Nonadiabatic effects in atom-surface charge transfer

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We present results of a joint experimental and theoretical study of the neutralization of Li$^+$ ions scattered off a Ag(100) surface. Experimental data and a complete dynamical treatment based on a wave-packet propagation approach demonstrate a pronounced nonadiabatic character of the electron transfer process. In particular we show that, while strong for a fixed projectile-surface distance, the effect of the Ag(100) projected band gap on the charge transfer is to a large extent ineffective in scattering in the energy range of a few hundred eV due to the finite interaction time.

The outcome of many reactive processes on surfaces is determined by electron tunneling and nonadiabatic phenomena. When atoms or molecules interact with a metal surface an electron can be exchanged between the atomic or molecular states and metal states of the same energy, leading to the change of the particle charge state, which can drive particular reactive channels. This process of resonant charge transfer (RCT) has been the subject of numerous experimental and theoretical studies over the past decade.[1–3] For the free-electron model of the metal, parameter-free approaches have been developed which provide adiabatic properties (energies and widths) of the atomic states for a fixed distance from the surface.[4–7] Using these parameter-free results as inputs in the treatments of the collisional RCT has become a standard procedure nowadays, often leading to a satisfactory description of experimental data.[8–12] However, one wonders if band structure effects for realistic surfaces can alter the characteristics of RCT and, furthermore, if knowledge of adiabatic (electronic structure) properties of the projectile-target system is enough to predict the outcome of reactive process or if nonadiabatic effects have to be taken into account.

To address these fundamental points, the (111) and (100) surfaces of the noble metals provide an ideal playground. The main peculiarities of their electronic structure are linked to the presence of a projected band gap (L gap and X gap, respectively) in the direction of the surface normal. These can be adequately modeled with 1D potentials, depending only on the electron coordinate perpendicular to the surface.[13] Recent wave-packet propagation (WPP) studies reported for H$^-$/Cu(111), Cs/Cu(100), and alkali/Cu(111) revealed that adiabatic properties such as energies and widths of the states for the fixed atom-surface distance are strongly affected by the projected band gap.[14–16] This is in agreement with time-resolved two-photon photoemission measurements[17,18] for alkali adsorbates.

However, a collision is a physical situation different from that of a static adsorbate. Indeed, a strong nonadiabaticity of the dynamics of the RCT process in the case of surfaces with a projected band gap has been theoretically predicted.[14,15] Above a certain critical velocity, a simple rate equation (RE) approach based on the *adiabatic* properties of the projectile states would fail completely.[14,15]

In this joint experimental and theoretical work on Li$^+$ ion scattering on Ag(100), *we demonstrate this nonadiabatic characteristic of the RCT process*. We show that the projected band gap (X gap) strongly modifies the energy and width of the Li(2s) level in front of the Ag(100) surface as compared to the case of the free-electron (jellium) target. Thus, very high Li$^+$ neutralization probabilities in the outgoing beam are predicted within an adiabatic RE approach. This is *not* confirmed by experimental data, which are close to the results of a full dynamical WPP treatment of the Li$^+$/Ag(100) charge transfer and also to those obtained using a free-electron description of the target. The present study thus demonstrates that (i) the dynamical behavior of the RCT process cannot be predicted from the knowledge of the characteristics of the static system, and (ii) above certain velocities, the effect of the target metal band structure disappears. These results, very important for the understanding and description of the RCT process and of RCT-mediated processes, could not be established fully before, because of the lack of a direct comparison between experimental data and detailed theoretical results on the same system.[19] *They in particular show that great caution should be exercised when performing an adiabatic treatment of chemical reaction dynamics on such surfaces.*

The experiments are performed in an ultrahigh vacuum (UHV) system described elsewhere.[20] Li ions are produced using a Li getter source. Ions scattered through 135° are energy analyzed with an electrostatic analyzer. Time-of-flight measurements can also be performed for a 116 cm flight length using a multianode channelplate detector, allowing simultaneous separate detection of ions and neutrals in continuous or pulsed beam modes. The crystal is cleaned by multiple cycles of small angle Ar bombardment and annealing. Crystal quality is ascertained by low-energy electron diffraction (LEED). AES and LEIS (low-energy ion scattering) using He ions are used for monitoring surface cleanliness. Li$^+$ neutralization probabilities are determined by measuring neutral fractions for a scattering configuration where the scattered particles leave normal to the surface.

Energy losses of scattered Li atoms and ions were investigated in LEIS and time-of-flight (TOF) measurements. Examples of TOF spectra of scattered atoms and ions are shown
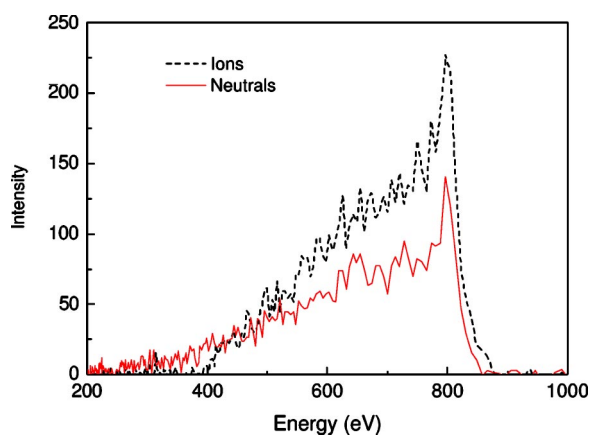
FIG. 1. Time of flight spectra of scattered Li ions and atoms for a 1 keV incident ion energy.

in Fig. 1, after conversion of the time scale into an energy scale. The spectra for neutrals and ions are fairly similar. At high energies one finds a peak related to surface scattered particles and a broad energy loss distribution resulting from particles penetrating into inner atomic layers. This lower energy tail becomes very large at the higher energies.

The neutral fractions are first made using a continuous beam, and a fraction averaged over energy losses is obtained. This fraction, measured in an incident ion energy range from 100 eV to 2 keV, is shown in Fig. 2. It is found to increase rapidly at low energies. Because of the large contribution of high energy losses at the higher incident ion energies, these neutral fractions were corrected using TOF spectra of scattered atoms and ions. The neutral fraction obtained after integration in the surface peak region is shown by full squares in Fig. 2. The corrected ion fraction lies a little lower than
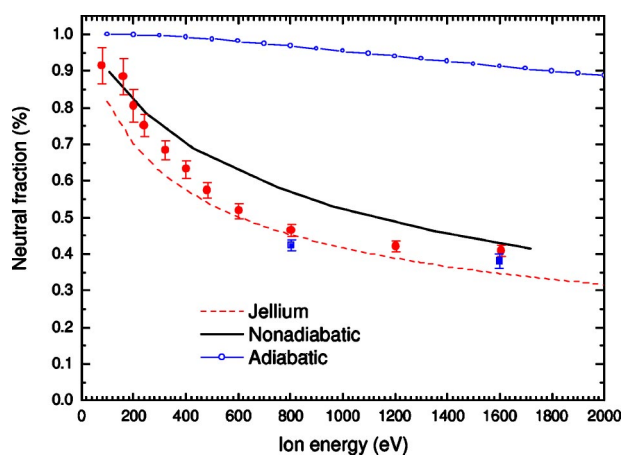

FIG. 2. Experimental and calculated neutralization probability for Li^+ leaving the surface along the surface normal with the indicated energy. Circles: experimental results for total fraction, squares–TOF corrected results. Solid line: results of the complete wave packet propagation treatment incorporating collision dynamics. Line and open circles: results of the rate equation calculation using the energy and width of the adiabatic state correlated with Li(2s) as calculated for the model Ag(100) surface (Fig. 3). Dashed line: results of the rate equation calculation using the energy and width calculated for the free-electron surface (Fig. 3).
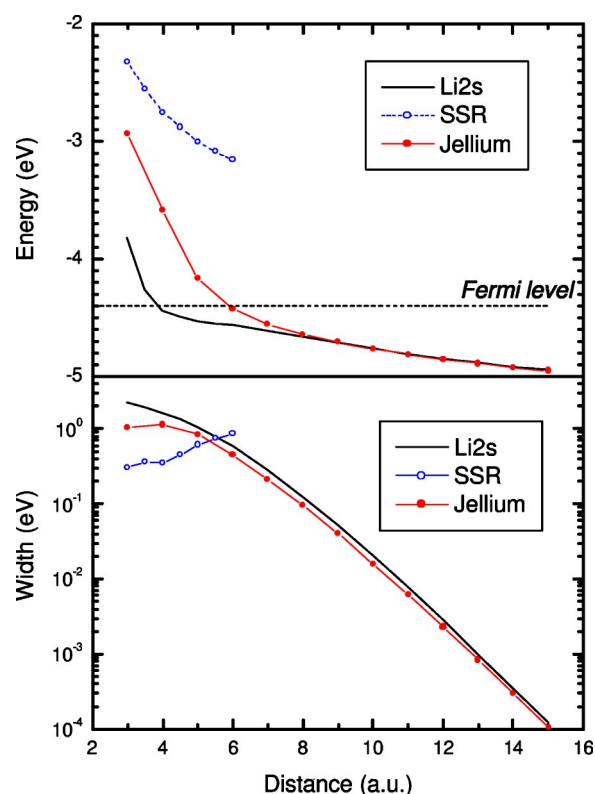

FIG. 3. Energies (a) and widths (b) of the quasi-stationary adiabatic states involved in the charge transfer between a Li(2s) level and a Ag(100) surface. The energy is measured with respect to the vacuum level. The data are presented as functions of the projectile-surface distance, measured from the image plane. Solid lines: results obtained with free-electron model. Lines with symbols denote results obtained for the model Ag(100) surface. Line with full circles: state correlated with Li(2s) level at infinite projectile-surface separation; Line with open circles: state correlated with surface state resonance. Thin horizontal dashed line represents the position of the Fermi level.

the summed fraction. The correction is not very large because, e.g., at 2 keV, although there is a large energy loss tail, most of the spectrum corresponds to energies where the ion fraction does not change significantly. At the lower energies this energy loss tail itself becomes less extended, so the ion fractions are not significantly affected.

Our theoretical study of the neutralization of Li^+ ions is based on a wave-packet propagation (WPP) approach described elsewhere.[15,16] We consider that, due to the large projectile-surface coupling, the memory of the initial charge state is lost and final charge states only depend on the outgoing trajectory.[2] The neutralization proceeds mainly in the region of projectile-surface separations where the energy of the Li(2s) quasistationary level is in resonance with occupied metal states below the Fermi level (see Fig. 3). At such distances from the surface the localized d bands of Ag do not contribute to the RCT. Excited states of Li projectile are too high in energy with respect to the Fermi level to be populated.[8,10] Consistent with the experimental procedure, we assume that the projectile follows a classical trajectory along the z axis normal to the surface. The time evolution of

the Li(2s) electron active in the RCT is followed quantum mechanically through direct on-the-grid-solution of the time-dependent Schrödinger equation, with the total potential, $V(t)$, given by

$$V(t) = V_{Li}(t) + \Delta V_{surf}(t) + V_{surf}. \qquad (1)$$

The first term stands for the electron–Li$^+$ ion core interaction.[10] The second term describes the electron interaction with the electrostatic image of the Li$^+$ ion core. The model potential proposed by Chulkov et al.[13] is used to describe the electron interaction with Ag(100) surface, $V_{surf}(z)$. It takes into account the periodicity of the crystal in the direction of the surface normal, and assumes free-electron motion parallel to the surface. It reproduces the main features of the Ag(100) surface: projected band gap (X gap) in the direction of the surface normal within $-2.89 \rightarrow +2.21$ eV energy range (energies are measured with respect to the vacuum level), the surface state resonance at -3.19 eV, and image potential states. We have also performed calculations with a free-electron modeling of Ag target. It is based on the model potential of Jennings et al.[21] Parameters of this potential are set consistently with the model Ag(100) surface.[13]

Two types of calculations have been performed. In the static calculation, the Li-surface distance is kept fixed and the energies and widths of the quasistationary states are obtained.[15] In the dynamic calculation, the Li projectile moves with respect to the surface, and we rely on the time-reversal symmetry to link the electron capture by a Li$^+$ receding from the surface to electron loss by a Li atom approaching the surface. First, we consider electron loss by a Li projectile impinging on the surface, and we use the flux method[22] to deduce the energy spectrum of the electron transferred into the metal, $R(E)$, from the WPP calculation. Provided that the impinging Li(2s) atom is completely ionized in the incoming trajectory, time reversal can be used to obtain the neutralization probability in the outgoing beam (electron capture) for a Li$^+$ projectile

$$p = \int_{-\infty}^{-\Phi} R(E)dE, \qquad (2)$$

where Φ is the surface work function. Spin statistics factors[10] have to be included since the Li$^+$ ion core is singlet, and so spin-up or spin-down electrons can be captured to form the two sublevels of the Li(2s) ground state. Correction for the spin statistics leads to the final result for the neutralization probability: $P = p + (1-p)p$.

In Fig. 3 we show the energies and widths of the quasistationary states calculated for various distances between Li atom and model Ag(100) and free-electron metal surfaces. For the free-electron metal surface, the energy and the width of the level, correlated with Li(2s) state at infinite projectile-surface separation, exhibit the usual behavior.[4,10] The energy roughly follows the $1/4Z$ behavior expected for a classical image potential shift. For large distances from the surface the width decreases roughly exponentially, reflecting the exponential variation of the couplings between the projectile state and metal continuum. At approximately $Z_C = 6$ a.u. from the image plane the Li(2s) level crosses the Fermi level of the

target. The work function was taken as 4.43 eV as given in the theoretical study[13] for Ag(100), and within the error bars of our experimental measurement of (4.4 ± 0.05) eV.[23] Thus, close to the surface, the equilibrium charge state of the projectile corresponds to a Li$^+$ ion. On the outgoing trajectory path, for 6 a.u. $\lesssim Z$ the Li(2s) level moves in resonance with occupied electronic states of the metal and neutralization sets in.

The results obtained with the static (immobile Li atom) WPP study, for the model Ag(100) surface, show a pronounced band structure effect. While for large projectile-surface distances a free-electron behavior is retrieved since the Li(2s) state is energetically well below the projected band gap, for small projectile-surface distances an avoided crossing structure appears. The lower adiabatic state is correlated with Li(2s) state at infinite projectile-surface separations. The width of this state is found to be larger than in the jellium case. The upper adiabatic state is correlated with a surface state resonance (see a discussion in Ref. 15). With decreasing projectile-surface distance, the Li(2s) character is transferred from the lower to the upper state. The latter enters into the projected band gap region and its width decreases.

Because of the avoided crossing structure the lower adiabatic state shifts above the Fermi level at much shorter distances ($Z_C = 3.8$ a.u.) than in the free-electron case. Assume now that the system evolves adiabatically and that its dynamics can be described with a rate equation approach. At each point of the trajectory, where the energy of the quasistationary state lies below the Fermi level, the neutralization rate is given by the corresponding width, $\Gamma(Z)$. The final neutral fraction is given by

$$P = \left(1 - \exp\left\{-\frac{2}{v}\int_{Z_C}^{\infty}\Gamma(Z)dZ\right\}\right), \qquad (3)$$

where v is the projectile velocity, and 2 stands for the spin statistics factor. Thus, because of the larger widths and smaller Z_c, one would predict that the band structure effect should lead to a higher neutralization probability as compared to the free-electron case.

In Fig. 2 we present the results for the Li neutral fraction in the outgoing beam obtained with this adiabatic assumption and using the static WPP results. The calculated neutralization probability is indeed very high, varying from 100% to 90% in the present projectile energy range. On the other hand, the dynamical WPP study for the model Ag(100) surface leads to a *much lower* neutralization probability. Comparison with experiment shows that *it is the dynamical approach which correctly describes neutralization demonstrating the existence of very strong nonadiabatic effects*. Thus, the RE approach based on "static" widths fails to correctly describe the RCT dynamics within the experimental energy range, and much lower projectile velocities are needed to reach the adiabatic behavior. The nonadiabatic behavior of the RCT during a collision tends to attenuate the effect of the band structure, so the Li$^+$ neutralization probabilities are quite close to the predictions obtained with the

RE approach for the free-electron model of the Ag surface, also shown in Fig. 2.

The physics underlying this nonadiabatic effect is the following. Consider electron escape from the projectile. For the free-electron metal the charge transfer rate is determined by the time required to tunnel through the potential barrier separating the projectile and the metal. This barrier is given mainly by the electron-projectile core interaction and electron interaction with image charges. It is basically the same for the free-electron metal and the realistic metal. The difference is due to the fate of the electron wave packet inside the metal. For the free-electron target, the electron is simply delocalized in the metal and no return to the projectile occurs. For the non-free-electron metal, reflections and thus interference arise due to scattering in the bulk. If the projectile motion is fast enough, it removes the interference effects and thus the effect of the target band structure on the RCT. In other words, the electron needs time to "probe" the target band structure and if this time is larger than the characteristic collision time, the target behaves as a free-electron one.[14,24]

In conclusion, this quest for band structure effects on electron transfer in particle surface interaction revealed two important features. The existence of the projected band gap leads to strong modifications in the adiabatic characteristics (energy, width) of the atomic state near the surface as compared to the free-electron metal case. On the other hand, our study shows that electron transfer is strongly nonadiabatic in our scattering conditions, so these adiabatic characteristics are not relevant for the proper description of the RCT dynamics in the present situation. The band structure effects almost disappear for the moving atom because of the finite interaction time; thus, a free-electron modeling of the experimental data obtained with non-free-electron like surfaces is successful. In a more general perspective these results indicate that care should be taken when using static adiabatic properties when describing *chemical reaction dynamics on realistic metal surfaces* when charge transfer plays a role.

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