Formation of Excited Hydrogen States in Stimulated Desorption from an Alkali-Promoted Surface

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The desorption of hydrogen from alkali-promoted surfaces has been studied with electron-stimulated desorption (ESD). Excited hydrogen states are found for work functions that are larger than the binding energies of the corresponding atomic levels. This finding is in direct contrast with the conventional image shift of neutral atomic levels near surfaces and indicates that the levels are instead downshifted near the surface. Calculations of the energy shift and broadening of atomic hydrogen levels in the vicinity of a potassium atom chemisorbed on a metal surface confirms such a downshift. A model is presented that accounts for the observed formation of excited H in ESD from alkali-promoted surfaces.

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Charge-transfer rates and their role in a number of dynamical processes occurring at or near a surface remain areas of considerable research activity.[1] In particular, charge transfer represents a decay channel for both ions and excited atoms in the vicinity of a surface and as such may be expected to play an important role in determining desorption rates for these different particles. In a recent paper we reported the observation of the desorption of excited hydrogen atoms from alkali-promoted surfaces.[2] In another study,[3] enhanced desorption rates of positive hydrogen ions from alkali-promoted surfaces were also reported. In our study,[2] it was found that the intensities of Lyman-α and Lyman-β radiation emitted in the decay of the excited states showed a considerable imbalance reflecting either a different initial excitation rate or, conversely, a different survival rate for the excited states on moving from the excitation to the deexcitation region.

In this Letter we report on an experiment to examine the role of charge transfer in determining the relative survival rates. By comparing the experimentally observed Lyman intensities, measured for the first time as a function of the Fermi-level position, with a calculation of the excited-state lifetimes in the vicinity of a surface we show that charge transfer is indeed the key factor. The close agreement between experiment and theory also serves to confirm the picture of the hydrogen interaction with an alkali-promoted surface provided by the calculation.[4,5]

In the simplest picture, the binding energies of the hydrogen excited levels will be reduced in the vicinity of a clean metal surface reflecting the relaxation and screening effects associated with the induced image interactions.[4,6] However, in the presence of coadsorbed alkali atoms, strong electrostatic fields will be induced. It has been suggested[7,8] that the dipole interaction between the hydrogen and alkali could lead to the excited levels moving to higher rather than lower binding energies. Such shifts would have the effect of allowing the observation of Lyman-α radiation at minimal alkali coverage.

The calculation employs a theoretical approach that has been described in detail elsewhere.[4,5] A one-electron approximation is used for the electrons and the clean metal is modeled by a jellium description ($r_s = 2$). The electron potential at position (r,z) can be written as

$$V^{\text{eff}}(\rho,z;Z) = V_0^s(\rho,z;Z) + \Delta V^s(\rho,z;Z) - \frac{1}{r} + \Delta V^{\text{K}}(\rho,z)\,, \qquad (1)$$

where (ρ,z) describe the electron coordinates and Z the position of the hydrogen nucleus. The first term V_0^s is the bare surface electron potential and the term ΔV^s is the potential induced by the proton. These terms are evaluated using a nonlocal-density functional approach and contain the image potentials induced by both the electron and the proton.[4] In the Coulomb term, r is the radial distance between the electron and the proton. The fourth term has not been included in previous calculations. It is the alkali-induced change in the surface potential and contains the direct interaction between the electron and the K, assumed to be fully ionized, and between the electron and the K image. The interaction between the electron and the K^+ is modeled using a pseudopotential[9] and the K^+ image is simply taken as a point charge. No account of the alkali-induced change in the exchange-correlation potential of the surface is taken. Such effects are local and will not influence the potential at the large hydrogen surface distances ($Z > 8$ a.u.). The present calculation was performed for the H placed along the surface normal through the chemisorbed K, the geometry demonstrated in Ref. 3. The Schrödinger equation for the combined system is solved using the complex scaling method described elsewhere.[4,5] This procedure yields directly the resonance energies, which

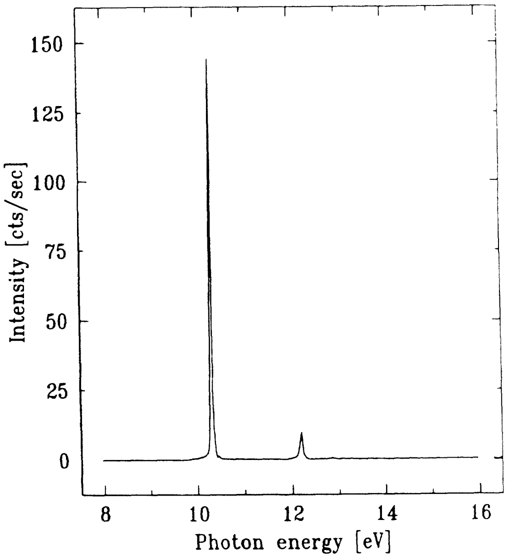

FIG. 1. Lyman spectrum showing the α (10.2 eV) and β (12.2 eV) radiation emitted from excited hydrogen atoms desorbed from an alkali-promoted metal surface.

contain a real part describing the binding energy and an imaginary part describing the tunneling rates between the atom and the surface.

The experiments were carried out using an apparatus that was originally designed for inverse-photoemission studies.[10] Briefly, the adsorbed hydrogen atoms are excited by a low-energy electron beam resulting in their desorption. The subsequent decay of the desorbed excited atoms is monitored by a spectrograph capable of detecting photons in the energy range from 10 to 30 eV. Low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES) were used to examine the surface order and cleanliness, respectively.

The Pt(001) surface was first cleaned by argon bombardment and annealing. Potassium was evaporated from an SAES getter to various coverages as determined by AES and the surface then exposed to a fixed amount of hydrogen, 5 L (where 1 $\mathrm{L}=10^{-6}$ Torrsec) in the present case. Such an exposure does not result in a saturated coverage. Having prepared the surface in this manner, the change in the work function from the clean-surface value was determined with the retarding-potential method using the low-energy electron gun.

In Fig. 1 we show a typical spectrum of the Lyman radiation emitted from excited hydrogen atoms desorbed from the potassium covered surface. The width of the lines, which are not observed in the absence of the alkali atoms, is determined entirely by the energy resolution of the spectrograph. As noted in our earlier study[2] the assumptions of equal excitation rates and equal survival rates should result in the Lyman lines having nearly equal intensities.

In Figs. 2(a) and 2(b) we show, respectively, our cal-

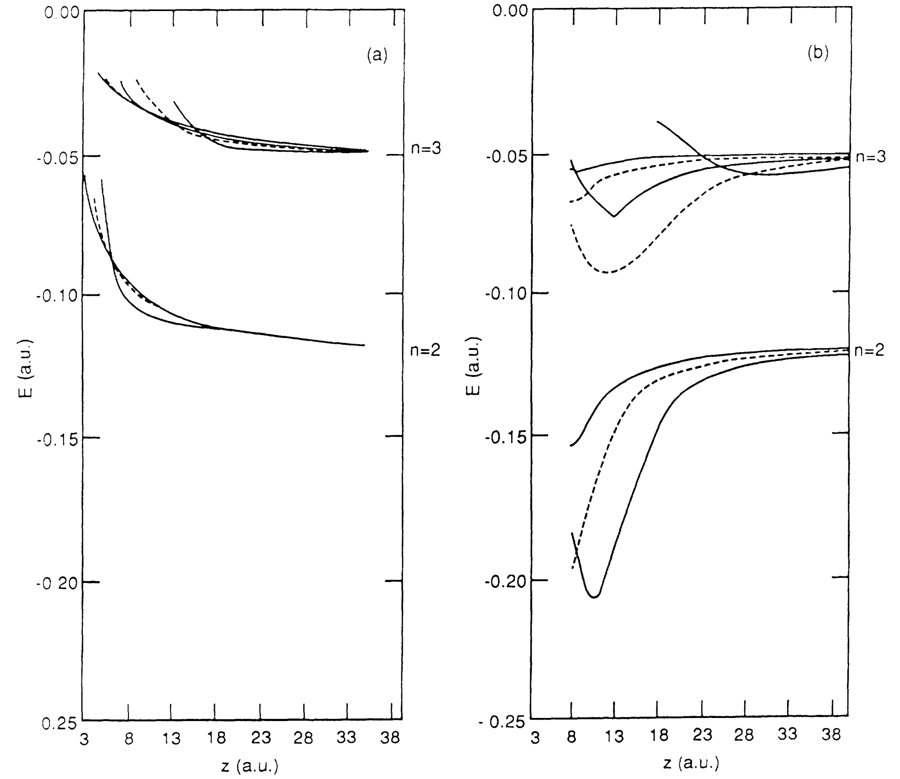

FIG. 2. Variation of the real part of the energy eigenvalues for the lowest H levels as a function of distance from the jellium edge for (a) a clean metal surface and (b) an alkali-covered metal surface. The solid curves are the $m=0$ states and the dashed curves the $m=1$ states.

culated energy-level shifts for the excited states of a hydrogen atom in the vicinity of a clean surface and in the vicinity of an alkali atom placed on that surface. As noted earlier, the strong electrostatic potential associated with the alkali atom in the latter case pushes the ionization levels of the hydrogen atom to higher binding energy. In addition, the splitting between the various H hybrid states is enhanced. The reason for this is that the alkali-induced dipole field in the surface region has larger curvature than the image potential. The different H hybrid states extend into different regions of space and thus experience a different surface potential. These different atomic hybrid orbitals can have very different widths because the tunneling probability is an exponential function of the distance from the surface. Analogous to the situation for H on a clean metal surface one can classify the different hybrids as hydrogenic Stark states.[4] Thus for the H ($n=2$) states there exists a long-lived state, ψ_2^-, oriented away from the surface and a short-lived state, ψ_2^+, oriented towards the surface. The two states derived from the atomic $2p_{x,y}$ orbitals are denoted ψ_2^0 and are oriented parallel to the surface. The H ($n=3$) states form six different hybrids that shift slightly differently and have very different widths. The calculated level broadenings of the H levels in the presence of the coadsorbed K are about an order-of-magnitude broader at a given surface distance than for H on the clean metal surface. Further details of the calculation will be presented elsewhere.

In Fig. 3 we show the experimentally observed intensities of Lyman-α and Lyman-β radiation as a function of work-function change. While no radiation is observed from the clean surface, Lyman α is observed almost immediately with minimal coverages of potassium. At higher coverages the Lyman β becomes more obvious in the spectrum but it never attains the intensity of the α radiation.

The experimental observations in Fig. 3 would not easily be explained with earlier descriptions with high charge-transfer rates.[11] An application of the standard theory for charge transfer[12] with short-lived atomic levels[13] would predict a nearly steplike onset of Lyman radiation when the substrate work function becomes smaller than the energy of the H ($n=2$) state. Thus the α radiation might be observable for the maximum change in work function but the β radiation would never be observed, the $3p$ level always being well above the Fermi level.

The population of excited atomic states after desorption can be calculated using the time-dependent Anderson model,[12,13] assuming a classical trajectory for the desorbing atom. The excited-state yield contains a memory term reflecting the survival of atomic excitations formed at the initiation of the desorption event and a dynamical contribution resulting from the formation of the excited state through resonant tunneling from the metal.[12] The H ($n=3$) levels lie above the Fermi level at all distances from the surface. Thus occurrence of any H ($n=3$) excited state must arise purely from the memory term. Only the most long lived of the H ($n=3$) states, ψ_3^-, can survive the passage out from the surface. The remaining H ($n=3$) states decay almost completely and are thus neglected. The ψ_2^- state is very long lived and only contributes to the H ($n=2$) yield through the memory term. For the description of the formation of the remaining H ($n=2$) terms we note that the ψ_2^+ level and the two ψ_2^0 levels have such short lifetimes that their memory terms are negligible and they will be populated immediately as they cross the Fermi level. It is adequate to treat these levels as a threefold degenerate ψ_2^0 level. The ψ_2^0 and ψ_2^+ states are the only states that can be formed by resonant tunneling from the metal. Since all other excited states except ψ_2^- and ψ_3^- will decay in the vicinity of the surface, the yield of positive ions, p^+, desorbing from the surface will be determined by the probability of formation of ψ_2^0 and ψ_2^+. The resulting expressions for the population of the H ($n=2$) and H ($n=3$) states thus read[13]

$$\begin{aligned}
n_3^-(\infty)_\phi &= k\Theta_K P_3^- e^{-\chi_3^-(Z_0)}, \\
n_2^-(\infty)_\phi &= k\Theta_K P_2^- e^{-\chi_2^-(Z_0)}, \\
n_2^0(\infty)_\phi &= k\Theta_K (1 - P_2^- e^{-\chi_2^-(Z_0)} - P_3^- e^{-\chi_3^-(Z_0)}) \\
&\quad \times \int_{Z_0}^{\infty} dZ\, f(\epsilon_2^0(Z),T) \frac{\Delta(Z)}{v_\perp} e^{-\chi_2^0(Z)}, \\
p_\phi^+ &= k\Theta_K - n_2^-(\infty) - n_2^0(\infty) - n_3^{\rm tot}(\infty),
\end{aligned} \tag{2}$$

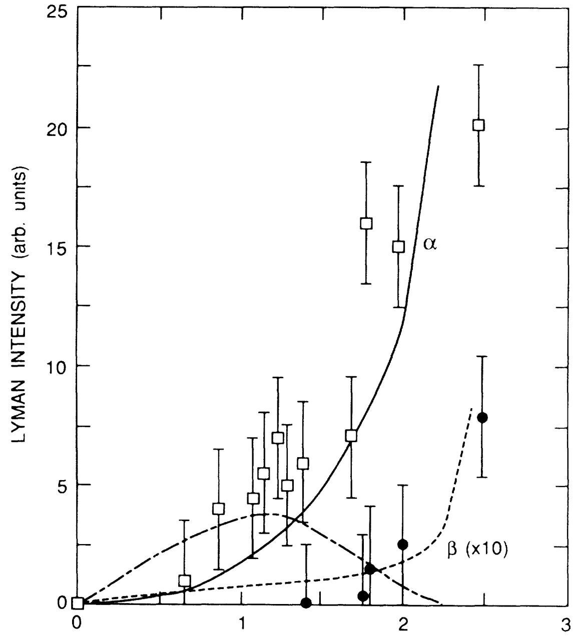

FIG. 3. Comparison of the experimentally measured Lyman α (open squares) and β (solid circles) intensities as a function of work-function change with a calculation of the same. The solid line is the calculated α intensity, the dashed line the calculated β intensity, and the variable dashed line the calculated desorbed positive-ion intensity.

where $f(\epsilon,T)$ is the Fermi function, T is the surface temperature (300 K), $\epsilon_a(Z)$ is the calculated H $(n=2)$ level shift, and $\chi(Z)$ is the outward integral (from Z to ∞) of the tunneling rate of the corresponding atomic level. Θ_K is the coverage of K on the surface and thus determines the work function. Calculations are performed assuming that the various excited states are populated with equal probability P. We assume that the H motion is perpendicular to the surface with a constant velocity, $v_\perp$, corresponding to 1-eV kinetic energy and a hydrogen surface bond distance of 8 a.u. corresponding to a H terminally bound to a chemisorbed K (Ref. 3) with a K-H bond length of 4 a.u.

In Fig. 3, for direct comparison with the experimental observations, we present the calculated Lyman-α and -β intensities based on calculated lifetimes and energy shifts using Eq. (1). The overall agreement between experiment and calculation is excellent. Both show the α and β states rising smoothly from zero-work-function change or zero alkali coverage. The β state shows a much lower rate with a slower increase with work function than the α state. The results can be qualitatively understood by noting that Eq. (2) for the yields of excited H contains a term proportional to the K coverage. At low work-function change the relation between the coverage and work function is linear. Thus the yield of H $(n=2,n=3)$ states will be linear in low work-function changes. At a work-function change of around 2 eV the slope of the work function versus coverage relation decreases leading to a correspondingly larger increase of the excited states. This effect dominates the $n=3$ state. The $n=2$ state increases even more rapidly due to increasing contribution from n_2^0 through resonant tunneling. In view of the calculational procedure, this latter observation suggests that both states can be occupied at an initially equal rate but charge transfer or resonant ionization determines the survival rate. We also show in Fig. 3 the rate of positive hydrogen-ion production resulting from the resonant ionization of the excited states. The ion production rate shown in the figure as a function of work-function change closely parallels that observed in the experiments of Lanzillotto *et al.*[3] A calculation assuming that the H is bound directly to the metal surface with a bond length of $Z_0=2$ a.u. shows no H $(n=3)$ states for work functions larger than 1.5 eV and no H $(n=2)$ states for work functions larger than 3.2 eV. While still a likely chemisorption position, desorption from the clean metal surface is not stimulated by electrons with the present energy, and we conclude that the desorbing H originates from a K-H-like surface complex as suggested in Ref. 3.

We note that the large difference in behavior calculated for the various components of the $n=2$ and $n=3$ states should result in a large polarization of the surviving states. Measurement of this polarization would further confirm the model.

In summary, the picture provided for the hydrogen interaction with alkali-promoted surfaces by the present study is that the hydrogen is terminally bonded to the alkali atom to form a hydride species. Desorption proceeds via excitation to the different excited states which, because of their radial extent, may be expected to be highly repulsive. The excited states are relatively long lived but the electrostatic potential of the alkali atom effectively serves to increase this lifetime by pushing the excited levels to higher binding energies. Positive ions, resulting from the resonance ionization of these excited levels, are observed at low alkali-atom coverages until the latter effect dominates.

The finding of large impurity-induced non-image-like atomic level shifts near alkali-covered metal surfaces has potentially important implications for the understanding of the microscopic mechanism of alkali promotion of transition metal catalysts.

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