Trajectory-Dependent Charge Exchange in Alkali Ion Scattering from a Clean Metal Surface

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We report the first evidence for trajectory-dependent neutralization of hyperthermal energy alkali ions scattered from a clean metal surface. We have scattered 7.5 and 50 eV Na^+ from Cu(001) and found that, for atoms leaving the surface with the same velocity and direction, the measured neutral fraction varies by a factor of 7 depending on the type of surface collision. The collision types are identified with scattering simulations. We suggest that coupling of the charge exchange and collision dynamics is responsible for the variations in neutralization.

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As charge exchange plays a key role in many dynamical processes at surfaces, such as trapping, molecular dissociation, and stimulated desorption, a better understanding of charge exchange mechanisms may eventually lead to advances in surface processing and catalysis. Additionally, a number of analytical techniques including secondary ion mass spectroscopy (SIMS) and low energy ion scattering spectroscopy (LEIS) depend on the detection of ions leaving a surface at low velocities. The quantitative accuracy of these techniques can rely on knowledge of the charge state distribution of the atoms leaving the surface. More fundamentally, charge exchange provides a way to probe the evolution of the electronic states of an atom approaching a surface. For these reasons charge exchange has received extensive experimental and theoretical investigation.

In general, charge exchange is a very complex process involving a number of different mechanisms for electronic rearrangement. Resonant [1] and Auger [2] mechanisms of charge exchange, and electron promotion in the collision with the surface [3], possibly followed by autoionization of excited neutrals [3], must all be considered. However, for alkalis scattered from metals at hyperthermal energies (a few to several hundred eV) a picture which includes only resonant charge exchange has been sufficient to explain measured charge state fractions [1,4].

For an alkali scattered from a metal surface at hyperthermal energies, the final charge state is thought to be determined on the outgoing portion of the trajectory by resonant charge exchange between the electronic states of the scattering atom and the surface [1]. Close to the surface, very high electron transition rates between the atom and surface force the electronic states of the atom and metal towards equilibrium occupancies independent of their initial fillings; i.e., the atom loses memory of its initial charge state. As the electron transition rates decrease along the outgoing trajectory, the electronic system evolves nonadiabatically. The evolution continues until the atom is far from the surface where the electron transition rates approach zero.

The final charge state depends on the velocity and angle of the outgoing trajectory. The same final velocity and angle can be produced by different types of collisions. Since the scattering collision occurs *at* the surface and the determination of the final charge state occurs on the outgoing part of the trajectory *at some distance* from the surface, it is generally assumed that the final charge state is independent of the type of collision. In this paper we present evidence to the contrary; in hyperthermal energy ion scattering from a clean surface, the scattered charge state depends on the type of collision.

These experiments were performed in a UHV chamber at a working pressure of 4×10^{-11} torr. The Cu(001) surface was cleaned using cycles of Ar^+ sputtering and annealing; cleanliness was verified with Auger electron spectroscopy, and surface order was checked with low energy electron diffraction. A well-collimated, monoenergetic beam of Na^+ ions, chopped at 10 kHz to permit time-of-flight velocity measurements, illuminates approximately 1 mm^2 of the sample with an average current of less than 2 pA. The beam is incident along the $\langle 100 \rangle$ azimuth. The detector, located in the plane defined by the crystal normal and the incident beam, converts neutral and charged scattered alkalis into positive ions for acceleration into a channel electron multiplier [5]. A set of biased apertures at the detector's entrance allows discrimination between charged and neutral species. All data were taken under conditions in which successive spectra did not show any changes due to sample contamination or damage. Further details of our beam line, scattering chamber, and time-of-flight detector can be found in Refs. [5,6].

For 50 eV Na^+ incident at 30° and scattering at 35° from the surface normal, Fig. 1 shows the ion and neutral spectra plotted as a function of the perpendicular component of the scattered velocity. The velocity is given in atomic units (1 a.u. velocity = 2.2×10^8 cm/s). Also shown is the corresponding neutral fraction. Note the large neutral fraction of the peaks at 0.002 a.u. Similar results have been observed at other geometries.

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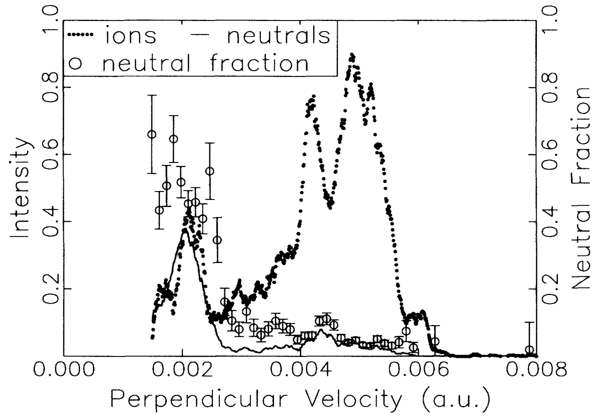

FIG. 1. Neutral atom and ion spectra for 50 eV Na^+ scattered from Cu(001) along the ⟨100⟩ azimuth, with $\theta_i = 30°$ and $\theta_f = 35°$. Circles with statistical error bars are the neutralization probability vs perpendicular velocity. Note the much larger neutralization for the low velocity peak.

With the SAFARI classical trajectory scattering simulation, we can associate each of the peaks in the spectra with specific types of collisions. Using a single potential, SAFARI simulations [7] reproduce measured energy and angular distributions for 7.5–400 eV Na^+ scattered from Cu(001). The potential is a sum of Hartree-Fock $(Na\text{-}Cu)^+$ pair potentials plus a saturated image potential [8]. For simulations at zero temperature [9], only limited regions of the surface unit cell scatter incident atoms into the detector. Each region contains impact parameters that produce trajectories with similar characteristics, such as final angle, velocity, collision dynamics, and energy loss. In a simulated spectrum, each region contributes amplitude to a single spectral peak.

Plotted in Fig. 2 are top and side views of representative trajectories for the spectra shown in Fig. 1; these trajectory types will be referred to by the letters (a)–(f), shown in Fig. 2. The peaks at a normal velocity of 0.0042 a.u. in Fig. 1 are due to trajectory type (a), while the wider peaks centered at 0.0052 a.u. result from trajectory types (b)–(d). The spectral peaks corresponding to these three types of trajectories cannot be resolved due to thermal broadening and the near-degenerate velocities of trajectory types (b) and (d). Our simulations indicate that trajectories which penetrate to the second layer, similar to type (f), account for approximately 90% of the intensity in the low velocity peaks at 0.002 a.u., with the remainder coming from trajectories of type (e), which involve multiple large-angle collisions with first layer atoms. The data shown in Fig. 1 were taken with the surface cooled to 160 K. Cooling reduces the thermal broadening of all the peaks but is particularly important for the low velocity peaks at 0.002 a.u., which disappear into the background at room temperature. Note that since low energy Cu atoms will not be efficiently ionized at the Pt surface in our detector, the detector is not sensitive to sputtered Cu.

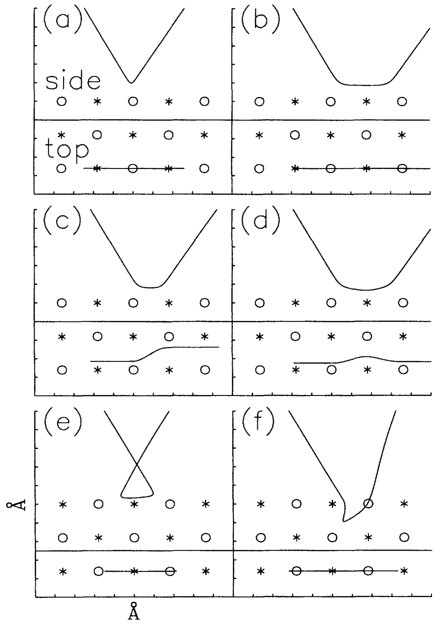

FIG. 2. Scattering trajectories for 50 eV Na^+ scattered from Cu(001) along the ⟨100⟩ azimuth, with $\theta_i = 30°$ and $\theta_f = 35°$. In each panel the atom enters from the left and exits to the right, the upper subpanel is a view along the crystal surface, and the lower subpanel is a view directly into the crystal surface. The open circles represent foreground atoms while the asterisks represent atoms in the next layer back.

We can now associate the measured neutral fractions for each spectral peak in Fig. 1 with particular trajectory types. In previous work Kimmel and Cooper [4] measured the neutral fraction for Na^+ scattered from Cu(001) as a function of both the incident velocity and scattering geometry. They found that, over the range of perpendicular velocities in Fig. 1, the neutral fraction scaled with final perpendicular velocity and varied from 0.06 to 0.09. In their analysis, for a given incident velocity, they averaged the neutral fraction in the scattered flux over the higher velocity peaks, which contain trajectory types (a)–(d) [10]. The same quantity for the data shown in Fig. 1 agrees with their results. In contrast, the neutral fraction of the lowest velocity peak in Fig. 1 is anomalously large.

As Kimmel and Cooper's results [4] indicate and we will show below, the anomalous neutralization in the lowest velocity peaks cannot simply be due to the small difference in perpendicular velocity, but instead depends on the type of collision with the surface.

We have tested this by comparing neutral fractions for different trajectory types scattered at the same final velocity. By decreasing the energy of the incident beam, the scattered velocities of trajectory types (a)–(d) can be reduced until they match those of the low velocity peaks in the 50 eV spectra. Figure 3 shows neutral and ion spectra for 7.5 eV Na^+ scattered with the same geometry and sample temperature as for the 50 eV spectra. Our

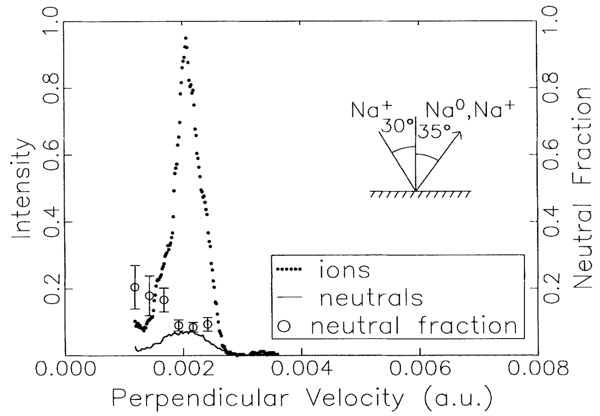

FIG. 3. Same as Fig. 1 for incident 7.5 eV Na^+. At the same final velocity this set of spectra shows a much smaller neutral fraction than the low velocity peak in Fig. 1.

simulations show that these spectra contain trajectory types (a)–(d) and that trajectory types (b) and (d) account for approximately 80% of the scattered flux. Trajectory types (e) and (f) do not occur for an incident energy of 7.5 eV because the effective surface potential is too smooth. In the 7.5 eV spectra, both thermal broadening and a longer incident pulse in the time-of-flight system prevent resolution of the peaks associated with the different trajectory types. For the single peak in these spectra, the neutral fraction is only 0.07, less than one-sixth of the neutral fraction measured at the same velocity in the 50 eV spectra.

Thus, we have two cases where scattered Na leaves the surface in the same direction with the same velocity, and yet undergoes dramatically different neutralization which depends on the type of collision. The collision associated with trajectory type (f) at 50 eV results in an anomalously large measured neutral fraction of 0.46, while the collisions associated with trajectory types (b) and (d) at 7.5 eV result in a measured neutral fraction, in agreement with previous measurements [4], of 0.07. Determining from these measurements the magnitude of the neutral fraction for a specific trajectory type is complicated somewhat by the change in scattering potential that occurs with neutralization. Neutralization eliminates the image potential, resulting in different final angular distributions for ions and neutrals which have undergone identical sets of collisions; the image potential shifts and broadens the ion angular distribution relative to that of the neutrals. Our analysis indicates that for the 50 eV case this effect increases the *measured* neutralization of the low velocity peak by a factor of 1.2. This does not explain the factor of 7 enhancement observed. At low velocities, the measured neutral fraction may deviate from the scattered neutral fraction due to image potential effects in the detector. Measurements show that these effects are also small and do not affect our conclusions.

If the charge state is determined on the outgoing trajectory, the collision can affect only the charge exchange through modification of the local electronic environment near the surface. To explain our results, we have considered two mechanisms, local electronic excitation of the surface and displacement of surface atoms, by which a collision could modify the local electronic environment.

When the Na atom is close to the surface, electrons excited above the Fermi level could enhance the neutralization probability by providing filled electronic states in resonance with the atom's ionization level; close to the surface, due to the image potential, the ionization level rises above the Cu Fermi level. In previous work, Kimmel and Cooper scattered 10 to 1600 eV K^+ from clean Cu(001) and found that the neutralization was negligible [4]. This agreed with a model which included only resonant charge exchange between the K ionization level and a Cu surface free of electronic excitations. At the higher energies in the K^+ scattering experiment, where electrons leaving the surface indicate the presence of electronic excitations, no neutralization was observed. While not conclusive, this does suggest that at our much lower incident energies, an electronic excitation mechanism will not explain the anomalous neutralization we have observed.

Now consider modification of the surface by the collision and its effect on the neutralization. A 7.5 eV Na^+ ion which undergoes the kind of surface collision associated with trajectory types (b) and (d) will lose approximately 4 eV of energy partitioned between two surface atoms. In contrast, a 50 eV Na^+ ion with a type (f) trajectory will lose approximately 47 eV of energy, also partitioned between two surface atoms. In the first case, there is only enough energy available to vibrationally excite the surface atoms; however, in the second case, the available energy is sufficient to create significant deformation of the lattice including the creation of adatoms or vacancies.

Previous work has shown that surface adatoms or vacancies will change the electrostatic potential just outside the surface, causing a reduction in the work function [11,12]. While the few localized atomic displacements produced in a single 50 eV collision with the surface will not change the work function, they do change the local electrostatic potential. A scattered atom which leaves the surface through this region of altered electrostatic potential is more likely to be neutralized [13,14]. For adsorbate-covered surfaces, it has been shown that adsorbate-induced variations in the local-electrostatic potential [13,14] influence the neutral fractions of scattered alkalis. For 1000 eV Cs^+ scattered from a cesiated W(110) surface, changes in the electrostatic potential due to lattice distortions localized near the collision site have been suggested to explain variations in the scattered neutral fraction with final angle [15].

To estimate the change in neutralization caused by atomic displacements, we have modeled the collision-induced change in local-electrostatic potential by placing a single dipole at the collision site. This is similar to previous studies in which an adsorbate overlayer was modeled by an array of dipoles [14]. Using a simple model of resonant charge exchange [16], we have calculated the neutralization as a function of dipole strength along a trajectory taken directly from our SAFARI [7] scattering simulation. We found that a 0.75 D dipole increased the neutral fraction of the 50 eV type (f) trajectory from 0.12 to 0.43. This dipole is comparable to those for adatoms [12] and vacancies [17]; thus, it seems reasonable to conclude that such a dipole can be formed from the atomic displacements induced by the collision. The calculated 0.75 D dipole represents an average over the effective dipoles for all the dynamic configurations of surface atoms created by the type (f) trajectories.

With the same size dipole, our model also predicts a change in neutralization from 0.07 to 0.23 for the 50 eV type (a) trajectory which is not seen in the data. This discrepancy between model and data is partially due to treating the collision-induced dipole as static. Simple binary collision kinematics show that the recoil velocities of the Cu surface atoms are comparable to the final velocity of the scattered Na atom; this implies that the dynamics of the dipole formation must be considered. The dynamics come into play via the variation among trajectory types in the time between first impact with and final departure from the surface. For example, consider the sequence of events for an ion with a type (f) trajectory: in the first collision, the ion decreases its velocity by transferring a large amount of energy to a single surface atom; then, the ion penetrates deeper into the surface where successive collisions further reduce its velocity; finally, the ion leaves the surface. During this sequence of events, the first surface atom hit in the collision has sufficient time to leave its lattice site and cause significant displacement of neighboring atoms, creating adatoms and vacancies. Contrast this with a type (a) trajectory where the scattering atom begins to leave the surface immediately after the first collision. In addition, the distance from the surface at which the final charge state is determined varies with scattered velocity. As the final velocity increases, this distance decreases. For a type (a) trajectory which leaves the surface faster, this further restricts the time available to form lattice displacements. Less time implies a smaller dipole and less neutralization.

These experiments and modeling provide evidence of coupling between the charge exchange and collision dynamics for an alkali atom scattering from a metal surface at hyperthermal energies. At the low scattered velocities in these experiments, the Na/Cu(001) system is very sensitive to small changes in the electronic environment at the surface. This sensitivity and a final scattering angle close to the surface normal explain why these effects have not been previously observed. Although the same perpendicular velocities have been obtained with higher incident energies by using grazing scattering geometries, the large velocity parallel to the surface means that the final charge state is determined far from the collision site, thus removing any correlation between the charge exchange and collision dynamics.

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