

Highly Charged Clusters of Fullerenes: Charge Mobility and Appearance Sizes

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Clusters of fullerenes (C_{60} , C_{70})_n are produced in a gas aggregation source and are multiply ionized in collisions with highly charged $Xe^{20+,30+}$ ions. Their stabilities and decay processes are analyzed with high-resolution time-of-flight mass spectrometry. Fullerene clusters in charge states up to $q = 5$ have been observed and appearance sizes are found to be as small as $n_{app} = 5, 10, 21,$ and 33 for $q = 2, 3, 4,$ and $5,$ respectively. The analysis of the multicoincident fragmentation spectra indicates a high charge mobility. This is in contrast to charge localization effects which have been reported for Ar_n^{q+} rare gas clusters. Clusters of fullerenes are found to be conducting when multiply charged.

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Fullerenes like C_{60} are tightly bound molecules, held together by strong covalent forces. When brought together at low temperatures they form clusters of fullerenes which are only weakly bound by van der Waals forces [1].

In the pioneering work of Martin *et al.* [1] the structures of singly and doubly charged $(C_{60})_n$ and $(C_{70})_n$ clusters have been analyzed leading to the conclusion that closed shell clusters with $n = 13$ and $n = 55$ are icosahedral. However, clusters with incomplete geometrical shells undergo structural transitions similar to those observed for other van der Waals clusters, like $(Ar)_n$. More recently, the same group has shown [2] that depending on the cluster temperature icosahedral as well as closed-packed and decahedral structures can be observed independent of the cluster charge. These structures have been confirmed by global-minima calculations for $(C_{60})_n$ clusters [3].

Concerning the behavior of pure and mixed clusters of C_{60} and C_{70} fullerenes, Hansen *et al.* [4] have shown that both types of fullerenes participate similarly in cluster formation and that they are characterized by similar binding energies and reactivities.

Many studies deal with the dimerization and the polymerization of C_{60} fullerenes [4–8]. It has been established that in this phase the most favorable bonding between two C_{60} molecules is accomplished by a $[2 + 2]$ cycloaddition [5,6,8,9]. In the case of the dimer C_{120} this leads to a binding energy of ≈ 0.3 eV with respect to the separated molecules; however, this local minimum is stabilized by a dissociation barrier of about 1.6 eV [5]. For C_{120}^2- a single-bonded structure has been predicted to be more stable [10].

The electrical communication between different fullerene molecules has been discussed in connection with

future optical and electronic applications [11,12]. In the case of neutral van der Waals-type clusters we expect a very low charge mobility and for singly charged rare gas clusters it has been shown that the charge is localized on a small number of atoms. The icosahedral Ar_{13}^+ cluster, as an example, is arranged around a linear Ar_3^+ core [13]. Very recently, charge localization effects have been reported for highly charged Ar clusters [14] leading to the production of highly charged atomic fragments up to charge states of seven (Ar^{7+}) measured in correlation with singly charged ones.

In the present work we report on an experimental study of highly charged clusters of fullerenes produced in collisions with highly charged ions. The main aspects concern the limit of stability of these loosely bound, multiply charged van der Waals clusters, their geometrical structure, and the phenomenon of charge mobility.

In the experiment a beam of neutral clusters of fullerenes is produced in a cluster aggregation source [15]. A mixture of C_{60}/C_{70} powder is evaporated in an oven at a temperature of ~ 550 °C. Aggregation of the vapor occurs by supersaturation in a cold He atmosphere (pressure of several mbar, temperature $T \sim 77$ K). The formed neutral clusters pass several differential pumping stages before interacting with the beam of highly charged ions ($Xe^{20+,30+}$). The charged reaction products are extracted from the interaction zone perpendicular to the two beams. The ion beam as well as the extraction voltage is pulsed (repetition rate: ~ 1 kHz; pulse width: 1 and 60 μs , respectively). The fullerene clusters are analyzed with a linear Wiley-McLaren time-of-flight mass spectrometer ($m/\delta m \sim 2500$). The particles are postaccelerated towards a conversion plate kept at voltages up to -25 kV in order to increase the detection efficiency. The electrons

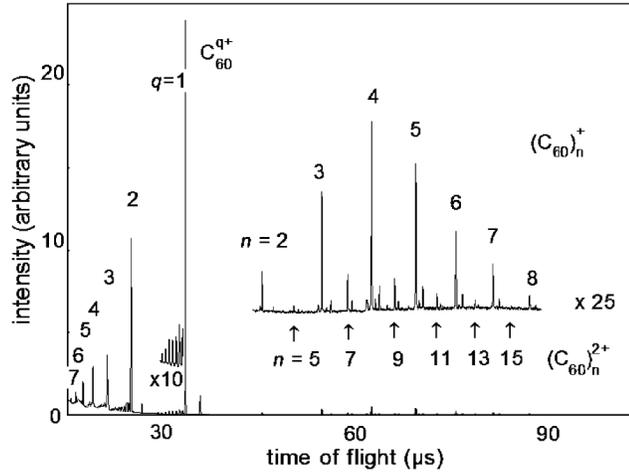


FIG. 1. Time-of-flight mass spectrum of fullerenes and fullerene clusters, ionized in collisions with Xe^{20+} projectiles at 400 keV. Arrows indicate positions of odd numbered doubly charged clusters ($T_{\text{oven}} = 525^\circ\text{C}$).

emitted from the conversion plate are focused on a channel plate. The signals are registered with a *multihit* time-to-digital converter on an event by event basis. Typical aggregation and drift times for neutral clusters between formation and interaction are of the order of several ms, whereas typical lifetimes between 10 and 40 μs are necessary for the ionized clusters in order to be registered as *stable* clusters.

Figure 1 shows a typical mass spectrum obtained in collisions of Xe^{20+} projectiles with neutral clusters of fullerenes. On the right-hand side contributions from singly and multiply charged clusters are present; on the left-hand side multiply charged fullerene monomers dominate the spectrum.

The spectrum looks similar to that reported for Ar clusters [14], with the exception that in the latter case no multiply charged clusters have been detected. As can be seen from the abundance of doubly charged clusters, the size distribution ends at about $n = 16$. However, at higher oven temperatures and hence higher vapor pressures in the cluster source, fullerene clusters containing up to 40 molecules have been detected.

Figure 2 gives a detailed view of the mass spectrum. The complexity is due to the presence of mixed clusters of C_{60} and C_{70} , as a mixture of these fullerenes has been used, and to the formation of multiply charged clusters. The analysis of the measured spectra leads to the following conclusions.

(i) Clusters in charge states up to $q = 4$ are identified as isolated peaks whereas contributions from 5 times charged clusters can be verified by a peak fitting procedure. The analysis of the mass spectra yields appearance sizes n_{app} as a function of the cluster charge (smallest cluster size observed in the experimental spectrum for a given charge state). The values are compared in Table I with typical values obtained for other types of clusters

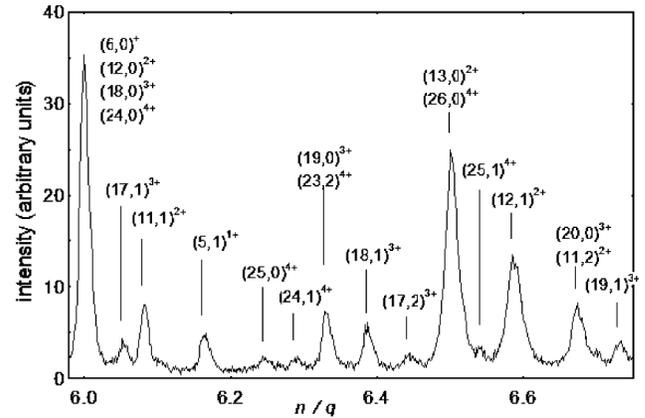


FIG. 2. Detailed view of a time-of-flight mass spectrum, showing contributions from multiply charged clusters. The notation (k, l) marks a cluster $(\text{C}_{60})_k(\text{C}_{70})_l$. $T_{\text{oven}} = 560^\circ\text{C}$.

like (Ar_n^{q+}) and (Na_n^{q+}) . Compared to other systems, the appearance sizes of fullerene clusters are rather small, as the size of the constituents is larger, as well as the polarizabilities and hence the binding energies. Thus, the competition between cohesive forces and Coulomb repulsion is more favorable for fullerene than for Ar and Na clusters. The observed difference in the appearance size for $q = 2$ for ionization by highly charged ions and by laser radiation is due to the lower energy transfer in collisions with highly charged ions as double ionization occurs already at very large impact parameters [15].

(ii) The analysis of mixed clusters shows that there is no remarkable difference between C_{60} and C_{70} molecules when forming clusters. The appearance sizes are more or less identical for $(\text{C}_{60})_n^{q+}$, $(\text{C}_{60})_{n-1}\text{C}_{70}^{q+}$, and $(\text{C}_{60})_{n-2}(\text{C}_{70})_2^{q+}$ for all observed charge states. Furthermore, the relative population of these mixed clusters corresponds approximately to a statistical population.

(iii) The mass spectra for individual charge states show peaks with enhanced intensity reflecting geometrical shell effects. For singly charged ions these intensity variations are not observed proving a low internal energy and the absence of evaporation processes. For $q = 2$ a slight increase occurs for $n = 13$, whereas a clearly enhanced intensity is observed for $n = 13, 19$, and 23 (for $q = 3$) and $n = 25$ and 29 (for $q = 4$). This indicates an increasing heating of the clusters with the degree of ionization.

TABLE I. Appearance sizes for various multiply charged clusters: (a) present values, (b) laser data from [1], (c) from [16], and (d) from [15].

q	$(\text{C}_{60})_n^{q+}$		$(\text{C}_{60})_{n-1}\text{C}_{70}^{q+}$	Ar_n^{q+}	Na_n^{q+}
	(a)	(b)	(a)	(c)	(d)
2	5	~ 25	5	91	25
3	10	\dots	11	226	49
4	21	\dots	22	\dots	72
5	(33)	\dots	(33)	\dots	92

The observed magic numbers correspond to the values communicated for $q = 1$ and 2 [1–4]. Thus, the structure of the fullerene clusters does not depend on the charge and corresponds to the structure of other neutral van der Waals clusters. This is true for the pure C_{60} as well as for the mixed (C_{60}, C_{70}) clusters.

These observations raise the question of charge mobility and to which extent the excess charge is mobile or localized in highly charged clusters of fullerenes. Information can be obtained from the analysis of the fragmentation spectra and the correlation between different charged fragments. Figure 1 shows multiply charged C_{60} molecules in charge states up to $q = 7$. However, this fact cannot be taken as an indication for charge localization as the primary cluster distribution contains also monomers and dimers to an unknown amount. On the other hand, surprisingly strong *evaporation series* of C_{60-2m}^{q+} ions are observed for low charge states (Fig. 1, $q = 1, 2$) which are totally absent in Xe^{20+}/C_{60} collisions. In order to further clarify the situation we regard in Fig. 3 mass spectra which correspond to a given multiplicity, which means where a given number of charged fragments has been detected per event.

When looking at the single-stop spectrum for $Xe^{25+}/(C_{60})_n$ collisions ($n = 1, 2, \dots$) [Fig. 3(b); one ion has been detected per event], we find a large similarity with the spectrum obtained in Xe^{20+}/C_{60} collisions [Fig. 3(a)]. In particular, the evaporation peaks C_{60-2m} disappear for the low charge states and very narrow peaks are measured in both cases. We therefore attribute the dominant part of this spectrum to the interaction with C_{60} monomers. The two-stops spectrum [Fig. 3(c)] contains contributions from intact fullerenes in charge states

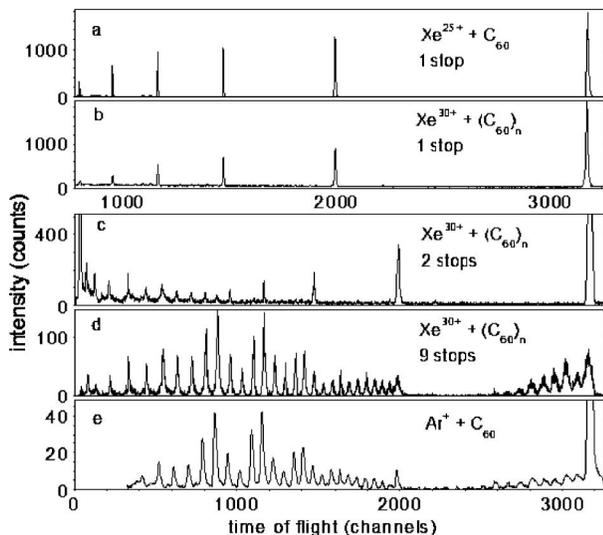


FIG. 3. Time-of-flight mass spectra: (a) $Xe^{25+} + C_{60}$, one stop; (b) $Xe^{30+} + (C_{60})_n$, one stop; (c) $Xe^{30+} + (C_{60})_n$, two stops; (d) $Xe^{30+} + (C_{60})_n$, nine stops; (e) $Ar^+ + C_{60}$, 2 keV, one stop.

up to $q = 5$ and small-size fragments ($C_n^+, n < 12$). The increased peak width (also visible for intact fullerenes) already indicates non-negligible kinetic energy releases during the fragmentation processes. The correlation between two fragments is analyzed in more detail in Fig. 4. It becomes evident that the two correlated fragments (C_{60}^{q+} or C_{70}^{q+}) tend to have a similar charge. Thus, C_{60}^+ fragments are measured in correlation with C_{60}^+ , or to a lower extent with C_{70}^+ and the doubly charged species C_{60}^{2+} and C_{70}^{2+} . On the other hand, C_{60}^{2+} shows a correlation with C_{60}^+ and C_{60}^{3+} , whereas for C_{60}^{3+} the dominant second fragments are C_{60}^{2+} and C_{60}^{4+} . Thus, the electric communication between neighboring charged fullerenes is rather high.

In the case of a high event multiplicity [see Fig. 3(d), nine stops; the cluster was ionized at least 9 times] the spectrum contains either singly charged fullerenes C_{60-2m}^+ or small-size fragments C_n^+ peaking at $n = 11$ and 15. An analysis shows a strong correlation either between the nearly intact molecules or the small fragments. Thus, a typical event where the cluster is ionized q times leads to the emission of q singly charged fullerenes which have lost one or several C_2 units or to the emission of q small singly charged fragments.

The distribution of the small fragments [Fig. 3(d)] is very similar to that obtained in low energy collisions of singly charged Ar^+ ions with C_{60} molecules [see Fig. 3(e) [17]]. In that case, the fragmentation is not charge induced but thermally activated. This comparison shows that the nine charges have to be well distributed over the cluster volume, as otherwise the charge-induced fragmentation of a highly charged fullerene molecule would lead to a fragment distribution which is peaked at C_1^+ as observed in close collisions between C_{60} monomers and slow highly charged ions (see, e.g., [18]).

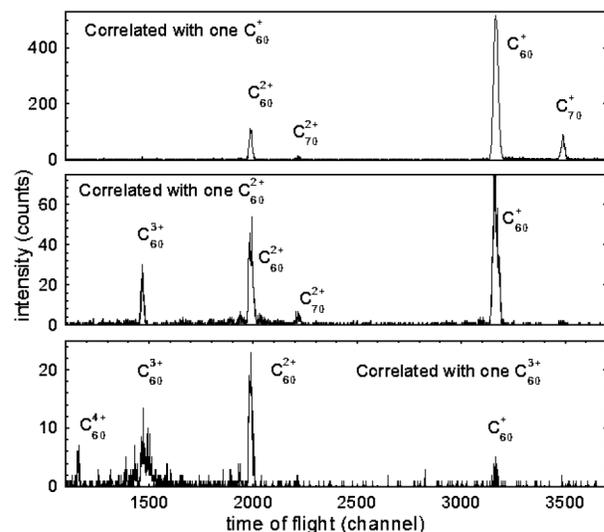


FIG. 4. Correlation spectra for two stops obtained in collisions between Xe^{30+} projectiles (600 keV) and $(C_{60})_n$ clusters (most likely $n = 2$).

How can the charge move in these multiply charged van der Waals clusters? The center distance between neighboring molecules is 10 Å in the neutral system; when singly charged, it is expected to become smaller due to the charge-induced dipole interaction. When treating two fullerene molecules as conducting spheres and developing the *classical over-the-barrier model* to describe the processes of charge transfer [19] we obtain critical distances for the transfer of the first electron which are 9.4, 9.8, 10.3, 11.0, and 11.7 Å for the charge states 1 to 5, respectively. Indeed, experimental studies with C_{60}^{4+} projectiles colliding with C_{60} have shown the validity of this model and have proven that a full electrical contact where both fullerenes share the charge equally is established at a center distance of 9.7 Å [20]. Thus, charged fullerenes in charge states ≥ 2 can communicate with their neighbors even at the equilibrium distance of the neutral fullerene cluster. But also for the charge 1 we might expect charge mobility when taking into account a slight reduction of the equilibrium distance due to the charge.

The ion-cluster interaction may be described by the following scenario: At large impact parameters the number of electrons captured by the projectile is low. Electrons will be taken most likely from the fullerene molecule which is closest to the projectile, but due to the charge mobility neighboring molecules might serve as electron donors as well. The charge will be distributed over several molecules and the multiply charged cluster becomes stable (depending on its size) as only a small amount of excitation energy has been transferred. At smaller impact parameters the cluster charge increases which will induce fragmentation processes characterized by singly or doubly charged fullerene molecules. At even smaller impact parameters both the charge and the transferred excitation energy increase. The charge and the electronic excitation energy are distributed rapidly in the cluster, which leads to a thermally activated fragmentation of low-charged fullerene molecules.

The different results obtained in multiply charged fullerene and Ar clusters might be related to the difference in the size and the polarizability of the corresponding building blocks. Thus, charged fullerene clusters are more strongly bound and do have critical distances for electron transfer which are larger or close to the equilibrium distance. Finally, the fragmentation time scale is expected to be slower due to the increased fullerene mass and the fact that charges on neighboring fullerenes can arrange in favorable positions (opposite sides) due to the high electron mobility on fullerene molecules, hereby reducing the effect of Coulomb repulsion.

In conclusion, we have shown that clusters of fullerenes can sustain excess charges up to $q = 5$ for rather small cluster sizes. The critical size for doubly charged clusters is much lower than that reported in laser experiments.

The correlated fragmentation spectra have shown that the charge is mobile within the cluster due to electron transfer processes, thus, these van der Waals clusters become conducting as soon as they are multiply charged. Furthermore, the geometrical structures of these clusters are found to be independent of the cluster charge and of the fact whether C_{60} or C_{70} molecules are used as building blocks.

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