VOLUME 86, NUMBER 23 PHYSICAL REVIEW LETTERS 4 JUNE 2001

Excitation and Fragmentation Mechanisms in Ion-Fullerene Collisions

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(Received 2 November 2000)

Electronic and vibronic excitations as well as fragmentation mechanisms in high energy ion (H^+, C^+, Ar^+) fullerene collisions are investigated within a fully microscopic approach, called nonadiabatic quantum molecular dynamics. The total kinetic energy loss of the projectile depends dramatically on ion mass, but, surprisingly, does not depend on the impact velocity for all ions in a certain range. This is in striking contrast to the predictions of the "stopping power" concept of solids, but explains apparently contradicting experimental observations. Signatures for nonstatistical fragmentation mechanisms are predicted.

DOI: 10.1103/PhysRevLett.86.5258 PACS numbers: 36.40.Qv, 31.15.Ew, 34.50.Bw

During the last decade, fullerene reactions became an exciting new field of collision physics and experiments involving photons, electrons, atoms, molecules, clusters, surfaces, ions, and highly charged ions have been performed (for recent reviews see [1,2]). In the case of ion-fullerene collisions, major experimental progress has been made recently by developing and applying novel multiparametric correlation techniques [3–7]. Systematic investigations as a function of ion mass, charge, and impact velocity [3–7] have provided significant new information about excitation, ionization, charge transfer, and, in particular, fragmentation mechanisms in these reactions. Thus, ion-fullerene collisions have proven to be ideal model systems to study electronic and vibronic excitation mechanisms including the fundamental process of electron-vibration coupling in atomic many-body systems with a large, but still finite number of degrees of freedom.

However, at present, there is by no means a commonly accepted interpretation of such experiments, and very different conclusions have been drawn about the excitation and fragmentation mechanisms. For example, Schlathölter *et al.* [7] found a strong velocity dependence of the fragmentation spectra (from evaporation to multifragmentation) in He^+ collisions in the impact velocity range of $v \approx 0.1-0.5$ a.u., and this behavior has been interpreted as the result of a continuous transition from vibrational to electronic excitation. In striking contrast, Opitz *et al.* [3] found complete velocity-independent fragmentation patterns for H^+ impact in the range of $v \approx 0.2-3.5$ a.u. exhibiting only evaporation processes, with maxima for the absolute cross sections around $v \approx 1.5$ a.u., and it has been argued that only electronic excitation occurs in these collisions. On the other hand, Reinköster *et al.* [4] observed velocity-independent multifragmentation spectra with different ions (He^+, Ar^{q+}, $q = 1, \dots, 3$) in a range ($v \gtrsim 0.4$ a.u.) where one may expect dominating electronic excitations. At a fixed impact velocity, however, the actual fragmentation patterns depend dramatically on ion mass and charge [4]. Obviously, a consistent interpretation of the ambiguous experimental observations, and thus a final and common understanding of the collision dynamics can be achieved only if the very initial phase of the reaction is definitely understood, i.e., the nature (electronical vs vibrational) and the total amount of the excitation energy transferred. This, however, is experimentally not accessible and theoretically unknown.

Because of the lack of microscopic calculations [8] the initial electronic and vibrational excitation energies have been estimated so far [3,5,7,9] by applying the macroscopic concept of the "stopping power" in solids [10,11]. In this paper we report on first microscopic studies of the excitation mechanisms in ion-fullerene collisions. Systematic investigations as a function of ion mass (H^+, C^+, Ar^+), impact velocity ($v = 0.01-0.5$ a.u.), impact parameter ($b = 0-10$ a.u.), and orientation of the cage are presented. It is shown that the absolute values as well as the relative contributions (electronical and vibrational) of the excitation energies depend dramatically on ion mass and strongly on the impact velocity in the range $v \approx 0.01-0.25$ a.u. Surprisingly, velocity-independent excitation energies are predicted above $v \gtrsim 0.25$ a.u. with dominating electronic transitions. This is at variance with the velocity-proportional stopping power concept in solids, but explains consistently the different experimental observations.

Concerning fragmentation it is well known today that statistical decay models [3,9,12–15] (where only the total amount of excitation energy determines the final mass distribution) are very successful in describing qualitatively the observed mass spectra. The present microscopic calculations explicitly show, however, that the fragmentation mechanism depends on both the total *amount* and the *nature* of excitation. Possible signatures to prove nonstatistical decay in future studies are discussed.

To study ion-fullerene collisions microscopically one has to consider the coupled dynamics of at least 240 excited and correlated electrons and $(183 - 6)$ nuclear degrees of freedom. A theory which, in principle, can cope with such situations is the so-called nonadiabatic quantum molecular dynamics (NA-QMD) [16]. In this approach, electronic and vibrational degrees of freedom are treated simultaneously and self-consistently by combining time-dependent density functional theory [17] with classical molecular dynamics (MD). It thus represents a quite general method to investigate different dynamical situations in atomic many-body systems where electronic excitation, direct ionization, and charge transfer, as well as the coupling to the nuclear motion (and vice versa), may occur. So far, the NA-QMD theory has been successfully applied for the description and interpretation of fragment correlations in collision-induced dissociation [18], charge transfer cross sections [19–21], as well as excitation and relaxation processes [22] in collisions of atoms with small sodium clusters Na_n ($n \leq 11$). It is used here, for the first time, to describe systems as large as fullerenes, which became possible by improving the underlying numerical procedure.

To obtain a first qualitative insight into the collision dynamics and in order to present an overview of the important reaction channels, snapshots of calculated collision scenarios at a fixed collision geometry (impact parameter $b = 2$ a.u.) are shown (Fig. 1). In Fig. 2, for the same events the time dependence of the kinetic energy of the ions in the center-of-mass system is presented.

In the case of proton impact, the projectile is backward scattered on the cage surface (Fig. 1) and, thereby, has lost about one-half of its initial kinetic energy (Fig. 2). At the same impact velocity, the carbon ion penetrates the first wall of the cage and is stopped and captured when colliding with the second wall inside the fullerene at $t \approx 40$ fs (Fig. 2). Because of the large excitation energy transferred, the endohedral complex is not stable and fragments in typically ~100 fs (Fig. 1). The argon ion penetrates the whole cage at this impact velocity and thereby is strongly deflected (third column in Fig. 1). The large amount of momentum and energy transferred to the carbon atoms (Fig. 2) leads to immediate fragmentation within time scales comparable with the interaction time of about 40 fs. At a velocity of $v = 0.45$ a.u., the argon ion penetrates the fullerene on a straight line within about 1 fs (last column in Fig. 1). No momentum transfer to the cage occurs, but the fullerene becomes electronically excited (see below). After about 45 fs (corresponding to about one-half of the breathing period of C_{60} [23]) the cluster starts visibly to vibrate (Fig. 1) and finally fragments, too (not shown).

The selected events in Figs. 1 and 2 correspond to cage-specific reaction channels that may occur in these collisions (surface scattering, capture, shot through with and without immediate fragmentation). From the depicted examples one may also draw first general conclusions about the excitation and fragmentation mechanisms:

First, in the two argon collisions ($v = 0.02$ and 0.45 a.u.) approximately an equal amount of excitation energy is being transferred to the fullerene (cf. Fig. 2). Its nature, however, is different (vibronic and electronic, respectively; cf. also discussion of Fig. 3) leading to entirely different time scales and mechanisms of fragmentation. It remains a stimulating question for future experiments,

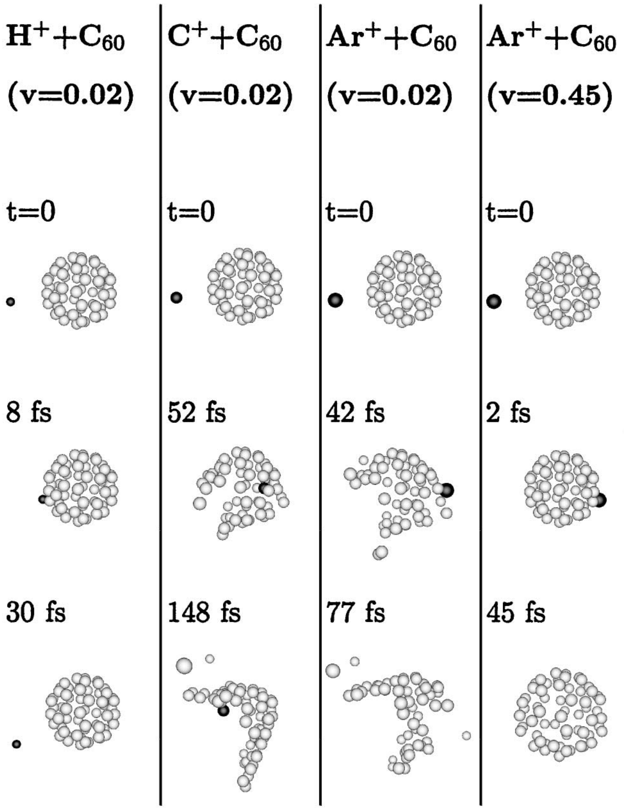

FIG. 1. Snapshots of the reaction dynamics as a function of time for a fixed collision geometry ($b = 2$ a.u.), different ions (H^+, C^+, Ar^+), and velocities ($v = 0.02$, 0.45 a.u.). The selected events represent cage specific reaction channels (see text).

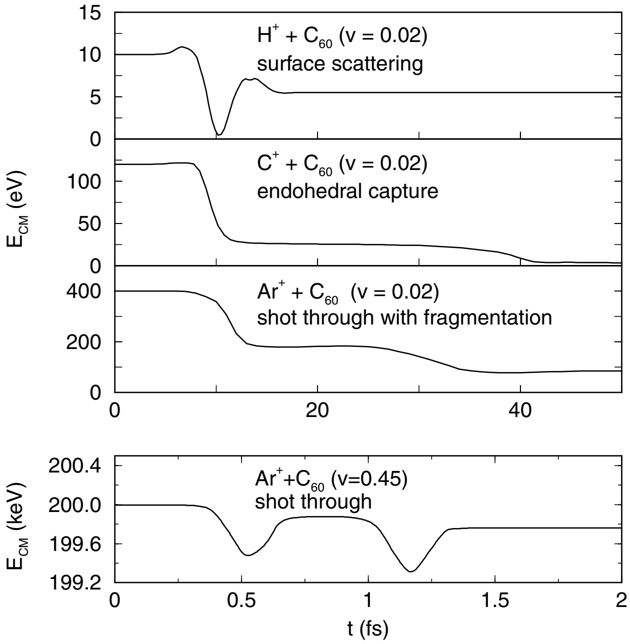

FIG. 2. Time dependence of the kinetic energies $E_{\mathrm{c.m.}}$ of the projectiles in the center-of-mass system for the same events shown in Fig. 1.

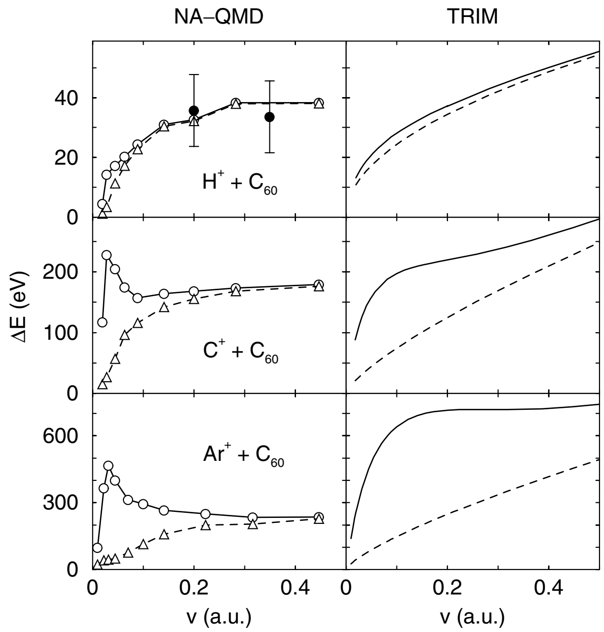

FIG. 3. Left: calculated (NA-QMD) total kinetic energy loss ΔE (open circles) and its electronic contribution (open triangles) as a function of impact velocity v for different ions (H^+, C^+, Ar^+) and fixed collision geometry with $b = 2$ a.u. Recent experimental data for $H^+ + C_{60}$ (filled circles with error bars) are also shown [3,24]. Right: for the same collision systems as shown left, the total kinetic energy loss (solid lines) and electronic contributions (dashed lines) as predicted by the nuclear and electronic "stopping power" concept calculated with the TRIM code [11].

whether this drastic distinction in the reaction dynamics can be seen directly in the final mass distributions, detected several μs after the collision and, thus, strongly affected by sequential decay processes [13–15]. We expect, however, significant differences in the angular distribution of the fragments due to the presence and lack of momentum transfer, during the very initial phase of the collisions (~fs), respectively.

Second, at a fixed impact velocity ($v = 0.02$ a.u.) the absolute values of the excitation energy depend drastically on ion mass, which is true in the whole velocity range considered as discussed in the following.

In Fig. 3, the total kinetic energy loss as well as its electronic contribution (resulting from excitation, direct ionization, and charge transfer processes) as a function of impact velocity and ion mass is shown. It is compared with predictions of the nuclear and electronic stopping power model of solids, calculated with the TRIM code [11], as well as with very recent experimental data of proton collisions [24].

Note, first of all, the quantitative differences in the absolute values of ΔE for the ions, which must result in qualitatively different fragment multiplicity distributions, as observed experimentally [4], also in fullerene-ion atom collisions [9]. Second, the transferred energy ΔE increases smoothly with v in the low velocity range ($v \lesssim 0.3$ a.u.) only for the proton collisions, whereas distinct maxima of ΔE are observed for heavier projectiles, resulting from first dominating and then decreasing vibrational energy transfer. This, together with the sensitive absolute values of ΔE as a function of ion mass, is in accord with the spectacular experimental findings (and given interpretation) of Schlathölter *et al.* [7], and also explains, at least qualitatively, the apparent differences in the fragmentation patterns between proton collisions and that of heavier ions [3,4,7]. Third, and most surprisingly, the microscopic calculations provide velocity-independent excitation energies with dominating electronic nature in the high velocity range of $v \approx 0.25$–0.5 a.u. for all ions. This is in striking contrast with the velocity-proportional electronic stopping power model [10,11] (right part of Fig. 3). We expect the reason for this saturation effect to be connected with the cage-specific collision geometry: Instead of a three-dimensional, homogeneous electron gas (used in the derivation of the stopping power [10,11]), fullerenes basically contain two-dimensional electronic density distributions, well defined and excited on a cagelike surface. A final theoretical understanding of this point, however, requires further, model investigations. But, in any case, the calculated values of ΔE explain nicely the velocity-independent fragmentation patterns observed in this range of v for different ions [3,4]. For proton impact, the calculated absolute values of ΔE are also in quantitative agreement with very recent experimental data [3,24].

To complete the microscopic analysis we present in Fig. 4 the dependence of the transferred energy on the impact parameter as well as on the orientation of the cage with respect to the collision axis. As a matter of fact, the electronic part of the energy loss shows a distinctly small variance as a function of the orientation of the cage (shown in the right part of Fig. 4 for $Ar^+ + C_{60}$, $v = 0.45$ a.u. collisions, but valid for all considered ions and impact velocities). This is expected to be the direct consequence of an approximately homogeneous electronic density distribution along the cage surface, in accordance with a jelliumlike approximation for the C_{60} structure [25]. However, as seen also in the right part of Fig. 4, there are a

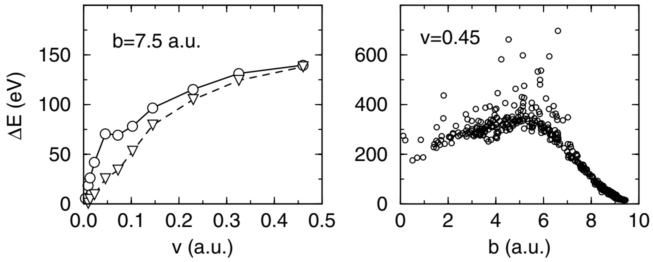

FIG. 4. Calculated energy losses for $Ar^+ + C_{60}$ collisions. Left: The same quantities as shown in Fig. 3, but for a near grazing collision with $b = 7.5$ a.u. Right: Total kinetic energy loss for $v = 0.45$ a.u. as a function of the impact parameter b and randomly selected orientations of the cage with respect to the collision axis.

few collision events exhibiting a distinctly larger energy loss as compared to the mean value, in particular, in the range of $b \approx 4-7$ a.u. They correspond to billiardlike collisions between the ion and individual carbon atoms on the fullerene cage, leading to direct fragmentation. Experimental evidence of this highly nonstatistical decay mechanism has been reported recently for fullerene-ion He (but not Ne or Ar) collisions [9] by detecting small signals of C_{59}^{+} fragments. Our analysis clearly shows that this mechanism exists also in collisions with fast Ar ions. However, because of the large amount of electronic energy transferred, it can be observed experimentally only by measuring directly the "knocked out" fast carbon atoms.

The impact parameter dependence of the absolute values of ΔE shows a maximum around $b \approx 4-6$ a.u., and ΔE vanishes for $b \gtrsim 10$ a.u. (right part of Fig. 4). The velocity dependence of ΔE is qualitatively the same for all impact parameters (as shown in Fig. 3) for b smaller than the cage radius, however, with an expected drastic decrease of the vibrational component if b exceeds the cage radius (as shown in the left part of Fig. 4).

In summary, from the presented microscopic calculations of ion fullerene collisions it is apparent that (i) the excitation mechanism is basically different from that in solids and is dominated by a saturation effect and (ii) the fragmentation mechanism depends on the amount and the nature of excitation leading to signals of nonstatistical decay in energy *and* angular resolved mass spectra.

This work was supported by the DFG through Schwerpunkt "Zeitabhängige Phänomene in Quantensystemen der Physik und Chemie." We are grateful to Eleanor Campbell and Preben Hvelplund for carefully reading the manuscript and for suggestions.

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