

Z Oscillations in Ion-Induced Fullerene Fragmentation

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Multiply charged ion-induced fragmentation and ionization of C_{60} is governed by electronic and nuclear stopping of the projectile as well as charge exchange. We have studied the collision dynamics as a function of the projectile atomic number Z ($2 \leq Z \leq 18$) for constant projectile velocity v at charge states $q = 2, 3$. Strong oscillations of electronic-stopping-related quantities such as ionization and fragmentation are observed. From the properties of the oscillations, we obtain information on the effective electron density of the fullerene.

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The physical properties of clusters, such as fullerenes, and other aggregates of intermediate size can vary over a wide range from those of isolated atoms to those of condensed matter. For ions passing by a cluster at large distances the cluster resembles an atom with many electrons. At smaller distances, we expect the situation to be more comparable to that of a solid. It is interesting to see to what extent essentially many-body phenomena can be observed in a system of finite size. Very recently, the concept of electronic stopping was invoked to explain experimental observations in ion-fullerene interactions: Larsson *et al.* [1] investigated collisions of Ar^{q+} ($v \approx 0.32$ a.u.) with C_{60} and found projectile energy losses of the order of several hundred eV, independent of the projectile charge state q . In an Ar^{8+} - C_{60} collision study ($v \approx 0.24$ a.u.), energy losses of about 350 eV were observed [2]. Also, in MeV collisions, Tsuchida *et al.* found indications for fragmentation due to electronic stopping [3].

However, exact measurements of the electronic stopping in multiply charged ion collisions with fullerenes are very difficult if not impossible. During the interaction the target charge state increases, giving rise to Coulomb repulsion of projectile and target especially on the outgoing trajectory. This repulsion manifests itself in a translational energy gain, dependent on the number of transferred and stabilized electrons [4] and the polarizability of the fullerene [5]. For Ar^{8+} projectiles ($v \approx 0.1$ a.u.) the average gain measured by Opitz *et al.* [6] amounts to 10–40 eV for 1–4 active electrons. The energy gains are superimposed on the energy losses.

A complementary approach of characterizing the electronic stopping is based on an evaluation of typical patterns in the fragmentation spectra. In a recent study on He^{q+} ($v = 0.1$ – 1 a.u.) collisions with C_{60} [7,8] we found evidence that electronic stopping of the projectile mainly leads to multifragmentation and collisional ionization of the fullerene, separable from, e.g., evaporation processes mainly caused by nuclear stopping. Multifragmentation and direct ionization can therefore be used as fingerprints of electronic stopping and are directly related to the amount of projectile translational energy transferred to internal modes of the target.

In ion-solid collisions, it was first observed that the electronic stopping power $S = dE/dx$ (i.e., the energy loss per trajectory unit length) oscillates with the projectile Z for $v < 1$ a.u. [9]. The bound states of the projectile are modified by the target electronic structure. These screening effects lead to a maximum in electronic stopping, e.g., in the range of $Z = 5$ – 8 ; closed shells lead to minima. The location of maxima and minima is affected by the target electron density; dilute electron gases lead to electronic stopping following the properties of unperturbed atoms [10,11]. Applying this to a fullerene target, an identification of the Z oscillations in fragmentation and ionization cross sections would stress the relevance of electronic stopping for the underlying excitation processes. Moreover, the location of the minima would indicate the effective density of the fullerene electron gas.

In this paper, we investigate electronic stopping effects and, in particular, the Z oscillations in collisions of multiply charged ions ($q = 2, 3$) with fullerenes as a function of the projectile atomic number Z ranging from 2–18.

The experiments are performed using multiply charged ions extracted from the KVI electron cyclotron resonance ion source. The source is floated on a potential between 2 and 20 kV to obtain an equal velocity of $v = 0.2$ and 0.25 a.u. for $q = 2$ and 3, respectively. The projectiles used in this study are He, B, C, N, O, F, Ne, Na, S, Cl, and Ar. In the collision chamber a fullerene oven is operated at around 700 K. C_{60} vapor effuses through a nozzle into the collision region where it is crossed by the projectile ion beam. A static electric field (200 V/cm) extracts the charged collision products into a reflectron-type time-of-flight mass spectrometer [12] (resolution ≈ 1500). For an extraction diaphragm of 4 mm, this results in a transmission of 100% up to ion kinetic energies of 2 eV. An increase of the extraction field to 400 V/cm changes the fragmentation yields by less than 10% even though the transmission threshold is shifted to 4 eV. This is in agreement with our earlier studies using O^{q+} projectiles [13] and with the results of Opitz *et al.* [6], who also found that just the C_2^+ fragments originating from superasymmetric fission [14] exhibit high kinetic energies of up to 5–10 eV.

The ions can be measured in coincidence with electrons emitted during the collisions, with charge resolved projectiles, or in a pulsed beam mode. Details of the experimental setup can be found in [15]. The relative cross sections presented in this study have been obtained using a pulsed beam in order not to discriminate events in which, e.g., no electron is emitted and thus no electron-ion coincidence can be measured.

Figure 1 displays time-of-flight spectra for $^{13}\text{C}^{2+}$ and $^{23}\text{Na}^{2+}$ projectiles. According to the classical overbarrier model [16], the distance at which the projectile captures the first electron from the fullerene mainly depends on the ionization potential of the fullerene and the projectile charge state. In other words, the absolute interaction cross section is roughly constant for $Z = 2-18$ at equal charge state. We can therefore use the total number of detected particles as a reference in discussing Fig. 1 and also to determine relative fragmentation as well as ionization yields. Both spectra in Fig. 1 are normalized to this total number of detected particles. Even though the projectiles are close in the periodic table, strong differences between the spectra are obvious. A clear change in the spectra when going from $Z = 6$ to $Z = 11$ is the strong decrease of the C_{60}^{2+} peak. However, the respective yield cannot be used as a measure for the stopping power since doubly charged fullerenes can either be formed in gentle collisions, where double electron capture is the dominant process, or as in close collisions where electronic stopping is important. The C_{60}^{3+} , on the other hand, cannot be formed by electron capture alone and is a fingerprint of a direct excitation following a

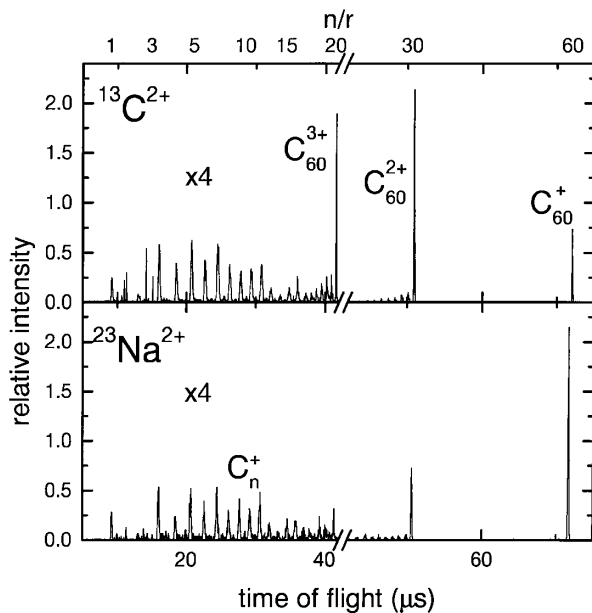


FIG. 1. Time-of-flight spectra of C_{60}^{r+} and fragment ions for projectiles $^{13}\text{C}^{2+}$ and Na^{2+} at $v = 0.2$ a.u. The intensity is normalized to the integral over all peaks. The top axis shows the n/r ratio with the number of C atoms n and the charge state r . The intensity in the low n/r region is multiplied by a factor of 4.

close projectile-fullerene collision. The same holds for the small C_n^+ fragments which are mainly due to multifragmentation processes. As already mentioned, both (collisional) ionization and multifragmentation of the fullerene could be identified as fingerprints of electronic stopping in He^{9+} collisions with C_{60} [7,8]. A closer look into the low n/r region of the spectra shows a dramatic decrease of the C_{60}^{3+} yield with Z increasing from 6 to 11. This decrease already indicates the Z dependence of the stopping power in ion-fullerene collisions. Before presenting the relative yields over the whole range of Z , the theoretical background of the Z oscillations should be discussed in more detail.

In the velocity range below 1 a.u., the electronic stopping of an ion traversing an electron gas scales linearly with v , and a friction coefficient can be defined via γ as $S = dE/dx = \gamma(r_s)v$ [17]. $r_s = (4\pi n_0/3)^{-1/3}$ is the density parameter with the electron density n_0 . (The density parameters for, e.g., solid Al and C are 2.07 and 1.59, respectively [10].) For a given density parameter, γ solely depends on the projectile atomic number Z . Density functional theory results for $\gamma(Z)$ at different values of r_s are plotted in Fig. 2 [10,18]. For all plotted friction parameters, clear oscillations of γ and therefore of the stopping power S can be seen. Besides the obvious fact that γ increases strongly with decreasing r_s , also the maxima and minima of the oscillation shift to larger Z . As brought up in the beginning, the minima at large r_s are found for $Z = 2$ and $Z = 10$, i.e., for closed shells. The decrease in collisional ionization from $Z = 6$ to $Z = 11$ can directly be recognized in Fig. 1, whereas the change in multifragmentation is less obvious from the raw data. The fact that the C_{60}^{3+} peak decreases stronger than the multifragmentation when going from $Z = 6$ to $Z = 11$ already indicates different effective electron densities for both processes.

For a more quantitative analysis of our data, we define relative cross sections for multifragmentation σ_f^q and for direct ionization σ_i^q as the relative yields of the various peaks with respect to the sum Y_{total} of all ions. This

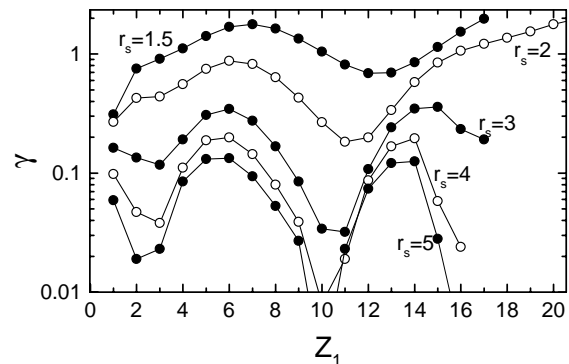


FIG. 2. The electronic friction coefficient γ as a function of Z for different density parameters r_s (from density functional theory calculations [10,18]).

sum consists of three components: parent ion peaks up to charge states $r = q + 1$, evaporation peaks up to $r = q$, and fragmentation peaks,

$$\sigma_f^q = \frac{\sum_{n=1}^{14} \int C_n^+}{Y_{\text{total}}}, \quad \sigma_i^q = \frac{\int C_{60}^{q+1}}{Y_{\text{total}}}. \quad (1)$$

The projectile charge state is denoted as q and just single direct ionization to C_{60}^{q+1} is taken into account.

All yields have been corrected for the (m/q) -dependent efficiency of our detector [13]. Changes of extraction field and reflectron settings do not affect the course of the oscillations, even though the transmission of the system might change. The results for doubly charged projectiles ($q = 2$) are displayed in Fig. 3. Oscillations of both cross sections are evident. The multifragmentation apparently consists of an oscillating contribution superimposed on a nonoscillating background. We performed molecular dynamics calculations which showed that the nuclear stopping increases linearly with projectile Z . For the heavier projectiles, the magnitude of the nuclear stopping can become comparable to the electronic stopping; i.e., direct vibrational excitation becomes strong enough to cause multifragmentation (in contrast to the case of light projectiles as He [7,8]). However, such strong nuclear stopping occurs only in large angle scattering events in which the target constituents considerably gain momentum in the projectile beam direction. In the experiment, thus, most of the fragments originating from nuclear stopping are not detected and cannot be evaluated quantitatively. The remaining of those fragments contribute to σ_f^q but show no oscillatory behavior.

The direct ionization, on the other hand, shows no such offset because it cannot be caused by nuclear stopping. More insight into both processes can be obtained from the location of the maxima. It is obvious from Fig. 3 that σ_f^2 and σ_i^2 peak at different Z values. For instance, the first maximum for σ_f^2 is found at $Z = 8$, whereas for σ_i^2 it is found at $Z = 7$. Comparing this to the data displayed in Fig. 2 reveals that multifragmentation is due to collisions with an effective electron density parameter $r_s < 1.5$, which is lower than the one of bulk carbon $r_s = 1.59$. This is in agreement with calculations of Puska and Nieminen [19] who used $r_s = 1.2$ for a jellium description of the fullerene. Direct ionization takes place in collisions where on the average the probed r_s is larger; i.e., the electron density is lower.

To guide the eye, the friction coefficients $\gamma(1.5)$ and $\gamma(2)$ from Fig. 2 data are plotted as dotted lines in Fig. 3. Apparently, multifragmentation takes place in collisions where the projectile passes the fullerene cage, thereby experiencing bulklike carbon properties, whereas direct ionization is limited to glancing collisions in which the projectile just passes through the electron "atmosphere" of the fullerene and the resulting exciting is too small to cause multifragmentation.

The impact parameters leading to multifragmentation and direct ionization, respectively, change with projectile charge state q . For $q = 3$ the cross sections σ_f^3 and σ_i^3 are plotted in Fig. 4. The multifragmentation (upper plot) shows a behavior similar to the doubly charged projectile case. For the direct ionization, however, the oscillatory

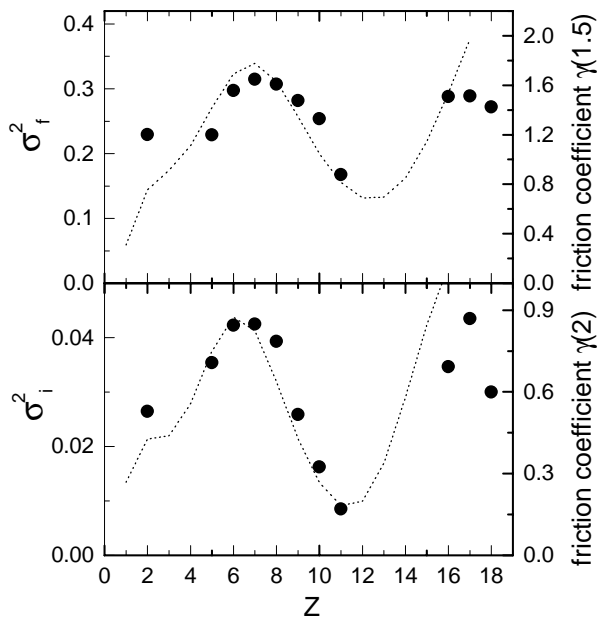


FIG. 3. Left axis: relative multifragmentation yields (upper plot) and C_{60}^{3+} yields (lower plot) for doubly charged ion impact. Right axis: friction coefficient γ for $r_s = 1.5$ and 2, respectively (dotted line).

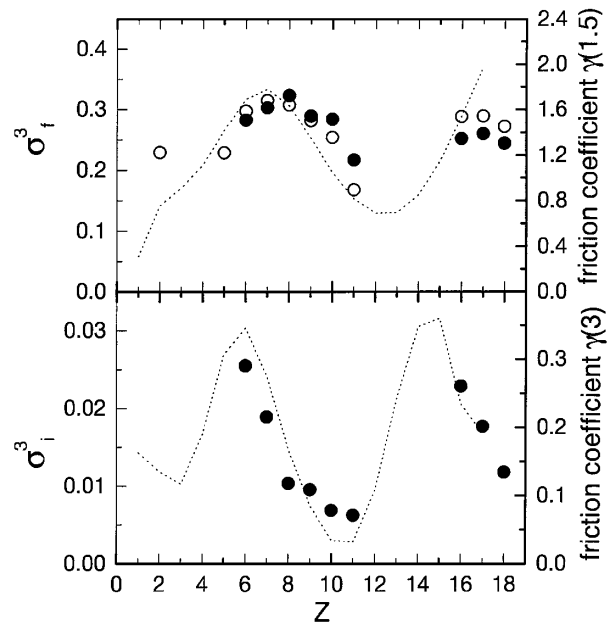


FIG. 4. Left axis: relative multifragmentation yields (upper plot) and C_{60}^{4+} yields (lower plot) for triply charged ion impact. The open symbols are taken from Fig. 3. Right axis: friction coefficient γ for $r_s = 1.5$ and 3, respectively (dotted line).

structure is shifted to lower Z as compared to the $q = 2$ case and now follows nicely the friction coefficient for $r_s = 3$, i.e., the lower electron densities. This indicates that, for higher projectile charge state q , ionization on the average takes place at larger impact parameters. Assuming an increasing electronic stopping with increasing projectile charge state q , indeed it has to be expected that the class of collisions for which the excitation energy is high enough for ionization but not yet sufficient for multifragmentation is, on the average, correlated with larger impact parameters.

A surprising conclusion from our experimental data is that a target as small as a C_{60} cluster has a sufficient size to be treated in terms of a statistical electronic stopping model. From the effective fullerene diameter of ≈ 20 a.u. and a projectile speed $v = 0.2$ a.u., an interaction time of about 2 fs can be deduced. This value is of the same order as the typical excitation times for an electron-hole pair of eV separation as well as the response time of the electron gas to screen the projectile. Very recently, Hattass *et al.* [20] have found comparably short charge equilibration times (7 fs) for, e.g., Th^{65+} penetrating 5 nm C foils. Shorter interaction times are crucial to study effects which are present in the preequilibrium range only: Juaristi *et al.* [21] investigated the dependence of the electronic stopping on projectile L - and K -shell vacancies on a 10 fs time scale. Theory predicts an increase of the stopping with increasing number of L -shell vacancies. Additional K -shell vacancies, however, should lead to weaker stopping. Ion-surface scattering experiments show only a weak influence of the L -shell filling; due to the fast filling rates ($\tau \approx 2$ fs) [22] most of the predicted variation is suppressed. Our results show that ion-fullerene collisions might be a tool to attack this problem: Interaction times on the 1 fs scale are feasible and characteristic features of the electronic stopping are still observable.

As an outlook, collisions of multiply charged ions with large (bio-)molecules might become a powerful tool also for mass spectrometry since the excitation of the molecules can be tuned by variation of Z and q , respectively.

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- [1] M. Larsson, P. Hvelplund, M. Larsen, H. Shen, H. Cederquist, and M. T. Schmidt, *Int. J. Mass Spectrosc.* **177**, 51 (1998).
- [2] S. Martin, J. Bernard, L. Chen, A. Denis, and S. Dessevelles, *Eur. Phys. J. D* **4**, 1 (1998).
- [3] H. Tsuchida, A. Itoh, K. MiYabe, Y. Bitoh, and N. Imanishi, *J. Phys. B, At. Mol. Opt. Phys.* **32**, 5289 (1999).
- [4] N. Selberg, A. Bárány, C. Biedermann, C.J. Setterlind, H. Cederquist, A. Langereis, M.O. Larsson, A. Wännström, and P. Hvelplund, *Phys. Rev. A* **53**, 874 (1996).
- [5] B. Walch, U. Thumm, M. Stöckli, C. Cocke, and S. Klawikowski, *Phys. Rev. A* **58**, 1261 (1998).
- [6] J. Opitz, H. Lebius, B. Saint, S. Jaquet, B. Huber, and H. Cederquist, *Phys. Rev. A* **59**, 3562 (1999).
- [7] T. Schlathölder, O. Hadjar, R. Hoekstra, and R. Morgenstern, *Phys. Rev. Lett.* **82**, 73 (1999).
- [8] T. Schlathölder, O. Hadjar, J. Manske, R. Hoekstra, and R. Morgenstern, *Int. J. Mass Spectrosc.* **192**, 245 (1999).
- [9] F. Eisen, *Can. J. Phys.* **46**, 561 (1968).
- [10] P.M. Echenique, R.M. Nieminen, J.C. Ashley, and R.H. Ritchie, *Phys. Rev. A* **33**, 897 (1986).
- [11] H. Winter, C. Auth, A. Mertens, A. Kirste, and M. Steiner, *Europhys. Lett.* **41**, 437 (1998).
- [12] B. Mamyrin, V. Karatev, A. Shmikk, and V. Zagulin, *Sov. Phys. JETP* **37**, 45 (1973).
- [13] T. Schlathölder, R. Hoekstra, and R. Morgenstern, *J. Phys. B, At. Mol. Opt. Phys.* **31**, 1321 (1998).
- [14] P. Scheier and T. Märk, *Phys. Rev. Lett.* **73**, 54 (1994).
- [15] H.O. Folkerts, F.W. Blik, M.C. de Jong, R. Hoekstra, and R. Morgenstern, *J. Phys. B, At. Mol. Opt. Phys.* **30**, 5833 (1997).
- [16] A. Niehaus, *J. Phys. B, At. Mol. Opt. Phys.* **19**, 2925 (1986).
- [17] A. Närmann, R. Monreal, P.M. Echenique, F. Flores, W. Heiland, and S. Schubert, *Phys. Rev. Lett.* **64**, 1601 (1990).
- [18] M.J. Puska and R.M. Nieminen, *Phys. Rev. B* **27**, 6121 (1983).
- [19] M.J. Puska and R.M. Nieminen, *Phys. Rev. A* **47**, 1181 (1993).
- [20] M. Hattass, T. Schenkel, A.V. Hamza, A.V. Barnes, M.W. Newman, J.W. McDonald, T.R. Niedermayr, G.A. Machicoane, and D.H. Schneider, *Phys. Rev. Lett.* **82**, 4795 (1999).
- [21] J.I. Juaristi, A. Arnau, P.M. Echenique, C. Auth, and H. Winter, *Phys. Rev. Lett.* **82**, 1048 (1999).
- [22] R. Díez Muiño, N. Stolterfoht, A. Arnau, A. Salin, and P.M. Echenique, *Phys. Rev. Lett.* **76**, 4636 (1996).