Imaging the Internal Electronic Structure of a Surface Adsorbate with Low Energy Ions

Jory A. Yarmoff,[1,*] Ye Yang,[1] and Zdenek Sroubek[2]

[1]*Department of Physics, University of California, Riverside, California 92521, USA*
[2]*Institute of Radio Engineering and Electronics, Academy of Sciences of Czech Republic,*
Chaberská 57, 182 51 Prague 8, Czech Republic

Time-of-flight spectra were collected for 2.5 keV $^7Li^+$ backscattered from Fe surfaces covered with submonolayers of iodine. Li singly scattered from the adatoms has a consistently larger neutral fraction than for scattering from the substrate, implying a region of positive charge atop the iodine. The neutral fraction decreases for off-normal exit angles, indicating a nonuniform charge distribution around the polarizable adsorbates. This demonstrates that ion scattering can image the internal electronic structure of an adatom and provides an explanation for anomalous work function changes.

The scattering of low energy (0.5–5 keV) ions from solids has traditionally been used to obtain the elemental composition [1] and detailed atomic structure [2,3] of the surface region. The surface electronic environment can also be probed, however, by measurements of the proportion of alkali ions that neutralize while scattering [4–9]. The neutralization probability is determined along the outgoing trajectory by resonant charge transfer between the alkali s level and the surface conduction band, and it depends primarily on the surface work function, or more precisely, on the local electrostatic potential (LEP) at the scattering site [10]. The LEP is critical when the surface potential is nonuniform, such as in the presence of adsorbates [6–8,11–14]. In this Letter, we demonstrate that neutralization in alkali ion scattering is actually sensitive to variations in the LEP on a subatomic scale, thus providing a means for mapping out the internal electronic structure of an adatom.

In previous ion scattering experiments, alkali atoms were deposited on metal surfaces to determine the effects that charged adsorbates have on the surface LEP [4–8]. An alkali adatom donates a substantial fraction of its charge to the substrate, thus reducing the surface work function by forming outward pointing dipoles. A reduced work function raises the neutralization probability for scattered alkali ions by increasing the overlap between the projectile ionization level and the surface bands [10]. When there are few adsorbates on the surface, the isolated dipoles form a spatially inhomogeneous LEP [15]. In prior work, we showed that Li ions singly scattered from the alkali adsorbates have a much larger neutralization probability than those scattered from substrate atoms because of a minimum in the LEP at each adatom site [6–8]. *Ab initio* calculations have verified this interpretation [12,13].

The behavior of halogens adsorbed onto metal surfaces might be expected to be opposite to that of alkalis as the surface work function should increase due to the inward pointing dipoles formed by negatively charged adsor-

bates. It has been observed, however, that the work function often decreases with halogen adsorption on metal surfaces, even though it is clear that the adsorbates are negatively charged [16–19]. There is no widely accepted explanation for this, although surface corrosion has been suggested as a possibility. Corrosion cannot, however, account for a decreased work function on single crystals, as halogens are most often positioned at well-defined sites above the outermost substrate atomic layer [20–23]. Low energy alkali ion scattering is an ideal tool to study the anomalous behavior of halogen adsorption, as it can probe the LEP specifically at the adsorption sites. We find that the LEP is actually decreased directly above the adsorbate due to internal polarization. This is the first experimental evidence that polarization contributes to the work function changes that accompany halogen adsorption.

The experiments were performed in an ultrahigh vacuum system described elsewhere [6]. The Fe single crystal surfaces were prepared by Ar^+ sputtering and annealing at 750 °C and checked with Auger electron spectroscopy and low energy electron diffraction. Iodine was deposited from a solid-state electrochemical cell [24], and the exposures are given by the time-integrated cell current (units of $\mu A\,min$). Surface work function changes were monitored by the secondary electron cutoff position during bombardment by 200 eV electrons.

Time-of-flight (TOF) spectra were used to provide the energy distributions of scattered ^7Li. The primary energy loss is due to elastic binary collisions between the projectile and isolated target atoms, which produces a distinct single scattering peak (SSP) for each element at the surface [1,3]. The incident ion energy (2.5 keV) was large enough so that any inhomogeneity in the surface potential could be detected [25]. $^7Li^+$ ions from a thermionic emitter were accelerated and deflected across an aperture to produce ∼40 ns pulses. The particles scattered at 168° were detected with a microchannel plate (MCP) after traversing a 0.57 m flight path. The entrance to the MCP

was held at ground to ensure equal collection efficiency for ions and neutrals. Deflection plates between the sample and detector were grounded in collecting the total yield; voltages were placed on the plates to deflect the ions and collect the scattered neutrals. Neutral fractions were calculated by subtracting the background due to multiply scattered ions, integrating the "neutrals only" and "total yield" SSP's, and then dividing [6,25].

Figure 1 shows the work function and single scattering neutral fractions obtained at normal incidence from Fe(110) and (100) as a function of iodine exposure. Although the coverages are not explicitly reported, they are in all cases below 1 monolayer. Upon iodine adsorption on Fe(110), the work function first decreases, but then increases so that the overall change is small. On Fe(100), the work function increases monotonically. The detailed shapes of the neutral fraction curves mimic the work function changes in that increases in work function correspond to decreases in the neutral fraction, and vice versa. The I SSP neutral fractions are, however, consistently larger by a factor of 2 to 3 than those of the Fe SSP. This is surprising for halogens—the potential above a negatively charged adsorbate is expected to be higher than that of the substrate, which should lead to a smaller neutral fraction. Instead, similar to alkali adsorbates, the adatom neutral fraction is larger than that of the substrate, which suggests that the surface potential is decreased at the halogen site. Note that the behavior of halogen adsorbates does not completely duplicate that of alkalis [6], as the adatom and substrate neutral fractions do not become equal at high coverage.
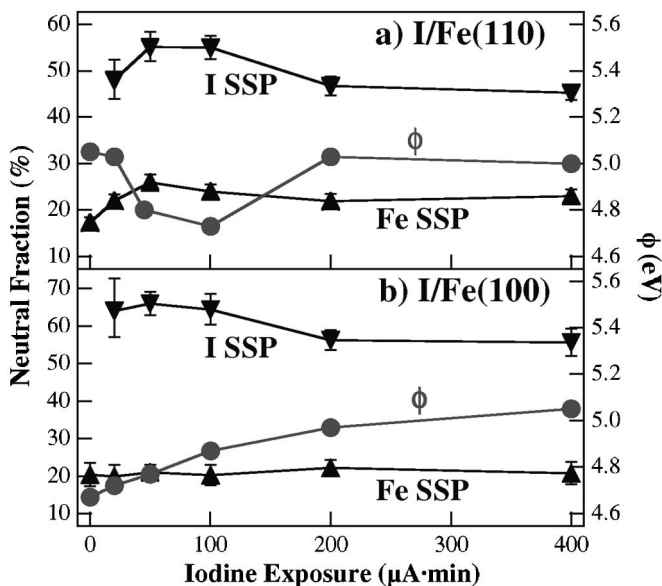
At first, it may appear straightforward to explain the large neutral fraction for scattering from halogens by considering the increased local electron density. Photoemission shows, however, that the occupied iodine states lie about 5.5 eV below the Fermi level [28], which places them well below the Li ionization level. Thus, resonant electron transfer between the filled iodine states and the Li level is not likely. The electrons involved in charge transfer during alkali ion scattering originate from the metal valence band so that the neutralization probability is determined by the local potential at the halogen site, and not by the total electron density [10].

The origin of the large neutral fractions measured for scattering from adsorbed halogens can be explained by considering the results of density functional calculations for Cl adsorbed on Ta(110) [29], Al(111), and Cu(111) [30]. Because halogens are polarizable, charge is not distributed uniformly within the adatom. Instead, the negative charge is attracted to its image in the substrate leaving a region of positive charge at the top of the adatom, as shown schematically in Fig. 2. This leads to the formation of an outward pointing dipole and a lowering of the LEP directly above the halogen. In contrast, for adsorbed alkalis, charge is transferred into the substrate so that alkali adatoms have relatively little polarizability. This difference between alkali and halogen adsorbates is clearly visible in the electron density plots shown for Na and Cl adatoms on metal surfaces in Ref. [30], which show a region of decreased electron density directly above the halogen. Thus, when Li backscatters from an adsorbed halogen, its neutralization probability is determined by the reduced LEP in that region.

The measured work function represents the average surface LEP. The work function changes that occur upon halogen adsorption result from a combination of the outward dipole formed from polarization within the adatom and the inward dipole formed by charge transfer from the substrate to the halogen. A third dipole caused by Smoluchowski smoothing within the substrate also contributes to the work function change [29]. Regardless

FIG. 1. Neutral fractions of $^7Li^+$ singly scattered from the I and Fe sites, along with the surface work function (ϕ) for I-adsorbed (a) Fe(110) and (b) Fe(100). The work function values for clean Fe(110) and Fe(100) were taken as 5.05 eV [26] and 4.67 eV [27], respectively.
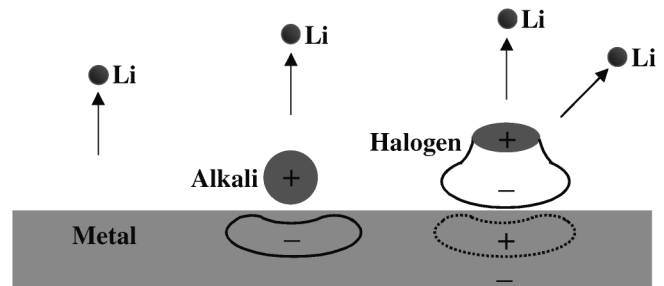

FIG. 2. Schematic diagram illustrating the internal electron density formed by alkali and halogen adsorption on metal surfaces. The outgoing trajectories of scattered Li are shown to illustrate how the dipoles formed from these charge distributions influence the potential experienced by the projectiles.

of the overall work function change, however, ion scattering neutral fractions are determined by the LEP above the scattering site. Note that the neutral fraction is always larger for backscattering from iodine sites on Fe and other materials whether the work function change is positive, such as on Fe(100), or negative, such as on Fe(110) [25]. This indicates that a reduced local potential occurs at the top of the halogen adatom even when it does not dominate the overall work function change.

Furthermore, ions exiting in an off-normal direction probe the side, rather than the top, of the adatom, as illustrated by the off-normal arrow in Fig. 2, and should thus be more sensitive to the downward-pointing dipole caused by charge transfer to the halogen. To test this idea, the angular dependences of the Li neutral fractions, shown in Fig. 3, were measured by tilting the sample with respect to (w.r.t.) the TOF detector. The circles in Fig. 3(a) show the neutral fraction for clean Fe(100) as a function of exit angle and, as expected, more grazing angles produce larger neutral fractions. In contrast, the I SSP neutral fractions collected from the I-covered surface *decrease* as the exit angle becomes more grazing, as shown in Fig. 3(b). This unusual behavior is opposite to that of the neutral fractions collected from the clean surface, from neutral or alkali adsorbates [25], or to our knowledge from any other previously measured system, and is contrary to the predictions of surface neutralization mechanisms. The only reasonable interpretation is that the scattered Li ions experience changes in the LEP
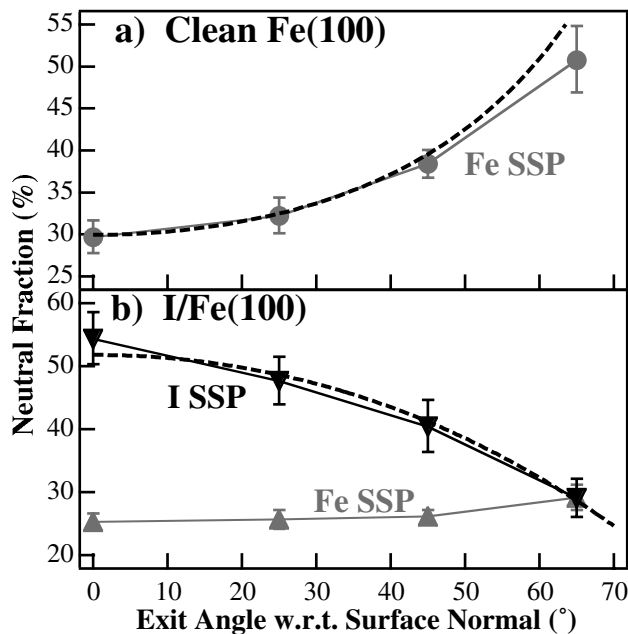

FIG. 3. Neutral fractions of $^7Li^+$ singly scattered from adsorbate and substrate sites shown as functions of the exit angle for (a) clean Fe(100) and (b) Fe(100) exposed to 50 μA min of I_2. The dashed lines are the semiquantitative theoretical estimates (see text).

across each individual halogen adatom. At the top of an adatom, the LEP is low as it is dominated by internal polarization, while the LEP at the side is increased due to the overall negative charge of the halogen. Note that the neutral fraction of the Fe SSP increases only slightly with the exit angle, as Li projectiles scattered from substrate atoms at grazing angles interact with nearby iodine adatoms along their outgoing paths.

The neutral fraction of scattered atoms is usually treated theoretically using the dynamical Newns-Anderson Hamiltonian [31,32], which describes the charge formation process in terms of the energy and virtual width of the valence level of the scattered projectile. The dependence of the width on the atom-surface distance is usually much stronger than the corresponding dependence of the energy of the level, which is mostly governed by the surface electrostatic potential. Thus, the width of the valence level determines the distance above the surface at which charge formation takes place. Under conditions in which the substrate can be represented by a free electron gas, this distance is laterally independent and the relevant velocity component is normal to the surface. For scattering from isolated impurities adsorbed above the surface, the total outgoing velocity is more relevant as the ionization would take place at a constant distance from the impurity. Under this approximation, the nonadiabatic neutralization N can be described by a simple analytical solution of the Newns-Anderson Hamiltonian,

$$ N = \left[1 - \exp\left(\frac{-C(\Delta E + \delta E)}{\nu_r}\right) \right] \times 100\%, \quad (1) $$

where ΔE is the potential difference between the substrate Fermi level and the projectile ionization level, and δE is the LEP modification induced by the adsorbate. The parameter C depends on the electronic structure of the substrate-projectile system, and ν_r represents the relevant velocity component of the scattered particle. Both ΔE and δE depend on the most probable distance for charge formation. In scattering from a metal surface with a laterally smooth electronic structure, the neutralization probability depends only on the normal component of the outgoing particle velocity [6,32], so that $\nu_r = \nu \cos\theta$, where ν is the total velocity and θ is the exit angle with respect to the surface normal. Assuming that $C\Delta E/\nu$ is constant for Li scattering from clean Fe, Eq. (1) was applied for scattering along the surface normal to determine that $C\Delta E/\nu = 0.356$. Using this value, the neutral fraction calculated from Eq. (1) is plotted vs exit angle by the dashed line in Fig. 3(a), which closely follows the experimental result.

For iodine adsorbates, the experimental evidence indicates that the adatom can be considered as a dipole positioned above the surface, rather than a point charge. δE in Eq. (1) therefore has a dipole character; i.e.,

$\delta E(I) = \frac{p^*(I)}{r^2}\cos\theta$, where $p^*(I)$ is the electrical dipole moment of the iodine adatom, and r is the distance from the adatom to the point where the charge exchange takes place. In addition, we assign a slight negative imbalance $\delta e^*(I)$ to the iodine dipole charge, as suggested by Fig. 2. This changes $\delta E(I)$ to $\frac{p^*(I)}{r^2}\cos\theta - \frac{\delta e^*(I)}{r}$. Since the adsorbate is positioned above the metal surface, we assume, as discussed above, that ionization occurs at a fixed distance from the adatom; i.e., r is constant and $v_r = v$. The dashed line in Fig. 3(b) was produced using this assumption, and by setting $\frac{Cp^*(I)}{vr^2} = 0.68$, $\frac{C\delta e^*(I)}{vr} = 0.24$, and $\frac{C\Delta E}{v}$ to the value 0.356 found for clean Fe. These fitting parameters yield an iodine charge imbalance $\delta e^*(I)/e^*(I) = 0.2$ and an iodine dipole length $d = 0.5r$. These are physically reasonable values in which the dipole approximation is satisfied, as $d < r$. The important conclusion to be drawn from this analysis is that a dipole on the surface with a charge imbalance produces a neutral fraction that decreases with more grazing exit angles.

Although this theoretical description is approximate, the good agreement between the calculation and experiment demonstrates that polarization of halogen adatoms is a real effect, and that it is likely responsible for the anomalous work function changes observed. Polarization of adsorbates may also play a role in other systems that display unusual work function behavior, such as oxygen adsorbed on Al or Mg surfaces [33,34].

We have shown that ion scattering neutral fractions are sensitive to the internal charge distribution of a single adatom. By collecting data as a function of both polar and azimuthal angles, it may be possible to map out three-dimensional variations in the LEP. Calculations would be valuable in quantitatively interpreting such data; for example, density functional theory can first be used to estimate the charge distributions for particular adsorption sites [29,30], and numerical analysis in terms of the parametric Newns-Anderson Hamiltonian [32] or other more sophisticated techniques [35] can then be applied to estimate neutral fractions for a particular charge distribution. The coordination of experimental results with such calculations could possibly lead to a method for mapping the electron density within a single adatom, thus providing microscopic information on adsorbates that is not accessible by other surface-sensitive techniques, such as scanning tunneling microscopy.

*Corresponding author.
Electronic address: yarmoff@ucr.edu

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