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

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C\textsubscript{60}\textsuperscript{2+} and C\textsubscript{60}\textsuperscript{+} ions are scattered under grazing incidence from an atomically clean and flat Be(0001) surface at keV energies. Distances for electron transfer are deduced from shifts of angular distributions for incident C\textsubscript{60}\textsuperscript{2+} and C\textsubscript{60}\textsuperscript{+} 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.

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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 (LEIS), 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 \cite{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 \cite{1, 5}, electron transfer involving highly-excited atoms/ions (Rydberg atoms, highly-charged ions) \cite{6, 7}, two-electron (Auger) processes \cite{3, 6}, or the interaction of extended objects, such as molecules or clusters, with surfaces \cite{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)) \cite{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 \cite{5}. For materials with a projected band gap \cite{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 \cite{18, 19}.

In this Letter, we report on electron capture during grazing scattering of hyperthermal C\textsubscript{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 \cite{20}, AFM (atomic force microscopy) or STM tips \cite{21}, or primary particles in SIMS \cite{22}, C\textsubscript{60} can be considered as a prototype for exploring molecule surface interactions \cite{8}.

Recent work on C\textsubscript{60} surface interactions has focused on the stability and fragmentation of the molecule in scattering experiments \cite{23–25}, on the structure of C\textsubscript{60} films on metal surfaces \cite{26}, or on the contact of an STM tip with a metal surface via an adsorbed C\textsubscript{60} molecule \cite{27}. From the analysis of shifts of angular distributions for scattered C\textsubscript{60} molecules of different charge due to the dielectric response of the metal \cite{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) \cite{29}.

In this work, we present studies with a Be(0001) target, a metal surface with a pronounced projected band gap \cite{17}. Different from the suppression of electron transfer for alkali atoms \cite{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\textsubscript{60}\textsuperscript{2+} and C\textsubscript{60}\textsuperscript{+} ions with energy \(E = 10\) keV under grazing polar angles of incidence \(\Phi_{\text{in}} \sim 1^\circ\) along a high-indexed (“random”) direction from an atomically clean and flat Be(0001) surface. Scattering proceeds in the regime of surface channeling \cite{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 \(E_{\text{in}} = E \sin^2 \Phi_{\text{in}}\) of the order of eV for keV projectiles. The parallel motion proceeds with constant kinetic energy \(E_{\parallel} = E \cos^2 \Phi_{\text{in}} \approx E\). The C\textsubscript{60} ion beams were produced by evaporation of C\textsubscript{60} pow-
Scattered projectiles were detected 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 ∆Φin < 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 about 680°C. The quality of the surface was monitored by Anger electron spectroscopy (AES), ion beam triangulation, and the shape of angular distributions [1]. For more details on the experimental setup, we refer to [24].

The effective distance for electron transfer is derived via the associated change of the interaction potential, which is a strictly monotonic function of distance here [1, 28]. We observe the complete neutralization of C²⁺ 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 C⁶₀⁺ (full circles) and C²⁺⁺ (full squares) ions under Φin = 0.76° from Be(0001). The distribution for incident C²⁺⁺ ions is shifted towards larger outgoing angles Φout, corresponding to enhanced outgoing normal energies E²⁺⁺ out = E sin² Φout. Owing to the differences of the potential barriers for singly and doubly charged projectiles, the neutralization of C²⁺⁺ ions proceeds via two successive resonant electron capture events at well-separated distances z²⁺⁺,+ and z⁺,0 [6, 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

ΔEgain = ΔV(z²⁺⁺,+) = V₄(z²⁺⁺,+) − V₂⁺(z₂⁺⁺,+) ,

where V₄ [V₂⁺] is the interaction potential for C²⁺⁺ [C⁶₀⁺] 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 V₂⁺ is more attractive than V₄, ΔEgain is positive which explains the shift of the angular distributions.

In Fig. 2, we show normal energies of outgoing projectiles E²⁺⁺ out derived from the peak positions of angular distributions (solid curves in Fig. 1 represent fits to Gaussian lineshapes) as function of incident normal energy E²⁺⁺ in for scattering of C²⁺⁺ (full squares) and C⁺⁺ (full circles) from Be(0001). In order to determine ΔEgain, the C⁺⁺ data is fitted with a 3rd 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 E²⁺⁺ in data for an incident normal energy E²⁺⁺ gain shifted by ΔEgain. The normalized sum of squared deviations χ² as function of ΔEgain is plotted in the inset of Fig. 2. From the minimum, we derive ΔEgain = (1.62±0.20) eV, where the uncertainty is dominated by systematic effects (the maximum system-
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\textsubscript{60} ion and the Be(0001) surface is sufficiently lowered for resonant electron transfer being classically allowed. The dielectric features of the C\textsubscript{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 a free-electron metal [29].

For Be(0001), we derive with this model \( z_{2+,+}^{\text{COB}} = 13.43 \) a.u. (atomic units), \( V_{2+}(z_{2+,+}^{\text{COB}}) = -2.10 \) eV, \( V_{+}(z_{2+,+}^{\text{COB}}) = -0.52 \) eV, and obtain \( \Delta V(z_{2+,+}^{\text{COB}}) = 1.58 \) eV in quantitative accord with our data \( \Delta E_{\text{gain}} = (1.62 \pm 0.20) \) eV, which corresponds to \( z_{2+,+} = (13.3 \pm 1.5) \) 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\textsubscript{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, \( V_{+}(z) = -1/4\varepsilon(z) \) \((V_{0}(z) \approx 0)\) at distances \( z \) relevant here. For \( E_{\text{kin}} \approx 6 \) 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 [35] and metal surfaces without projected band gap \( \Delta V(z_{+,0}) = 0.9 \) eV, Cu(100) [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 \((y \parallel, z \parallel \text{normal to surface})\) for the present critical distances of electron transfer \( z_{2+,+}^{\text{COB}} = 13.43 \) a.u., \( z_{2+,+}^{\text{COB}} = 12.45 \) a.u. for doubly (upper panel) and singly charged C\textsubscript{60} ions (lower panel), respectively. At these 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 \( |\vec{k}|\) 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 $\theta$ of $\vec{k}$ with respect to the surface normal is calculated to $\theta = \arccos(k_z/k) \approx 37^\circ$ [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 ($\theta \geq 37^\circ$) 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 $z^\text{COB}$ in an efficient electron transfer. The experimental data is in accord with an efficient capture of electrons from the Fermi level of Be(001) surfaces with a projected band gap \cite{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.

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