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Dynamical Auger charge transfer of noble gas atoms and metal surfaces

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The ionization of noble gas atoms with keV energies scattered under grazing angles of incidence of about 2° from atomically clean and flat metal surfaces is assigned to a two-electron Auger ionization process. Auger ionization, the inverse process of Auger neutralization, is a dynamical process that converts kinetic energy from the projectile to the electronic excitations. In this work, we present first realistic calculations of Auger ionization rates. In molecular-dynamics simulations for grazing scattering of He atoms from Al(111), we demonstrate that our theoretical results are in quantitative accord with threshold behavior and angular dependencies of measured ion fractions.

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Charge-transfer reactions between atomic particles and metal surfaces are important processes in different fields of physics and chemistry. The atomic binding energy and the electronic structure of the surface determine the outcome of atom-surface collisions in a decisive manner. While charge-transfer reactions of particles of low atomic binding energy as, e.g., alkali atoms, with metal surfaces, have been extensively studied experimentally and are well understood theoretically on the basis of resonant electron transfer,[1–3] a similar degree of understanding has not been achieved so far concerning reactions for atoms of higher electronic binding energy. This is largely due to the fact that here charge transfer proceeds via two-electron Auger processes.[2,4,5] In Auger neutralization (AN), a metal electron neutralizes the ion with the excess energy and momentum being transferred to another metal electron or a plasmon. In the inverse process of Auger ionization (AI), an electron bound to the projectile is excited to an unoccupied state of the metal accompanied by excitation of another metal electron or a plasmon.[2,6–8] The particle velocity sets a fundamental difference between these two types of Auger processes. AN can operate as long as the atomic level is below the Fermi level also for the atom at rest, while AI requires a minimum of kinetic energy of the projectile to excite the electronic system. In the case of molecules, conversion of vibration to electron excitation of the solid has recently been observed to be an efficient mechanism for energy transfer.[9]

The problem of charge transfer between noble gas ions/atoms and metal surfaces has been extensively studied. In this respect, He/Al is considered as a model system, since He is the simplest noble gas atom and Al the prototype of a nearly free-electron metal. In spite of its apparent simplicity, the microscopic understanding of this problem has been a puzzle only resolved recently. Experimental findings[4,10–18] and theoretical calculations of AN rates[17,19–25] are in accord only if the atomic energy level is substantially modified near the surface.[12,15,18,21,22,24–26] This former theoretical and experimental effort was focused on the understanding of the AN process at low energies where reionization by the inverse process of AI can be generally neglected and ion fractions result from an incomplete neutralization of incident ions. Earlier experimental results on the ionization of neutral atoms[7,8] agree with simple theoretical estimates[6] for the existence of a kinetic-energy threshold below which AI is forbidden, but a full theory is still lacking. In this Brief Report, we show theoretical and experimental evidence that AI is an efficient contribution to charge transfer for the system He/Al for small perpendicular velocities with a threshold in parallel energy of 4–5 keV. We present first microscopic calculations of the rate for Auger ionization of He in front of Al as a function of distance from the surface, energy of the ground state, and projectile velocity. With these results as input we perform molecular-dynamics simulations on ion fractions for comparison with our experiments. The calculations reproduce the observed kinetic-energy threshold, the overall magnitude of the ion fractions, and their increase with kinetic energy. This detailed treatment thus demonstrates that AN and AI have to be considered for the quantitative description of charge transfer between keV noble gas atoms and molecules and metal surfaces, which is important for surface-analysis techniques using atoms/ions as a probe.[2,4]

Auger capture and loss are inverse processes. Using the simple electronic model of a metal surface (jellium model), the transition rate for AN has been calculated in Ref. 19, including one-electron and multielectron channels. For AI we follow a similar approach, however, take into account the kinetic energy of the projectile. Since the angle of incidence with respect to the surface is small, we assume a projectile motion parallel to the surface with velocity $\mathbf{v}$ at a distance z_a. Atomic units (a.u., $e=\hbar=m=1$) are used if not otherwise stated.

The initial state of the bound electron in the rest frame of the solid is

$$|\Phi_a\rangle = \phi_a(\mathbf{x}-\mathbf{v}t, z-z_a)e^{i\mathbf{x}\cdot\mathbf{v}}e^{-i[E_a+(1/2)v^2]t}, \qquad (1)$$

with $\phi_a(\mathbf{x},z)$ being the wave function of the bound electron in the rest frame of the ion, $(\mathbf{x},z)$ are the electron coordinates parallel and perpendicular to the surface, respectively, and E_a being the electron binding energy. A Galilean transformation from the metal frame to the atomic frame is straightforward for a jellium metal, since the metallic wave functions are plane waves in the parallel coordinate $\mathbf{x}$. Then, following Ref. 19, the rate per spin orientation for Auger loss is obtained from

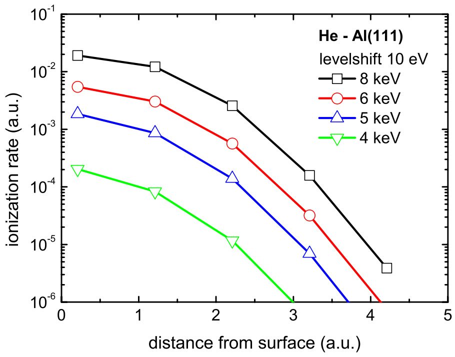

FIG. 1. (Color online) Auger ionization rates as a function of distance to topmost surface layer z_a for constant He 1s level shift of +10 eV and parallel energies indicated.

$$\frac{1}{\tau_{\mathrm{AL}}}(\mathbf{v},z_a)=2\sum_{|\mathbf{k}+\mathbf{v}|>k_F}\int_0^\infty d\omega\int\frac{d\mathbf{q}}{(2\pi)^2}\int dz\int dz'\\ \times[-\mathrm{Im}\,\chi(\omega,q;z,z')]V(\mathbf{k};\mathbf{q},z)\\ \times V^*(\mathbf{k};\mathbf{q},z')\,\delta(E_a-E_k-\omega-\mathbf{q}\cdot\mathbf{v}), \qquad (2)$$

with the matrix elements given by

$$V(\mathbf{k};\mathbf{q},z)=\frac{2\pi}{q}\langle\phi_a(\mathbf{x},z_1-z_a)|e^{i\mathbf{q}\cdot\mathbf{x}}e^{-q|z_1-z|}|\mathbf{k}\rangle, \qquad (3)$$

where $|\mathbf{k}\rangle$ is the final metal state of wave vector $\mathbf{k}$ and energy $E_k=\frac{1}{2}k^2$ to which the initially bound electron is scattered. Both states are made orthogonal by using the orthogonalized-plane-wave (OPW) method. In Eq. (2), k_F is the Fermi wave vector and the metal excitations accompanying the process, of energy ω and wave vector $\mathbf{q}$, are summed up giving the imaginary part of the electronic susceptibility $\chi(\omega,q;z,z')$ of the surface, which is consistently calculated in the model. In Eq. (3), the matrix elements are obtained by integration in the coordinates $(\mathbf{x},z_1)$. As reference, distances are measured with respect to the first atomic layer of Al. Then the jellium edge for Al(111) is at 2.21 a.u. Energies of the He 1s level will be referred to its value in vacuum of −24.6 eV. In Eq. (2), energy conservation implies that frequency and wave vector are related via the Doppler relation $\omega'=\omega+\mathbf{q}\cdot\mathbf{v}$. As a consequence, different from previous assumptions,[2,6–8] there is no clear-cut threshold for the kinetic energy of the projectile below which the Auger loss process is energetically forbidden. Rather, the $\mathbf{q}\cdot\mathbf{v}$ term always yields a finite probability although it can be negligibly small depending on the distance of the projectile to the surface and its kinetic energy.

In Fig. 1 we plot the AI rates of He in front of Al as a function of distance for a fixed value of the 1s level shift of +10 eV and for four kinetic energies of 4–8 keV. The exponential decrease in the rate with distance is the consequence of the strong screening of the surface owing to excitations of electrons with large wave vectors $\mathbf{q}$ needed at small velocities. The magnitude of the rates shows a pronounced increase in kinetic energy. In Fig. 2 we show AI rates as a function of the He 1s level shift for a fixed distance to the surface of z_a=1.21 a.u. The rate is found to increase with decreasing ionization potential as expected. The increase is steeper for lower kinetic energies. Theoretically[24] and experimentally[15] derived He 1s level shifts in front of Al(111) as a function of distance from the surface, depicted in Fig. 2, show pronounced variations close to the surface. As a consequence, the analysis of experimental data on ion fractions requires detailed calculations on the trajectories for atoms/ions during their interaction with the surface, where the energy level varies along the trajectory.

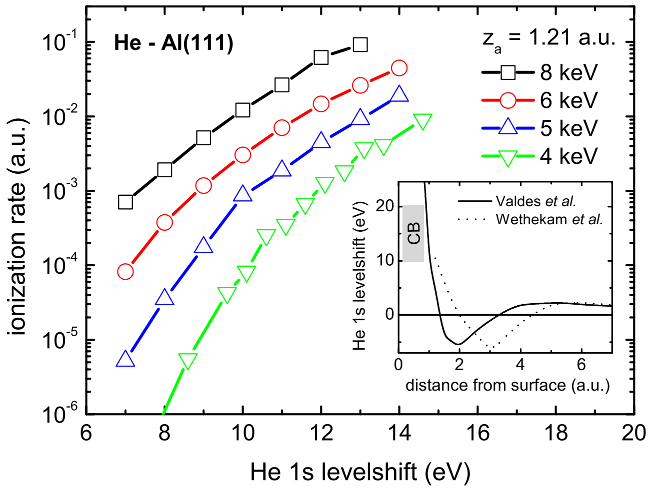

FIG. 2. (Color online) Auger ionization rates at z_a=1.21 a.u. as a function of He 1s level shift for parallel energies indicated. Inset: theoretical (solid curve) (Ref. 24) and experimental (dotted curve) (Ref. 15) He 1s level shift as a function of distance from the surface. Shaded region: energy range for occupied states of conduction band (CB) of Al(111).

We perform combined Monte Carlo and molecular-dynamics simulations of charge state and trajectory for scattered projectiles. For each time step of the calculations, the Newton equations of motion for the projectile and the Al target atoms as well as the rate equation for electron capture or loss are solved using a fourth-order Runge-Kutta method. The final charge state of the projectile is determined by reference of the calculated charge fraction to a random number. For the He^0-Al interaction we use the Moliere potential with a modified Firsov screening length by O'Connor and Biersack.[27] The interaction potential for charged projectiles is constructed from the potential for atoms reduced by the level shift.[2,5,15,21] The surface is represented by clusters of Al atoms centered below the projectile including correlated thermal displacements (for details see Ref. 28). We use the Auger neutralization rate as calculated with a linear combination of atomic orbitals (LCAOs) method in Ref. 24 which reproduces the experimental fractions of surviving ions obtained for incident energies of 1–2 keV (Refs. 15 and 18) better than the jellium rates. Since the main difference between the jellium and LCAO calculations of AN in Ref. 24 is due to orthogonalization effects, we consistently correct the jellium rates for AI by the same factor that brings the rates for AN from the jellium to the LCAO values. Perfect agreement with the measured surviving ion fractions is achieved for LCAO rates enhanced by an additional factor 1.31 and we present results for the original as well as for rates ad-

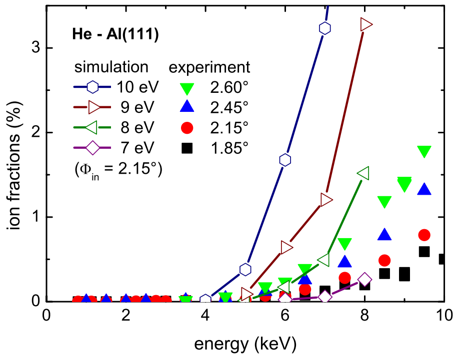

FIG. 3. (Color online) Full symbols: measured ion fractions as a function of energy for scattering of He atoms from Al(111) under grazing angles of incidence indicated. Curves with symbols: results from simulations for constant level shifts indicated for grazing angle of incidence of 2.15°. For details see text.

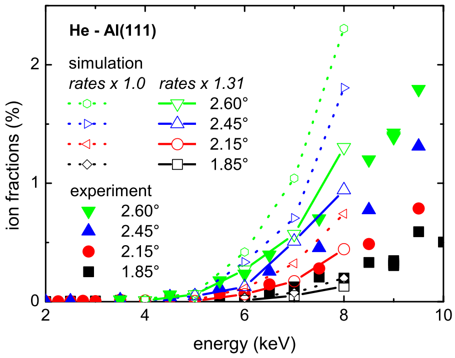

FIG. 4. (Color online) Ion fractions from experiments (full symbols) and simulations (curves with symbols) as a function of energy for grazing angles of incidence indicated. For details see text.

justed by a factor 1.31. Note that this factor is obtained from a different experimental case. A 30% deviation in the rates is not serious in view of the complexity of the problem. This could be due to deficiencies of the jellium calculations and/or of the interaction potentials used. We note that ion fractions depend exponentially on the values of the rates along the trajectory. The rates also depend exponentially on distance to the surface and level shift (Figs. 1 and 2). Therefore, a very good quantitative agreement between theory and experiment is difficult to obtain. However, the theory for the AI rate should be improved by going beyond the jellium model. In calculations of the energy-level variation of He in front of Al,[21,22,24] the He atom was assumed to be in front of an Al atom of the first layer. The strong promotion of the 1*s* level is caused by its interaction with the 2*s* - and 2*p*-core electrons of Al. Therefore, we consider the loss rate to depend on the energy level via the total distance between He and an Al atom, i.e., $E_a(d=\sqrt{z_a^2+x_a^2})$, with $E_a(d)$ given in Ref. 24 for perpendicular incidence.

In our experiments we have scattered He^0 atoms (produced via resonant charge transfer in a gas target mounted in the beamline of a small ion accelerator) with energies of some keV under grazing angles of incidence of about 2° from an atomically clean and flat Al(111) surface. The surface was prepared by cycles of grazing sputtering with 25 keV Ar$^+$ ions and subsequent annealing. Charge states and angular distributions for scattered projectiles were measured using biased electric-field plates and a microchannel plate detector (Roentdek GmbH, Kelkheim-Ruppertshain). For details concerning the experimental setup and the preparation of the surface, we refer to Refs. 2, 15, and 18. In Fig. 3 we show measured ion fractions as a function of projectile energy for grazing angles of incidence of 1.85°–2.6°. The ion fractions show a thresholdlike behavior at about 4–5 keV and increase with energy and angle of incidence. This observation is in qualitative accord with main characteristics of our AI rates which also show a pronounced increase with energy. Projectiles scattered under larger angles of incidence reach distances closer to the surface with larger level shifts and AI rates compared to projectiles scattered under smaller angles. The angular dependencies of the data are also in qualitative accord with AI as relevant ionization mechanism.

Before presenting our full calculations, we demonstrate the efficiency of the AI mechanism by performing simulations assuming a *constant* energy level of He (no distance dependence). Then we fix upward shifts of the He 1*s* level of 7–10 eV and compare the calculated ion fractions with experiments. From Fig. 3 it is evident that constant level shifts of about 7–8 eV reproduce the order of magnitude and the trend of the experimental data. Such values of the level shift are consistent with previous theoretical[21,22,24,26] and experimental work.[15,22,29] Here, it is important to stress that an upward shift of the He level of about 10 eV at Al(111) brings the level to the bottom of the conduction band (cf. Fig. 2). Thus, the results of Fig. 3 unambiguously show that He can be efficiently ionized by Auger loss before the competing resonant mechanism[22,29] can even occur. Ion fractions from our full calculations and the experimental data are shown in Fig. 4. Whereas for the parameter-free theoretical calculations the agreement with experiment is reasonable, the energy threshold as well as the increase in the ion fractions with incident energy and angle are reproduced on a quantitative level for the slightly modified rates (factor 1.31) for all angles of incidence. We conclude that in the simulations incident neutrals reach distances to the surface where the energy level of He has been substantially promoted and efficient Auger loss is present. Neutral projectiles with sufficient kinetic energies can even reach distances to the surface where the shifted level might resonate with the conduction band, such that resonant processes[22,29] can take place. However, the good agreement between theory and experiment shown in Fig. 4 implies the relevance of the Auger loss mechanism. In passing we note that simulations using the experimentally retrieved level shifts of Refs. 15 and 18 do also provide the correct order of magnitude and trends of the experimental data. This again points to the importance of the AI mechanism as a general one, independent of details of the atom-surface interaction.

In conclusion, we have presented first realistic calculations of Auger ionization rates for noble gas atoms in front of a metal surface. Based on our theoretical rates we have performed molecular-dynamics simulations of charge transfer for keV He atoms scattered under grazing angles of incidence of about 2° from Al(111). The resulting ion fractions are in quantitative accord with our experiments. Even if the details of charge transfer will depend on the exact combination of level shift and interaction potential between atom and the surface, the results of the present calculation free from adjustable parameters show that the mechanism of kinematically induced Auger loss is an efficient ionization mechanism that has to be considered in the description of charge transfer.

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