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Energetics in charge-separation processes of highly charged fullerene ions

S. Tomita,* H. Lebius,† A. Brenac, F. Chandezon, and B. A. Huber†
Départment de Recherche Fondamentale sur la Matiére Condensée (DRFMC), CEA-Grenoble, 17 rue des Martyrs,
38054 Grenoble Cedex 9, France

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We have measured the kinetic energy release for the decay ${C_{60}}^{q+} \rightarrow {C_{60-2m}}^{(q-1)+} + {C_{2m}}^{+}$ for charge states $q=4$–8 and $m=1$ and 2. The measured kinetic-energy release increases linearly with the fullerene charge state. The estimates of the barrier heights, deduced from the kinetic-energy releases, agree well with the observations regarding the stability and the competition between charge separation (C_2^+ emission) and neutral C_2 emission of highly charged fullerenes.

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I. INTRODUCTION

The stabilities of finite-size systems against repulsive Coulomb potentials and the corresponding decay mechanisms play an important role in a large variety of fundamental phenomena. Thus, these processes have been studied for charged microdroplets, metal clusters, fullerenes, and atomic nuclei. Because of the high stability of spherical C_{60} molecules, the decay of multiply charged C_{60} ions has been studied by several authors, both theoretically [1–3] and experimentally [4–18] during the last decade. The highest charge state for stable ${C_{60}}^{q+}$ has been predicted to be $q=16$ by Seifert *et al.* [1], $q=13$ by Bastug *et al.* [2] and higher than $q>10$ by Cioslowski *et al.* [3]. Experimentally, ${C_{60}}^{7+}$ was observed in electron-impact collision [4], ${C_{60}}^{9+}$ in collisions with slow Bi^{44+} ions [13], and ${C_{60}}^{10+}$ in collisions with Xe^{25+} ions [12]. More recently, fullerene ions of ${C_{60}}^{11+}$ and ${C_{60}}^{12+}$ have been observed in experiments using an infrared intense femtosecond laser [19].

The different decay channels of these highly charged fullerene ions attract much interest as well. In particular, it has been shown that for medium charge states of the fullerene ion ${C_{60}}^{q+}$ ($q=3$–7), the process of the emission of small charged carbon clusters (asymmetric fission) plays an important role. In order to explain the experimental values for the kinetic-energy release occurring for charge separation of highly charged fullerene ions, ${C_{60}}^{q+} \rightarrow {C_{60-2m}}^{(q-1)+} + {C_{2m}}^{+}$, the charge-separation process has been described as a two-step mechanism where an electron is recaptured by the multiply charged fullerene from an emitted C_2 dimer (auto-charge-transfer model) [5,11]. In this model, the existence of a crossing point within a reasonable distance is required and the charge-separation process is dependent on the neutral evaporation as discussed in detail in Ref. [11]. Thus, the electron recapture probability determines the branching ratio between the two decay channels: charge separation and evaporation. On the other hand, if ${C_2}^{+}$ emission is considered as a direct process, the stability of the multiply charged fullerene is described in terms of a reaction barrier, and the height of this barrier has to be compared with the activation energy for C_2 emission in order to explain the competition between charge separation and evaporation.

In this paper we present experimental results on the kinetic-energy release for the decay reactions ${C_{60}}^{q+} \rightarrow {C_{60-2m}}^{(q-1)+} + {C_{2m}}^{+}$ for $q=4$–8, and $m=1$ and 2. The results are used to estimate the height of the reaction barrier. These estimates yield a good qualitative agreement with the experimental observations concerning the stability of highly charged fullerene ions with respect to the competition between the emission of neutral and charged C_2 dimers.

II. EXPERIMENT

Highly charged fullerene ions ${C_{60}}^{q+}$ were prepared in collisions between highly charged Xe ions (Xe^{25+}) and neutral C_{60} molecules at a collision energy of 280 keV. The highly charged ions were provided by the AIM (Accélerateur d'Ions Multicharges) facility in Grenoble. The ion beam was pulsed at a repetition rate of 10 kHz, yielding ion-beam pulses of 300 ns in width. Bulk C_{60} was heated to $\sim 520\,^{\circ}\mathrm{C}$ in an oven to produce a molecular beam of C_{60}, which crossed the projectile ion beam in the interaction region of a Wiley-McLaren time-of-flight mass spectrometer. The extraction field of 77.1 V/cm was applied 100 ns after the ion beam had passed through the interaction region. The fullerene ions and the fragments produced in the collision were extracted and analyzed with respect to their mass-to-charge ratios in the time-of-flight mass spectrometer. By using this delay, the peak profiles are mainly determined by the kinetic-energy releases in the fragmentation processes. The mass-analyzed recoil ions were detected with a "multistop" electronic acquisition device which allowed us to treat the data event by event for different decay processes. More details of the experimental procedure are given elsewhere [20,21].

III. RESULTS AND DISCUSSION

In Fig. 1, we show a spectrum of fragment ions obtained in collisions between Xe^{25+} ions and C_{60} molecules. Highly charged fullerene ions ${C_{60}}^{q+}$, as well as small fragment ions

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*Present address: Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark. Electronic address: tomita@phys.au.dk

†Present address: CIRIL-GANIL, Rue Claude Bloch, B.P. 5133, F-14070 Caen Cedex 05, France.

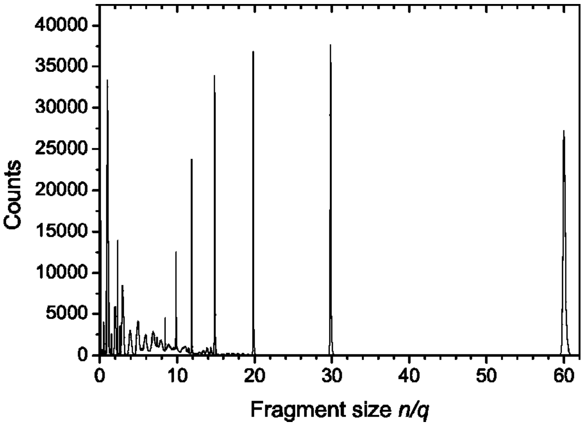

FIG. 1. Time-of-flight spectrum of fragment ions C_n^{q+} obtained in the collision between Xe^{25+} and C_{60}.

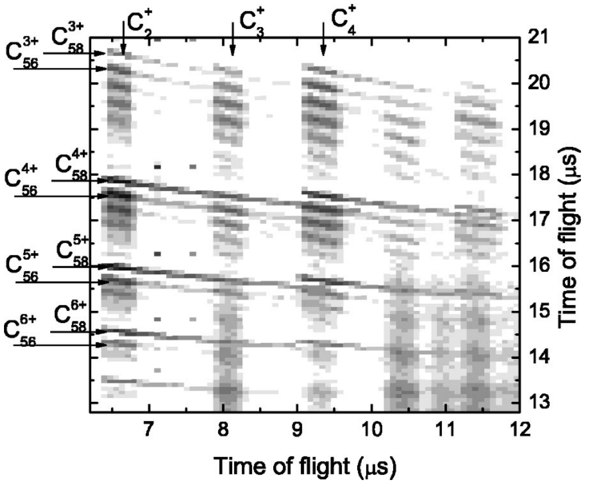

FIG. 3. Two-dimensional histogram showing the correlation between two fragment ions. The horizontal axis shows the time-of-flight of the small fragment ion and the vertical axis gives that of the second heavy fragment ion. Individual flight times are indicated by arrows.

C_n^+ $(1 \leqslant n \leqslant 11)$, are clearly observed. The peak widths of the C_n^+ fragments are much wider than those of C_{60}^{q+} because of the high kinetic-energy releases in the Coulomb explosion process [22]. Intact highly charged fullerene ions, such as C_{60}^{q+}, are easily observed up to $q=7$. For $q>7$, the spectrum is dominated by small fragments C_n^+ which are mainly produced through multifragmentation processes. Therefore, the higher charged fullerenes are more clearly seen when we plot only those events which are characterized by one stop per start (see Fig. 2). In this spectrum the peaks of small fragments are strongly suppressed, and highly charged fullerene ions up to C_{60}^{9+} are clearly identified. In the present data the highest charge state is 9 as observed by Jin *et al.* [13], although C_{60}^{10+} ions have been observed with Xe^{25+} projectiles [12], probably under more favorable experimental conditions.

In the present paper we will concentrate on the charge separation of highly charged fullerene molecules. In order to specify a decay channel, the correlation between two fragment ions in the same event has to be analyzed. In Fig. 3 we show the spectrum for two stop signals. The horizontal axis gives the time-of-flight of the first fragment and the vertical axis gives the time-of-flight of the second fragment. The two-dimensional spectrum shows coincidences between small and large fragment ions. The binary charge separation channels leading to the products $C_{60-2m}^{(q-1)+}+C_{2m}^+$, can be clearly identified for $m=1$ and 2, $q=4-8$. The tails from these channels, extending to larger drift times, are due to the delayed emission of C_{2m}^+ ions during acceleration of the recoil ions.

For these charge-separation events we constructed the corresponding histograms, i.e., the integrated peak intensity as a function of the time of flight. Figure 4 shows an example of such a gated spectrum for the event $C_{60}^{5+} \rightarrow C_{58}^{4+} + C_2^+$. The peak for C_2^+ has a rectangular shape accompanied by a tail due to delayed emission of C_2^+ with a corresponding lifetime of the order of several microseconds [7]. The rectangular shape is due to the kinetic-energy of the emitted C_2^+ ion. Chen *et al.* [8,9] also reported similar spectra for the decay of C_{60}^{5+} ions. However, in their case the rectangular profile was often modified by a larger exponen-

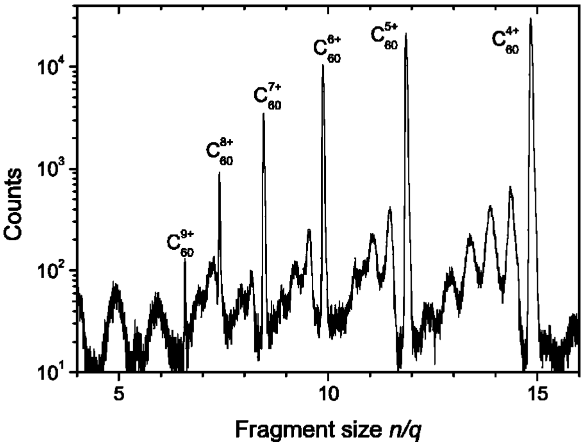

FIG. 2. Time-of-flight spectrum of fragment ions C_n^{q+} obtained by plotting events which contain only one stop signal.

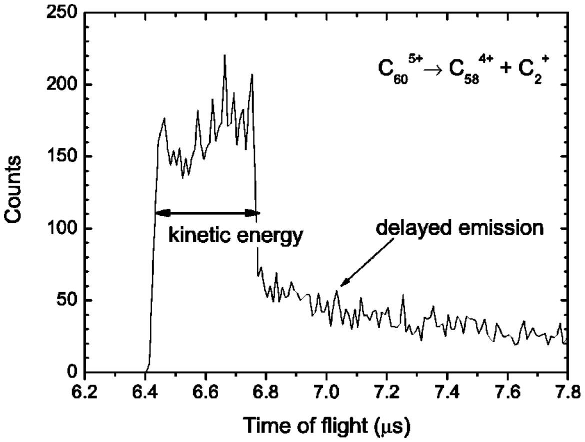

FIG. 4. The gated spectrum for the charge separation channel of $C_{58}^{4+}+C_2^+$.

TABLE I. Kinetic-energy releases for the charge-separation reaction $C_{60}{}^{q+} \rightarrow C_{60-n}{}^{(q-1)+} + C_n{}^{+}$.

	Kinetic energy (eV)	
Charge q	$C_2{}^{+}$	$C_4{}^{+}$
4	4.8±0.4	5.3±0.4
5	7.2±0.8	7.7±1.1
6	8.9±0.9	9.4±0.8
7	11.7±1.5	10.6±1.2
8	12.5±3.3	

tial time-of-flight profile due to the delayed charge-separation effect that becomes more important in the case of continuous extraction [14,15]. Due to the delay between collision and extraction, the peak shape is determined in the present work by the kinetic-energy of the fragment ion. This makes it possible to measure the kinetic energy release for the higher charged fullerene ions up to $C_{60}{}^{8+}$. The kinetic energy release has been determined by measuring the width of the time-of-flight spectrum, Δt, and by using the following relation obtained from Ref. [23]:

$$\Delta t = \frac{2}{\epsilon}\sqrt{\frac{2mE}{q}}, \tag{1}$$

where ϵ is the extraction field, m is the mass, q is the charge state of the ion, and E is its kinetic energy. The accuracy of Eq. (1) has been checked by measuring the kinetic energies for the Coulomb breakup of multiply charged nitrogen molecules, $N_2{}^{q+} \rightarrow N^{(q-r)+} + N^{r+}$, and comparing the results with those of Ref. [24]. In addition, we have also performed simulations with the SIMION trajectory program [25] to ensure that the geometrical efficiency of the spectrometer is close to 100% for the kinetic energies measured in this work [22].

The kinetic-energy releases for the charge-separation channels, $C_{60}{}^{q+} \rightarrow C_{60-2m}{}^{(q-1)+} + C_{2m}{}^{+}$, as obtained from the widths of the gated spectra for $q=4$–8 and $m=1$ and 2 are summarized in Table I. One remarkable result is the similarity of the kinetic-energy releases for $C_2{}^{+}$ and $C_4{}^{+}$ emission, even though the activation energy for neutral C_2 emission should be much smaller than that for C_4 because C_2 emission is the main decay channel of C_{60}. Similar results were obtained earlier by other groups [8,10]. These results imply that the kinetic-energy release is mainly determined by electrostatic repulsion. In Fig. 5 we show the kinetic-energy release for the emission of $C_2{}^{+}$ as a function of the charge state of the parent $C_{60}{}^{q+}$ ion together with results from Ref. [5]. The present analysis shows a linear increase with charge state, and a linear fit gives the following relation for the kinetic-energy release:

$$E_{kin}(C_{58}{}^{(q-1)+} + C_2{}^{+}) = 2.16q - 3.8 \ \text{eV}. \tag{2}$$

In general, the two measurements agree with each other except that our kinetic-energy release for $C_{60}{}^{7+}$ is somewhat higher. Scheier *et al.* have measured the unimolecular decay of $C_{60}{}^{q+}$ with the aid of a tandem mass spectrometer. In that case, the $C_{60}{}^{q+}$ ions had to survive the time scale of several microseconds in order to be selected as a precursor ion. In the present experiment it is the other way round as we analyze the decay of highly charged fullerene ions which decay within the first several hundred nanoseconds. In order to be observed as a charge-separation event within the rectangular peak shape, they have to decay before extraction occurs. Thus, the internal energies of the sampled fullerene ions are quite different in the two experiments. This fact should influence the charge separation rate but should have less or no influence on the kinetic-energy release.

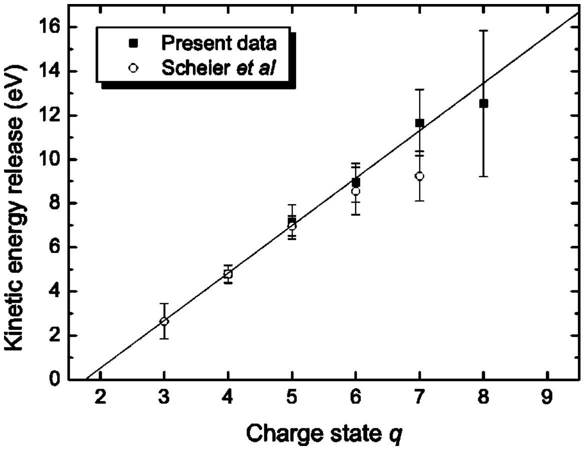

FIG. 5. Kinetic-energy release for the decay $C_{60}{}^{q+} \rightarrow C_{58}{}^{(q-1)+} + C_2{}^{+}$ as a function of initial charge state q. Full squares are the present data. Open circles are results from Ref. [5].

The absolute values of the measured kinetic-energy releases are too small to be explained by a simple Coulomb repulsion model, as pointed out earlier [5,11]. A possible explanation is based on the auto-charge-transfer mechanism where an electron is captured by the highly charged fullerene from the emitted neutral C_2 dimer. In this two-step process the decay rate is linked to the C_2 emission rate, and the branching ratio between neutral and charged C_2 emission is determined by electron recapture probability. Thus, the kinetic-energy release contains information about the crossing point of the potential curves for evaporation and charge separation, in particular, on the distance where charge transfer occurs. The involved molecular potential curves describe the systems $C_{58}{}^{q+} + C_2$ and $C_{58}{}^{(q-1)+} + C_2{}^{+}$ [11]. On the other hand, if we assume a direct emission of $C_2{}^{+}$ (single-step process), the charge separation is independent of, but still competing with, evaporation; and it is the height of the fission barrier which should be compared to the activation energy for C_2 emission. The measured kinetic-energy release does not allow to distinguish between the two mechanisms; however, particularly for higher charge states, where the fission barrier becomes very low, we favor a single-step mechanism as in this case a crossing point may not exist [26].

In order to further discuss the energetics of the charge-separation process of highly charged fullerenes, we first consider the activation energy for C_2 emission. Assuming that there are no strong structural differences between multiply charged C_{60} ions and the neutral system, we can estimate the activation energy for the emission of neutral C_2 dimers from ${C_{60}}^{q+}$ by considering only the difference of the ionization energies,

$$D({C_{58}}^{q+}+C_2)=D({C_{58}}^{+}+C_2)-\sum_{q'=2}^{q}[I_{q'}(C_{60})-I_{q'}(C_{58})]. \tag{3}$$

Here, $D({C_{58}}^{q+}+C_2)$ corresponds to the dissociation or activation energy of the C_2 evaporation process, and $I_q(C_{60})$ and $I_q(C_{58})$ to the ionization potential of $C_{60}^{(q-1)}$ and $C_{58}^{(q-1)}$, respectively. The dissociation energy of ${C_{60}}^{+}$ is $D({C_{58}}^{+}+C_2)=9.8$ eV [27]. As discussed in Ref. [28], the qth ionization energy of C_{60} is well approximated by that of a charged conducting sphere, which can be expressed as

$$I_q(C_{60})=W+(q-1/2)/a, \tag{4}$$

where a is the radius of C_{60} and W is bulk work function. Within this model of a charged conducting sphere the ionization potential of other fullerenes can be scaled with their size. Thus, for C_{58} the ionization energy is estimated with a slightly smaller radius, which conserves the surface charge density,

$$I_q(C_{58})=\sqrt{60/58}(q-1/2)+W. \tag{5}$$

This scaling results in only a small difference with respect to the ionization energy for C_{60}, and we will neglect it in the following discussion. Thus we use the same ionization energy for C_{58} as for C_{60} and the dissociation energy for neutral C_2 loss from ${C_{60}}^{q+}$ should depend on its charge state very weakly, i.e., $D({C_{58}}^{q+}+C_2)\sim 9.8$ eV for all q. This approximation is supported by the experimental results for the activation energy for ${C_{60}}^{2+}$ where only a small difference has been observed compared to that for ${C_{60}}^{+}$ [27,29].

In the present work we use a slightly different expression for the ionization energy for fullerenes,

$$I_q(C_{60})=3.85+3.39q \quad \text{eV}, \tag{6}$$

which has been used by Walch *et al.* [30] based on Dirac-Fock-Slater calculations by Bastug *et al.* [2]. The difference in energy levels between ${C_{58}}^{q+}+C_2$ and ${C_{58}}^{(q-1)+}+{C_2}^{+}$ is given by the difference of the ionization energies, $I_q(C_{58})-I(C_2)$, where $I(C_2)=11.41$ eV [31]. Thus, the difference in energy between the initial state ${C_{60}}^{q+}$ and the asymptotic final state ${C_{58}}^{(q-1)+}+{C_2}^{+}$, ΔE_q, is given by

$$\Delta E_q=D({C_{58}}^{q+}+C_2)+I(C_2)-I_q(C_{58})\simeq 17.36-3.39q \quad \text{eV}. \tag{7}$$

The height of the reaction barrier, B_q, is determined from the measured kinetic-energy release,

$$B_q=\Delta E_q+E_{kin}({C_{58}}^{(q-1)+}+{C_2}^{+})\simeq 13.56-1.23q \quad \text{eV}. \tag{8}$$

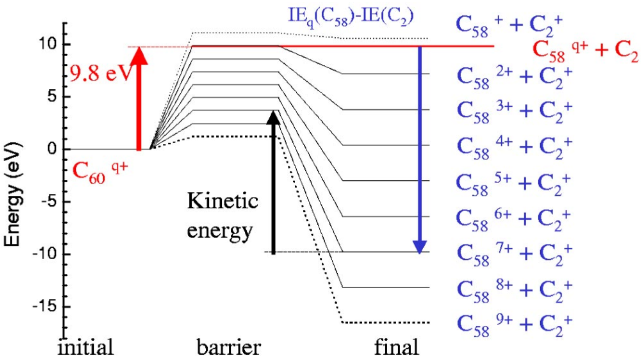

FIG. 6. Energy levels for the decay of highly charged fullerenes compared to the initial state. Barrier heights for ${C_2}^{+}$ emission are estimated with Eq. (8). Arrows indicate $D({C_{58}}^{q+}+C_2)$, ΔE_q [Eq. (7)], and kinetic-energy release $E_{kin}({C_{58}}^{(q-1)+}+{C_2}^{+})$ for the case of $q=8$.

In Fig. 6 the barrier heights obtained by using Eq. (8) and the kinetic-energy release according to Eq. (2) are shown as a function of the charge state q. As can be seen, the height of the reaction barrier for ${C_{60}}^{2+}$ (extrapolated curve) is larger than the activation energy of neutral C_2 emission, and for this case evaporation should dominate the charge separation process. This finding agrees well with the experimental result obtained by Scheier *et al.* [5] who did not observe ${C_2}^{+}$ emission, from ${C_{60}}^{2+}$. For $q=3$, the barrier height becomes equal to the activation energy, and thus we expect that evaporation and charge-separation should become competitive, which was also observed experimentally [15,16]. With increasing charge state the barrier height becomes much lower than the neutral dissociation energy, which strongly favors the emission of singly charged dimers. For ${C_{60}}^{9+}$, the intermediate energy level still lies above the initial state and a stabilizing barrier of about 2.5 eV exists. In Fig. 6 we also show the extrapolated results for ${C_{60}}^{10+}$ as a dotted line. In this case the estimation of the barrier height for ${C_{60}}^{10+}$ yields a small value (1.3 eV). A further extrapolation shows that the limit of stability is reached for charge states between 11 and 12. However, it should be noted that the detection of intact, highly charged fullerene ions requires very low internal energies of the ionized system and short experimental time scales, so that the system can survive during the analyzing time of several microseconds. The internal energy of C_{60} at 700 K can be estimated to be 3.9 eV by using scaled vibrational frequency calculated by Stanton and Newton [32] with a reduction by 10% [33]. Together with the energy transfer in the ionizing collision, this will provoke high charge-separation rates for highly charged fullerenes, and most of the ions initially formed in very high charge states will have decayed on their way to the detector. The fact that ${C_{60}}^{12+}$ has been observed experimentally [19] might indicate that the estimated ionization energies should be replaced by more precisely calculated ones [34] or that vibrational excitations after the charge-separation processes have to be taken into account [35]. Furthermore, the highest charge state for stable ${C_{60}}^{q+}$ is directly related to the value of dissociation energy of C_{60}. If $D({C_{58}}^{q+}+C_2)\geqslant 11$ eV, ${C_{60}}^{12+}$ can be stable.

The results described above, in particular the interpretation of the binary decay by a reaction barrier, explain the experimental results very well considering the simplicity of the argument. A similar discussion concerning the sequential loss of charged fragments from $C_{60}{}^{5+}$ has also been used successfully by Chen *et al.* [9]. In both investigations, their studies and the present work, the direct emission model explains experimental results very well. Furthermore, the high mobility of charges on the fullerene surface (as demonstrated in many fragmentation and collision studies of highly charged fullerenes [36–38]), and the Coulomb repulsion between individual surface charges will favor the direct formation of a charged fragment as soon as it tries to leave the multiply charged system, provided that the reaction barrier is lower than the evaporation energy. In addition, the reaction barrier concept has been applied very successfully for metallic sodium clusters [39]. In that case, evaporation (emission of a neutral monomer) and charge separation (emission of small size charged fragments, dominated by a singly charged trimer) have been shown to be independent, competitive processes. The low kinetic-energy releases in the C_{60} case and hence the low reaction barriers might be due to the large polarizability of both the fullerene and the fragment molecule or to a strong structural deformation taking place during the emission of the charged particle. The role of the polarizabilities of the fragments $C_{58}{}^{q+}$ and $C_2{}^{+}$ are discussed in detail in Ref. [26]. In this paper, additional measurements of kinetic-energy releases using a two-dimensional imaging technique rather than a time-of-flight peak shape analysis are presented. These data agre quite well with the results of the present paper.

IV. CONCLUSIONS

We have measured the kinetic-energy release for the fragmentation process $C_{60}{}^{q+} \rightarrow C_{60-2m}{}^{(q-1)+} + C_{2m}{}^{+}$ for $q = 4–8$ and $m=1$ and 2 by coincident detection of both fragments. The kinetic-energy releases for $4 \leqslant q \leqslant 7$ agree well with earlier experimental results. For fullerenes in higher charge states, the kinetic-energy release continues to increase linearly. The estimation of barrier heights is in agreement with observations of the competition between the evaporation of neutral C_2 and the emission of charged $C_2{}^{+}$ ions. The present analysis shows that the concept of a reaction barrier can explain the stability limit and the competition with the neutral evaporation channel as well as the auto-charge-transfer model. The low kinetic-energy releases and low reaction barriers might be caused by the large polarizability of the fullerene or by strong structural deformation taking place during the emission of charged particles.

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