DIET of Neutral Excited State Hydrogen from Alkali Halide Surfaces

L.T. Hudson[1], *A.V. Barnes*[1], *J.L. Rose*[1], *N.H. Tolk*[1], *G. Betz*[2], *W. Husinsky*[2], *E. Wolfrum*[2], *and P. Wurz*[2]

[1]Department of Physics and Astronomy, Vanderbilt University,
Nashville, TN 37235, USA
[2]Technische Universität Wien, Institut für Allgemeine Physik,
Wiedner Hauptstr. 8–10, A-1040 Wien, Austria

Abstract. 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, time of irradiation, and sample temperature. The measurements indicate that the adsorption of hydrogen which leads to the stimulated emission of neutral, excited-state hydrogen is contingent upon surface damage induced by the incident radiation. Specifically, H_2 adsorbs dissociatively at surface sites containing a non-stoichiometric excess of alkali metal. This hydrogen may come from the gas phase or from a source which has accumulated in the bulk of these compounds during the course of the experiment. Incident electrons or photons can then induce a valence excitation to a neutral, antibonding state of the surface alkali hydride molecule leading to the desorption of atomic hydrogen.

1. Introduction

One of the prime objectives in surface physics is to understand the nature of the surface bond and the processes leading to its formation and rupture. 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. The hydrogen-alkali halide surface system is one such system that exhibits large electronically-stimulated desorption yields of excited hydrogen atoms upon exposure at room temperature to gaseous H_2. The goal of this work is the determination and elucidation of the fundamental interactions of hydrogen with alkali halide surfaces while under electron and photon bombardment which lead, ultimately, to the emission of H*. Specifically, this goal encompasses the identification of the site at which bonding occurs, whether the adsorption is physical or chemical, associative or dissociative, and the bond-breaking processes involved in desorption of excited hydrogen atoms from these surfaces.

2. Experimental Methods

The PSD experiments utilized the Vanderbilt/SRC (Synchrotron Radiation Center) beamline at the University of Wisconsin. This is a 6-meter toroidal grating monochromator which provided well resolved UV radiation from 10 to 200 eV with a

---

Springer Series in Surface Sciences, Vol. 19
Desorption Induced by Electronic Transitions, DIET IV
Editors: G. Betz · P. Varga

first-order flux of about 10^{11} photons/sec/mm^2. During these measurements, the entrance and exit slits were opened wide, giving an energy resolution of 100 to 200 meV. Samples were prepared by cleaving in air and heating in vacuum at 400°C for several hours so as to remove adsorbed atmospheric water [1]. The experimental chamber supported a base pressure of 5×10^{-11} Torr; during measurements the chamber was backfilled with research grade H_2 gas at pressures not exceeding 1×10^{-6} Torr. Visible fluorescence emitted as a result of UV-photon impact was collimated by a lens system parallel to and just in front of the surface and focused onto the slits of a 0.3m McPherson spectrometer (1200/mm grating) and photomultiplier combination with subsequent signal processing with photon-counting electronics. The Balmer alpha (H_α, n=3 to 2) fluorescence yields from desorbing H atoms presented below represent the counting rate above background, normalized to incident photon flux.

The electron irradiation measurements were performed using a low energy electron gun (10 to 350 eV) based on the design of Stoffel and Johnson [2]. Sample charging and irreproducible energy threshold measurements at low energies were eliminated by overlaying the crystal faces with an electrically grounded 80% transmission molybdenum mesh.

3. The Surface Morphology and Stoichiometry

The alkali halide surfaces studied here are far from being atomically smooth checkerboards of alkali and halogen ions. Both cleaving the sample and subjecting it to radiation cause dramatic deviations in the surface stoichiometry and irregularities in the surface structure. In particular, the halogen species is preferentially sputtered, leaving the surface metal-rich. This radiation-induced accumulation of excess metal on the surfaces of alkali halides has been extensively documented using a wide variety of surface-sensitive techniques including AES [3,4], soft x-ray emission spectroscopy [5], EELS [6,7], EPR [8], secondary electron and scanning Auger electron microscopy (SEM and SAM) [9].

4. Time, Energy, and Temperature Dependent Measurements

During the initial irradiation of a freshly cleaved and baked sample and in the presence of H_2, fluorescence spectra exhibit little or no emissions from desorbing hydrogen. The ESD H* yields, however, grow dramatically in time and then saturate. Each of the five alkali halide compounds examined has displayed this effect. The time evolution of H* tracks qualitatively the results of studies of the electron-induced metallization of alkali halide surfaces [4,7]. While the ESD signal of H* saturates on the time scale of one to a few hours, in the photon irradiation experiments it took one to a few days. The flux of incident photons was about two orders of magnitude less than that of the ESD experiments.

The ESD energy thresholds for the desorption of H* are shown in Figure 1. The energy axis has *not* been corrected for the contact charging due to transfer of

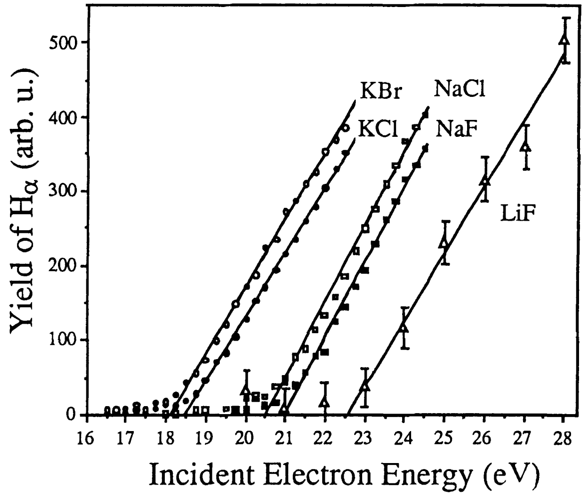

Figure 1. ESD energy thresholds for the desorption of H*(n=3) from five alkali halide surfaces

electrons between the cathode of the electron gun and sub-bandgap surface states of the sample [10]. This is not a factor in PSD and in light of those results, the absolute electron energy calibration is considered accurate to within an electron volt. The thresholds are grouped according to the alkali of the compound. That the thresholds from surfaces containing the same alkali are not identical is attributed to contact potential differences since this shift is not observed in PSD.

In Figure 2(a), the yield of H_α due to photon irradiation of KCl exhibits a prominent resonance centered around 20 eV. To determine the contribution to this signal by incident photons of second or higher order, a tin-foil filter (1500 Å thick) dependent yields of H_α from KCl, KBr and LiF are also shown in Figure 2(b) normalized to the relative flux transmitted by this filter. These results have been scaled for comparison. Scaled error bars are also shown. This shows that the resonance from KCl (black dots) is in fact the primary energy threshold for the emission of H^*(n=3). The resonance from KBr (open squares) is identical in position and width to that from KCl. A resonance from LiF begins around 23 eV and is truncated in this measurement by the transmission of the filter. Without the filter this resonance is found to be centered at about 24 eV. Due to signal strength requirements, the resonant yields from NaCl and NaF were taken without the Sn filter. The counting rates were small, yet reproducible. These two resonances occur at the same energy and with similar widths.

Note that the results from compounds containing the same alkali constituent are essentially identical. The thresholds from the sodium halides occur at incident photon energies between the potassium and lithium halides in agreement with the ESD thresholds. Further, the low energy onset of each resonance agrees to within an electron volt with the corresponding ESD threshold.

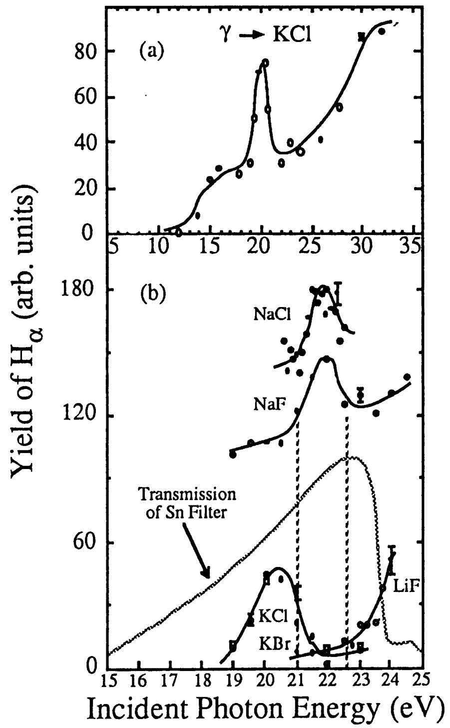

Figure 2.
(a) H*(n=3) desorption yield from KCl without filtering higher order incident photons. (b) H*(n=3) yields from KCl (black dots), KBr (open squares) and LiF with a Sn filter (transmission shown) inserted into the beam. Also shown are yields from NaCl and NaF without use of the Sn filter.

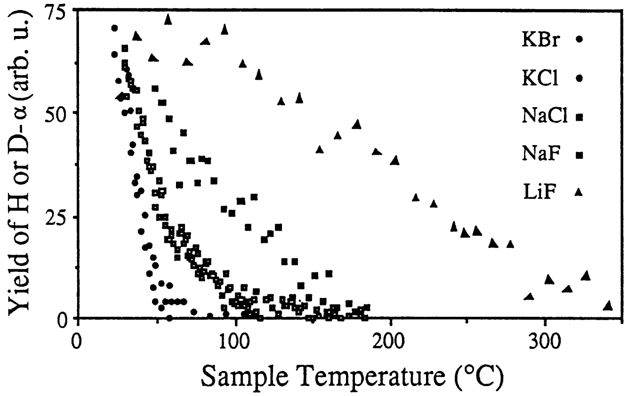

Figure 3. Temperature dependence of the desorption yields of H* from five alkali halide surfaces while irradiating with zero-order photons.

The temperature dependence of desorbing H* is displayed in Figure 3 from KCl, KBr, NaCl, NaF, and LiF surfaces under "white-light" photon irradiation. All of the yields were taken in the presence of about 10^{-7} Torr of H_2 and while increasing the temperature of the samples except that from KCl. The KCl data were acquired as the sample was cooled. The yields have been scaled for purpose of display since the unnormalized desorption rates of H_α from the potassium halides were about three to six times greater than those from the other compounds; this scaling did preserve the relative ordering of these yields as displayed on the temperature axis. Electron irradiation experiments yielded similar results.

The following observations follow by inspection of Figure 3:

(1) in all cases the yield of H* is diminished by heating, but this diminution occurs at different temperatures for different alkali halide compounds, the sequence being KBr < KCl < NaCl < NaF < LiF,

(2) the temperatures at which these desorption yields approach the noise-level are lowest for the potassium halides, higher for the sodium halides and highest for lithium fluoride, and finally,

(3) the ordering described in (2) is the same as the ordering of the heats of vaporization of these three metals, *viz.* K (0.80 eV) < Na (0.92 eV) < Li (1.40) [11].

5. The Desorption Precursor and the Mechanism of Desorption

The temperature regime over which H* yields are depleted is especially telling since many of the possible precursor states of the desorbing hydrogen would be completely unaffected by this thermal change. Chemisorbed atomic hydrogen could reside indefinitely bonded to K or Cl (≈2eV) at 125°C. In contrast, the exceedingly brief residence time (≈1ps) of physisorbed H or H_2 on KCl (≈30meV) [12] implies that these precursors are inconsequential under the conditions of these experiments.

The temperature intervals over which the yields of H* are diminished agree well with the observed temperature intervals found by Roy *et al.* [13] over which electron-induced excess potassium, sodium and lithium are thermally depleted by evaporation from their respective alkali halide surfaces. They measured the temperature dependent peaks in EELS spectra associated with surface and volume metal plasmons from the surfaces of electron-irradiated alkali halide compounds. These peaks from KBr were completely removed at 100°C, those from KCl at 110°C; NaCl, 200°C; NaF, 235°C; and LiF, 315°C (*cf.* Figure 3). This is in good agreement with an AES study by Szymonski *et al.* [14] of NaCl. They measured the ratio of Na to Cl Auger peak heights as a function of sample temperature and found the surface to be metal rich below 200°C compared to the stoichiometric ratio measured at higher temperatures.

These observations argue strongly that the diminishing yield of H* with temperature is not due to the thermal removal of physisorbed or chemisorbed H or H_2. Instead it is related (in first order) to the removal of excess metal from the surface. The role of the alkali constituent of the compound is also apparent in the time and energy dependent measurements. The time dependent measurements of H* suggest that these yields are correlated with the time evolution of surface metallization. The ESD energy thresholds from compounds containing the same alkali constituent agree within uncertainties in contact charging. Furthermore, the PSD energy thresholds are identical for compounds bearing the same alkali.

It is reasonable, therefore, to conclude from the temperature, time, and energy dependent results that H_2 dissociation occurs at and is contingent upon the existence of radiation-induced metal-rich surface sites and that the ultimate desorption precursor is a surface alkali hydride molecule.

When assigning DIET mechanisms to neutral-particle desorption, one must in general consider the possibility of direct resonance or Auger neutralization of desorbing ions as they recede from the surface. In this study, however, the neutral atoms are emitted in an excited state, typically $n = 3$ is measured. This state in hydrogen is only 1.5 eV below the vacuum. There are no electrons in the surface states of the alkali metals or alkali halides energetically available for neutralization of an ion into such a highly excited state. Therefore mechanisms of *ion* emission are not considered here. Gas-phase excitation of ground state hydrogen atoms is also improbable. Alkali halide surfaces under photon bombardment at the energies which gave threshold H_α resonances emit no secondary electrons energetic enough to excite ground-state hydrogen to $n=3$ (12.1 eV) [15]. Several mechanisms for ESD and PSD of neutral atoms and molecules correlate the energy thresholds and structure of desorption yields of excited atoms with core-level ionization [16], bulk and surface exciton creation [17], and vibrational excitation [18] of adsorbed molecules. The threshold energies for H^* in the present study, however, show no systematic correlation to the core-excitation/ionization or excitonic energies of hydrogen, the alkali metals, the alkali halides or vibrational excitation of the alkali hydrides.

A one-dimensional Franck-Condon model of valence excitation is often applied to desorption of gases from metal surfaces. This so called Menzel-Gomer-Redhead (MGR) model [19] has been applied extensively to the results of photon [20] and electron [21] stimulated desorption of neutral molecules from metal surfaces.

This valence excitation model predicts many features which are consistent with the results of desorption of H^* from a surface alkali hydride molecule. In such a model, the first step in the desorption of H^* is a vertical excitation within the Franck-Condon region from the alkali hydride ground state to an antibonding state. Previous applications of this model often specified excitation to an ionic repulsive state. Here desorption is expected to follow direct excitation to a neutral antibonding state. This follows since the desorption of protons which are subsequently neutralized as they recede from the surface is unlikely as discussed above. If this excitation is sufficiently localized, the molecule will dissociate emitting H^* with a kinetic energy determined by the point on the upper curve to which the molecule was excited and the level of the asymptote of the upper curve at infinite nuclear separation. If all the excited hydrogen atoms produced in this manner escape from the surface, then the H^* yield as a function of incident photon energy is a reflection of the square of the ground state alkali hydride wavefunction through the potential energy curve of the antibonding state. This would result in PSD resonance structure at threshold with typical Franck-Condon mediated widths [22] as shown here for desorption from KCl. Such a mechanism is also consistent with non-resonant ESD thresholds due to the inelastic nature of electron-particle interactions.

The time, temperature and energy dependent results strongly indicate that the H^* desorption precursor is a surface alkali hydride molecule. The observations presented above argue against desorption of H* which is thermal, initially ionic or ground-state, or desorption which is induced by momentum transfer, core-excitations or excitons. The location in energy of the observed thresholds and the shapes and widths of the features associated with these thresholds are consistent, however, with an MGR-valence-excitation model of desorption.

The desorption mechanism proposed here is primarily a surface interaction and independent of the substrate or the origin of the alkali hydride surface species. To confirm this, preliminary desorption experiments have been performed from a surface on which alkali metal and hydrogen were coadsorbed. A glass slide was dosed with potassium from a SAES getter and then exposed to gaseous hydrogen. The PSD excitation function exhibited a pronounced resonance at the incident photon energies that produced this feature during PSD of the potassium halide samples. The yield was also suppressed as the metal was evaporated from the substrate. These results support the desorption precursor and valence excitation mechanism proposed for the desorption of excited hydrogen atoms from alkali metal surfaces with hydrogen overlayers.

This research has been sponsored by The Air Force Office of Scientific Research under contracts F49620-86-C-0125 and F49620-88-C-0080 and the Office of Naval Research under contract N00014-87-C-0146.

References

1. J. Estel, H. Hoinkes, H. Kaarmann, H. Nahr, and H. Wilsch, Surf. Sci. **54**, 393 (1976), G. Boato, P. Cantini, and L. Mattera, Surf. Sci. **55**, 141 (1976).
2. N. G. Stoffel and P. D. Johnson, Nuc. Instr. Methods A **234**, 230 (1985).
3. P. W. Palmberg and T. N. Rhodin, J. Phys. Chem. Solids **29**, 1917 (1968).
4. H. Tokutaka, M. Prutton, I. G. Higginbotham, and T. E. Gallon, Surf. Sci. **21**, 233 (1970).
5. K. L. Tsang, C. H. Zhang, T. A. Callcott, and D. L. Ederer, Phys. Rev. B **35**, 8374 (1987).
6. G. Singh and T. E. Gallon, Solid State Commun. **51**, 281 (1984).
7. L. S. Cota Araiza and B. D. Powell, Surf. Sci. **51**, 504 (1975).
8. G. C. Fryburg and R. A. Lad, Surf. Sci. **48**, 353 (1975).
9. Q. Dou, D. W. Lynch, and A. J. Bevolo, submitted to Surf. Sci.
10. L. Ernst, Solid State Commun. **19**, 311 (1976), L. Ernst, Nuovo Cimento **39**, 797 (1977).
11. *CRC Handbook of Chemistry and Physics*, R. C. Weast, ed. (CRC Press, Inc., Boca Raton, 1988), p. F-65.
12. H. Hoinkes, Rev. Mod. Phys. **52**, 933 (1980).
13. G. Roy, G. Singh, and T. E. Gallon, Surf. Sci. **152/153**, 1042 (1985).
14. M. Szymonski, J. Ruthowski, A. Poradzisz, Z. Postawa, and B. Jørgensen, *Desorption Induced by Electronic Transitions - DIET II*, edited by W. Brenig and D. Menzel (Springer, New York, 1985), p. 160.
15. W. Pong and J. A. Smith, Phys. Rev. B **9**, 2674 (1974).
16. 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).
17. R. F. Haglund, Jr., A. V. Barnes, M. H. Mendenhall, N. H. Tolk, and D. E. Ramaker, to be submitted to Phys. Rev. B, P. Fuelner, T. Müller, A. Puschmann, and D. Menzel, Phys. Rev. Lett. **59**, 791 (1987), F. Coletti, J. M. Debever, and G. Zimmerer, J. Physique Lett. **45**, L-467 (1984).

18. J. Heidberg, H. Stein, E. Riehl, and A. Nestman, Z. Phys. Chem. **121**, 145 (1980), T. J. Chuang, J. Chem. Phys. **76**, 3828 (1982).
19. P. A. Redhead, Can. J. Phys. **42**, 886 (1964), D. Menzel and R. Gomer, J. Chem. Phys. **41**, 3311 (1964).
20. R. O. Adams and E. E. Donaldson, J. Chem. Phys. **42**, 770 (1965).
21. D. Menzel, Ber. Bunsenges. Physik. 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).
22. M. Higo and T. Ogawa, Chem. Phys. **44**, 279 (1979), J. Kurawaki, K. Ueki, M. Higo, and T. Ogawa, J. Chem. Phys. **77**, 3071 (1983), T. Ogawa, J. Kurawaki, and M. Higo, Chem. Phys. **61**, 181 (1981).