

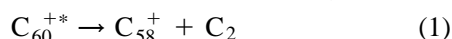
Direct Evidence for the Sequential Decay $C_{60}^{z+} \rightarrow C_{58}^{z+} \rightarrow C_{56}^{z+} \rightarrow \dots$

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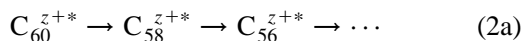
Using a two sector field mass spectrometer in combination with a crossed beams ion source we have obtained direct experimental evidence that C_{60} fragment ions such as C_{58} , C_{56} , C_{54} , ... produced by electron impact ionization of C_{60} may be formed by unimolecular decay of the C_{60} parent ion involving sequential loss of C_2 . Moreover, by comparing experimental and theoretical breakdown graphs the overriding conclusion is that in the case of C_{56}^{z+} production (with $z = 1, 2, 3$) sequential loss of two C_2 units dominates over the loss of a single C_4 unit. [S0031-9007(96)01297-5]

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Despite numerous recent studies [1], the energetics and dynamics of the fragmentation of excited fullerene ions remains a matter of controversy. On the one side reported dissociation energies for the unimolecular decay reaction



range from about 4.0 eV [2] up to about 14 eV [3], the most likely value being 7.1 eV [4] as confirmed recently in two independent studies [5,6]. In contrast, the formation mechanism for smaller fragment ions such as C_{56}^{+} , C_{54}^{+} , ..., C_{30}^{+} produced either by collision induced dissociation of C_{60}^{+} [7–10], by photon [11,12], electron [13–15], or heavy ion impact [16] ionization of C_{60} is still a controversial issue. Whereas in all cases large yields of even-sized fragment ions have been observed (also for ions with charges larger than $z = 1$ [14]), it has remained unclear whether these fragment ions result from sequential loss of C_2 units via



or from the ejection of larger molecular carbon units (e.g., C_4 , C_6 , ...) via



with $m = 2, 3, \dots$. The occurrence and the relative reaction probability for these two reaction routes will depend on the excitation energy of C_{60}^{z+*} and, hence, on the time since its formation. So far, however, there exist conflicting experimental results. Several mass spectrometric studies [4,17,18] have provided evidence that C_{60}^{+*} may lose the equivalent of four carbon atoms in a given experimental time window, but it was not possible to directly distinguish between reactions (2a) and (2b). Some authors argued that sequential decay prevails [1,4–6,10]. Other authors, however, have claimed conclusive evidence against a successive statistical evaporation of C_2 [12,18,19]; they consider ejection of larger neutral fragments such as C_4 as the only essential reaction route [20]. As neutral fragments are rather difficult to identify [22] experimental evidence against or in favor of sequential C_2 emission has been so far only indirect. Concerning theoretical investigations it has been conjectured that even-sized fragments larger than C_2 are efficiently produced via an “unzipping” mechanism

[23]. On the other hand, molecular dynamics simulations of highly excited C_{60} have revealed C_2 loss and, at a low rate, loss of C and C_3 [24] or even two C_2 units [25], but larger fragments were never observed. It is interesting to note that C_2 fragments of fullerenes, produced in an argon microwave plasma, appear to provide a novel, efficient approach to synthesize fine-grained diamond without the addition of hydrogen or oxygen [26].

In this Letter, we present direct experimental evidence for the decay of C_{60}^{z+} into C_{56}^{z+} by sequential ejection of two C_2 units via reaction (2a) for singly, doubly, and triply charged C_{60} precursor ions. Specifically, we find in the present studies that the precursor ions C_{60}^{z+} decay into C_{58}^{z+} in a first experimental time window, and that these product ions C_{58}^{z+} decay subsequently into C_{56}^{z+} in a second experimental time window available in our double focusing mass spectrometer by decoupling the analyzing fields [27]. Moreover, using RRKM type calculations we can demonstrate that under the present experimental conditions the major contribution to the C_{56}^{z+} fragment ion current is due to the sequential loss of two C_2 units via reaction (2a), whereas reaction (2b) constitutes only a minor reaction channel.

The present measurements were performed with a double-focusing sector-field mass spectrometer with a mass range of 10 000 amu at a nominal acceleration voltage of 3 kV [14]. Pure C_{60} powder was evaporated in a temperature-controlled oven typically operated at around 900 K. After entering the ion source via a skimmer and another collimator the effusive C_{60} beam was crossed at right angles with an electron beam typically operated at an energy of 200 eV and electron currents of up to 1 mA (for details of the ion production see Refs. [14,28]). The resulting ions were extracted perpendicular to both the fullerene and electron beam, and accelerated into the mass spectrometer. In the present “reversed geometry” variant of the spectrometer the ions are first analyzed in terms of their momentum in a magnetic sector field and then in terms of their energy in a subsequent electric sector field. The combined action of these two analyzing fields constitutes a double-focusing high-resolution mass analyzer.

Essential for the present work is the possibility to study quantitatively unimolecular dissociations in the two field free regions of this mass spectrometer [27,29] by decoupling the two analyzing fields. The first field free (1ff) region is located between the end of the acceleration region and the beginning of the magnetic sector field (length 61 cm) and the second field free (2ff) region between the end of the magnetic sector field and the beginning of the electric sector field (length 33.3 cm). A metastable decay of an ion m_1^{z+} (produced in the ion source) into m_2^{z+} can be monitored either in the 1ff region by tuning the magnetic sector field to a nominal mass $m^* = m_2^z/zm_1$ and the electric sector field E to a nominal field $E^* = m_2E/m_1$ or in the 2ff region by tuning the magnetic sector field to m_1^{z+} and the electric field $E^* = m_2E/m_1$ (with E being the correct sector field to detect m_1^{z+}). This corresponds to the usual operating mode for the detection of single metastable dissociations [29]. Here we employed an alternative operating mode to detect successive unimolecular decay reactions, i.e., a possible decay of m_1^{z+} into m_2^{z+} in the 1ff region followed by decay of this m_2^{z+} ion into m_3^{z+} in the 2ff region is detected by tuning the magnetic sector field to $m^* = m_2^z/zm_1$ and the electric sector to $E^* = m_3E/m_1$. In this case only those m_3^{z+} ions will be detected which arise from the two successive decay steps in the 1ff and 2ff regions, respectively. Under typical operating conditions a singly charged C_{60} ion will pass the 1ff region in the time interval from 7.7 to 31.2 and the 2ff region from 49 to 60.8 μ s. Possible collision induced fragmentation with background gas (pressures in the 1ff region are below 4×10^{-6} Pa) has been shown to be negligible in the present study.

Using the technique outlined above we have studied for singly, doubly, and triply charged parent ions the occurrence of the metastable decay reactions



in the 1ff and 2ff regions, respectively, and, in addition, the sequential reaction (2a) using both regions simultaneously. Figure 1 shows a representative set of mass spectrometric data obtained for the C_{60}^{2+} parent ions by scanning the electric sector voltage (MIKE scan technique, see Ref. [29]). The top panel shows the parent ion peak at the electric sector voltage of about 512 V and the two product ion peaks (multiplied by factors of 10 and 350, respectively) corresponding to the production of the C_{58}^{2+} and C_{56}^{2+} ions via reactions (3a) and (3b) in the 1ff region detected at the correspondingly lower voltages. The spectrum in the middle corresponds to similar data taken for the 2ff region. Finally, the left part of the bottom panel shows those C_{56}^{2+} ions whose formation is identified as a sequential decay, where C_{60}^{2+} decaying to C_{58}^{2+} in the 1ff region is selected by the magnetic sector field (C_{58}^{2+} produced only by this reaction is shown in this panel designated as 58^{2+}) and the subsequent decay of this fragment ion C_{58}^{2+} to C_{56}^{2+} in the 2ff region is selected by the electric sector field giving

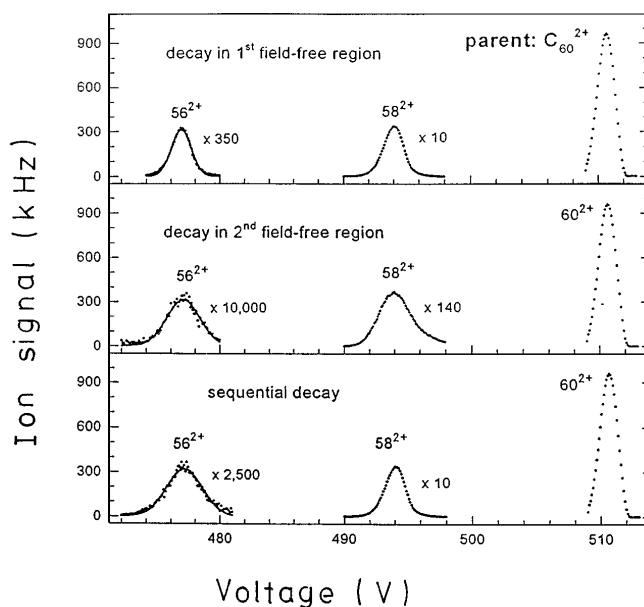


FIG. 1. Mass spectra of C_{60}^{2+} parent ions and fragment ions C_{58}^{2+} and C_{56}^{2+} formed from C_{60}^{2+} ions by unimolecular decay in the 1ff and 2ff regions (top and middle panels, respectively). The left peak in the bottom panel identifies formation of C_{56}^{2+} fragment ions through sequential emission of two C_2 units in two different time windows.

the peak designated C_{56}^{2+} . Similar spectra have been obtained for the singly and triply charged C_{60}^{z+} ion and also for the dissociation of C_{58}^{z+} into C_{56}^{z+} and C_{54}^{z+} , thereby confirming the results presented in Fig. 1.

The peak in the bottom panel designated 56^{2+} constitutes therefore a clear proof for the occurrence of sequential decay reactions (2a). If C_{56}^{2+} is, however, produced via reaction (3b) in either the 1ff region or the 2ff region (labeled C_{56}^{2+} in the top and middle panels), the reaction mechanism [either reaction (2a) or (2b)] and the neutral products formed (either C_2 or C_4) remain unknown. Although the different peak heights in Fig. 1 designated 56^{2+} give already some indication on the relative probability of the sequential reaction (2a) as compared to the direct ejection of an intact C_4 unit (i.e., the sequential decay as witnessed by peak 56^{2+} in the bottom panel is about a factor of 4 stronger than the decay C_{60}^{2+} to C_{56}^{2+} in the 2ff region), due to the unknown discrimination in the 1ff and 2ff regions and the occurrence of competing decay processes such as the emission of photons [30,31] (radiative cooling) and the emission of electrons [32] (delayed ionization), it is not possible to analyze quantitatively the data shown in Fig. 1. Therefore one important question still to be addressed is if for a given time window the sequential route (2a) is more likely than the unimolecular loss of a C_4 unit (2b). In the following we will demonstrate that the dominant unimolecular dissociation channel for excited C_{60} ions decaying to C_{56} ions is the sequential evaporation of C_2 units via reaction (2a).

Evidence for this conclusion is obtained by comparing measured (see Fig. 2) and calculated (see Fig. 3)

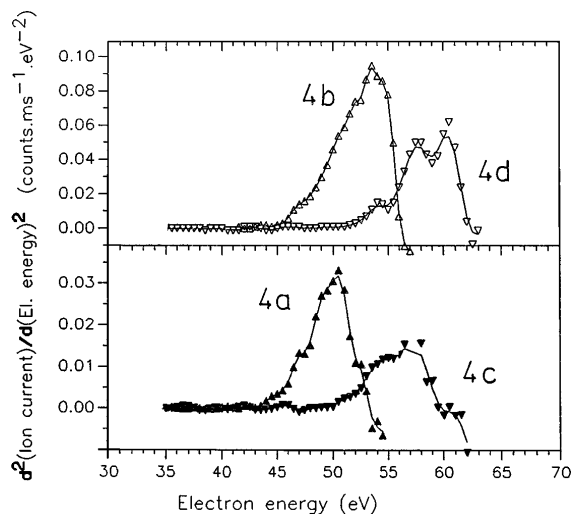
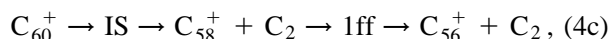
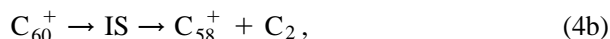
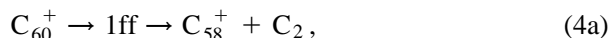


FIG. 2. Experimental breakdown graph of the C_{60}^+ ion. Upper part: breakdown curves for the C_{58}^+ (designated Δ) and C_{56}^+ (designated ∇) fragment ions formed in the ion source by reactions (4b) and (4d), respectively. Lower part: breakdown curves for C_{58}^+ ions (designated filled \blacktriangle) formed in the 1ff reaction (4a) and for C_{56}^+ ions (designated filled \blacktriangledown) formed by the sequential decay in the ion source and 1ff region by reaction (4c).

breakdown curves for singly charged C_{60} ions decaying in the ion source (IS) (between 0 and 1 μ s after formation of the parent ion) and the 1ff region (between 7.7 and 31.2 μ s after formation of the parent ion) by unimolecular dissociation reactions:



(where x is either a C_4 unit or two single C_2 units). The experimental breakdown curves corresponding to reactions (4a) to (4d) shown in Fig. 2 were obtained in a standard procedure taking the second derivatives of the measured C_{58}^+ and C_{56}^+ ionization efficiency curves, i.e., the corresponding ion peak values as given in Fig. 1 versus electron energy (for details see Ref. [4]). The calculated breakdown curves shown in Fig. 3 were obtained by a procedure outlined in detail in Ref. [4]. This involves solving the corresponding kinetic equations using fragmentation decay rate constants calculated with the statistical RRKM theory assuming the transition state model (TS-1) described in [5]. The only independent parameters needed for these calculations are the respective activation energies for the C_2 and C_4 loss. The activation energy $E_a(C_{60} \rightarrow 58)$ has been derived as outlined in [4] by fitting the experimental breakdown curve for reaction (4b) yielding 7.2 eV in good agreement with [4] and [5] and a recent study by Lifshitz and co-workers [6]. The activation energies $E_a(C_{58} \rightarrow 56)$ and $E_a(C_{56} \rightarrow 54)$ for the loss of C_2 from C_{58}^+ and C_{56}^+ , respectively, have been obtained using the rela-

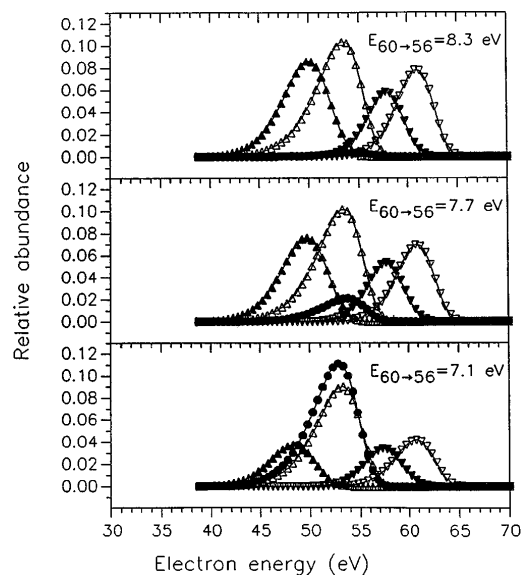


FIG. 3. Calculated breakdown graph of the C_{60}^+ ion (RRKM theory). Curves for reactions (4a)–(4c) designated as in Fig. 2. The two different possibilities for the neutral product x in the case of reaction (4d) assuming either sequential C_2 loss or C_4 loss are designated Δ and \bullet , respectively. Calculated results are shown for three different values of $E_a(C_{60} \rightarrow 56)$.

tive binding energies derived from measured metastable fractions in an independent study of Klots [33] and are in good agreement with recent data reported in Ref. [5]. The activation energy $E_a(C_{60} \rightarrow 56)$ is not known very well. According to Stanton [34], the adiabatic energy necessary for the elimination of a C_4 unit from C_{60}^+ is by 7.2 eV lower than that for the successive emission of two C_2 units (see also a detailed discussion of the energetics of small carbon clusters in [35]). Nevertheless, to study the influence of this critical parameter on the shape and position of the calculated breakdown curves, we used in the present calculation three reasonable values [5,34,36,37] of $E_a(C_{60} \rightarrow 56)$, i.e., 7.1, 7.7, and 8.3 eV.

When properly normalized, the breakdown curves describe the fragmentation branching ratios as a function of the deposited electron energy. Therefore, each breakdown curve has the shape of a relatively narrow peak extending over the range of energies where a given fragmentation reaction occurs with sufficient probability. When comparing measured and calculated breakdown curves we can in principle judge the agreement in the energy position of the maxima and the agreement in their relative abundance. The latter is, however, possible only for breakdown curves pertaining to the same region of the mass spectrometer due to possible discrimination effects for the various regions. As can be seen by comparing curves given in Figs. 2 and 3 there is not only an excellent agreement for reaction (4b) [used for obtaining the activation energy $E_a(C_{60} \rightarrow 58)$; see above], but also for reaction (4a). Moreover, the C_{58}^+ breakdown curve for reaction (4a) peaks at an energy about 3 eV lower than that for reaction (4b) as expected for a unimolecular decay reaction occurring at later times after

initial ion production. More importantly, there exists also very good agreement for the reaction sequence (4c) leading to C_{56}^+ . Finally, the measured breakdown curve for reaction (4d) agrees very well with the calculated curve assuming x to be two independently lost C_2 units, while it cannot be fitted at all by assuming x to be a C_4 unit. This conclusion is valid for all values of $E_a(C_{60 \rightarrow 56})$ used in the calculations, i.e., at an activation energy of 7.1 eV the maximum of the calculated breakdown curve is approximately 8 eV lower than that of the measured curve for reaction (4d), at higher values of this activation energy the maximum of the calculated breakdown curves is still approximately 5 eV below the experimental data, and, in addition the relative abundance has decreased dramatically. This therefore demonstrates that also in the case of reaction (4d)—where the reaction takes place in the ion source and cannot be analyzed experimentally in terms of its decay mechanism—the major contribution to the C_{56}^+ fragment ion current is sequential loss of two C_2 units whereas contribution of the single step C_4 loss reaction is negligible.

Therefore, in concluding we have obtained direct experimental evidence that fragment ions of C_{60}^{z+} are produced by unimolecular decay involving the sequential loss of C_2 . Moreover, by comparing experimental and theoretical breakdown graphs the overriding conclusion is that in the case of C_{56}^+ production (via electron impact ionization of C_{60}) sequential loss of two C_2 units dominates over the loss of a single C_4 unit.

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- [1] C. Lifshitz, *Mass Spectrom. Rev.* **12**, 261 (1993).
- [2] E. Kolodney, B. Tspinyuk, and A. Budrevich, *J. Chem. Phys.* **102**, 9263 (1995).
- [3] R. L. Whetten and C. Yertzian, *Int. J. Mod. Phys.* **6**, 3801 (1992).
- [4] M. Foltin, M. Lezius, P. Scheier, and T. D. Märk, *J. Chem. Phys.* **98**, 9624 (1993).
- [5] 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).
- [6] J. Laskin, H. A. Jiminez-Vazquez, R. Shimshi, M. Saunders, M. S. de Vries, and C. Lifshitz, *Chem. Phys. Lett.* **242**, 249 (1995).
- [7] R. J. Doyle and M. M. Ross, *J. Phys. Chem.* **95**, 4954 (1991).
- [8] R. Hvelplund, L. H. Andersen, H. K. Haugen, J. Lindhard, D. C. Lorents, R. Malhotra, and R. Ruoff, *Phys. Rev. Lett.* **69**, 1915 (1992).
- [9] T. Rauth, O. Echt, P. Scheier, and T. D. Märk, *Chem. Phys. Lett.* **247**, 515 (1995).
- [10] R. D. Beck, J. Rockenberger, P. Weis, and M. F. Kappes, *J. Chem. Phys.* **104**, 3638 (1996).
- [11] P. Wurz and K. R. Lykke, *J. Phys. Chem.* **96**, 10 129 (1992).
- [12] H. Hohmann, C. Callegari, S. Furrer, D. Grosenick, E. E. B. Campbell, and I. V. Hertel, *Phys. Rev. Lett.* **73**, 1919 (1994).
- [13] S. W. McElvany, M. M. Ross, and J. H. Callahan, *Acc. Chem. Res.* **25**, 182 (1992).
- [14] P. Scheier, B. Dünser, and T. D. Märk, *J. Phys. Chem.* **99**, 15 428 (1995).
- [15] B. Dünser, M. Lezius, P. Scheier, H. Deutsch, and T. D. Märk, *Phys. Rev. Lett.* **74**, 3364 (1995).
- [16] T. LeBrun, H. G. Berry, S. Cheng, R. W. Dunford, H. Esbensen, D. S. Gemmel, E. P. Kantner, and W. Bauer, *Phys. Rev. Lett.* **72**, 3965 (1994).
- [17] P. Radi, T. L. Bunn, P. R. Kemper, M. E. Molchan, and M. T. Bowers, *J. Chem. Phys.* **88**, 2809 (1988).
- [18] D. R. Luffer and K. H. Schram, *Rapid Commun. Mass Spectrom.* **4**, 552 (1990).
- [19] K. J. McHale, M. J. Polce, and C. Wesdemiotis, *J. Mass Spectrom.* **30**, 33 (1995).
- [20] See also the observation that charge separation reactions of highly charged fullerene ions involve the ejection of intact C_4^+ and C_6^+ units [14,21].
- [21] B. Dünser, P. Scheier, and T. D. Märk, *Chem. Phys. Lett.* **236**, 271 (1995).
- [22] K. R. Lykke, *Phys. Rev. A* **52**, 1354 (1995).
- [23] R. V. Vandenbosch, *J. Phys. Chem.* **99**, 14 868 (1995); R. L. DeMuro, D. A. Jelski, and T. F. George, *J. Phys. Chem.* **96**, 10 603 (1992).
- [24] Y. Xia, Y. Xing, C. Tan, and L. Mei, *Phys. Rev. B* **52**, 110 (1995); S. Serra, S. Sanguinetti, and L. Colombo, *Chem. Phys. Lett.* **225**, 191 (1994).
- [25] C. Xu and G. E. Scuseria, *Phys. Rev. Lett.* **72**, 669 (1994).
- [26] D. M. Gruen, S. Liu, A. R. Krauss, J. Luo, and X. Pan, *Appl. Phys. Lett.* **64**, 1502 (1994).
- [27] P. Scheier and T. D. Märk, *Phys. Rev. Lett.* **59**, 1813 (1987); L. P. Hills, J. H. Futrell, and A. L. Wahrhaftig, *J. Chem. Phys.* **51**, 5255 (1969).
- [28] P. Scheier and T. D. Märk, *Phys. Rev. Lett.* **73**, 54 (1995).
- [29] R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, *Metastable Ions* (Elsevier, Amsterdam, 1973).
- [30] R. Mitzner and E. E. B. Campbell, *J. Chem. Phys.* **103**, 2445 (1995).
- [31] J. Laskin, J. M. Behm, K. R. Lykke, and C. Lifshitz, *Chem. Phys. Lett.* **252**, 277 (1996).
- [32] G. Walder, K. W. Kennedy, and O. Echt, *Z. Phys. D* **26**, S288 (1993).
- [33] C. E. Klots, *Z. Phys. D* **21**, 335 (1991).
- [34] R. E. Stanton, *J. Phys. Chem.* **96**, 111 (1992).
- [35] K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).
- [36] J. M. L. Martin, J. P. Francois, and R. Gijbels, *J. Comp. Chem.* **12**, 52 (1991).
- [37] J. D. Watts, J. Gauss, J. F. Stanton, and R. J. Bartlett, *J. Chem. Phys.* **97**, 8372 (1992).