PHYSICAL REVIEW B VOLUME 62, NUMBER 15 15 OCTOBER 2000-I

Electron- and photon-stimulated desorption of atomic hydrogen from radiation-modified alkali halide surfaces

L. T. Hudson
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

N. H. Tolk and C. Bao
Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235

P. Nordlander
Department of Physics, Rice University, Houston, Texas 77251

D. P. Russell
Department of Physics, University of Texas at El Paso, El Paso, Texas 79968

J. Xu
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

(Received 8 May 2000)

The desorption yields of excited hydrogen atoms from the surfaces of KCl, KBr, NaCl, NaF, and LiF have been measured as a function of incident photon and electron energy and flux, time of irradiation, dosing pressure of H_2 and sample temperature. As these surfaces are exposed to H_2 gas during electron or photon bombardment, the fluorescence from excited hydrogen atoms ejected from the surface is monitored. The desorption yields are found to be contingent upon surface damage induced by the incident particle radiation, leading to dissociative adsorption at surface sites containing an excess of alkali metal. A desorption mechanism is presented in which incident electrons or photons induce a valence excitation to a neutral, antibonding state of the surface alkali hydride molecule complex, leading to the desorption of hydrogen atoms possessing several eV of kinetic energy.

I. INTRODUCTION AND BACKGROUND

One of the prime objectives in surface physics is to understand the nature of the surface-adsorbate bond, including mechanisms of bond making and bond breaking. As the hydrogen atom serves as a paradigm for atomic physics, so adsorption and desorption of hydrogen is a natural and profitable choice for investigation of the most basic adsorbate-surface interactions. Recently, interest has been attached to studies of adsorption and desorption of hydrogen and solid surfaces such as Si, SiO_2, diamond, and GaN.[1] In contrast to the small hydrogen signatures characteristic of most surface science spectroscopies, the hydrogen–alkali-halide surface system has been found to exhibit large electronically stimulated desorption yields of excited hydrogen atoms upon exposure at room temperature to gaseous H_2. The goal of the present work is to determine the fundamental interactions of hydrogen with surfaces that can lead to the desorption of H* under electron and photon bombardment. Insights derived from this work include the preconditions for room-temperature hydrogen adsorption on alkali halide surfaces, the physical nature of the bond, and the mechanism of desorption.

To understand better these fundamental interactions, we have measured the excitation functions as well as temperature, incident particle flux, dosing pressure of H_2 and time dependencies of the electron- and photon-stimulated desorption (ESD, PSD) yields of neutral hydrogen from several different alkali halide surfaces. The observed behavior of the hydrogen yields correlates well with the identity of the alkali constituent of the sample as well as the metal's time-dependent accumulation on the surface, due to radiation damage, and subsequent removal by active heating. Measurements were also performed with an alkali-metal-dosed glass surface which exhibited a similar excitation function in the absence of a halogen component. We conclude that free-surface metal is required for hydrogen adsorption and a direct, wavelength-dependent desorption mechanism is involved in the photon-stimulated emission of neutral, excited-state hydrogen from these systems: *viz.* a resonant, valence excitation to neutral dissociative levels of the surface alkali hydride molecule or complex. An analogous electron-stimulated desorption mechanism is also proposed.

Knotek[2] correlated incident electron energy thresholds of protons desorbing from metal-oxide surfaces with *core-level* ionization potentials. This correlation permitted the identification of hydrogen bonded to reduced-valency metal ions on the surface, and demonstrated that electronically stimulated desorption can be a surface-, site-, and adsorbate-specific probe. Recently, Romberg *et al.*[3] showed atom-selective bond breaking of N_2 chemisorbed on Ru(001) surfaces. In that study, synchrotron radiation was tuned to give rise to desorption of either neutral N or N_2, and this was attributed to inducement of core excitations of the two N atoms in different chemical environments. The present study shows that ESD and PSD of neutral hydrogen atoms following *va-*

lence excitations of surface species can provide energy-selective bond breaking and bonding-site information.

Molecular and atomic hydrogen as point defects in the bulk of alkali halides have been well characterized,[4] but very little work to date has dealt with the desorption of hydrogen from alkali halide or alkali metal surfaces. Parks, Shirley, and Loubriel studied the emission of H^+ from alkali fluorides under photon bombardment.[5] They postulated that hydrogen, as an intrinsic impurity in their study, was photon activated in the bulk, migrated to the surface, formed a bond with an alkali atom, and finally desorbed due to a photon-induced core excitation followed by Auger decay. In contrast, the first observation of PSD of H* from alkali halide surfaces[6] required continuous dosing of the surface with gaseous H_2. The present study of neutral hydrogen desorption reveals that hydrogen bonding to a simple-metal surface can serve as a prototypical physical system involving a *direct* bond-breaking process in contrast to bulk-mediated desorption mechanisms.

II. EXPERIMENT

The ESD and PSD experiments were conducted in ultrahigh-vacuum chambers evacuated by a 220-l per second ion pump system with a base pressure of 1.3×10^{-8} Pa $(10^{-10}$ Torr). During hydrogen desorption measurements, research-grade (99.9999% pure) H_2 gas was dosed through a capillary, so as to maintain a partial pressure of about 1.3×10^{-5} Pa $(10^{-7}$ Torr) within the vacuum chamber. The desorption experiments were performed on the (100) faces of single-crystal KCl, KBr, NaCl, NaF, and LiF. These compounds are readily procured, easily cleaved, and were chosen so as to include combinations of three different alkali and three different halogen components. H* desorption signals were generally most intense from the potassium halides; consequently KCl data are shown here as representative in those cases where the only difference between different substrate compounds was signal strength. The samples were grown from the melt, and prepared by cleaving in air and heating in vacuum at 400 °C for several hours to remove adsorbed atmospheric water.[7] Above 25 °C, the sample temperature was controlled by a resistive button heater, and measured with a chromel-alumel thermocouple attached to a copper sample holder.

Fluorescence emitted as a result of electron or photon impact with a sample surface was collected by one- or two-lens systems which had an optic axis parallel to and just in front of the surface. This fluorescence was then focused through the slits of a 0.3 m (f/5.3) grating spectrometer (1200/mm grating) and photomultiplier tube combination with subsequent signal processing with photon-counting electronics. The spectrometer and the 1200-line/mm grating and photomultiplier tube efficiencies permitted observation of emissions in the 200–800 nm region. The H* yields presented as a function of various experimental parameters represent the counting rate above background, normalized to the incident particle flux.

The electron irradiation measurements were performed using a low-energy electron gun (10–350 eV) based on the design of Stoffel and Johnson.[8] The electron gun was constructed from gold-plated copper electrodes insulated from each other by ceramic spacers. An osmium-coated dispenser cathode is heated internally and emits thermal electrons with an energy spread of ≈0.1 eV. The beam energy could be varied under computer control. The incident electron flux at 20 eV was nominally 20 μA, focused to a spot about 2–3 mm in diameter. To eliminate problems of sample charging which could cause irreproducible excitation threshold measurements at low electron energies, the crystal faces were overlaid with an electrically grounded 80% transmission molybdenum mesh for the ESD measurements. The electron beam was incident at 45° from the sample normal, which also tends to reduce such charging.[9]

The PSD experiments utilized the 6-m TGM (toroidal grating monochromator) beamline at the University of Wisconsin's Synchrotron Radiation Center. This is a 6-m toroidal grating monochromator that provides a first-order flux of about 10^{11} photons/s mm^2 on a 20-mm^2 spot (particle current density ≈0.04 μA/mm^2). During these measurements, the entrance and exit slits were opened wide, giving an energy resolution of 100–200 meV. The photon beam was incident along the surface normal. The zero-order (undispersed) flux is about two orders of magnitude larger than that of first order. During measurements that employed zero-order light, an 80-nm-thick aluminum filter (bandpass 17–70 eV) was used to block visible radiation from the spectrometer. The energy-dependent measurements reported here employed a low-energy grating permitting first-order radiation to be tuned from 7 to 35 eV.

III. RESULTS

A. Spectra

Figure 1 shows fluorescence spectra from KCl while dosing the surface with hydrogen (ESD) or deuterium (PSD) at a partial pressure of $\approx1.3\times10^{-8}$ Pa $(10^{-7}$ Torr). The top spectrum was produced by white-light irradiation (25–70 eV); the lower spectrum is due to a 50-μA electron beam (7 μA/mm^2) with an incident energy of 350 eV. In the PSD spectrum, one observes the first resonance line from desorbing excited-state potassium atoms, a couple of the Balmer lines from desorbing atomic deuterium (e.g., D_α, $n=3\rightarrow2$,6563 Å), broadband fluorescence characteristic of the bulk, and the 0-0 emissions of the hydroxyl radical OD*$(A\ {}^2\Sigma^+\rightarrow X\ {}^2\Pi)$. The ESD spectrum is similar except that due to the radiation history of this sample, the K* emissions are below the experimental detection limit. While not explored with all of the samples of this study, we did observe an inverse relationship between the desorption yields of H* and the excited alkali signals in the ESD of KCl and LiF. This is discussed briefly in Sec. IV A.

B. Time dependence

If the active dosing of H_2 is terminated, the ESD yield of excited-state hydrogen decays with time. The total cross section σ_T for the electronic desorption of hydrogen in all possible final charge and excitation states can be derived from this decay time.[10] One such ESD measurement from KCl at 350 eV gives $\sigma_T\approx10^{-17}$ cm^2.[11] Hence, this physical system exhibits relatively large desorption yields since typical total ESD cross sections for various adsorbate-adsorbent systems are $\leqslant10^{-17}$ cm^2.[12]

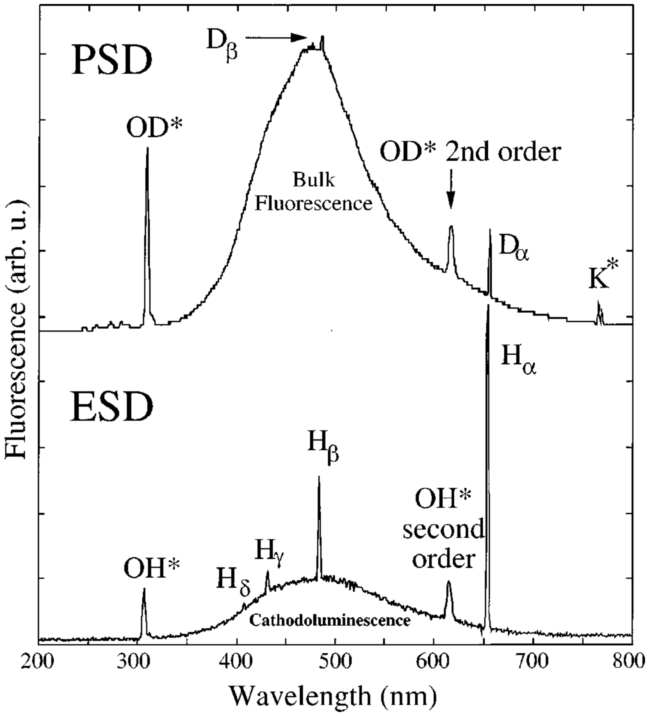

FIG. 1. Fluorescence spectra taken under photon (top) and electron (bottom) irradiation of KCl. The PSD spectrum was produced with white light (25–70 eV) while dosing the surface with a partial pressure of 1.3×10^{-5} Pa(10^{-7} Torr) of deuterium; the ESD spectrum is due to a 350-eV, 50-μA electron beam (7 μA/mm^2), while dosing with hydrogen at 1.3×10^{-5} Pa(10^{-7} Torr).

The hydrogen desorption signals also vary in time during the initial irradiation of a freshly cleaved and baked sample. At the initial stages of sample irradiation while dosing gaseous H_2, all of the alkali halide compounds examined have displayed little or no desorbing H*, followed by growth and saturation of H* yields as electron or photon irradiation is continued. Heating the samples can reverse this phenomenon, as discussed in Sec. III D. Figure 2 shows the time evolution of H_α signals from a KCl crystal which had been heated for 10 h at 400 °C, and then allowed to cool to room temperature. At $t=0$, 125-eV electron irradiation was initiated at 240 μA (34 μA/mm^2) in the presence of a 1.3×10^{-5} Pa (10^{-7} Torr) partial pressure of hydrogen.

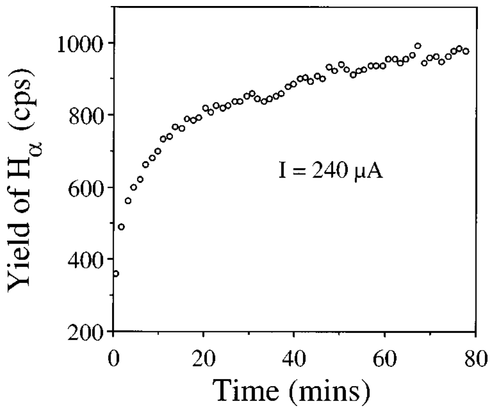

FIG. 2. The time evolution of the H* desorption yield from KCl at room temperature under 125-eV electron irradiation. $t=0$ follows 10 h of sample heating at 400 °C without electron bombardment or hydrogen dosing. At $t=0$ the background pressure of H_2 was brought to 1.3×10^{-5} Pa (10^{-7} Torr), and electron irradiation commenced with a beam current of 240 μA (34 μA/mm^2).

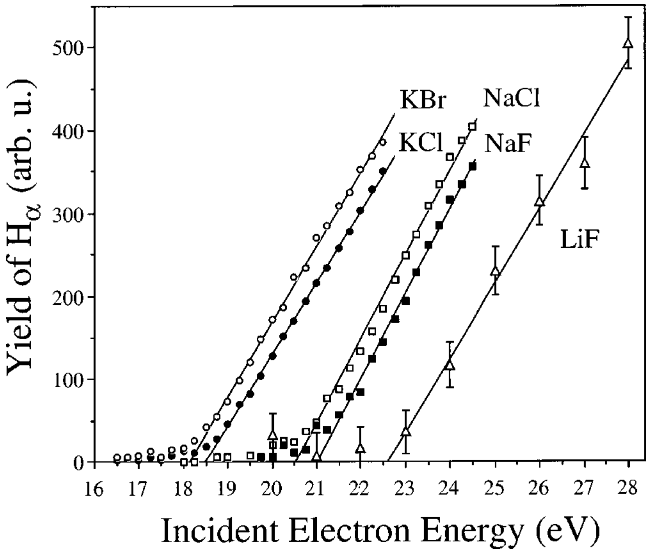

FIG. 3. Comparison of ESD thresholds of H_α from five alkali halide surfaces. All of the data except LiF represent the sum of four consecutive trials, which gives counting statistical error bars on the order of the size of the plotting symbols used. The beam current was 35 μA (5 μA/mm^2); the partial pressure of H_2, 1.3×10^{-5} Pa(10^{-7} Torr). For presentation, the data from KCl were scaled by 0.6, and those from LiF by 6.3.

C. Energy dependence

A comparison of the ESD excitation functions of H* are shown in Fig. 3 for each of the targets used in this study. The energy axis has *not* been corrected for the contact potential difference between gun and target.[13] This is not a factor in PSD, and, in light of those results, the absolute electron energy calibration for these ESD measurements is considered accurate to within an eV. The data were acquired while dosing continuously at room temperature with about 1.3×10^{-5} Pa (10^{-7} Torr) of H_2. Because of the different cross sections for the production of desorbing H*, in Fig. 3 the KCl results are scaled by a factor of 0.6, and the yield of LiF by 6.3 for presentation. Of note here is the grouping and ordering of the thresholds (or, rather, extrapolations of the linear part of the excitation functions) according to the identity of the alkali component of the compound being irradiated. Again, the observation that the ESD thresholds are not equal from surfaces containing the same alkali species is attributed to contact potential differences, or residual sample charging, and no such shift is observed in the corresponding PSD excitation functions, as shown below.

The incident photon energy dependence at room temperature of desorbing H* is displayed in Fig. 4. In Fig. 4(a), the yield of H_α, due to irradiation of KCl, exhibits a prominent resonance centered around 20.4 eV. To determine the contribution to this signal by incident photons of second or higher order, a tin-foil filter was inserted into the path of the incident photon beam. This filter passes only first-order light up to about 24 eV. The data in Fig. 4(b) show the resonance

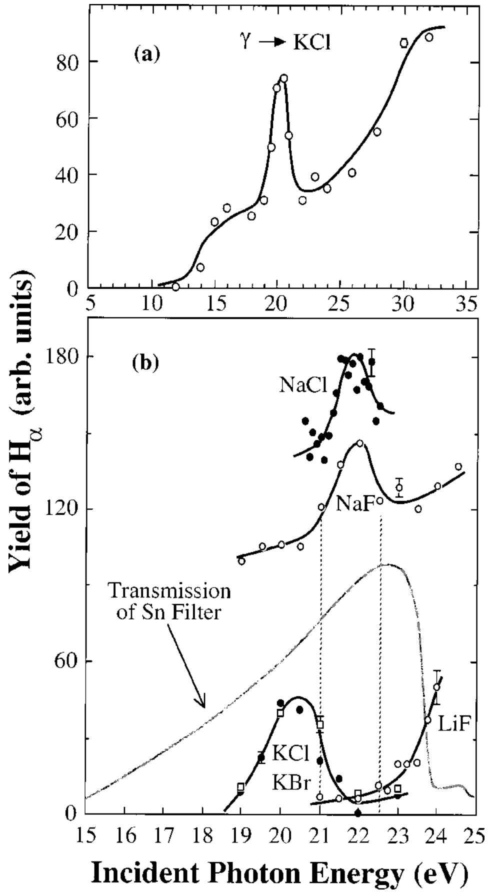

FIG. 4. Desorption yield of excited hydrogen atoms as a function of incident photon energy and normalized to incident photon flux. (a) Yield from photon irradiation of KCl without filtering higher-order light. (b) Yields from KCl (black dots), KBr (open squares), and LiF with a Sn filter in the path of the incident beam and from NaCl and NaF without a filter. The Sn filter passes only first-order light with the transmission function shown. The error bars shown are typical for each excitation function and indicate uncertainty due to counting statistics.

from KCl (black dots) to be the primary energy threshold for the emission of $H^*(n=3)$. A similar resonance from KBr (open squares) is identical in position and width to that from KCl. A resonance threshold from LiF is observed, and without the cutoff of the Sn filter (not shown), is found to be centered at about 24 eV. Due to relatively small desorption cross sections, the resonances from NaCl and NaF were taken without the filter. These two resonances are centered at about 21.8 eV, and have similar widths. The error bars shown represent statistical counting uncertainties. Again there is a clear correlation between the resonant energy thresholds for H* desorption and the identity of the alkali constituent of the compound.

To test that the excitation functions from at least the potassium halides were independent of the halogen constituent, a glass slide was dosed *in situ* with potassium metal forming an opaque layer. The potassium-dosed glass surface was then exposed to hydrogen and monochromatized UV photons. The photon-energy-dependent yield of excited hydrogen atoms was resonant (Fig. 5), and occurred at the same energy and with the same width as the results from the potassium halides. No H* desorption was observed from untreated glass.

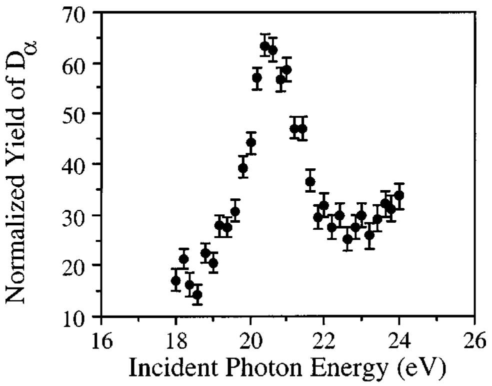

FIG. 5. Incident photon energy dependence of the desorption yield of D_α from a potassium dosed glass surface. Second-order light contributes the nonzero background signal. The error bars shown represent uncertainty due to counting statistics.

D. Temperature dependence

As mentioned previously, the H* signals could be removed from the fluorescence spectra by heating the sample substrate. This was found for all five of the samples studied. The exact shapes of the temperature dependencies were a function of sample history and the rate of heating. For example, if the temperature were raised rapidly, the desorption yield might show an initial increase before decreasing as is commonly observed in the thermally programmed desorption technique. Also, the level of the high-temperature asymptote was higher from samples which had been exposed longer to particle irradiation and hydrogen dosing. It is possible that there is a time-dependent source of hydrogen that accumulates in the bulk of alkali halides during the active dosing of hydrogen. H_2 is known to diffuse about 30 Å/s at 150 °C in KCl.[14] As the temperature is slowly lowered, as in Fig. 6, over a 2-h period, the desorbing H* signals increase for both ESD and PSD of KCl. In addition, after the samples returned to room temperature, the desorption yields were observed to return to their room-temperature levels. The ESD data were acquired using an ultraviolet spectrometer, and the strength

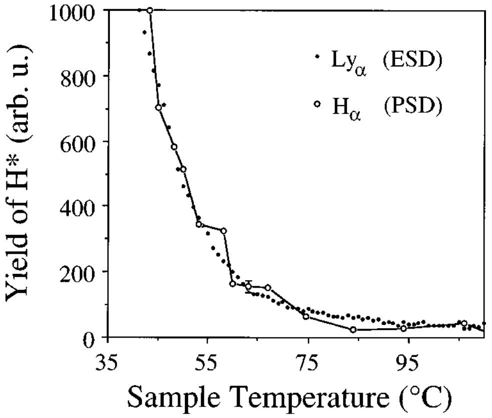

FIG. 6. Comparison of H* yields from KCl under electron (300 eV and 80 μA into 7 mm^2) and photon (zero-order light) irradiation while slowly lowering the substrate temperature. Ly_α denotes the $n=2-1$ transition of atomic hydrogen at 1216 Å, and H_α the transition from $n=3$ to 2 at 6563 Å. The two data sets were normalized at 50 °C.

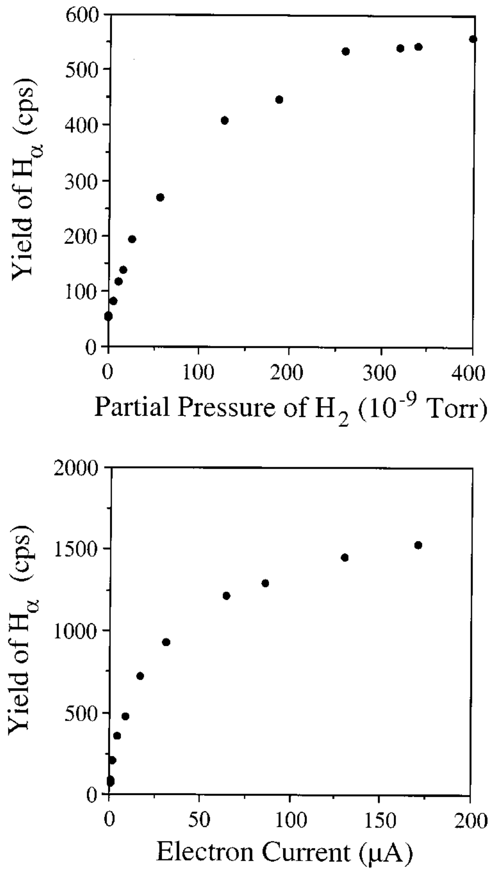

FIG. 7. Pressure and current-dependent measurements of H_α during ESD of KCl. Top: electron-beam current $I=160\,\mu A$ (23 $\mu A/mm^2$), electron-beam energy $E=125\,eV$. Bottom: the partial pressure of H_2P is 1.3×10^{-5} Pa(10^{-7} Torr), and the electron beam energy $E=125$ eV.

of the hydrogen Lyman alpha line was recorded ($n=2-1$, 1216 Å). These two data sets were normalized at 50 °C. In another measurement, the temperature of a KCl sample was lowered from room temperature to −145 °C, resulting in a factor of 4 increase in H* emissions as compared to the yields at room temperature under the same irradiation conditions.

An important substrate dependence was observed in both the ESD and PSD temperature-dependent measurements: when the substrate temperature was slowly stepped higher, maintaining thermal equilibrium, desorbing H* signals from the potassium halides were found to have generally disappeared from fluorescence spectra by about 100 °C, from the sodium halides by about 200 °C, and from LiF by about 300 °C. This will be discussed in Sec. IV B in relation to the vapor pressures of alkali metals.

E. Pressure and current dependencies

Typical pressure and current dependent measurements are shown in Fig. 7 for ESD from KCl. The yields of H_α rise and then tend toward saturation with increasing H_2 dosing pressures and incident electron current. This behavior is qualitatively consistent with sources and sinks of an adsorbate on any adsorbate-substrate system. In the present study, then, the desorption yield does not remain linear at high currents and constant pressure because it is rate limited by the arrival of new surface hydrogen. At high dosing pressures and constant current, the desorption yield is limited by the availability of adsorption sites. Similar behavior was found in the PSD of H* as a function of H_2 pressure. The PSD yield of H_α from KCl was found to be linear with the current measured on a gold diode, as the beamline entrance slits were adjusted from 400 to 3000 μm. This zero-order flux, however, has a neutral particle current of about two orders of magnitude less than that of the ESD electron currents that produced saturation.

IV. DISCUSSION AND CONCLUSIONS

A. Time dependence

The time evolution of H* mirrors the results of studies of the metallization of alkali halide surfaces. When alkali halide samples are exposed to photons above the band-gap energy, halogen atoms are preferentially sputtered,[15] leading to a partially metallized surface at room temperature. This photon-induced accumulation of excess alkali metal then evaporates thermally from the surface[16] at a rate determined by its creation (related to incident flux and migration rates of bulk defects), vapor pressure, and substrate temperature.

If incident electrons or photons are energetic enough to produce electron-hole pairs in alkali halide samples, defects are efficiently produced, leading to sample erosion and surface modification. Cota Araiza and Powell[17] documented the evolution of surface metallization during electron irradiation of alkali halides. They used electron-energy-loss spectrometry (EELS) to monitor the surface and bulk (volume) plasmon peaks associated with both the alkali halide and the free alkali metal at the surface. During bombardment of a KCl surface which had previously been cleaved in air and baked in vacuum, the EELS peak associated with the potassium metal bulk plasmon increased dramatically, and saturated after about 60 min. During the same elapsed time the surface and bulk plasmon signals associated with bulk KCl decreased. This was interpreted as the growth of free metal on the surface severe enough to mask much of the bulk from the electronic probe. The study of Cota Araiza and Powell also reported the same time evolution of the lithium surface plasmon during irradiation of LiF. The Li bulk plasmon, however, did not appear until the sample was heated above room temperature. This suggested that on LiF at room temperature the excess metal remained atomically thin. Upon heating it then became mobile enough to aggregate and give rise to the bulk plasma oscillations. The time evolution of free lithium metal was also documented on the surface of LiF due to photon bombardment.[18] Finally, Auger electron spectroscopy (AES) was also used to document the temporal evolution of the KCl surface during ESD. Tokutaka *et al.*[19] measured the time evolution of the potassium and chlorine AES peaks during irradiation with 1.5-keV electrons of intensity 2 $\mu A/mm^2$. They reported that the chlorine signal decreased while the potassium signal increased slightly until a metal-rich equilibrium was achieved after 45 min.

As mentioned in Sec. III A, desorption yields of excited-state alkali atoms were observed to be anticorrelated with the desorption yields of H*. It is not thought that the introduction of hydrogen quenches the desorption or excitation of the alkali species. Incoming electronic energy imparted to areas of the surface which are metallized is not localized sufficiently to result in desorption of metal. Hence, the K* present in the PSD spectrum of Fig. 1 along with a relatively *D** signal weak (with respect to the desorbing H* in the ESD spectrum) is thought to be indicative of a weakly modified (metallized) KCL surface under an incident photon flux which is low relative to our electron-irradiation studies.

B. Temperature dependence

The results of the temperature-dependent measurements may also be understood in terms of changes in the surface stoichiometry as a result of incident particle irradiation. The temperature ranges through which electron-induced, excess potassium, sodium, and lithium are thermally depleted from the surfaces of their corresponding alkali halides was studied in Ref. 20 using EELS. Peaks in EELS spectra associated with surface and bulk plasmons of free alkali metal were seen to decrease and disappear from the surface of KBr by 100 °C, from KCl by 110 °C, from NaCl by 200 °C, from NaF by 235 °C, and from LiF by 315 °C. This is in good agreement with the ranges in which we found H* to be depleted from the potassium halides (≈100 °C), sodium halides (≈200 °C), and LiF (≈300 °C). These observations strongly suggest that diminution of the H* desorption yields with increasing substrate temperature is not due to direct thermal desorption of physisorbed or chemisorbed hydrogen, rather the H* yields are correlated with the creation and subsequent thermal removal of excess surface alkali metal.

C. Desorption precursor

We turn now to a discussion of the site(s) of hydrogen adsorption and H* desorption. Partial pressures of $H_2 > 1.3\times10^{-5}$ Pa (10^{-7} Torr) can evolve H_2O from vacuum-system surfaces, thereby creating the possibility that desorbing hydrogen was initially deposited by water rather than directly by H_2.[21] The desorption yields of H*, and, from the potassium halides of this study, the yields of OH*, are correlated with the introduction of H_2, and each shows the same dependence upon H_2 partial pressure. One must consider OH as a primary desorption precursor of H*; however, this would seem unlikely since the ratio of H* and OH* was observed to vary widely on both sides of unity as a function of sample, sample history, and compound. The desorbing H* and OH* are detectable in our pressure dependencies at H_2 partial pressures in the mid-10^{-7}-Pa (10^{-9}-Torr) range, and increase by a factor of six, tending toward saturation by 1.3×10^{-5} Pa (10^{-7} Torr). Over this same H_2 pressure range, residual gas analysis within our vacuum system revealed less than a 10% increase of all other background gases including O, OH, H_2O, CO, and CO_2. Above about 1.3×10^{-5} Pa (10^{-7} Torr), we find that background water begins to increase markedly, consistent with the findings of Ref. 21 that proton desorption due to adsorption of evolved water was only observed at H_2 dosing pressures greater than 1.3×10^{-5} Pa (10^{-7} Torr). Since the desorption yields of H* (and OH*) are found to be uncorrelated with the evolution of water and other residual gases as H_2 dosing pressure is varied, we conclude that molecular hydrogen is reacting directly with the surface. Desorbing OH* was detected only from the potassium halides of this study. Here surface hydroxides are formed from H_2 reaction with oxygen impurities, probably forming surface K-O-H.

Since the energy thresholds for desorption of H* are grouped by the identity of the alkali atom of the adsorbent, and both the H* and OH* yields appear correlated with the creation and removal of excess metal on the surface, the most likely desorption precursor of H* is a metal hydride (M-H) or, at least from the potassium halides of this study, metal hydroxide (M-O-H). Above some incident particle energy, one would expect at least a component of desorbing H* to originate from M-O-H where present, and so the question becomes whether the M-H species is formed at all, and dominates or whether the catalytic process of this study necessarily requires the presence of surface oxygen impurities. The large variation of the relative yields of H* and OH* suggests the existence of an independent M-H formation channel. OH* was not observed from NaCl, NaF, and LiF under similar experimental conditions. The exclusive M-O-H desorption precursor is also unlikely, since the energy thresholds of H* from compounds containing a different alkali constituent differ in energy by several eV. A comparison of the spacing of resonant thresholds, as in Fig. 4, is an indication of the difference between bonding and antibonding energy levels of desorption precursor systems. It is difficult to account for a 3–4-eV separation of thresholds due to rupturing the O-H bond, as the M-O-H metal is changed from potassium to lithium. Such a spacing of H* thresholds is not unreasonable if due to a valence excitation of surface MH species as discussed below.

Hence we propose that H_2 dissociation occurs at, and is contingent upon, metal-rich surface sites. While dissociation of H_2 is thermodynamically favorable on a lithium surface, it is not expected to occur on smooth, defect-free potassium and sodium surfaces.[22] However, as mentioned above, three-dimensional islands[17,21] form on these surfaces, reflecting the tendency of atomically thin metal layers to aggregate. Due to the incommensurability with the underlying lattice, such a metallic overlayer on an alkali halide surface will contain a high concentration of defects, greatly enhancing the probability of dissociation.[23] That the energy thresholds are identical (in the PSD results where surface charging does not affect incident particle energy) for compounds bearing the same alkali component further suggests that the surface alkali hydride molecule or alkali hydride complex is also the ultimate desorption precursor of hydrogen. Similar conclusions have also been drawn in electron-stimulated desorption experiments of protons[24] and H*,[25] both from alkali-promoted Ni and Pt surfaces, respectively.

D. Desorption mechanism

When assigning a mechanism to neutral particle desorption, one must in general consider the possibility of resonant tunneling or Auger neutralization of desorbing ions as they recede from the surface. In this study, however, we seek a mechanism for photodesorption of *excited* neutral atoms. Since the uppermost filled levels of the alkali metals and alkali halide surface states are energetically below the $n=3$ level of atomic hydrogen, we immediately discount desorp-

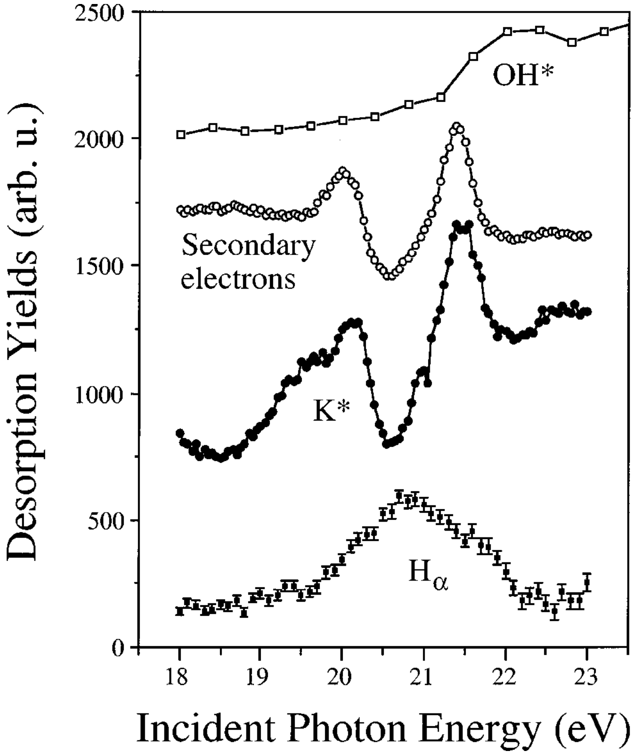

FIG. 8. Comparison of the photon-stimulated energy-dependent yields of OH*, secondary electron yield, K*, and H_α from KCl.

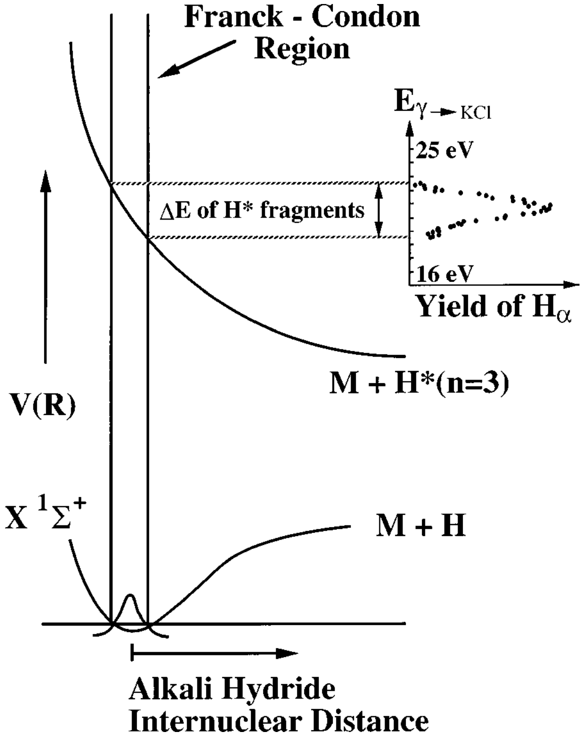

FIG. 9. Schematic of the one-dimensional Franck-Condon model excitation proposed for the electron- and photon-stimulated desorption of H* from alkali halide surfaces. A valence excitation to a neutral, antibonding state of a surface alkali hydride molecule complex leads to the desorption of excited hydrogen atoms with several electron volts of kinetic energy. Also shown is an experimental excitation function of H* desorbed by photons from KCl.

tion by the Knotek-Feibelman[26] or other Auger-stimulated desorption mechanisms,[27] which in some physical systems have been shown to result in ion emission. This observation also excludes models of primary valence excitations of the surface-adsorbate complex to repulsive[28] or attractive[29] ionic states, which lead to subsequent neutralization and desorption arising from crossings with occupied energy-level surfaces.

Only a few PSD mechanisms for excited neutral atoms or molecules have been proposed. The desorption yields of excited alkali atoms from alkali halide surfaces exhibit energy thresholds and structure which are correlated to metal core-level ionization[30] and exciton creation. In the case of KCl, potassium excitons (reflected in the structure of the desorption excitation function of K*) occur in the vicinity of the H* PSD excitation resonance, as shown in Fig. 8.[31] However, the threshold energies for H* in the present study show no systematic correlation to either the core-excitation or exciton-creation energies of hydrogen, the alkali metals or the alkali halides; nor to features in the excitation functions of bulk fluorescence, total electron yield, or excited- or ground-state alkali atoms. A recent study[3] of the PSD of N and N_2 from Ru(001) surfaces attributed the core excitation of nitrogen energy levels as the first step of the desorption process.

In contrast to these indirect processes leading to desorption, a mechanism of direct excitation to the repulsive state of the adsorbate-substrate complex has been applied to the results of photon-[32] and electron[33] -stimulated desorption of neutral molecules from metal surfaces. Here we assign a direct valence excitation mechanism to the present measurements of electron- and photon-stimulated desorption of neutral atoms from a surface. The antibonding H* $(n=3)$ state can be very long lived in the vicinity of a metal surface,[34] thereby enabling the desorption and detection of H* $(n=3)$. This desorption mechanism would result in resonant PSD thresholds with typical Franck-Condon-mediated widths, as measured here and shown schematically in Fig. 9. At present, no experimental or theoretical values are available for the high-lying, dissociative excitation states of gas-phase alkali hydride molecules, but energy thresholds up to 25 eV are reasonable for such valence excitations. In contrast to the selective bond-breaking capability of photons, the inelastic nature of electron interactions would be expected to result in linear excitation threshold functions, such as measured in Fig. 3.

The valence excitation mechanism proposed above predicts the desorption of hydrogen atoms with several eV of kinetic energy. The energy distribution of these desorbates was not measured directly, but the fluorescence techniques employed here permitted measurement of the Doppler profile of the fluorescence lines emitted by the excited hydrogen atoms as they receded from the surface. The spectral profile of the H_α and H_β lines in these experiments are Gaussian, with a full width at half maximum of a little more than 0.1 nm after correction for experimental resolution. This is much broader than that of hydrogen atoms in thermal equilibrium (≈9 pm at 400 K, H_α),[35] or that due to the natural lifetime of the excited state (≈ 160 ns, $\Delta\lambda \approx 10^{-6}$ nm, H_α).[36] Assuming that pressure broadening is not significant, this width is then principally due to Doppler broadening.

The Doppler profile of H_β (desorbing H* with $n=4-2$, 4861 Å) due to 150-eV electron irradiation of KCl was taken in second order, for improved resolution, with a 1200 l/mm grating blazed at 7500 Å. The instrumental resolution in this region was estimated by using the 4046-Å line of Hg from room lights, also in second order. The corrected width due to Doppler broadening was found to be 1.1 Å. From the geometry employed, a lower bound on the average transverse velocity corresponds to a kinetic energy of 6 eV. This is quite similar to the average energies of excited hydrogen atoms $(n=4)$ fragmented during electron dissociative excitation of gas-phase H_2,[37] HCl,[38] NH_3,[39] and CH_4 (Ref. 40) at comparable incident electron energies and is consistent with valence excitation to high-lying, antibonding molecular states. At these relatively large velocities we expect the survival probability of the most long-lived H* states to be finite.

In summary, the time-, temperature-, and energy-dependent desorption yields of neutral hydrogen atoms from alkali halide surfaces suggest that these surfaces are initially inert to gaseous H_2, but as radiation damage produces surface metallization, it is rendered vulnerable to adsorption and alkali hydride formation. The electronic desorption mechanism postulated here, namely, a direct valence excitation to a neutral, dissociative excitation state of the surface alkali hydride, then leads to the electronic ejection of energetic atomic hydrogen.

ACKNOWLEDGMENTS

The authors acknowledge the able assistance of the staff at the University of Wisconsin's Synchrotron Radiation Center. This work was supported in part by The Air Force Office of Scientific Research, the Office of Naval Research, and the Robert A. Welch Foundation.

---

[1] A. Pusel, U. Wetterauer, and P. Hess, Phys. Rev. Lett. **81**, 645 (1998); E. T. Foley, A. F. Kam, J. W. Lyding, and Ph. Avouris, *ibid.* **80**, 1336 (1988); E. Pehlke and M. Scheffler, *ibid.* **74**, 952 (1995); Kyeongjae Cho, Efthimios Kaxiras, and J. D. Joannopoulos, *ibid.* **79**, 5078 (1997); V. J. Bellitto and B. D. Thoms, Phys. Rev. B **60**, 4821 (1999); A. Hoffman, M. Petravic, G. Comtet, A. Heurtel, L. Hellner, and G. Dujardin, *ibid.* **59**, 3203 (1999); S. Vijayalakshmi, H. T. Liu, and Z. Wu, *ibid.* **58**, 7377 (1998); H. Akazawa, M. Sugiyama, S. Maeyama, M. Oshima, and Y. Watanabe, *ibid.* **57**, 4883 (1998).

[2] M. L. Knotek, Surf. Sci. Lett. **91**, L17 (1980); Surf. Sci. **101**, 334 (1980).

[3] R. Romberg, N. Heckmair, S. P. Frigo, A. Ogurtsov, D. Menzel, and P. Feulner, Phys. Rev. Lett. **84**, 374 (2000).

[4] A. S. Marfunin, *Spectroscopy, Luminescence and Radiation Centers in Minerals* (Springer-Verlag, New York, 1979), p. 267.

[5] C. C. Parks, D. A. Shirley, and G. Loubriel, Phys. Rev. B **29**, 4709 (1984).

[6] L. T. Hudson, A. V. Barnes, N. J. Halas, R. F. Haglund, Jr., M. H. Mendenhall, P. Nordlander, N. H. Tolk, Y. Wang, and R. A. Rosenberg, in *Desorption Induced by Electronic Transitions—DIET III, 1987*, edited by M. L. Knotek and R. H. Stulen (Springer, New York, 1988), p. 274.

[7] J. Estel, H. Hoinkes, H. Kaarmann, H. Nahr, and H. Wilsch, Surf. Sci. **54**, 393 (1976); G. Boato, P. Cantini, and L. Mattera, *ibid.* **55**, 141 (1976).

[8] N. G. Stoffel and P. D. Johnson, Nucl. Instrum. Methods Phys. Res. A **234**, 230 (1985).

[9] C. G. Pantano and T. E. Madey, Appl. Surf. Sci. **7**, 115 (1981).

[10] T. E. Madey and J. T. Yates, Jr., J. Vac. Sci. Technol. **8**, 525 (1971).

[11] L. T. Hudson, Ph.D. thesis, Vanderbilt University 1989.

[12] T. E. Madey and J. T. Yates, J. Vac. Sci. Technol. **8**, 525 (1971).

[13] L. Ernst, Solid State Commun. **19**, 311 (1976); Nuovo Cimento **39**, 797 (1977).

[14] A. E. Hughes and D. Pooley, J. Phys. C **6**, 2094 (1973).

[15] P. D. Townsend, R. Browning, D. J. Garlant, J. C. Kelly, A. Mahjoobi, A. J. Michael, and M. Saidoh, Radiat. Eff. **30**, 55 (1976).

[16] N. G. Stoffel, R. Riedel, E. Colavita, G. Margaritondo, R. F. Haglund, Jr., E. Taglauer, and N. H. Tolk, Phys. Rev. B **32**(10), 6805 (1985).

[17] L. S. Cota Araiza and B. D. Powell, Surf. Sci. **51**, 504 (1975).

[18] K. L. Tsang, C. H. Zhang, T. A. Callcott, E. T. Arakawa, and D. L. Ederer, Phys. Rev. B **35**, 8374 (1987).

[19] H. Tokutaka, M. Prutton, I. G. Higginbotham, and T. E. Gallon, Surf. Sci. **21**, 233 (1970).

[20] G. Roy, G. Singh, and T. E. Gallon, Surf. Sci. **152/153**, 1042 (1985).

[21] E. Bauer and H. Poppa, Surf. Sci. **99**, 341 (1980).

[22] J. Paul and F. M. Hoffmann, Surf. Sci. **194**, 419 (1988).

[23] G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell University Press, Ithaca, NY, 1981), pp. 488–491.

[24] A.-M. Lanzillotto, M. J. Dresser, M. D. Alvey, and J. T. Yates, Jr., J. Chem. Phys. **89**, 570 (1988).

[25] P. D. Johnson, A. J. Viescas, P. Nordlander, and J. C. Tully, Phys. Rev. Lett. **64**, 942 (1990).

[26] M. L. Knotek and P. J. Feibelman, Phys. Rev. Lett. **40**, 964 (1978); P. J. Feibelman and M. L. Knotek, Phys. Rev. B **18**, 6531 (1978); M. L. Knotek, V. O. Jones, and V. Rehn, Phys. Rev. Lett. **43**, 300 (1979).

[27] D. R. Jennison and D. Emin, Phys. Rev. Lett. **51**, 1390 (1983); D. E. Ramaker, J. Vac. Sci. Technol. A **1**, 1137 (1983); *Desorption Induced by Electronic Transitions—DIET-I, 1982*, edited by N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey, Springer Series in Chemical Physics Vol. 24 (Springer, New York, 1983), and references therein.

[28] P. A. Redhead, Can. J. Phys. **42**, 886 (1964); D. Menzel and R. Gomer, J. Chem. Phys. **41**, 3311 (1964).

[29] P. R. Antoniewicz, Phys. Rev. B **21**, 3811 (1980).

[30] N. H. Tolk, M. M. Taum, J. S. Kraus, T. R. Pian, W. E. Collins, N. G. Stoffel, and G. Margaritondo, Phys. Rev. Lett. **49**, 812 (1982); N. G. Stoffel, R. Riedel, E. Colavita, G. Margaritondo, R. F. Haglund, Jr., E. Taglauer, and N. H. Tolk, Phys. Rev. B **32**, 6805 (1985).

[31] The total electron yield and K* measurements were graciously provided by P. H. Bunton and R. F. Haglund, Jr.

[32] R. O. Adams and E. E. Donaldson, J. Chem. Phys. **42**, 770 (1965).

[33] D. Menzel, Ber. Bunsenges. Phys. Chem. **72**, 591 (1968); P. Feulner, R. Treichler, and D. Menzel, Phys. Rev. B **24**, 7427 (1981); P. Feulner, D. Menzel, H. J. Kreuzer, and Z. W. Gortel, Phys. Rev. Lett. **53**, 671 (1984).

[34] P. Nordlander and J. C. Tully, Phys. Rev. Lett. **61**, 990 (1988).

[35] K. Ito, N. Oda, Y. Hatano, and T. Tsuboi, Chem. Phys. **17**, 35 (1976).

[36] A. Corney, *Atomic and Laser Spectroscopy* (Clarendon, Oxford, 1977), p. 113.

[37] R. S. Freund, J. A. Schiavone, and D. F. Brader, J. Chem. Phys. **64**, 1122 (1976).

[38] M. Higo and T. Ogawa, Chem. Phys. **44**, 279 (1979).

[39] J. Kurawaki and T. Ogawa, Chem. Phys. **86**, 295 (1984).

[40] T. Ogawa, J. Kurawaki, and M. Higo, Chem. Phys. **61**, 181 (1981).