# Absolute Charge Transfer and Fragmentation Cross Sections in $He^{2+}$-$C_{60}$ Collisions

A. Rentenier,[1] L. F. Ruiz,[2] S. Díaz-Tendero,[2] B. Zarour,[3] P. Moretto-Capelle,[1] D. Bordenave-Montesquieu,[1] A. Bordenave-Montesquieu,[1] P. -A. Hervieux,[4] M. Alcamí,[2] M. F. Politis,[5] J. Hanssen,[3] and F. Martín[2]

[1]*Laboratoire de Collisions, Agrégats et Reactivité, UMR 5589 CNRS, Université Paul Sabatier 3, 31062 Toulouse, France*
[2]*Departamento de Química, C-9, Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[3]*L.P.M.C., Université de Metz, Technopôle 2000, 1 Boulevard Arago, 57078 Metz Cedex 03, France*
[4]*Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue Loess, 67034 Strasbourg, France*
[5]*I.M.P.M.C., Université Pierre et Marie Curie, 140 rue de Lourmel, 75015 Paris, France*

(Received 16 October 2007; published 5 May 2008)

We have determined absolute charge transfer and fragmentation cross sections in $He^{2+} + C_{60}$ collisions in the impact-energy range 0.1–250 keV by using a combined experimental and theoretical approach. We have found that the cross sections for the formation of $He^+$ and $He^0$ are comparable in magnitude, which cannot be explained by the sole contribution of pure single and double electron capture but also by contribution of transfer-ionization processes that are important even at low impact energies. The results show that multifragmentation is important only at impact energies larger than 40 keV; at lower energies, sequential $C_2$ evaporation is the dominant process.

DOI: 10.1103/PhysRevLett.100.183401 PACS numbers: 36.40.Sx, 36.40.Qv, 82.30.Fi

Collisions of highly charged ions with $C_{60}$ have been intensively studied for more than one decade (see [1–4], and references therein). In these collisions, several $C_{60}$ electrons may be ionized or transferred to the charged projectile, thus leading to the formation of multiply charged $C_{60}^{q+}$ fullerenes [5–10]. Theory [11] has predicted that charges as high as $q = 14$ might be observable. However, as $C_{60}^{q+}$ ions are usually produced in excited states, they can undergo fragmentation by emitting one or several fragments. The complex fragmentation patterns observed in these processes are mostly determined by the charge, excitation energy, structure, and relative stability of the different fullerene fragments [3].

The existing experiments [5–10] show that charge transfer, ionization, excitation, and fragmentation compete in a wide range of impact energies. In this work, we consider the collision of $^4He^{2+}$ ions with $C_{60}$ in the region of impact energies 0.1–250 keV, in which charge transfer is the dominant process and the resulting neutral and singly and doubly charged $C_{60}$ preferentially decays by emission of neutral $C_2$ molecules [6,10,12]. At these impact energies, all electronic processes (electron capture, ionization, excitation) are much faster than fragmentation [13]. Thus, fragmentation can be considered as a postcollisional process in which the energy deposited by the collision in $C_{60}$ is transferred to the nuclear (dissociative) degrees of freedom. Therefore, the mass spectrum associated with charge transfer in ion-$C_{60}$ collisions is determined by two parameters: (i) the charge transfer cross sections $\sigma_{CT}$ and (ii) the collision energy deposit $E_{dep}$. The former determines the proportion of the different $C_{60}^{q+}$ ions produced in the collision and the latter the ensuing fragmentation. Both quantities are not easy to determine either theoretically or experimentally. This is due to the large number of active electrons and nuclear degrees of freedom involved, which implies the detection in coincidence of many particles and makes fully quantum dynamical theoretical approaches unfeasible.

Very recently, Chen *et al.* [10] have been able to measure $E_{dep}$ in low energy $H^+ + C_{60}$ collisions by analyzing in coincidence the kinetic energy loss of the scattered $H^-$ anion and the time of flight of the recoil $C_{60}^{2+}$ ion. This provides a direct measure of the energy deposit following double capture without additional modeling. In contrast, absolute cross sections have been measured for $H^+ + C_{60}$ only at very high impact energy [14] (see also [15]), where charge transfer is no longer the dominant process. Absolute values of $\sigma_{CT}$ in the low impact-energy region, which are necessary to provide a reference for future measurements, are still unknown.

In this Letter, we report on absolute measurements and theoretical calculations of charge transfer cross sections in $He^{2+} + C_{60}$ collisions at low impact energies. The experimental and theoretical cross sections are in reasonable agreement with each other, thus reinforcing the quantitative value of our predictions. The measurements cover a wide range of impact energy (3–250 keV) and make use of multicoincidence techniques to separate the different fragmentation channels. The theory explains the various charge transfer mechanisms and provides the energy deposit that eventually leads to fragmentation.

Experiments have been performed on our 150 kV accelerator in Toulouse, equipped with a radio-frequency ion source; $^4He^{2+}$ isotopic helium gas was used inside. It is often considered that a pure $^4He^{2+}$ ion beam cannot be produced with such equipment because of the overlap with the nearby contaminant $H_2^+$ beam, which has about the same $m/q$ ratio (2.0007 and 2.0151, respectively). However, the quality of our beam line allows us to separate these two beams as shown in Ref. [16], so we are confident

 

of our identification of collisional processes. For time-of-flight purposes, the beam is pulsed and impinges an effusive $C_{60}$ target produced by an oven heated at about 450 °C. Recoil ions (ionized $C_{60}$ and smaller fragments) created by the collision are extracted by a pulsed (10 ns rise time) 600 V cm$^{-1}$ electric field perpendicular to the projectile beam direction and are analyzed by a time-of-flight (TOF) cell with a second-order time focusing. A postacceleration of 3 kV just before the multichannel plate detector (MCP) allows for a better detection efficiency, especially for the slowest $C_{60}^{+}$ fragments. Also, a negatively biased grid is used in front of the MCP in order to repel electrons and increase the detection efficiency from 60% (open area ratio) up to 95% [17]. Delay between the beam pulse and the extraction one is chosen in such a way that $He^{2+}$ projectiles cross the collision zone without any deviation in order to see always the same target density. Time-of-flight spectra are registered in an event by event mode by a FastComptek 7885 (5 ns resolution) multistop module. Delays, trigger generation, and mixing of signals are done by using two CO4020 Ortec modules. More details can be found in Ref. [18].

An example of the spectrum obtained at 20 keV collision energy is given in Fig. 1(a). The figure shows the formation of (i) small carbon clusters via multifragmentation (MF) processes (notice the well-known even-odd oscillations), (ii) intact $C_{60}^{q+}$ ions resulting from pure charge transfer, and (iii) $C_{60-2n}^{q+}$ fullerene ions resulting from fission and evaporation processes. The partial spectrum associated with processes (ii) and (iii) at 20 keV is shown in Fig. 1(b): No evaporation from $C_{60}^{+}$ is seen and only a little from $C_{60}^{2+}$ and $C_{60}^{3+}$ [regions labeled EV2 and EV3 in Fig. 1(b)].

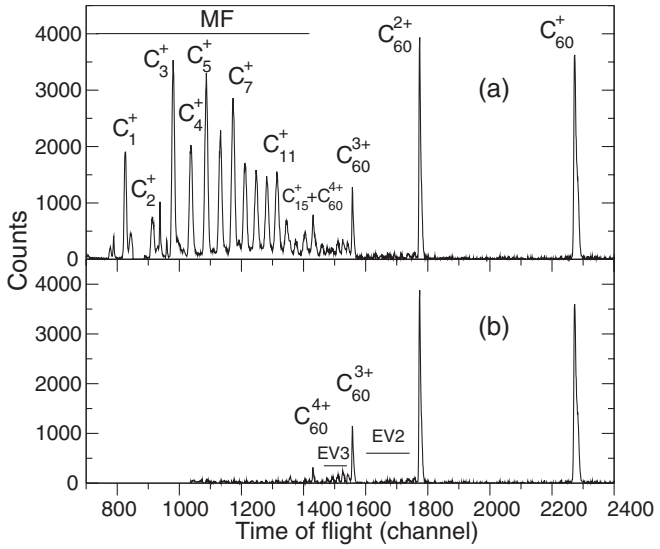


FIG. 1. Time-of-flight spectrum for the $^4He^{2+} + C_{60}$ collision at 20 keV impact energy. (a) Total (inclusive) spectrum; (b) partial spectrum corresponding to the emission of a single ion ($C_{60}^{q+}$ evaporation sequences).

Absolute cross sections have been obtained by renormalizing to charge production cross sections in $H^+ - C_{60}$ collisions [14,15] (see [19] for details). Afrosimov *et al.* [20,21] have measured relative cross sections for the charge changing process $^3He^{2+} + C_{60} \rightarrow {}^3He^{i+} + C_{60-2n}^{j+} + C_{2n}^{k+} + [i + j + k - 2]e^-$. For simplicity, in the absence of fragmentation (i.e., in the absence of $C_{2n}^{k+}$), we will use the notation $(ij)$, where $i$ and $j$ are, respectively, the projectile and target charge after the collision; a subscript $fr$ will be added when fragmentation occurs. From these measurements, one can deduce cross sections (in arbitrary units) for the formation of intact $C_{60}^{q+}$ ions in charge transfer reactions and the production of $He^+$ and $He^0$. The relevant $(ij)$ processes contributing to each cross section are listed below:

$$C_{60}^{+} = (11), \qquad C_{60}^{2+} = (12) + (02), \qquad C_{60}^{3+} = (13) + (03), \tag{1}$$

$$He^{+} = (11) + (12) + (13), \tag{2}$$

$$He^{0} = (02) + (03) + (04) + (02)_{fr} + (03)_{fr} + (04)_{fr}.$$

Formation of $C_{60}^{2+}$ is mainly due to (12) reactions which include transfer ionization or double capture into He doubly excited states that later decay by autoionization $[He^0(2\,\mathrm{ln}l') \rightarrow He^+(1s) + e^-]$. Formation of stable $C_{60}^{3+}$ is mainly due to double transfer ionization (03) at energies below 30 keV and to transfer-double ionization (13) at higher energies. It must be noted that the sum of cross sections corresponding to nonfragmented $C_{60}^{q+}$ is a good approximation to the cross section for $He^+$ production. All cross sections from Afrosimov *et al.* [20,21] have been renormalized to our absolute values for the production of nonfragmented $C_{60}^{2+}$ at 90 keV equivalent energy for the $^4He^{2+}$ isotope. Figure 2 shows good agreement between the two sets of data. Hence, we can deduce absolute cross sections for producing $He^+$ and $He^0$ more suitable for comparison with theoretical results. Uncertainties of our absolute values are estimated to be 50%.

We have also carried out theoretical calculations by using the method of Ref. [22]. This method has led to absolute charge transfer and fragmentation cross sections in good agreement with the experimental measurements for collisions of positively charged lithium and sodium clusters with alkali atoms [13,22–24]. The method has been described in detail in Ref. [22]. Therefore, only a brief account is given here. The only nuclear degree of freedom included in the calculations is the relative distance $R$ between the cluster and the projectile [25]. This is a good approximation because, in this collision, charge transfer occurs far away from the target. However, multifragmentation produced in frontal collisions with the target cannot be described. According to the present experimental results, this is a minor dissociation channel at impact ener-

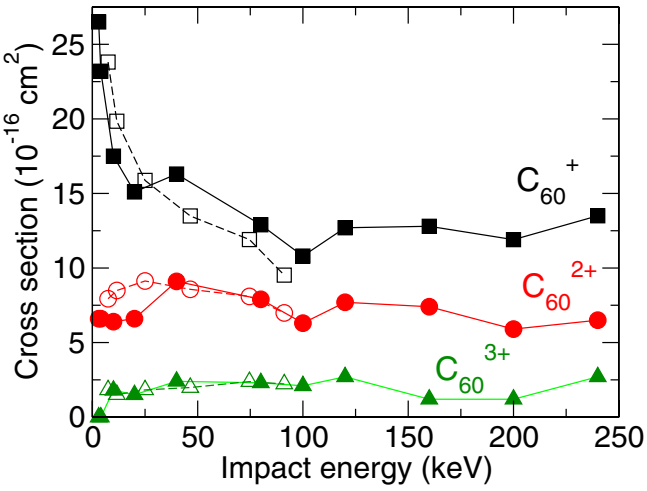


FIG. 2 (color online). Cross sections for production of intact $C_{60}^{q+}$ ions. Solid symbols: Our results; hollow symbols: results of Afrosimov *et al.* [20,21] normalized as explained in the text. Square, circle, and triangle: $C_{60}^+$, $C_{60}^{2+}$, and $C_{60}^{3+}$, respectively.

gies lower than 10 keV; hence, our calculations are restricted to the energy interval 0.1–10 keV. We use the hollow-sphere jellium model of Puska and Nieminen [26] to represent the ionic core potential of the cluster. Hence, only the $C_{60}$ $\pi$ electrons are considered. Then, following Ref. [22], we use the semiclassical impact parameter approach in which the electrons are described quantum mechanically and the relative projectile-target motion classically. An additional simplification is that electrons are treated as independent particles. We have used the ''molecular close-coupling'' formalism to solve the semiclassical time-dependent Schrödinger equation. From the calculated one-electron amplitudes, inclusive many-electron transition probabilities have been obtained as explained in Ref. [27]. In particular, we have evaluated $P(He^+)$ and $P(He^0)$, which are the probabilities of producing $He^+$ and $He^0$ irrespective of the fate of all of the other electrons. Then the energy deposit $E_{dep}$ associated with $P(He^+)$ has been evaluated as explained in Ref. [22]. From $E_{dep}$, the evaporation rate constants have been evaluated by using two methods: the microscopic and microcanonical statistical theory of Weisskopf [28] as implemented in Ref. [29] and the Arrhenius model as implemented in Ref. [10]. These models have been successfully used to describe fragmentation of small carbon clusters and $C_{60}$ ions, respectively. Hence, the proportion of the different fragments at a given TOF is easily obtained [22].

Preliminary results obtained with a reduced basis of molecular states have been reported in Ref. [25]. In the present work, a much larger basis has been used, which ensures a reasonable convergence up to an impact energy of ~10 keV. This is important to account for ionization processes occurring at the higher impact energies. The calculated and measured cross sections for $He^+$ and $He^0$ formation are shown in Fig. 3. They are in reasonable agreement in the region where they overlap. Both theory and experiment predict that $He^+$ and $He^0$ cross sections are comparable in magnitude for a wide range of impact energies and comparable to the geometrical cross section ($\sim 56 \times 10^{-16}$ cm$^2$). As we have seen, this is not the case for the cross sections leading to $C_{60}^+$ and $C_{60}^{2+}$ (see Fig. 2). The difference between the $C_{60}^+$ and $He^+$ cross sections given in Figs. 2 and 3 is due to transfer ionization [processes (12) + (13) in Eq. (2)].

Figure 4(a) shows the variation of the relevant molecular orbitals of the $(C_{60} - He)^{2+}$ system with $R$ and Fig. 4(b) the calculated $E_{dep}$ as a function of impact parameter $b$ for $C_{60}^+$ ions produced at an impact energy of 0.1 and 10 keV. As can be seen, the energy deposit is important even at large $b$, which is the consequence of electron transfer from the inner $\pi$ orbitals of $C_{60}$ (mainly, the $p$, $d$, and $f$ ones) to the empty $He^+(n = 2)$ orbitals at $R < 25$ a.u. [see Fig. 4(a)]. Thus charge transfer already occurs when the projectile is far away from $C_{60}$ (the radius of the latter is ~8 a.u.). Since charge transfer creates one or several holes in the inner $\pi$ orbitals of $C_{60}$, the resulting charged fullerene will lie in an excited state. The presence of a hole in these inner $\pi$ orbitals implies an excitation energy of the order 0.3–0.4 a.u. [i.e., ~8–11 eV; see Fig. 4(a)]. This is the dominant process at $b > 17$ a.u. [see Fig. 4(b)]. At smaller $b$, $E_{dep}$ is significantly larger, implying that electron capture is accompanied by the simultaneous excitation or ionization of other $\pi$ electrons as, e.g., in transfer ionization. Transfer ionization is expected to be negligible at very low impact energy; thus, the difference between the energy deposit at 0.1 and 10 keV [see Fig. 4(b)] is mostly due to that process. Therefore, the calculated $E_{dep}$ at higher impact energies not only describes excitation of $C_{60}^+$ but

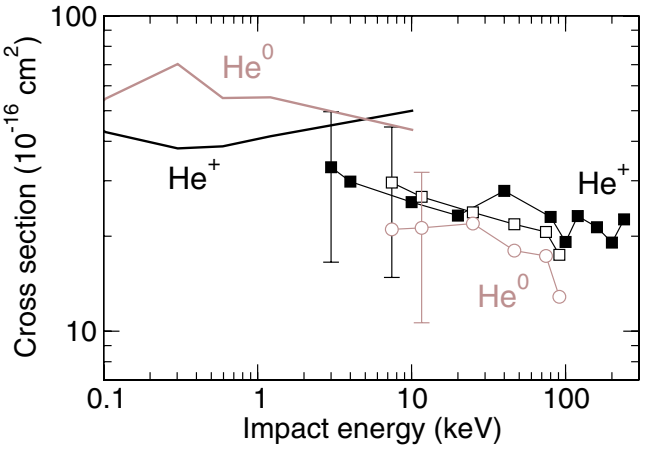


FIG. 3 (color online). Cross sections for production of $He^+$ and $He^0$. Solid lines: Present theoretical results; solid symbols: present experimental results; hollow symbols: experimental results of Afrosimov *et al.* [20,21] normalized as explained in the text.

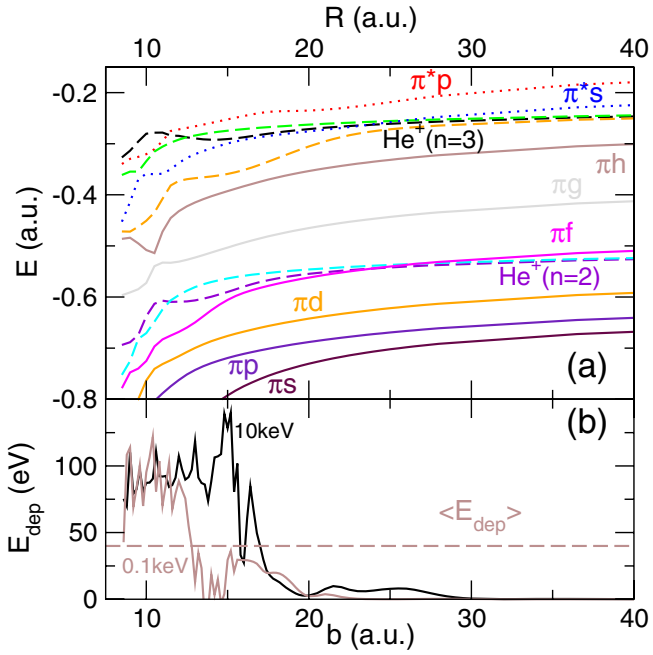


FIG. 4 (color online). (a) Correlation diagram for the relevant molecular orbitals of $(C_{60}\text{-He})^{2+}$ denoted by their character at infinite separation. Solid lines: Occupied orbitals at the beginning of the collision; dashed lines: orbitals dissociating into $He^+$ ones; dotted lines: orbitals dissociating into empty $C_{60}$ ones. (b) Collision energy deposit in $C_{60}^+$ as a function of impact parameter at 0.1 and 10 keV. Dashed line: Average value at 0.1 keV. Notice that $R = b^2 + v^2t^2$, where $v$ is impact velocity and $t$ is time.

also of $C_{60}^{q+}$ ($q \geq 2$) formed in transfer ionization. In other words, only at low impact energies is the energy deposited in $C_{60}^+$ close to the calculated $E_{\text{dep}}$ ( $\sim 40$ eV at 0.1 keV); at 10 keV, it is approximately half of the calculated $E_{\text{dep}}$.

For $b < 20$ a.u., the energy deposit is larger than the energy required to evaporate a single $C_2$ unit from $C_{60}^+$ (which is 10.6 eV [30]). However, the present experiment (and that of Ref. [10]) shows that, at impact energies smaller than 10 keV, almost no $C_{58}^+$ is observed. This is confirmed by our Weisskopf and Arrhenius calculations of the fragmentation branching ratios for a TOF of $\sim 3$ $\mu$s, which lead to almost 100% intact $C_{60}^+$ for an energy deposit smaller than 50 eV (in good agreement with the $C_{60}^{2+}$ fragmentation patterns reported in Ref. [10]).

In summary, we have presented a combined theoretical and experimental study of charge transfer and fragmentation in collisions of slow $He^{2+}$ ions with $C_{60}$ that has allowed us to determine absolute charge transfer and fragmentation cross sections for this reaction. These results could be used as a reference in future experimental work involving other ion-$C_{60}$ collisions. The agreement between theory and experiment supports the validity of our conclusions.

We thank the CCC-UAM and CIEMAT for computer time. This work was supported by the DGI Projects No. FIS2006-00298, No. FIS2007-60064, and No. CTQ2004-00039/BQU.

[1] E. E. B. Campbell and F. Rohmund, Rep. Prog. Phys. **63**, 1061 (2000).
[2] C. Lifshitz, Int. J. Mass Spectrom. **200**, 423 (2000).
[3] E. E. Campbell, *Fullerene Collision Reactions* (Kluwer Academic, Dordrecht, 2003), 1st ed.
[4] I. V. Hertel, T. Laarmann, and C. P. Schulz, Adv. At. Mol. Opt. Phys. **50**, 219 (2005).
[5] G. Senn, T. D. Märk, and P. Scheier, J. Chem. Phys. **108**, 990 (1998).
[6] S. Martin *et al.*, Phys. Rev. A **62**, 022707 (2000).
[7] S. Tomita *et al.*, Phys. Rev. A **67**, 063204 (2003).
[8] H. Cederquist *et al.*, Phys. Rev. A **67**, 062719 (2003).
[9] A. Rentenier *et al.*, J. Phys. B **36**, 1585 (2003).
[10] L. Chen *et al.*, Phys. Rev. Lett. **98**, 193401 (2007).
[11] S. Díaz-Tendero, M. Alcamí, and F. Martín, Phys. Rev. Lett. **95**, 013401 (2005).
[12] S. Matt *et al.*, Eur. Mass Spectrom **5**, 477 (1999).
[13] C. Bréchignac *et al.*, Phys. Rev. Lett. **89**, 183402 (2002).
[14] H. Tsuchida *et al.*, J. Phys. B **31**, 5383 (1998).
[15] A. Reinkoster *et al.*, Phys. Rev. A **64**, 023201 (2001).
[16] P. Moretto-Capelle *et al.*, J. Phys. B **31**, L423 (1998).
[17] B. Deconihout *et al.*, Appl. Surf. Sci. **94/95**, 422 (1996).
[18] A. Rentenier *et al.*, J. Phys. B **37**, 2429 (2004).
[19] P. Moretto-Capelle *et al.*, Phys. Scr. **T110**, 325 (2004).
[20] V. V. Afrosimov *et al.*, Tech. Phys. **43**, 358 (1998).
[21] V. V. Afrosimov *et al.*, Fullerene Sci. Technol. **6**, 393 (1998).
[22] P. A. Hervieux *et al.*, J. Phys. B **34**, 3331 (2001).
[23] B. Zarour *et al.*, J. Phys. B **33**, L707 (2000).
[24] C. Bréchignac *et al.*, Phys. Rev. A **68**, 063202 (2003).
[25] L. F. Ruiz *et al.*, Int. J. Quantum Chem. **86**, 106 (2002).
[26] M. J. Puska and R. M. Nieminen, Phys. Rev. A **47**, 1181 (1993).
[27] H. J. Lüdde and R. M. Dreizler, J. Phys. B **18**, 107 (1985).
[28] D. H. E. Gross, Rep. Prog. Phys. **53**, 605 (1990).
[29] S. Díaz-Tendero *et al.*, Phys. Rev. A **71**, 033202 (2005).
[30] S. Díaz-Tendero, M. Alcamí, and F. Martín, J. Chem. Phys. **123**, 184306 (2005).