Sequential Reaction Channels of Metastable C_{60}^{4+}

B. Dünser, O. Echt,* P. Scheier, and T. D. Märk

Institut für Ionenphysik, Leopold Franzens Universität, Technikerstrasse 25, A-6020 Innsbruck, Austria

(Received 31 July 1997)

We employ a two-sector-field mass spectrometer to identify sequential, unimolecular dissociation channels of C_{60}^{4+}. In addition to sequential "monomer evaporations" (loss of two C_2 units), we observe two novel sequential channels which involve fissionlike events: loss of C_2^+ followed by evaporation, and sequential loss of two C_2^+ units. [S0031-9007(97)04493-1]

PACS numbers: 36.40.Qv, 34.80.Gs

Strongly bound, highly excited finite atomic systems may emit electrons, neutral particles, or a continuous spectrum of photons. These phenomena are the molecular analogs of thermionic emission, evaporation, and blackbody radiation, respectively [1–3]. In addition, *multiply* charged systems may undergo fission; i.e., they may eject charged rather than neutral fragments, analogous to nuclear fission [4,5]. Fission of atomic nuclei is usually accompanied by other reactions: emission of prompt and delayed neutrons, beta decay, or emission of gamma quanta and, occasionally, of alpha particles [6]. Alpha decay, which itself may be considered a special case of fission [6–9], transforms heavy radionuclides such as U-238 or Np-237 through long decay chains into stable nuclides. In this Letter we shall present the first experimental evidence for the occurrence of analogous, sequential fissionlike processes [10], in multiply charged fullerenes.

Fission of *atomic clusters* is observed for fissility parameters well below 1.0; i.e., fission is, like monomer evaporation (but unlike spontaneous nuclear fission), a statistical, thermally activated process [11]. There is a range of experimental conditions under which both channels are active. For example, the frequently quoted "critical size" $n_c(z)$ of z-fold multiply charged clusters represents a lower bound to their observability under typical experimental conditions; it marks the size for which the fission barrier and the heat of evaporation are approximately equal. Spontaneous (i.e., unimolecular, statistical) fission as well as evaporation have been identified in the vicinity of $n_c(z)$ [12,13]. Either process will bring about a reduction in the effective vibrational temperature. Nevertheless, if the system is sufficiently large this reduction will be small, and the cluster may decay further within the observational time window. Sequential decay reactions have, in fact, been observed for multiply charged fullerenes C_{60}^{z+} and C_{58}^{z+}. They did not, however, involve fissionlike processes because the charge states of parent and daughter were identical [14]. On the other hand, previous reports about evaporation following fission of van-der-Waals and alkali clusters involved *induced* fission; the multiply charged parent clusters were heated by collisions [15,16], by photon ionization [17], or by photon absorption [18].

In the present study we demonstrate that spontaneous, "fissionlike" reactions of fullerenes [10] may be followed either by evaporation or by another fissionlike event. Specifically, we investigate with a two-sector-field mass spectrometer spontaneous (unimolecular) decay of C_{60}^{4+} into C_{58}^{3+} in the first field-free region,

$$C_{60}^{4+} \xrightarrow{1\text{ff}} C_{58}^{3+} + C_2^+, \tag{1a}$$

and subsequent unimolecular reactions in the second field-free region,

$$C_{60}^{4+} \xrightarrow{1\text{ff}} C_{58}^{3+} + C_2^+ \xrightarrow{2\text{ff}} C_{56}^{3+} + C_2^+ + C_2, \tag{1b}$$

$$C_{60}^{4+} \xrightarrow{1\text{ff}} C_{58}^{3+} + C_2^+ \xrightarrow{2\text{ff}} C_{56}^{2+} + 2C_2^+, \tag{1c}$$

where regions 1ff (first field-free region) and 2ff (second field-free region) correspond to time windows $3.8 \leq t \leq 15.6$ μs and $24.5 \leq t \leq 30.4$ μs, respectively, measured with respect to the time at which the parent ion C_{60}^{4+} was formed by electron impact ionization in the ion source of the mass spectrometer. In other words, we observe reactions which follow the initial, spontaneous reaction (emission of C_2^+) with a delay of about 10 to 25 μs.

In the preceding paragraph we have used the term "fissionlike" because loss of C_2^+ from highly charged fullerenes has been shown to proceed in three steps: (i) Statistically driven evaporation of C_2, (ii) electron transfer from the neutral dimer to the remaining fragment at a distance of several Å, and (iii) separation of the charged fragments by Coulomb repulsion leading to large, experimentally accessible kinetic energies [19,20]. These auto-charge-transfer (ACT) reactions are distinct from genuine fission encountered in other atomic clusters, but the net result, and the energy balance of the reaction, are the same.

Fission in 1ff [reaction (1a)] competes with evaporation [19,20]

$$C_{60}^{4+} \xrightarrow{1\text{ff}} C_{58}^{4+} + C_2, \tag{2a}$$

which may be followed by another evaporative event,

$$C_{60}^{4+} \xrightarrow{1\text{ff}} C_{58}^{4+} + C_2 \xrightarrow{2\text{ff}} C_{56}^{4+} + 2C_2, \tag{2b}$$

0031-9007/97/79(20)/3861(4)$10.00

i.e., two sequential, spontaneous evaporations like those reported previously for singly, doubly, and triply charged C_{60} [14].

A fourth type of sequential reactions,

$$C_{60}^{4+} \xrightarrow{1ff} C_{58}^{4+} + C_2 \xrightarrow{2ff} C_{56}^{3+} + C_2 + C_2^+, \qquad (2c)$$

i.e., evaporation followed by fission, could not be identified, however.

The present measurements were performed with a double-focusing two-sector-field mass spectrometer (reversed geometry) with a mass range of 10 000 amu at a nominal acceleration voltage of 3 kV [19]. C_{60} powder of 99.99% purity was evaporated in a temperature-controlled oven typically operated at 950 K. After entering the modified Nier-type ion source via a skimmer and collimator, the effusive molecular beam was crossed at right angles by an electron beam typically operated at an energy of 200 eV and electron currents of up to 1 mA. Details about the efficient production of highly charged fullerenes have been reported elsewhere [19]. The resulting ions (charge state z) were extracted from the ion source by a weak electric field and accelerated to a translational energy of $3z$ keV. After passing through a first field-free region (1ff, length 61 cm), the ions are momentum analyzed by a magnetic sector before entering a second field-free region (2ff, length 33.3 cm). Next, the ions are energy analyzed by an electric sector field and detected by an electron multiplier operated in the single-ion counting mode.

Unimolecular dissociation occurring in the two field-free regions of this mass spectrometer is identified by decoupling the two analyzing fields [21]. Consider the reaction $(m_1, z_1) \rightarrow (m_2, z_2)$ occurring in the 1ff region, i.e., metastable decay of a parent ion of mass m_1 and charge state z_1, fully accelerated to an energy $3z_1$ keV. The reaction is monitored by tuning the magnetic sector to a nominal mass $m^* = m_2^2 z_1 / z_2^2 m_1$ and the electric sector to a nominal field $E^* = E m_2 z_1 / m_1 z_2$ where E denotes the sector field necessary to transmit the parent ion. If, however, the product ion (m_2, z_2) undergoes further decay into (m_3, z_3) in the 2ff region, after the magnet but before the electric sector, then it will only pass the electric sector at a nominal field $E^* = E m_3 z_1 / m_1 z_3$. Our previous experiments on sequential reactions [14,22] had been restricted to those for which $z_1 = z_2 = z_3$.

In principle, fragmentation may also be induced by collisions with background gas. Its relative contribution will depend on the pressure (in our case, below 4×10^{-6} Pa in the 1ff region and 4×10^{-6} Pa in the 2ff region), and on the probability of the unimolecular reaction being considered. We have verified that collision-induced contributions to the reactions presented in this Letter are negligible. The shift of electron energy thresholds for the formation of product ions, studied in different regions of the mass spectrometer, clearly shows that collisions do not contribute significantly [14].

Figure 1 presents direct evidence that spontaneous fission of C_{60}^{4+} may be followed either by evaporation or by another fissionlike event. Panel (a) displays a mass spectrum of the C_{60}^{4+} parent ion [mass-to-charge ratio 180.0 Thomson for the $(C\text{-}12)_{60}^{4+}$ isotopomer]. This ion coincides with $(C\text{-}12)_{15}^{+}$, but the peaks at fractional mass-to-charge ratios (180.25, 180.50, and 180.75 Thomson) are solely due to C_{60}^{4+} containing one to three C-13 isotopes which have a natural abundance of 1.1%. They can be used to deconvolute the mass spectrum [19]. The dashed line in Fig. 1(a) represents the intensity of C_{60}^{4+} isotopomers corrected for the contamination by C_{15}^{+} isotopomers. It should be noted that spectra of product ions discussed below do not suffer from this kind of contamination even though the apparent resolution is poorer, because the "nominal masses" m^* and translational energies of fragment ions from C_{15}^{+} are different from those being considered for C_{60}^{4+}.

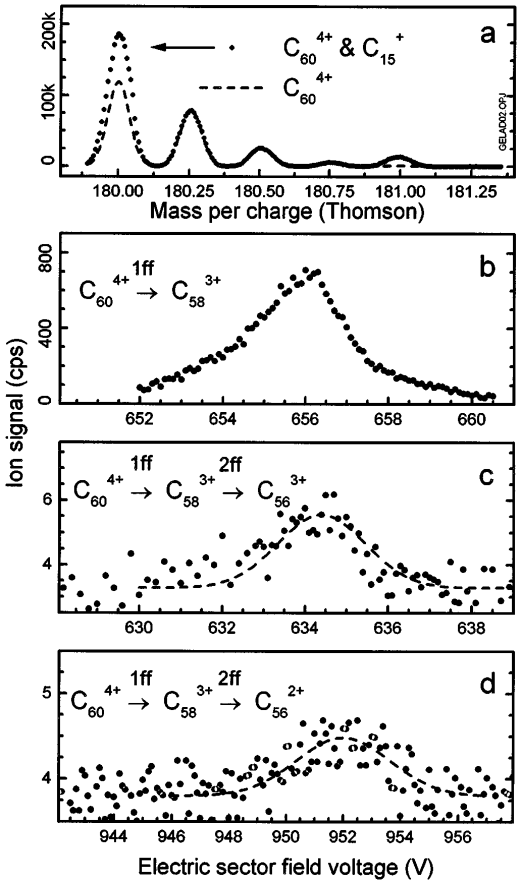

FIG. 1. Mass spectral evidence for unimolecular reactions following fissionlike ejection of C_2^+. (a) Parent ion C_{60}^{4+} with (dots) and without (dashed curve) contamination by C_{15}^{+}. (b) Loss of C_2^+ from C_{60}^{4+} in the 1ff region. (c) and (d) Fission followed by evaporation [reaction (1b)] and by fission [reaction (1c)], respectively. Dashed lines in panels (c) and (d) are drawn to guide the eye.

Figure 1(b) shows a scan of the electric sector field [MIKE (mass analyzed ion kinetic energy) scan [21]] with the magnet being tuned to the C_{58}^{3+} daughter ion, produced via reaction (1a), which forms a peak at a sector field voltage of 656 V. The same MIKE scan

reveals two additional peaks [Figs. 1(c) and 1(d)] which are themselves fragments of the C_{58}^{3+} fragment, formed in the second field-free region. The one at 634.5 V is due to C_{56}^{3+} [reaction (1b), Fig. 1(c)] and the other one at 952 V is due to C_{56}^{2+} [reaction (1c), Fig. 1(d)]. The probabilities of these reactions are approximately as follows: 0.6% for fission in the 1ff region, 0.76% for evaporation in 2ff, and 0.13% for fission in 2ff. These values specify the intensity of the product ions relative to their immediate precursors. The overall probabilities of the sequential reactions (final product ions relative to C_{60}^{4+}) are, therefore, 0.0046% and 0.00078% for reactions (1b) and (1c), respectively. These values have been evaluated from the experimental data taking into account the different peak widths, which in turn reflect the kinetic energy being released in the reactions.

Figure 2 presents analogous measurements identifying reaction (2b). Panel 2(a) displays the C_{60}^{4+} parent ion, which undergoes unimolecular decay into $C_{58}^{4+} + C_2$ in the 1ff region with a probability of 3.9% [reaction (2a), Fig. 2(b)]. This daughter ion decays further into C_{56}^{4+} in 2ff with a probability of 0.77% [Fig. 2(c)], i.e., sequential evaporation of two C_2 units from C_{60}^{4+} [reaction (2b)] occurs with a probability of 0.030%.

Reaction (2c), evaporation followed by fission, could not be identified with sufficient certainty. The second step of this reaction might be expected to proceed with enhanced probability, because the reduction in size of a highly charged atomic cluster increases its fissility [4,5]. (A similar enhancement is expected for auto charge transfer reactions, because the potential energy curves for the two relevant reactions, evaporation of neutrals versus fission, cross at a shorter separation, leading to a reduced energy of the intermediate state.) On the other hand, the first evaporative step reduces the thermal excitation of the complex. A weak peak at the expected electric sector field voltage has been observed, but we cannot exclude that it relates to another reaction, namely, loss of C_4^+ from C_{56}^{4+} in the 2ff region. The C_{52}^{3+} product ion from this reaction features a broad kinetic energy distribution [23,24], masking any other nearby daughter ion peaks.

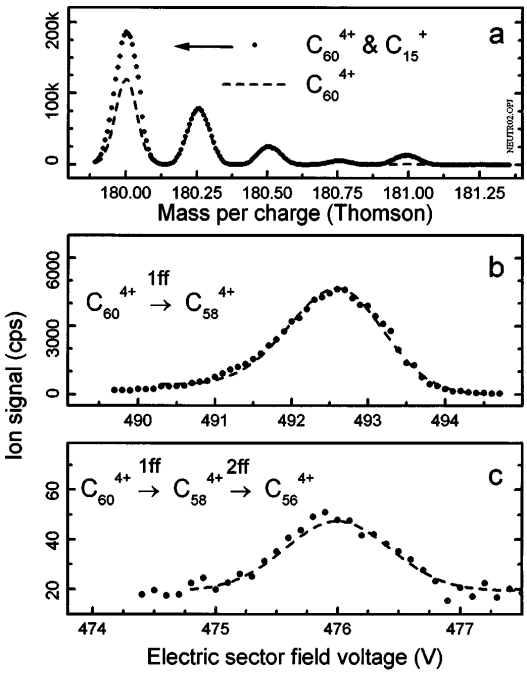

FIG. 2. Mass spectral evidence for sequential evaporation of two C_2 units. (a) Parent ion C_{60}^{4+} with (dots) and without (dashed curve) contamination by C_{15}^{+}. (b) Evaporation of a single C_2 unit in the 1ff region. (c) Evaporation of C_2 in the 1ff region followed by another evaporative event in the 2ff region [reaction 2(b)]. Dashed lines in panels (b) and (c) are drawn to guide the eye.

We have previously determined the probabilities of competing reactions, evaporation versus "fission," for metastable C_{60}^{z+} with charge states $3 \leq z \leq 6$ [19]. The current results allow us to investigate the intriguing question if the history of a metastable ion, i.e., the type of reaction by which it was formed, influences these probabilities, or their branching ratios. Such an effect may arise for the following reasons:

(1) In the second step of the sequential reactions (1b) and (1c), we are dealing with C_{58}^{3+}, a system of reduced size (relative to C_{60}^{3+}). For genuine fission (escape of C_2^+ across a fission barrier) this reduction in size would, within a simple liquid-drop approximation, be accompanied by a reduction in the height of the barrier. However, the activation energy for the competing reaction, evaporation of neutral C_2, would probably not change significantly, provided the relatively weak size dependence of evaporation energies for neutral and singly charged fullerenes, for $n \leq 60$, carries over to higher charge states [25–28].

(2) Fission as well as evaporation would yield a fullerene fragment ion of reduced thermal (vibrational) energy. For any subsequent reaction, this would enhance the branching ratio in favor of the energetically less costly reaction.

(3) If, however, loss of C_2^+ proceeds via ACT instead of genuine fission, then the fullerene fragment ion could be considerably hotter than the same fragment ion produced by some other mechanism. A detailed consideration of the energy balance, taking into account experimentally determined kinetic energy release data as well as ionization energies of C_2 and estimated electron affinities of C_{58}^{z+}, reveals that the thermal excess energy of the C_{58}^{3+} product ion of ACT [reaction (1a)] would be larger by about 4 eV than that of C_{58}^{4+}, produced from the same precursor (C_{60}^{4+}) by evaporation [reaction (2a)] [29,30].

In order to identify any of the above-mentioned effects, one would need to compare the reaction probabilities of C_n^{z+} ions, produced by two different, experimentally selected mechanisms. Exactly these kinds of data are not available, but we can compare the decay of C_{58}^{3+} produced by a specific reaction (C_2^+ loss), with the decay of an ensemble of C_{58}^{3+} produced by a superposition of unspecified reactions (C_2^+ loss and/or evaporation). These latter types of data have been recorded recently, a branching ratio of about 6×10^{-4} for C_2^+ loss relative to evaporation (C_2

loss) was obtained [31,32]. This contrasts with a branching ratio of $0.13/0.76 = 0.17$ for reaction (1c) versus (1b) found in the present work; i.e., our data reveal an enhancement of the C_2^+ loss channel by a factor of about 300. Even if one concedes that the individual reaction probabilities carry experimental uncertainties of some 50%, it is obvious that the ensemble of C_{58}^{3+}, produced via reaction (1a), exhibits an increased tendency for further C_2^+ loss.

In summary, we have identified sequential unimolecular reactions involving the ejection of one or two small, charged units. These types of reactions had not been observed so far for any kind of atomic cluster. It is, in spite of the profound differences between "spontaneous" reactions of atomic clusters and of atomic nuclei, tempting to draw a formal analogy between these new decay modes of multiply charged fullerene ions, and sequential alpha decay of heavy radionuclides (which also involves competition with another reaction channel, namely, β^- decay). Furthermore, the history of metastable fullerene ions, C_{58}^{3+}, has been shown to have a dramatic effect on the branching ratio of subsequent reactions.

This work was partially supported by the Österreichischer Fonds zur Förderung der Wissenschaftlichen Forschung, The Bundesministerium für Wissenschaft und Verkehr and The Jubiläumsfonds der Österreichischen Nationalbank, Wien, The EURATOM/OEAW Association, Wien, and The Fonds Zur verstärkten Förderung von wissenschaftlichen Auslandsbeziehungen, Leopold Franzens Universität, Innsbruck.

*Permanent address: Department of Physics, University of New Hampshire, Durham, NH 03824.

[1] C. E. Klots and R. N. Compton, Surf. Rev. Lett. **3**, 535 (1996); K. Hansen and O. Echt, Phys. Rev. Lett. **78**, 2337 (1997); R. Deng, G. Littlefield, and O. Echt, Z. Phys. D **40**, 355 (1997).

[2] C. E. Klots, J. Phys. Chem. **92**, 5864 (1988); P. Fröbrich, Ann. Phys. **6**, 403 (1997).

[3] U. Frenzel, U. Hammer, H. Werstje, and D. Kreisle, Z. Phys. D **40**, 108 (1997); R. Mitzner and E. E. B. Campbell, J. Chem. Phys. **103**, 2445 (1995); A. A. Vostrikov, D. Y. Dubov, and A. A. Agarkov, JETP Lett. **63**, 963 (1996).

[4] O. Echt and T. D. Märk in *Clusters of Atoms and Molecules II*, edited by H. Haberland, Springer Series in Chemical Physics (Springer-Verlag, Berlin, 1994), Vol. 56, p. 183.

[5] U. Näher, S. Bjørnholm, S. Frauendorf, F. Garcias, and C. Guet, Phys. Rep. **285**, 245 (1997).

[6] E. Segre, *Nuclei and Particles: An Introduction to Nuclear and Subnuclear Physics* (W. A. Benjamin, Reading, MA, 1977), 2nd ed.

[7] D. N. Poenaru, M. Ivascu, and A. Sandulescu, J. Phys. G **5**, L169 (1979); A. Sandulescu, J. Phys. G **15**, 529 (1989).

[8] In nuclear physics one usually distinguishes between (more or less symmetric) fission and emission of alpha particles, but these processes may be viewed as extreme modes of a more general phenomenon, linked by the recently discovered superasymmetric fission (cluster decay).

[9] A. Sandulescu and W. Greiner, Rep. Prog. Phys. **55**, 1423 (1992).

[10] By "fission" of multiply charged fullerenes we shall mean any process in which a charged fragment ion, such as C_2^+, C_4^+, C_6^+, etc., is emitted.

[11] U. Näher, S. Frank, N. Malinowski, U. Zimmermann, and T. P. Martin, Z. Phys. D **31**, 191 (1994).

[12] O. Echt, D. Kreisle, E. Recknagel, J. J. Saenz, R. Casero, and J. M. Soler, Phys. Rev. A **38**, 3236 (1988).

[13] K. Leiter, D. Kreisle, O. Echt, and T. D. Märk, J. Phys. Chem. **91**, 2583 (1987).

[14] P. Scheier, B. Dünser, R. Wörgötter, D. Muigg, S. Matt, O. Echt, M. Foltin, and T. D. Märk, Phys. Rev. Lett. **77**, 2654 (1996); M. Foltin, O. Echt, P. Scheier, B. Dünser, R. Wörgötter, D. Muigg, S. Matt, and T. D. Märk, J. Chem. Phys. **107**, 6246 (1997).

[15] N. G. Gotts and A. J. Stace, Phys. Rev. Lett. **66**, 21 (1991).

[16] W. A. Saunders, Phys. Rev. Lett. **64**, 3046 (1990).

[17] C. Brechignac, P. Cahuzac, F. Carlier, M. Defrutos, R. N. Barnett, and U. Landman, Phys. Rev. Lett. **72**, 1636 (1994).

[18] U. Näher, H. Göhlich, T. Lange, and T. P. Martin, Phys. Rev. Lett. **68**, 3416 (1992).

[19] P. Scheier, B. Dünser, and T. D. Märk, J. Phys. Chem. **99**, 15 428 (1995).

[20] P. Scheier, B. Dünser, and T. D. Märk, Phys. Rev. Lett. **74**, 3368 (1995).

[21] R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, *Metastable Ions* (Elsevier, Amsterdam, 1973).

[22] P. Scheier and T. D. Märk, Phys. Rev. Lett. **59**, 1813 (1987).

[23] B. Dünser, P. Scheier, and T. D. Märk, Chem. Phys. Lett. **236**, 271 (1995).

[24] G. Senn, B. Dünser, P. Scheier, and T. D. Märk, Chem. Phys. Lett. **266**, 276 (1997).

[25] C. E. Klots, Z. Phys. D **21**, 335 (1991).

[26] B. L. Zhang, C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **46**, 7333 (1992).

[27] J. Laskin and C. Lifshitz, Int. J. Mass Spectrom. Ion Proc. **138**, 95 (1994).

[28] R. Wörgötter, B. Dünser, P. Scheier, T. D. Märk, M. Foltin, C. E. Klots, J. Laskin, and C. Lifshitz, J. Chem. Phys. **104**, 1225 (1996).

[29] B. Dünser, Ph.D. thesis, University of Innsbruck, 1997.

[30] In the extreme case of large precursor charge states ($z \geq 6$), the product of ACT could become even hotter than its parent ion.

[31] G. Senn, Diploma thesis, University of Innsbruck, 1997 (unpublished).

[32] All decay probabilities quoted in the present Letter are evaluated by properly taking into account individual peak widths and positions (see Ref. [33] for details). Our current values may therefore differ from values reported before [19] which were merely based on peak amplitudes.

[33] P. Scheier, G. Senn, S. Matt, and T. D. Märk, Int. J. Mass Spectrom. Ion Proc. (to be published).