PHYSICAL REVIEW B **81**, 121416(R) (2010)

Resonant electron capture by C_{60} ions at a metal surface with projected band gap

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(Received 5 March 2010; published 31 March 2010)

C_{60}^{+} and C_{60}^{2+} ions are scattered under grazing incidence from an atomically clean and flat Be(0001) surface at kilo-electron-volt energies. Distances for electron transfer are deduced from shifts of angular distributions for incident C_{60}^{+} and C_{60}^{2+} projectiles, which reflect changes in the interaction potentials at the instants of electron transfers. These distances are consistent with classical over-the-barrier model results indicating that the suppression of charge transfer, observed for atomic projectiles in front of metal surfaces with a projected band gap, is absent for fullerenes.

DOI: 10.1103/PhysRevB.81.121416 PACS number(s): 79.20.Rf, 79.60.Bm, 78.30.Na

The understanding of charge transfer of atoms and molecules in front of solid surfaces plays an important role in many fields as surface analysis, heterogeneous catalysis, secondary-ion mass spectrometry (SIMS), low-energy ion scattering, scanning tunneling microscopy (STM), or plasma wall interactions. During the last decade, a large body of work has been devoted to studies on the basic mechanisms.[1–7] Whereas electron tunneling between atoms/ions and surfaces with "simple" electronic structure (e.g., free-electron metals) is well understood, recent studies address effects of the electronic band structure,[1,5] electron transfer involving highly excited atoms/ions (Rydberg atoms, highly charged ions),[6,7] two-electron (Auger) processes,[3,6] or the interaction of extended objects, such as molecules or clusters, with surfaces.[8]

A process of considerable interest in recent years is the suppression of electron transfer between alkali atoms and metal surfaces with projected band gap [e.g., Cu(111), Ag(111)].[9–16] Based on two-photon (pump-probe) photoemission experiments and wave-packet propagation calculations, a quantitative understanding of lifetimes of excited adsorbate-localized states has recently been established.[5] For materials with a projected band gap,[17] experiments on electron transfer involving molecules or clusters are rare. Theoretical wave-packet propagation studies have recently predicted pronounced dependencies of electron-transfer rates between metal surfaces with projected band gap and adsorbate islands and atom chains on their size and shape.[18,19]

In this Rapid Communication, we report on electron capture during grazing scattering of hyperthermal C_{60} ions from a Be(0001) surface. We have studied the effect of the projected band gap on electron capture by a large molecule. Based on its symmetrical shape, well-known physical properties, and the relevance of carbon nanostructures for a variety of applications, e.g., future electronic devices,[20] atomic force microscopy or STM tips,[21] or primary particles in SIMS,[22] C_{60} can be considered as a prototype for exploring molecule surface interactions.[8]

Recent work on C_{60} surface interactions has focused on the stability and fragmentation of the molecule in scattering experiments,[23–25] on the structure of C_{60} films on metal surfaces,[26] or on the contact of an STM tip with a metal surface via an adsorbed C_{60} molecule.[27] From the analysis of shifts of angular distributions for scattered C_{60} molecules of different charge due to the dielectric response of the metal,[1,28] we have recently provided detailed information on the distance for electron capture of a positively charged fullerene in front of a free-electron metal surface, Al(100).[29]

In this work, we present studies with a Be(0001) target, a metal surface with a pronounced projected band gap.[17] Different from the suppression of electron transfer for alkali atoms[5,9–16] (see also below), we observe within the detection limits of our method no effect of the band gap on charge transfer. Whereas for atoms, the potential barrier between projectile and surface strongly favors transfer of electrons with large normal momentum corresponding to a strong suppression of the coupling of projectile states to electronic states of the surface outside the band gap (angular dependencies of transition matrix elements), the barrier for a large molecule in conjunction with its extended shape results in a pronounced overlap with states outside the band gap, i.e., an efficient electron transfer.

In the experiments, we have scattered C_{60}^{+} and C_{60}^{2+} ions with energy $E=10$ keV under grazing polar angles of incidence $\Phi_{in} \sim 1°$ along a high-indexed (random) direction from an atomically clean and flat Be(0001) surface. Scattering proceeds in the regime of surface channeling[1] with negligible energy transfer to the surface and widely decoupled motions of projectiles parallel and normal with respect to the surface. The impact with the surface proceeds with an energy for the motion along the surface normal $E_z^{in}=E \sin^2 \Phi_{in}$ on the order of electron volt for kilo-electron-volt projectiles. The parallel motion proceeds with constant kinetic energy $E_{\|} = E \cos^2 \Phi_{in} \approx E$. The C_{60} ion beams were produced by evaporation of C_{60} powder in an electron cyclotron resonance ion source operated with Ar gas and a small ion accelerator. By means of a set of slit systems, which separate differential pumping stages in order to maintain a pressure of some 10^{-11} mbar in the UHV target chamber, the incoming beams were collimated to a divergence $\Delta\Phi_{in} < 0.03°$. Scattered projectiles were detected by means of a position sensitive microchannel plate detector (Roentdek GmbH, Kelkheim-Ruppertshain) with an angular resolution of about 0.01°. The surface was prepared by cycles of grazing sputtering with 25 keV Ar^{+} ions and subsequent annealing to

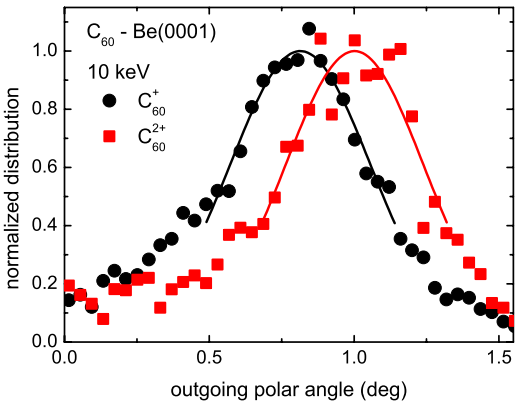

FIG. 1. (Color online) Normalized angular distributions as function of polar exit angle Φ_{out} for scattering of C_{60}^{2+} (squares) and C_{60}^{+} (circles) with $E=10$ keV under $\Phi_{in}=0.76°$ from Be(0001). Solid curves: Gaussian fits of maxima.

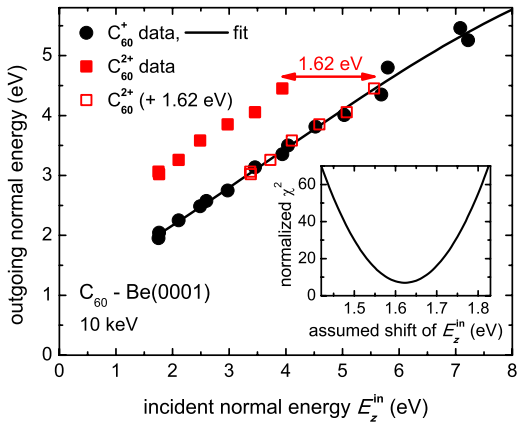

FIG. 2. (Color online) Outgoing normal energy E_z^{out} as function of incident normal energy E_z^{in} derived from maxima of polar angular distributions as shown in Fig. 1 for scattering of C_{60}^{2+} (full squares) and C_{60}^{+} ions (full circles) with $E=10$ keV from Be(0001). Curve: fit of C_{60}^{+} data. Open squares: C_{60}^{2+} data plotted as function of incident normal energy E_z^{in} shifted by 1.62 eV which corresponds to minimum of χ^2. Inset: χ^2 as function of assumed shift ΔE_{gain} of E_z^{in} for C_{60}^{2+}. For details see text.

about 680 °C. The quality of the surface was monitored by Auger electron spectroscopy, ion-beam triangulation, and the shape of angular distributions.[1] For more details on the experimental setup, we refer to Ref. 24.

The effective distance for electron transfer is derived via the associated change in the interaction potential, which is a strictly monotonic function of distance here.[1,28] We observe the complete neutralization of C_{60} ions during scattering with the surface, a clear indication for the efficient neutralization of ions on the incoming part of the trajectory.

In Fig. 1, we show polar angular distributions for scattering of C_{60}^{+} (full circles) and C_{60}^{2+} (full squares) ions under $\Phi_{in}=0.76°$ from Be(0001). The distribution for incident C_{60}^{2+} ions is shifted toward larger outgoing angles Φ_{out}, corresponding to enhanced outgoing normal energies $E_z^{out}=E\sin^2\Phi_{out}$. Owing to the differences of the potential barriers for singly and doubly charged projectiles, the neutralization of C_{60}^{2+} ions proceeds via two successive resonant electron capture events at well-separated distances $z_{2+,+}$ and $z_{+,0}$ (Refs. 6 and 29–31) with a common final step of neutralization for singly and doubly charged incident ions. Electron capture is associated with a change in interaction potential for the projectile in front of the surface, resulting in a gain of normal energy. The difference of this energy gain for doubly and singly charged incident ions is given by $\Delta E_{gain}=\Delta V(z_{2+,+})=V_+(z_{2+,+})-V_{2+}(z_{2+,+})$, where $V_+[V_{2+}]$ is the interaction potential for $C_{60}^{+}[C_{60}^{2+}]$ in front of the surface. Resonant charge transfer proceeds in a region of distances where the interaction potentials are well approximated by the concept of classical image charges[1,28] (see also below). As V_{2+} is more attractive than V_+, ΔE_{gain} is positive which explains the shift of the angular distributions.

In Fig. 2, we show normal energies of outgoing projectiles E_z^{out} derived from the peak positions of angular distributions (solid curves in Fig. 1 represent fits to Gaussian line shapes) as function of incident normal energy E_z^{in} for scattering of C_{60}^{2+} (full squares) and C_{60}^{+} (full circles) from Be(0001). In order to determine ΔE_{gain}, the C_{60}^{+} data is fitted with a third-order polynomial (solid curve), which shows a linear behavior in the region relevant here, but takes into account the inelasticity of the scattering process at larger energies (not shown).[24] This curve is compared to the C_{60}^{2+} data for an incident normal energy E_z^{in} shifted by ΔE_{gain}. The normalized sum of squared deviations χ^2 as function of ΔE_{gain} is plotted in the inset of Fig. 2. From the minimum, we derive $\Delta E_{gain}=(1.62\pm0.20)$ eV, where the uncertainty is dominated by systematic effects (the maximum systematic uncertainty is due to the definitions of the incoming beams).

The analysis of the experimental results is performed in the framework of an extended classical over-the-barrier (COB) model[30] by Zettergren *et al.*[31] In this model, electron transfer is initiated at a critical distance where the potential barrier between the C_{60} ion and the Be(0001) surface is sufficiently lowered for resonant electron transfer being classically allowed. The dielectric features of the C_{60} ion are modeled by a conducting sphere, the surface by a conducting plane characterized by its work function. Details on the electronic structure, such as a projected band gap, are not directly included. Polarization effects are treated in the framework of series of image charges.[31] The model has been successfully applied to the description of charge transfer between fullerenes and other fullerenes, highly charged ions, or biomolecules.[32–34] It also yields an accurate description of electron transfer between C_{60} ions and an Al(100) surface, a prototype of a free-electron metal.[29]

For Be(0001), we derive with this model $z_{2+,+}^{COB}=13.43$ a.u. (atomic units), $V_{2+}(z_{2+,+}^{COB})=-2.10$ eV, $V_+(z_{2+,+}^{COB})=-0.52$ eV, and obtain $\Delta V(z_{2+,+}^{COB})=1.58$ eV in quantitative accord with our data $\Delta E_{gain}=(1.62\pm0.20)$ eV, which corresponds to $z_{2+,+}=(13.3\pm1.5)$ a.u. From this agreement within our experimental uncertainties, we conclude that a suppression of electron transfer as found for atoms is not present here.

For a discussion on the physical mechanisms of our finding, we consider the effect of the projected band gap of the Be(0001) surface on charge transfer for atoms. From shifts of angular distributions for scattering of neutral and singly

charged Na ions (energy level comparable to energy of electrons captured by C_{60} ions), we derive the distance of electron transfer $z_{+,0}$ from the difference of interaction potentials $\Delta V(z_{+,0})=V_0(z_{+,0})-V_+(z_{+,0})$, using the classical image charge potential, $V_+(z)=-1/4z[V_0(z)\approx 0]$ at distances z relevant here. For $E_z^{\text{in}}\approx 6$ eV, we measure $\Delta V(z_{+,0})=(1.1\pm 0.1)$ eV.[35] This relates to $z_{+,0}=(6.2\pm 0.6)$ a.u.. which is considerably smaller than the prediction of the COB model $z_{+,0}^{\text{COB}}=9.3$ a.u., $\Delta V(z_{+,0}^{\text{COB}})=0.73$ eV. On the other hand, experimental data for the free-electron metal Al(111) yield $\Delta V(z_{+,0})=0.75$ eV,[1] i.e., $z_{+,0}=9.1$ a.u., in good accord with the COB model prediction. Similar differences in $\Delta V(z_{+,0})$ for the Be(0001) surface [$\Delta V(z_{+,0})=(1.3\pm 0.1)$ eV (Ref. 35)] and metal surfaces without projected band gap [$\Delta V(z_{+,0})=0.9$ eV, Cu(100) (Ref. 36)] are found for Li projectiles. Also in this case, the value for a surface without projected band gap is in accord with the COB model prediction $\Delta V(z_{+,0}^{\text{COB}})=0.77$ eV. In passing we note that the projected band gap of the Be(0001) surface closes at −3.8 eV with respect to vacuum, so that Cs atoms with an ionization energy of 3.9 eV do not show this effect.[35] We therefore conclude that the effect of the projected band gap of the Be(0001) surface on charge transfer for atomic projectiles can be detected by our method.

For atomic projectiles in front of metal surfaces with projected band gap, the main reason for the suppression of resonant charge transfer is the potential barrier between projectile and surface.[5] This barrier strongly favors charge transfer for electrons with large components of the wave vectors normal to the surface and suppresses the coupling to states with large parallel momentum (transition matrix elements show pronounced angular dependence[5]). In case of a projected band gap, charge transfer for atoms is dominated by the latter and thus inefficient.

In order to understand the basic mechanism for the absence of such an effect of the projected band gap on charge transfer for the fullerene, we show in Fig. 3 potential-energy contour plots for an active electron (y parallel, z normal to surface) for the present critical distances of electron transfer $z_{2+,+}^{\text{COB}}=13.43$ a.u. and $z_{+,0}^{\text{COB}}=12.45$ a.u. for doubly (upper panel) and singly charged C_{60} ions (lower panel), respectively. At those distances, the potential barrier along the surface normal is lowered to the work function $W=(5.2\pm 0.2)$ eV of the Be(0001) surface (measured here via photoemission). In referring to results from wave-packet propagation calculations, electron transfer for an atomic projectile at a surface with projected band gap is dominated by electronic states $|\vec{k}\rangle$ of the surface outside the band gap with maximum normal momentum k_z (maximum spill out of the wave function).[5] For capture of an electron $|\vec{k}\rangle$ from the Fermi level of Be(0001), the tilt angle θ of $\vec{k}$ with respect to the surface normal is calculated to $\theta=\arccos(k_z/k)\approx 37°$,[17] whereas for a jellium metal surface, electron transfer can proceed along the surface normal ($\theta\approx 0$).

The overlap of electrons $|\vec{k}\rangle$ from the Fermi level outside the band gap ($\theta\geq 37°$) with final states of the fullerene can be illustrated by tilted classical pathways depicted by solid (dotted) arrows whether electron transfer is allowed (forbidden). From the size of the C_{60} ion, it is evident, that the critical distances for a classical electron transfer along the normal and tilted paths coincide, so that Fermi electrons outside the projected band gap can efficiently couple to unoccupied states localized at the surface of the fullerene. Therefore, the angular dependence of charge transfer is weak and the suppression of charge transfer for single atoms in front of surfaces with projected band gap is absent. The large phase space including surface-localized states with large parallel momentum results at the critical distance z^{COB} in an efficient electron transfer. The experimental data is in accord with an efficient capture of electrons from the Fermi level. As a consequence, in front of a Be(0001) surface, the projected band gap has a minor effect on charge transfer for C_{60} ions.

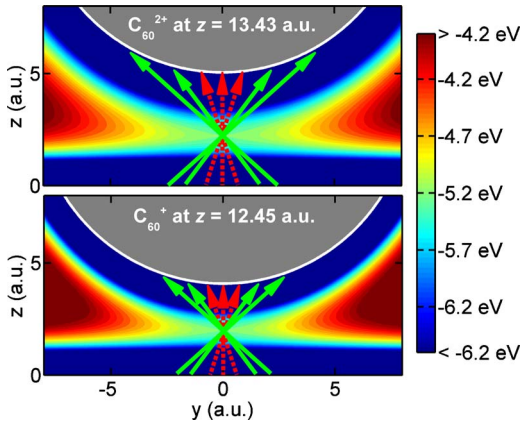

FIG. 3. (Color online) Potential energy for active electron (color scale) as function of distance y parallel and z normal to Be(0001) surface for C_{60} ions (fullerene: gray area and section of white circle) in indicated charge state and at indicated critical positions z^{COB} ($y=0$). Allowed/forbidden electron transfer paths under angles $\theta\approx 0°$ and $\theta\geq 37°$ with respect to surface normal for work function $W=5.2$ eV shown by solid/dotted arrows. Normal transfer ($\theta\approx 0°$) blocked by projected band gap of Be(0001). For details see text.

In conclusion, we have studied resonant electron capture for C_{60}^{2+} ions in front of a Be(0001) surface via shifts of angular distributions for incident C_{60}^{2+} and C_{60}^{+} ions. We observe no signature for a suppression of electron transfer as found for atomic particles in front of metal surfaces with a projected band gap.[5,9–16] This finding is in accord with a model that assigns the differences for atomic particles and fullerenes to the shape of the potential and the spatial extension of the molecule. We hope to stimulate with our results a more detailed theoretical analysis of this fundamental aspect on the interactions of large molecules with surfaces.

Financial support by the Deutsche Forschungsgemeinschaft (DFG) (Project No. Wi 1336) and the Swedish Research Council is gratefully acknowledged. We thank K. Maass and A. Schüller for their assistance in the preparation of the experiments.

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