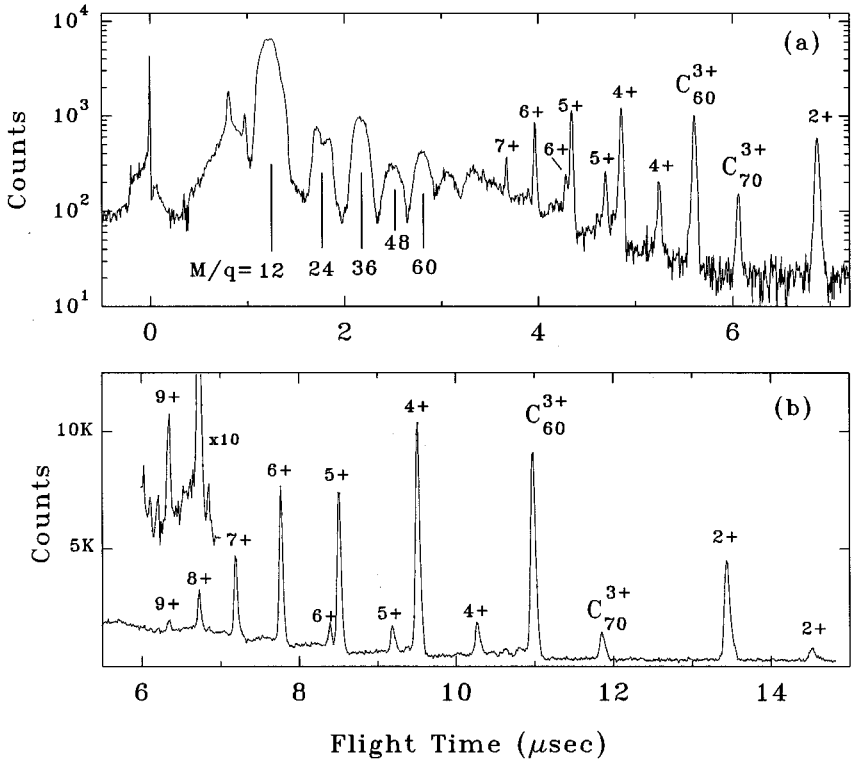

FIG. 1. Time-of-flight spectra from impact of (a) $v=0.2$ a.u. Bi^{20+} and (b) $v=0.30$ a.u. Bi^{44+} on the fullerene beam (see text).

same M/q). With the relatively strong field of $E=266$ V/cm, one does not observe $C_{60}{}^{7+}$ ions for projectiles with charge $Q<17$, and a $C_{60}{}^{8+}$ peak with a convincing intensity did not appear for $Q<28$, because these small peaks are masked by the overlapping light-fragment spectrum. To improve their visibility, E was reduced by a factor of 4 to lower the collection efficiency for light fragments, which have high initial velocities. This had relatively little effect on collecting the low-energy fullerene ions and electrons with energy <5 eV. Figure 1(b), obtained with a $^{209}Bi^{44+}$ ion beam and $E=66.5$ V/cm, shows clearly $C_{60}{}^{q+}$ with q from 2 to 9. ($C_{70}{}^{7+}$ is coincident with $C_{60}{}^{6+}$, and $C_{70}{}^{8+}$ is buried in the right wing of the $C_{60}{}^{7+}$ peak.)

With increasing projectile charge Q, the relative yield of high-charge fullerene ions increases, shifting the mean charge of the distribution to higher values. We find that the fullerene charge distributions can be described by a Q-dependent binomial distribution, where the fraction of ions with charge q is

$$f_q=\frac{C!}{q!(C-q)!}p^q(1-p)^{C-q},$$

with $C(Q)$ and $p(Q)$ parameters obtained from fits to the observed distributions. This approach has been used to describe recoil-ion charge distributions observed in highly charged ion-atom collisions [9]. It follows from the assumption that, from a total of C electrons, each may be captured independently onto the projectile with probability p. Regardless of the validity of these assumptions for the case of capture from fullerenes, the binomial form is useful for description and extrapolation of the observations. Figures 2(a) and 2(b) show $C(Q)$ and $p(Q)$ obtained from fits to the observed distributions of intensities in the fullerene ion peaks, and Fig. 2(c) shows the observed and fitted charge distributions for $Q=46$. For small Q, $C\cong Q$, but as Q increases the growth of C slows. Extrapolation of a smooth fit to the C vs Q data indicates the approach to a limiting value $C\approx 11$ at large Q, while p extrapolates to near 0.5. This suggests that the fullerene structure can support, at most, a total charge of ≈ 11 units; roughly 1 per six carbon nuclei. Treating the fullerene as a perfectly conducting sphere of radius $\alpha^{1/3}$ (polarizability $\alpha=618$ a.u.^{3} [10]) yields a maximum positive surface charge density $\rho_S\cong 0.012$ a.u.$^{-2}$.

To learn more about the stability of the $C_{60}{}^{q+}$ ions, their flight times were varied by changing the extraction field. The intensity of fullerene ion peaks was compared to that of $C_{60}{}^{2+}$ as a function of their time of acceleration. This is used, rather than their total flight time, because decay channels in which a neutral or charged dimer is emitted [11] do not diminish a particular peak if the decay occurs in the drift region of the ion TOF spectrometer, e.g., if the process $C_{60}{}^{7+}\rightarrow C_{58}{}^{6+}+C_2{}^{+}$ occurred in the drift region, the heavy $C_{58}{}^{6+}$ fragment would arrive at essentially the same time as the precursor $C_{60}{}^{7+}$ ion and no decay would be seen (barring a significant difference in the detection efficiency between the parent and fragment ions, not expected for $q>2$ [2]). This is not the case if decay occurs during the acceleration time which varied from 2–6 μsec in these measurements. These studies showed that, for $q<8$, lifetimes are longer than 20 μsec, and that at $q=8$ the lifetime is at least 5 μsec (no measurements were made for $q=9$). The lifetime for slow fission of a fullerene ion is dependent upon its state of internal excitation (not defined in this work); hence these measurements place lower limits on the lifetimes of the ground-state ions.

The classical barrier model (CMB) for multiple electron transfer predicts that, to capture q electrons, the projectile

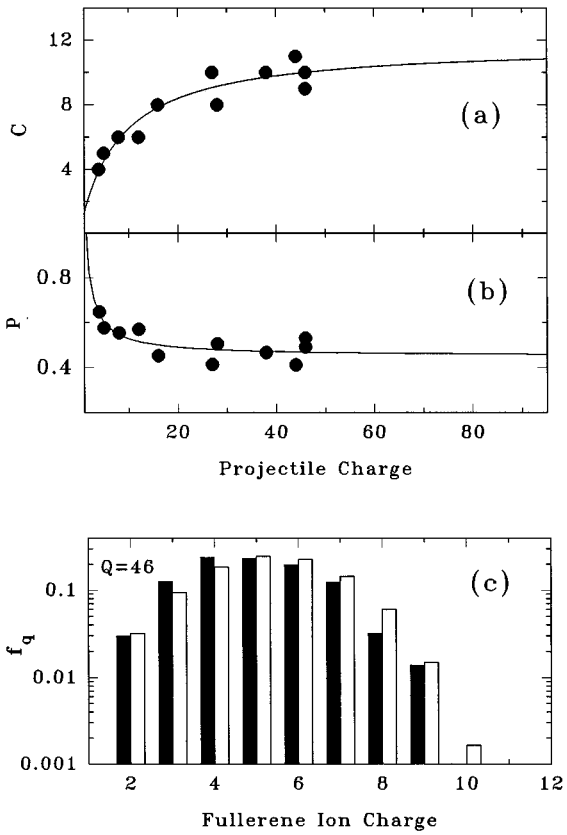

FIG. 2. Results of application of the binomial distribution to observed fullerene ion charge fractions. (a) and (b) show the parameters C and p which give best fits to the observed distribution of fractions for the range of projectile charges Q used. The curves are constructs to represent the data and suggest values expected for higher projectile charges. (c) shows the observed (solid bars) and binomial-distribution fitted (open bars) fractions for $Q=46$ for fullerenes with $q>1$.

ion must approach to within a radius R_q where the classical potential barrier for movement of an electron from the fullerene $q+$ ion to the projectile drops below the binding energy (ionization potential I_q) for that electron. Our observations suggest that removal of ≈ 11 electrons will result in prompt fragmentation of the fullerene structure. Since, on the side opposite the projectile ion, the positive surface charge density may exceed ρ_s at separations which exceed R_{11}, one expects that for a range of internuclear separations, outside R_{11}, both electron capture and fragmentation are probable. Taking πR_{10}^2 as an estimate of the cross section for fragmentation and πR_2^2 to estimate the total cross section for production of fullerene ions with $q>1$, the relative intensity of fragment to fullerene ions would be roughly $n_f(R_{10}/R_2)^2$, with n_f the mean fragment multiplicity. From the TOF spectra obtained with projectiles of charge $Q \geq 12$, the ratio of integrated intensities in the fullerene ion peaks to that in the fragments is approximately independent of Q with an average value of 11 ± 1.5. The CMB [12] shows $(R_{10}/R_2)^2$ to vary slightly from 0.27 to 0.31 over the range $Q=15-50$; this calculation used $I_{10}=43$ eV obtained from a linear extrapolation of the measured values for $q \leq 3$ (values obtained agree with calculations of Yannouleas and Landman [13] which extend to $q=12$). One thus obtained $n_f \approx 37$; consistent with the view that many light ion fragments are produced following close but noncontacting collisions. Recently, Wörgötter *et al.* [14] measured I_4 to be significantly above a linear extrapolation of measured values for $q \leq 3$. A quadratic extrapolation of the I_q, including the I_4 value of Wörgötter *et al.*, predicts $I_{10}=116$ eV; this yields $(R_{10}/R_2)^2$ values which decrease from 0.11 at $Q=15$ to 0.06 at $Q=50$, and resulting values for n_f from 100 to 180; this suggests that I_{10} is less than 116 eV. Values for R_{10} derived from $I_{10} \approx 55-60$ eV, together with the observed ratios of fragments to fullerene ions, yield $n_f \approx 60$ (i.e., complete disintegration).

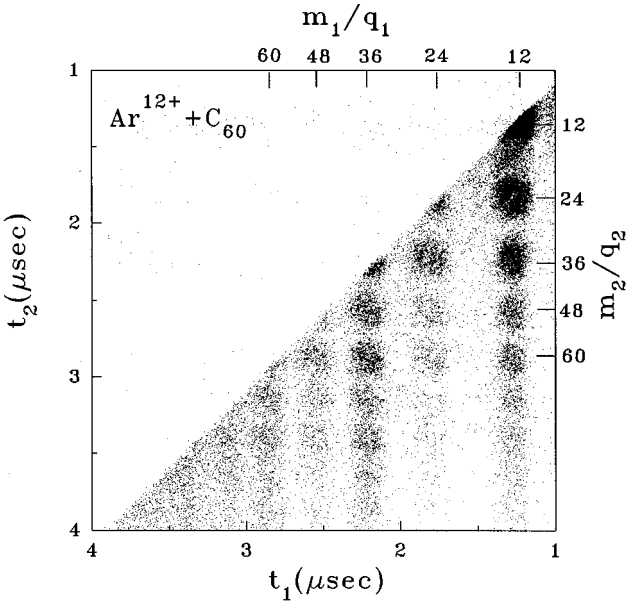

FIG. 3. First ion vs second ion arrival times, t_1 vs t_2, for fragments produced by 120-keV Ar^{12+} impact, with $E=266$ V/cm.

Details of the prompt fragmentation of the fullerene ions are present in "double hit" time-of-flight spectra, where the arrival times, t_1 and t_2, of the first and second ions are recorded. Eland [15,16] has described the study of the patterns observed in scatter plots of t_2 vs t_1 resulting from photofragmentation of molecules; the same methodology is applicable to fullerene fragments observed here where there is a higher likelihood of producing multiply charged fragments. In t_2 vs t_1 plots, we observe an array of "spots" at positions corresponding to $\mu_1=m_1/q_1$ and $\mu_2=m_2/q_2$ values with m_1 and m_2 multiples of the atomic carbon mass. Figure 3 shows an example from 120-keV Ar^{12+} impact. As developed by Eland [15,16] and Simon *et al.* [17], the shape of the intensity distribution in a particular spot provides clues to the fragment energies and masses. Figure 4(a) shows an example for the $\mu_1,\mu_2=12,24$ (amu/e) spot pattern from impact of 80-keV Ar^{8+}. This pattern is consistent with the breakup of energetic precursor fragments (kinetic energy E_0) into two charged pieces, with release of energy E_{12}, one of which may further decompose into charged and neutral parts with negligible energy release. That is,

$$C_M{}^{q_1+q_2}(E_0) \rightarrow C_{m_1}{}^{q_1} + C_{m'}{}^{q_2} + E_{12}$$

followed by $C_{m'}{}^{q_2} \rightarrow C_{m_2}{}^{q_2} + C_{m'-m_2}$. For a particular breakup of this kind, the t_1 and t_2 points fall within paral-

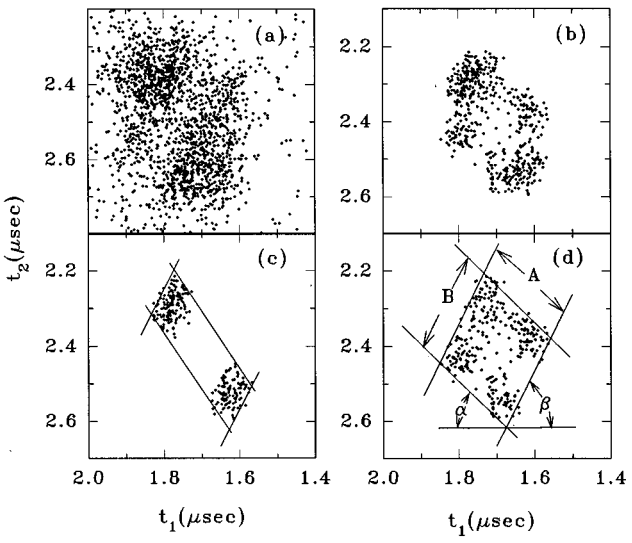

FIG. 4. (a) Enlarged view of the "spot" from fragments with $\mu_1=12$ (amu/e), and $\mu_2=24$ (amu/e) from impact of 80-keV Ar^{8+} projectiles, and $E=133$ V/cm. (b) is a superposition of two Monte Carlo simulations, shown in (c) and (d), which resembles the data in (a). See the text for details of this analysis.

lelograms as indicated in Figs. 4(c) and 4(d). From the slopes of the sides one obtains $M/m_2=1+(\mu_1/\mu_2)\tan\alpha$ and $\mu_2/\mu_1=\tan\beta$; from the ratio of the sides one has $A/B=\sqrt{E_{12}/E_0}$. Figure 4(b) is a superposition of two simulations constructed from the slope information in 4(a), μ_1 and μ_2, the geometry and potentials on the TOF spectrometer, and adjusted values for E_0 and E_{12}; it closely resembles the observation. Figures 4(c) and 4(d) show the two components of the simulation; 4(c) is the process

$$C_7^{(5-n)+}(2\ \text{eV})\rightarrow C_4^{2+}+C_3^{(3-n)+}+30\ \text{eV},$$

$$C_3^{(3-n)+}\rightarrow C_{3-n}^{(3-n)+}+C_n,$$

where n may be 0, 1, or 2 and C_4^{2+} is the second fragment in the detected pair. The results are independent of n, but a likely choice is $n=2$, yielding the lowest charged precursor, i.e., $C_7^{3+}\rightarrow C_4^{2+}+C_1^{+}+C_2$. Figure 4(d) depicts the breakup:

$$C_6^{3+}(12\ \text{eV})\rightarrow C_4^{2+}+C_2^{+}+12\ \text{eV},\quad C_2^{+}\rightarrow C^{+}+C.$$

A complete analysis of all of the patterns of correlated double hits for the wide range of projectiles used in this study is beyond the scope of this paper. However, we point out that there are curious alternations in the intensity patterns; e.g., events with $m_1/q_1=24$ are less probable than those with 12 or 36 (see Fig. 3). The two-particle correlations depend upon the way in which the fullerene breaks, a potentially complex process (there are 966 466 different fragment-mass combinations obtainable from 60 units). Fragment multihit time-of-flight measurements can provide a detailed description of the outcome of this process, and perhaps, as in the case of nuclear fragmentation [18], show the way to a particularly simple representation. Significant differences may exist in the fragmentation dynamics of low-velocity, highly charged ion impact studied here, and similar studies [19] at much higher impact velocities (where, e.g., charge capture is much less important).

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[1] C. W. Walter, Y. K. Bae, D. C. Lorents, and J. R. Peterson, Chem. Phys. Lett. **195**, 543 (1992).
[2] B. Walch, C. L. Cocke, R. Voelpel, and E. Salzborn, Phys. Rev. Lett. **72**, 1439 (1994).
[3] P. Scheier and T. D. Märk, Phys. Rev. Lett. **73**, 54 (1994).
[4] S. Petrie, J. Wang, and D. K. Bohme, Chem. Phys. Lett. **204**, 473 (1993).
[5] T. D. Märk and P. Scheier, Nucl. Instrum. Methods Phys. Res. Sect. B **98**, 469 (1995).
[6] U. Boesl, R. Weinkauf, and E. W. Schlag, Int. J. Mass Spectrom. Ion Processes **112**, 121 (1992).
[7] U. Thumm, J. Phys. B **27**, 3515 (1994).
[8] U. Thumm, J. Phys. B **28**, 91 (1995).
[9] C. L. Cocke and R. E. Olson, Phys. Rep. **205**, 153 (1991).
[10] M. J. Puska and R. M. Nieminen, Phys. Rev. A **47**, 1181 (1993).
[11] P. Scheier, B. Dünser, and T. D. Märk, Phys. Rev. Lett. **74**, 3368 (1995).
[12] A. Bárány and C. J. Setterlind, Nucl. Instrum Methods Phys. Res. Sect. B **98**, 184 (1995).
[13] C. Yannouleas and U. Landman, Chem. Phys. Lett. **217**, 175 (1994).
[14] R. Wörgötter, B. Dünser, P. Scheier, and T. D. Märk, J. Chem. Phys. **101**, 8674 (1994).
[15] J. H. D. Eland, Acc. Chem. Res. **22**, 381 (1989).
[16] J. H. D. Eland, Laser Chem. **11**, 259 (1991).
[17] M. Simon, T. Lebrun, R. Martins, G. G. B. de Souza, I. Nenner, M. Lavollee, and P. Morin, J. Phys. Chem. **97**, 5228 (1993).
[18] L. G. Moretto *et al.*, Phys. Rev. Lett. **74**, 1530 (1994).
[19] T. LeBrun, H. G. Berry, S. Cheng, R. W. Dunford, H. Esbensen, D. S. Gemmell, and E. P. Kanter, Phys. Rev. Lett. **72**, 3965 (1994).