Observation of the Septuply Charged Ion $C_{60}{}^{7+}$ and Its Metastable Decay into Two Charged Fragments via Superasymmetric Fission

P. Scheier and T. D. Märk

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

(Received 28 February 1994)

The existence of $C_{60}{}^{7+}$ and spontaneous decay of this ion via the superasymmetric fission reaction $C_{60}{}^{7+} \rightarrow C_{58}{}^{6+} + C_2{}^{+}$ have been observed and studied by isotope-resolved two-sector-field mass spectrometric techniques, thereby allowing the unambiguous identification of the septuply charged fullerene ion and the experimental determination of the rather large kinetic energy release of 9.7 ± 2.2 eV for the separating fragment ions.

PACS numbers: 36.40.+d, 34.80.Gs, 35.20.Wg

In this Letter we report the observation and identification of the septuply charged $C_{60}{}^{7+}$ fullerene ion produced by electron impact ionization of C_{60} and the study of properties such as its production mechanism, stability, and related quantities. Following recent reports of the existence of quintuply and sextuply charged fullerene ions [1–4] in accordance with predictions from theoretical considerations by Bohme and co-workers [5] the existence of the $C_{60}{}^{7+}$ ion exceeds these theoretical predictions [5]. Moreover, the present example constitutes the highest charged molecular parent ion that is formed via electron impact ionization. Although gas-phase ion chemistry of multiply charged cations, in particular the area of dictations, has advanced rapidly in the past decade [6], much less attention has been directed to date towards polyatomic cations with more than two charges. Whereas triply charged molecular positive ions have been known for some time [7], the unusual structural features and the surprising possible kinetic stability (inhibition of the Coulombic repulsion by an energy barrier which is sufficiently high to permit experimental observation) of quadruply charged molecular ions have been predicted only recently by the *ab initio* calculations of Radom and co-workers [8].

The stability of multiply charged large aromatic molecules is not surprising, but the existence of rather small multiply charged molecules can only be explained in terms of (i) valence forces leading to local minima in the otherwise repulsive Coulomb states or of (ii) charge-polarization states correlating for heteronuclear diatomic species AB to $A^{2+} + B$ [9]. In contrast to these ions, a large number of multiply charged cluster ions $X_n{}^{z+}$ (with X either an atom or a molecule) has been recently observed and reported [10] with charge states up to $z = 4$ [10, 11]. These multiply charged cluster ions are observed only if their sizes exceed a critical size $n_c(z)$ for which the Coulombic repulsion between the singly charged cluster constituents (distributed over the cluster surface) is smaller than the bonding forces. The lowest observed sizes for multiply charged molecular clusters (with $z \geq 3$) are $n_c(3) = 52$ and $n_c(4) = 92$ for C_6H_6 clusters [12], thus defining a limit for $n_c(z)/z$ of approximately 17 atoms per charge. The present study pushes this limit to approximately 8.5 atoms per charge in the septuply charged molecule $C_{60}{}^{7+}$. In addition, we were also able to observe and to study quantitatively in the metastable time regime the spontaneous decay of $C_{60}{}^{7+}$ into two charged fragment ions thus allowing us to deduce the translational energy release.

The measurements were carried out in a double-focusing, sector-field mass spectrometer of reversed geometry with a mass resolution of up to 25 000 and a mass range of 10 000 Dalton at a nominal acceleration voltage of 3000 V [3, 4]. The C_{60} powder was evaporated in a temperature-controlled oven (set to 890 K in the present study) and introduces as an effusive beam via a small orifice into the modified Nier-type ion source. The ionizing electrons can have energies varying from close to 0 up to 1000 eV with an energy spread of approximately 0.5 eV. As a compromise between a desired high mass resolution (in order to distinguish the various isotopes of the septuply charged $C_{60}{}^{7+}$ ion from interfering coincidences of possible singly and multiply charged fragment ions of C_{60}; see discussion in Refs. [3, 4]) and a high sensitivity (as the relative abundance of septuply charged carbon fullerenes was expected to be below 10^{-5} [3, 4]) a mass resolution of approximately 1000 to 2000 was used. Moreover, it was necessary to use high energy electrons (around 200 eV) and extremely high electron currents (up to 1 mA).

These large electron currents, however, generate a strong negative space charge in the ionization region. Thus positively charged ions produced by a primary ionization event will be trapped by this space charge for a rather long time (up to 10 μs according to ion trajectory calculations) and so additional electron collisions can occur. It is only under these conditions that we were able to detect $C_{60}{}^{7+}$ and therefore we have to conclude that these highly charged fullerene ions are produced almost exclusively by multiple electron impact ionization processes (highly charged sodium cluster ions were produced by a similar multistep photoionization process [13]). This conclusion is supported by the fact that for low electron cur-

0031-9007/94/73(1)/54(4)$06.00

rents (single collision conditions at 30 μA electron current) the mass spectrometric abundances of higher charge states of C_{60} decrease rather rapidly with increasing z (i.e., for $z \geq 5$ below our detection limit), whereas for high electron currents (and an electron energy of 200 eV) the abundances of the higher charge states decrease much less with increasing z (see Fig. 1) due to the production of these ions via electron-ion interactions (the cross sections for these processes are rather large and peak at approximately 200 eV [14]).

Nevertheless, the overriding conclusion from the present study is the existence of septuply charged fullerene ions which live long enough (approximately 30 μs) to be detected in our mass spectrometer system. Figure 2 shows as an example a section of a high resolution mass spectrum of ions produced by electron impact ionization of C_{60} where the first isotopomer of the $C_{60}{}^{7+}$ ion can be identified unambiguously, i.e., $\frac{1}{7}$ Dalton below the $({}^{13}C_2{}^{12}C_{15})^{2+}$ ion at 103 Dalton there appears a peak corresponding to the ${}^{12}C_{60}{}^{7+}$ ion. The second, weaker (approximately 67.4% of the first isotope peak [3,4], isotopomer ion ${}^{13}C^{12}C_{59}{}^{7+}$ coincides at 103 Dalton with the doubly charged fragment ion ${}^{13}C^{12}C_{15}{}^{2+}$. The third, even more weak (approximately 22.3% of the first isotope peak [3,4]), isotopomer ion ${}^{13}C_2{}^{12}C_{58}{}^{7+}$ at 103 $\frac{1}{7}$ Dalton is located very close to the ${}^{12}C_{43}{}^{5+}$ ion at 103 $\frac{1}{5}$ Dalton and thus cannot be seen perfectly resolved (a full separation would need a mass resolution of 3600 or better). A number of repeat mass spectra taken under various experimental conditions confirm these identifications.

As this observation of septuply charged fullerene ions goes beyond the theoretical predictions and expectations of Bohme and co-workers [5] (see discussion below), an additional test on the existence of this ion has been carried out. The idea behind this test is that we assume that this ion can be produced in the ion source in reasonable amounts and that these ions then decay on their way to detection due to possible spontaneous or induced dissociations, and then to use these dissociation reactions to establish the identity or nonidentity of these ions. If such dissociations occur in the field-free regions of our instrument, they can be readily detected and studied by proper tuning of the analyzing fields [15]. Figure 3 shows as an example a mass-analyzed high voltage (HV) scan around the position (dashed line in Fig. 3) on the energy scale corresponding to the reaction

$$C_{60}{}^{7+} \rightarrow C_{58}{}^{6+} + C_2{}^{+}. \qquad (1)$$

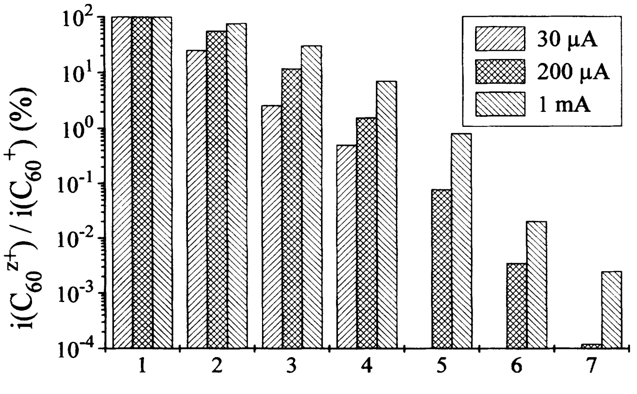

FIG. 1. Normalized ion currents $C_{60}{}^{z+}/C_{60}{}^{+}$ versus charge state z for three different electron currents obtained for electron impact ionization of the neutral parent C_{60} at 200 eV.

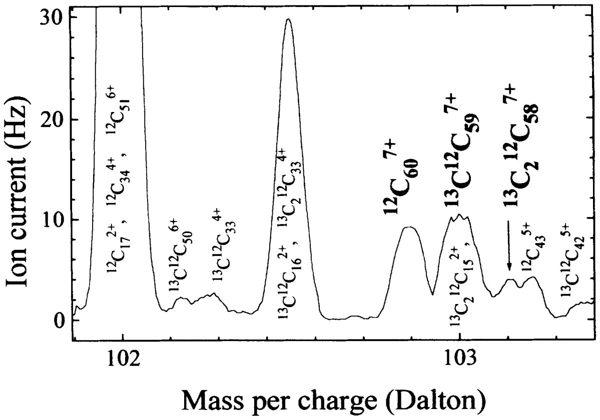

FIG. 2. Section of a high resolution mass spectrum of C_{60}.

The observed peak exhibits the typical dished-peak shape [15] indicating a metastable transition associated with a rather large energy release. Because of the shape of this peak and additional evidence from its gas pressure behavior, it can thus be concluded that the parent ion of this transition is indeed metastable, i.e., decaying in this case by the superasymmetric spontaneous fission reaction (1). Other possible spontaneous decay reactions were too weak to be detected with the parent ion signal available, and it can be concluded from this and further studies with other fullerene ions that the asymmetric fission reaction (1) is besides neutral C_2 (monomer) evaporation [16] the dominant dissociation pathway for this parent ion in the metastable time regime.

The observation of reaction (1) not only provides a simple and reliable second method of identification $C_{60}{}^{7+}$, but the characteristic peak shape (measured for the first time for such an ion) also provides the opportunity to gain information on the structure and decay of $C_{60}{}^{7+}$. For a simple charge separation process like reaction (1) the translational energy release T can be calculated from the corrected width of the metastable peak ΔV (i.e., taking into account the width of the parent ion peak) using the relation [15]

$$T = \frac{q_1^2 m_2^2 eV}{16 q_2 m_1 m_3} \left(\frac{\Delta V}{V} \right)^2, \qquad (2)$$

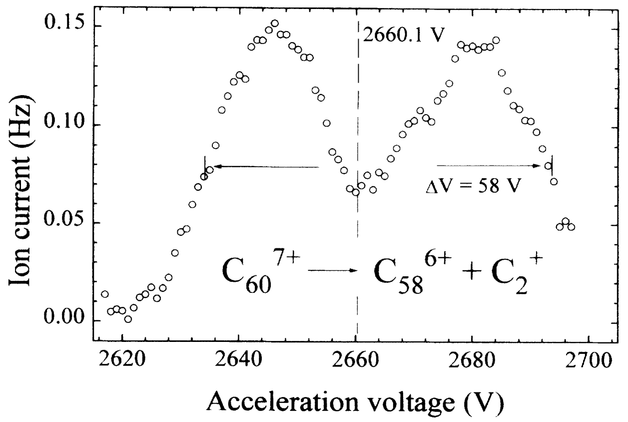

FIG. 3. Metastable peak associated with the spontaneous decay reaction $C_{60}^{7+} \rightarrow C_{58}^{6+} + C_2^+$ plotted by the HV scan technique (see text). Note the large release of kinetic energy apparent from the huge metastable peak width ΔV.

where q_1 is the charge of the mother ion, m_1 the mass of the mother ion, q_2 the charge of the detected daughter ion, m_2 the mass of the detected daughter ion, m_3 the mass of undetected fragment ion, and V the acceleration voltage.

In the simple case of two separating point charges q_1 and q_2 and under the assumption that other contributions (internal energy of the activated complex, non-Coulombic portion of the reverse activation energy) will be negligible relative to the Coulombic repulsion [15], the measured energy release may be used to derive the intercharge distance in the transition state from the relation

$$T = T_{\mathrm{Coul}} = \frac{1}{4\pi\varepsilon_0} \frac{q_2(q_1 - q_2)e^2}{R}. \qquad (3)$$

The kinetic energy release of 9.7 ± 2.2 eV determined here from the corrected metastable peak width of 45 ± 5 V corresponds according to Eq. (3) to an apparent intercharge distance between the two fragments at the instance of separation of 8.9 ± 2.4 Å. This apparent distance is much larger than the radius of the parent neutral, $r(C_{60}) = 3.5$ Å [17], and very likely also than that of the polycation, because Hrusak and Schwarz [18] demonstrated recently that in the case of C_{60}^{2+} the Coulombic repulsion only leads to an increase in the radius of about 2.2%. This result (i.e., the significant difference between the radius of C_{60} and the apparent intercharge distance of the separating fragments in the fission process, which changes only slightly to a distance of 8.5 Å when taking into account the expected charge distribution of the septuply charged ion; see Fig. 4) needs further experimental and theoretical studies before final interpretation of this decay process will be possible. While we recognize the desirability of this, we turn now to the question of the unexpected stability of C_{60}^{7+} despite the current belief that C_{60} ions are only stable against Coulomb repulsion up to $z = 6$.

According to Peterson and co-workers [19] the observed stability of C_{60} polycations up to $z = 4$ indicates that charge shielding and/or delocalization inhibits the fragmentation, because following the model of Bennemann and co-workers [20] (which proposes that the criterion for Coulombic decay of multiply charged metallic, ionic or van der Waals–type clusters is that the Coulombic repulsion between the charged fragments exceeds the binding energy of 4.6 eV for C_2 in C_{60} [21] that a spherically symmetric C_{60}^{4+} ion would be unstable against Coulombic decay. Bohme and co-workers [5], however, recently pointed out that the arguments of Peterson and co-workers ignore the difference in character between the chemical bonding within the fullerene frame and the electrostatic repulsion between the multiple charges. Bohme and co-workers argue that in the case of C_{60}^{4+} the chemical bonding between the two charged fragments will be essentially dissipated at a separation of the C_2^+ from the surface of the remnant fullerene cage of 2 to 3 Å, whereas at this separation considerable Coulombic repulsion of 5.5 eV or more remains for the C_2^+ from the Coulombic repulsion of 7.55 eV for a symmetric charge distribution on the fullerene cage surface. The Coulomb energy thus released over this separation, to counteract the chemical bonding, is only approximately 2.0 eV, which is not sufficient to permit this fragmentation. Similar arguments have been advanced by Bohme and co-workers for the likely stability of C_{60}^{5+} and C_{60}^{6+} against Coulombic repulsion.

In order to explain the present results, however, it is necessary to extend these arguments of Bohme and co-workers in such a way that it is possible to account for the existence of the septuply charged fullerene ion. They used as a basis for the Coulomb energy release a total Coulomb energy calculated for a C_{60} polycation of radius equal to that of the parent neutral, upon which all charges are at any point in time at the maximum mutual separation attainable upon a sphere of this size. For C_{60}^{7+} this optimization procedure gives a pentagonal bipyramidal charge configuration (depicted in Fig. 4) leading to a total Coulomb energy of 59.42 eV amounting to an increase in V_{tot} from C_{60}^{6+} to C_{60}^{7+} of 18.34 eV. As the Coulombic

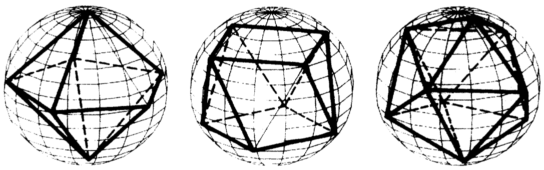

FIG. 4. Depiction of calculated charge distribution for an idealized spherically symmetric C_{60}^{7+}, C_{60}^{8+}, and C_{60}^{9+} from left to right.

repulsion between a pentagonal charge and the other six is with 17.14 eV larger than the repulsion of 16.60 eV for a charge located at the pole position, the energetical most favorable dissociation path is the ejection of the pentagonal charge. Following Bohme and co-workers, at a distance of 3 Å, however, where the chemical bonding will be dissipated, at least 11.98 eV remains from the original Coulomb repulsion. Thus Coulomb energy released over this distance is about 5.1 eV, which is still smaller than the generally accepted value for the binding energy of C_2 or C_2^+ to C_{58} in the order of 7 eV [22]. This energy release is therefore not sufficient to promote immediate Coulomb explosion unless the bonding energy is much weaker than in the neutral or singly charged C_{60}. We expect that high-level theoretical calculations on C_{60}^{7+} will support this view in accordance with the present experimental findings.

In conclusion, we have observed by isotope-resolved mass spectrometry the production of C_{60}^{7+} via multiple-electron impact ionization of the neutral parent C_{60}. Some of these ions live long enough to reach after 30 μs flight time from the ion source through the analyzer the detector of the mass spectrometer system, whereas others decay in the metastable time regime via a spontaneous superasymmetric fission reaction. For this dominant decay reaction into a singly charged C_2^+ and a sextuply charged fullerene fragment cage the kinetic energy release could be determined by HV-scan mass spectrometry to be approximately 9.7 ± 2.2 eV, which is as expected much larger than the average product kinetic energy release of 0.43 ± 0.05 eV and 0.415 ± 0.05 in the case of neutral C_2 evaporation from C_{60}^+ and C_{60}^{2+}, respectively [23].

This work was partially supported by the Österreichischer Fonds zur Förderung der Wissenschaftlichen, Wien, Austria.

[1] R.J. Doyle and M.M. Ross, J. Phys. Chem. **95**, 4954 (1991).

[2] B. Walch, C.L. Clocke, E. Salzborn, and R. Völpel, in Proceedings of the International Conference on the Physics of Highly Charged Ions, Manhatten, 1992 (to be published).

[3] P. Scheier, R. Robl, B. Schiestl, and T.D. Märk, Chem. Phys. Lett. **220**, 141 (1994).

[4] P. Scheier and T.D. Märk, Int. J. Mass Spectrom. Ion. Proc. Lett. **133**, L5 (1994).

[5] S. Petrie, J. Wang, and D.K. Bohme, Chem. Phys. Lett. **204**, 473 (1993).

[6] W. Koch, F. Maquin, D. Stahl, and H. Schwarz, Chimica **29**, 376 (1985).

[7] T.D. Märk, Int. J. Mass Spectrom. Ion Phys. **55**, 325 (1983); L. Morvay and I. Cornides, Int. J. Mass Spectrom. Ion Proc. **62**, 263 (1984); S. Singh, R.K. Boyd, F.M. Harris, and J.H. Beynon, Int. J. Mass Spectrom. Ion Proc. **66**, 167 (1986); G.W. Burdick, J.R. Appling, and T.F. Moran, J. Phys. B **19**, 629 (1986); D. Mathur, in *Electronic and Atomic Collisions*, edited by H.B. Gilbody, W.R. Newell, F.H. Read, and A.C.H. Smith (Elsevier, New York, 1988), pp. 623–630.

[8] M.W. Wong, R.H. Nobes, and L. Radom, Rapid Comm. Mass Spectrom. **1**, 3 (1987).

[9] R.W. Wetmore, R.J. LeRoy, and R.K. Boyd, J. Phys. Chem. **88**, 6318 (1984); P.R. Taylor, Mol. Phys. **49**, 1297 (1983); H. Helm, K. Stephan, T.D. Märk, and D.L. Huestis, J. Chem. Phys. **74**, 3844 (1981).

[10] O. Echt, in *Physics and Chemistry of Small Clusters*, edited by P. Jena, B.K. Rao, and S.N. Khanna (Plenum, New York, 1987), pp. 623–638.

[11] There are two notable exception to this z limit i.e., Henkes and Isenberg [(W. Henkes and G. Isenberg, Int. J. Mass Spectrom. Ion Phys. **5**, 249 (1979)] reported the observation of fivefold ionized huge nitrogen clusters (without definitive mass analysis) and Martin and co-workers [13] recently determined the critical appearance size for sodium clusters up to $z = 7$ with $n_c(7) = 448 \pm 10$ and the existence of stable highly charged sodium clusters with z up to 14.

[12] M.Y. Hahn, K.E. Schriver, and R.L. Whetten, J. Chem. Phys. **88**, 4242 (1988).

[13] T.P. Martin, U. Näher, H. Göhlich, and T. Lange, Chem. Phys. Lett. **196**, 113 (1992); U. Näher, H. Göhlich, T. Lange, and T.P. Martin, Phys. Rev. Lett. **68**, 3416 (1992).

[14] R. Völpel, G. Hofmann, M. Steidl, M. Stenke, M. Schlapp, R. Trassl, and E. Salzborn, Phys. Rev. Lett. **71**, 3439 (1993).

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

[16] P.P. Radi, M.T. Hsu, M.E. Rincon, P.R. Kemper, and M.T. Bowers, Chem. Phys. Lett. **174**, 223 (1990).

[17] J.M. Hawkins, A. Meyer, T. Lewis, S. Loren, and F.J. Hollander, Science **252**, 312 (1991).

[18] J. Hrusak and H. Schwarz, Chem. Phys. Lett. **205**, 187 (1993).

[19] C.W. Walter, Y.K. Bae, D.C. Lorents, and J.R. Peterson, Chem. Phys. Lett. **195**, 543 (1992).

[20] D. Tomanek, S. Mukherjee, and K.H. Bennemann, Phys. Rev. B **28**, 665 (1983).

[21] Note that the binding energy used in this estimate is much lower than recent data [M. Foltin, M. Lezius, P. Scheier, and T.D. Märk, J. Chem. Phys. **98**, 9624 (1993)], thus leading to an underestimation of the binding force relative to the Coulomb repulsion.

[22] Foltin, Lezius, Scheier, and Märk (Ref. [21]).

[23] C. Lifshitz, M. Iraqi, T. Peres, and J.E. Fischer, Int. J. Mass Spectrom. Ion Proc. **107**, 565 (1991).