Neutralization of Charged Fullerenes during Grazing Scattering from a Metal Surface

S. Wethekam and H. Winter*
Institut für Physik, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 6, D-12489 Berlin, Germany

H. Cederquist
Department of Physics, Stockholm University, SE-106 91 Stockholm, Sweden

H. Zettergren
Departamento de Química, C-9, Universidad Autónoma de Madrid, 28049 Madrid, Spain
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The neutralization of C_{60}^{+} and C_{60}^{2+} fullerenes with keV energies is studied for grazing scattering from a clean and flat Al(001) surface. From the measured shifts between the angular distributions for scattered projectiles of different incident charge, we derive image-charge interaction energies, which relate to the distances of electron transfer for C_{60}^{+} and C_{60}^{2+}. These neutralization distances are in accord with a classical over-the-barrier model taking into account the image-charge effects of the Al target and the polarization of the fullerene.

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Owing to their specific features, fullerenes are interesting objects for a variety of studies and applications [1]. This holds, in particular, for cluster-impact phenomena where the nearly spherical shape, the simple electronic structure, and the high fragmentation energies provide a good basis for detailed investigations using projectiles of substantially higher complexity than, e.g., single atoms or ions. A considerable body of work has been performed on gas phase collisions making use of fullerenes as targets (see, e.g., [2,3]) and as projectiles *and* targets [4–6]. Studies on C_{60} scattering from solid surfaces show increasing activities over recent years [7–13] and have been focused mainly on angular distributions, fragmentation, and electron emission for impact on metal and graphite surfaces.

In view of the broad interest in electron-transfer phenomena for scattering of neutral or charged atoms and molecules from surfaces (see, e.g., [14,15], and references therein), the important aspects of electron transfer for larger projectiles (such as fullerenes and other clusters) have been paid little attention so far. Interesting studies were performed by Hillenkamp, Pfister, and Kappes [10] on charge fractions after scattering of C_{60}^{+}, C_{76}^{+}, and C_{84}^{+} from a graphite surface and by Bekkerman *et al.* [11,12] on the formation of negative C_{60}^{-} ions during scattering of hyperthermal (projectile energies of up to some 10 eV) neutral C_{60} from a carbonized nickel surface. Making use of the effect of the attractive force owing to the image charge on ion trajectories [16], an effective distance for the formation of C_{60}^{-} on the outgoing path of about $25a_0$ (a_0 = Bohr radius) was derived. Recently, Tamehiro *et al.* [13] analyzed the neutralization of C_{60}^{+} ions grazingly scattered from a KCl(001) surface by measuring fractions of ions that survive the scattering event in their initial charge state. A more general understanding of charge transfer at surfaces for larger molecules, fullerenes, or clusters has not been worked out so far.

The enhanced complexity involved in studies on charge transfer at surfaces for fullerenes (and clusters in general) is mainly due to the presence of internal excitations as well as to delayed emission processes of electrons and/or fragmentation. Here C_{60}^{q+} ions are of particular interest, since for these species well-defined trajectories (with negligible fragmentation) can be achieved under specific scattering conditions. Furthermore, fullerenes have highly symmetric structural and well-known physical properties which provide good perspectives for model descriptions. In this Letter, we present studies on the neutralization of keV C_{60}^{+} and C_{60}^{2+} fullerenes during grazing scattering from an Al(001) surface. We compare our experimental data on image-charge acceleration with calculations using a variant of the classical over-the-barrier model by Zettergren *et al.* [17] in which the mutual electronic responses of the metal surface *and* the fullerene projectile (modeled as a conducting sphere) are taken into account.

In the experiment, we have scattered C_{60}^{+} and C_{60}^{2+} fullerene ions with keV energies (produced by evaporation of C_{60} powder in a 10 GHz electron cyclotron resonance ion source) from a clean and flat Al(001) surface under grazing angles of incidence of typically $\Phi_{in} = 1°$. Under these conditions, scattering proceeds in the regime of surface channeling [18] where projectiles are reflected in front of the topmost surface layer following well-defined trajectories [15]. The target surface was prepared by cycles of grazing sputtering with 25 keV Ar^{+} ions followed by annealing to about 500 °C for 10 minutes. This procedure results in a clean and very flat target surface with a mean width of terraces larger than 100 nm [15]. The direction of the incident beam was aligned along a high index crystallographic direction in the surface plane of the target (''ran-

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dom orientation'') in order to avoid effects of axial surface channeling [19]. Scattered projectiles were recorded at a distance of 66 cm behind the target using a position-sensitive channel plate detector where outgoing ions in different charge states could be separated by means of a set of electric-field plates.

When charged projectiles approach a metal surface, their trajectories are affected by image-charge interactions. The resulting attractive force leads to an increase of the perpendicular component of the velocity vector of incoming projectiles. This force vanishes at the instant of projectile neutralization. The resulting enhancement of the perpendicular velocity is equivalent to a gain of normal energy. Based on the image-charge potential for ions in front of metal surfaces, one can deduce from the normal energy gain the effective distance of neutralization on the incident trajectory [16] as shown for singly, multiply, and highly charged *atomic* ions during scattering from metal and insulator surfaces [20–23]. Information on the related charge-transfer mechanisms has motivated the ion-surface over-the-barrier charge transfer model [22,24].

In Fig. 1, we show angular distributions for the scattering of 7 keV C_{60}^{+} (solid circles) and C_{60}^{2+} (open circles) fullerene ions from an Al(001) surface under a grazing angle of incidence $\Phi_{in} = 1.0°$. We did not succeed with our setup to produce neutral C_{60} beams without substantial excitation and fragmentation. In order to obtain a reference for the angle of incidence, we scattered neutral Ar atoms with keV energies which are specularly reflected from the surface. The angular distributions for the neutralized C_{60}^{+} and C_{60}^{2+} fullerenes have a full width at half maximum of about 0.5 degrees, which shows that scattering proceeds along well-defined trajectories. Owing to the small grazing angle of incidence, the effective energy for projectile impact on the surface is given by the energy for the motion along the surface normal (z axis) $E_z = E_{proj}\sin^2\Phi_{in}$. For the data shown in Fig. 1, E_z is small ($E_z \approx 2$ eV), and no fragmentation of scattered fullerenes could be detected. Scattered fullerenes were mostly neutral, and only about 1% had a single positive charge. The intensity of C_{60}^{-} was below the detection limit of our setup (10^{-3}). A striking feature in Fig. 1 is the angular shift between the distributions for C_{60}^{2+} and C_{60}^{+}. As outlined above, we attribute this shift to the different attractive forces for C_{60}^{2+} and C_{60}^{+} projectiles on their incident trajectories prior to neutralization.

By adjustment of the projectile beam energy and the angle of incidence Φ_{in}, we have varied the normal energy E_z. The experimental normal energies for the scattered projectiles were then deduced as functions of E_z from the maxima of the angular distributions for the scattered neutralized C_{60}^{+} and C_{60}^{2+} fullerenes. In Fig. 2, we have plotted these outgoing normal energies as function of the incoming normal energies E_z for C_{60}^{+} (solid circles) and C_{60}^{2+} (open circles) projectiles. The solid line indicates specular reflection (elastic scattering) where the scattering angle equals the incident angle. We find that singly charged clusters are scattered subspecularly, whereas C_{60}^{2+} clusters are scattered at slightly larger outgoing angles and normal energies than C_{60}^{+} for the same E_z.

The observed image-charge effects are closely related to charge transfer and the neutralization of the incident charged fullerenes, since the electronic rearrangement on

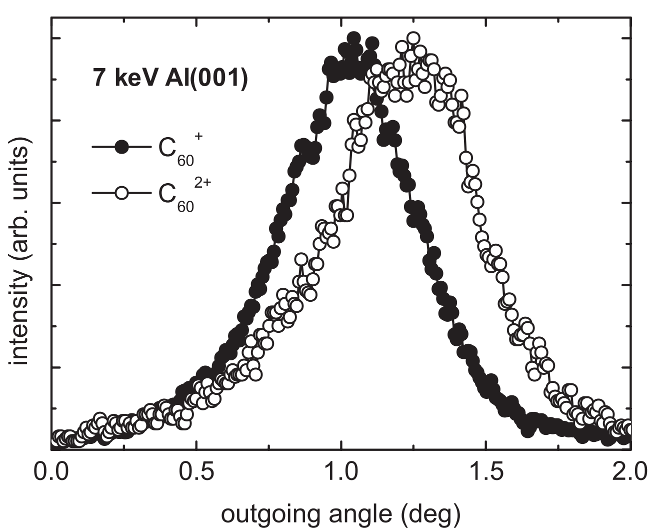

FIG. 1. Intensities of neutralized projectiles as a function of outgoing polar angles for scattering of 7 keV C_{60}^{+} (solid circles) and C_{60}^{2+} (open circles) on Al(001) for $\Phi_{in} = 1.0°$. Angular shift is attributed to differences in image-charge effects on C_{60}^{+} and C_{60}^{2+} trajectories.

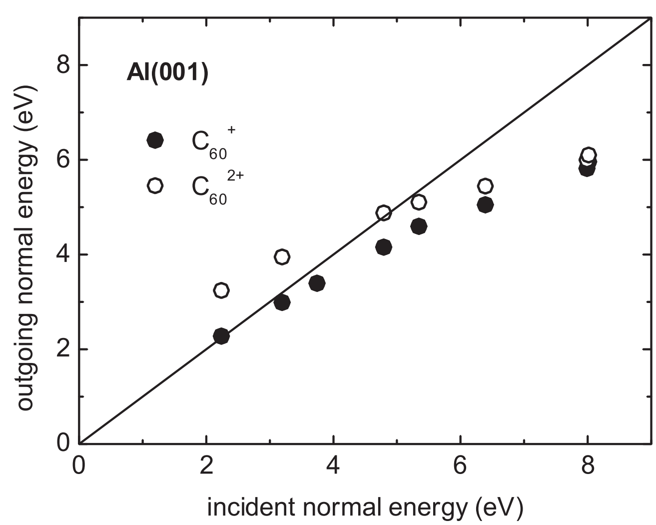

FIG. 2. Measured normal energies of outgoing fullerenes as a function of incident normal energies E_z for scattering and neutralization of C_{60}^{+} (solid circles) and C_{60}^{2+} (open circles) from Al(100). The solid line indicates specular reflection. Experimental uncertainties correspond to the size of the symbols.

the metal surface and the fullerene can be considered to relax at the instant of fullerene neutralization. For the analysis of the present data, we employ the classical *over-the-barrier model* originally developed for electron transfer between spherical objects [17] (such as two fullerenes) and let one of the sphere radii tend to infinity. This model has been used successfully to describe charge transfer in C_{60}^{q+}-C_{60} collisions [5,17] and charge transfer between highly charged ions and clusters of fullerenes [24] or biomolecules [25] and for charge transfer from fullerene dimers [26].

The basic feature of the over-the-barrier approach is the onset of charge transfer, if the total potential barrier between the projectile and the target is lowered to potential energies such that *resonant* electron transfer is classically allowed. The corresponding distance between the collision partners is considered as the effective distance of formation for ions of the next lower charge. The sequence leads eventually to fully neutralized projectiles. The dielectric response, generally described by the concept of image charges, plays an important role for the modeling of the potential barrier. For atomic ions, this interaction is incorporated by considering the (point) charge and the image charge of the ion core and the image charge of the active electron. For C_{60}^{q+} ions, the problem is more complex, as the large polarizability of the fullerene has to be taken into account. This problem can be solved analytically by using an infinite series of image charges in two spheres [17]. Here we will employ this method and expand one of the sphere radii to infinity in order to describe the dielectric response of the Al surface. The projectile sphere radius is set to $a = 8.37a_0$, extracted from the classical expression for the ionization energies of q-times positively charged conducting spheres $\mathrm{IE}(q) = W(C_{60}) + (q + 0.5)/a = (7.106 + 3.252q)$ eV, in fair accord with recent density-functional theory calculations [27].

For the doubly charged C_{60}^{2+}, we made use the model by Zettergren *et al.* [17] with a work function for Al(001) $W = 4.4$ eV (measured here via photoemission) to calculate the distance for the first electron transfer to be $z_1 = 14.8a_0$. At this distance, the potential energy difference compared to infinite separation is $V^{q=2+}(z = z_1 = 14.8a_0) = -1.88$ eV, while for C_{60}^{+} we have $V^{q=1+}(z = z_1 = 14.8a_0) = -0.47$ eV. Thus, the difference in normal energy gain for C_{60}^{+} and C_{60}^{2+} scattering is $1.88 - 0.47 = 1.41$ eV. Electron transfer for C_{60}^{+} projectiles is predicted closer to the surface at $13.3a_0$, where $V^{q=1+}(z = z_2 = 13.3a_0) = -0.53$ eV. The approximation using a point-charge fullerene gives neutralization distances of $z_1 = 12.7a_0$ and $z_2 = 9.2a_0$. Then the difference in normal energy gain between doubly and singly charged projectiles is 1.60 eV.

In Fig. 3, we show the measured outgoing normal energy as a function of normal energy corrected for image-charge effects by means of calculated energy gains for electron-transfer distances of $14.8a_0$ and $13.3a_0$, respectively. Now the data sets for singly and doubly charged fullerenes fall on a universal curve with energies systematically below those for specular reflection (solid line). The correction based on a point-charge cluster leads to slight systematic shifts between the data sets for different projectile charge (see also Fig. 4). Since most neutralized fullerenes are

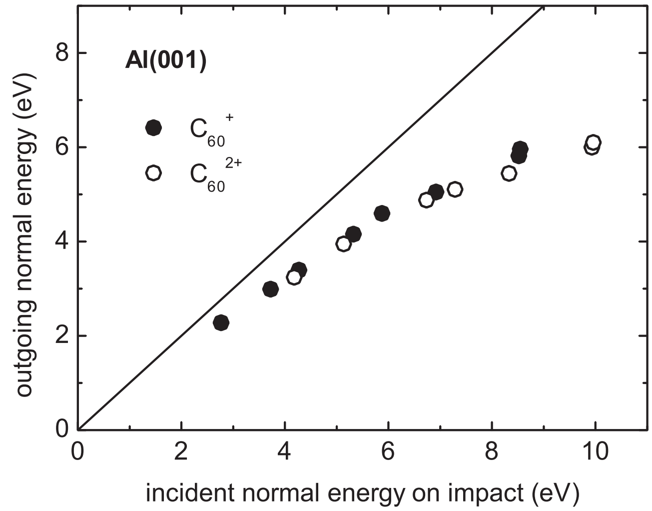

FIG. 3. Measured outgoing normal energies of neutralized C_{60}^{+} (solid circles) and C_{60}^{2+} (open circles) after grazing scattering from Al(100) as a function of normal energies *after* image-charge acceleration. C_{60}^{+} and C_{60}^{2+} incident energies have been corrected with respective model values for normal energy gains (0.53 and 1.94 eV, respectively). The solid line indicates specular reflection. Experimental uncertainties correspond to the size of the symbols.

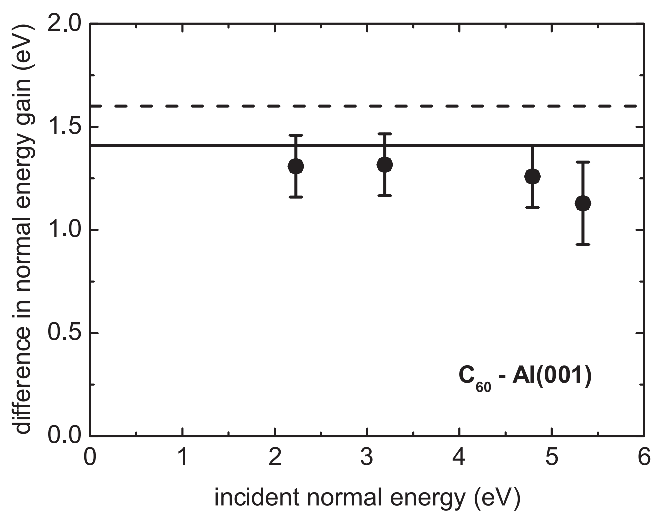

FIG. 4. Difference in experimental normal energy gains for C_{60}^{+} and C_{60}^{2+} fullerene ions as functions of incident normal energies. Solid line: Model prediction [17] for full polarization effects included (1.41 eV). Dashed line: Model prediction for pointlike projectile (1.60 eV).

found to be intact after scattering, the lower normal energies on the outgoing trajectories have to be attributed to collision-induced internal excitations as deduced from the analysis of fragment spectra [28]. The energy transfer to the crystal lattice [9,15] is negligible here, since inelastic contributions are independent of the grazing angle of incidence for constant normal energy (not shown).

For a more detailed discussion, we eliminate effects of internal excitations by considering the differences in normal energy gains for doubly and singly charged fullerenes as plotted in Fig. 4. Using the present model, we find for point-charge and spherically shaped projectiles [17] $\Delta E(z_1) = V^{q=1+}(z_1) - V^{q=2+}(z_1) = 1.60$ (dashed horizontal line) and 1.41 eV (solid horizontal line), respectively. Despite its simplicity (neglecting electron tunneling and dynamics), the present model catches the essentials of electron-transfer and image-charge effects of fullerenes in front of (neutral) metal surfaces. The comparison with our experiments seems to show that the polarization of the fullerene has to be taken into account. However, experiments with enhanced accuracy and calculations taking into account the collision dynamics are needed to further support this interesting issue.

In the present work, we consider the first information on distances of electron transfer of C_{60}^{2+} and C_{60}^{+} ions in front of a metal surface as a key result. From an analysis based on a classical over-the-barrier charge transfer model for a polarizable projectile sphere of finite size, we derive distances for electron transfer between about $13a_0$ and $15a_0$. These distances are in fair agreement with measured shifts of angular distributions for C_{60}^{+} and C_{60}^{2+} projectiles. From our model, we expect the final neutralization to occur at a distance of $13.3a_0 - 6.7a_0 = 6.6a_0$ (fullerene cage radius $6.7a_0$) between the closest C atom in the fullerene and the surface. We note that the distance of neutralization is a factor of 2 smaller than deduced for the formation of negatively charged fullerenes [12]. The consistent correction of image-charge effects implies for increasing normal energies an enhanced transfer of normal energy to internal excitations of the fullerene projectiles.

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*To whom all correspondence should be addressed. winter@physik.hu-berlin.de

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