

Photon-stimulated desorption of H^+ ions from OH on Ti and Cr: Comparison with bulk solid H_2O

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An interpretation and comparison of photon-stimulated desorption yields of H^+ ions from OH on Ti and Cr and from bulk solid H_2O indicate that desorption occurs through two entirely different mechanisms. The first involves an intramolecular excitation of the OH adsorbate producing a H^+ yield similar to that in bulk H_2O . The second involves metal core-level excitation followed by Auger decay and is an example of molecular adsorbate dissociation arising from a metal-substrate Auger decay. This is a further generalization of the Knotek-Feibelman model applicable for desorption in ionic systems.

The electron- or photon-stimulated desorption (ESD, PSD) of positive ions from various surfaces has been shown to occur, at sufficiently high incident energies, by core-level excitation of a surface atom followed by Auger decay. Within the Knotek-Feibelman (KF) model¹ for ionic systems, the role of the Auger process is the creation of a positive ion at an initially negative-ion site. The expulsion of the positive ion results from the reversal of the Madelung potential experienced by the ion. The early work on metal oxides also indicated the necessity for maximal valency of the metal cation to prevent intra-atomic decay of the metal core hole, and force the interatomic decay that produces the O^+ ion.^{1,2} Generalization of the Auger stimulated desorption (ASD) process to covalent systems, such as SiO_2 ,³ requires a mechanism of localization of the two final-state holes onto a bond orbital, a condition necessary to provide the Coulomb potential for expulsion of a fragment ion from the bond orbital cluster. Such a mechanism is provided within the Cini-Sawatsky⁴ or configuration-interaction theory,⁵ which indicates that localization of the valence holes results when the Coulomb correlation energy U is greater than the covalent interaction or bandwidth. Of course, for small diatomic molecules in the gas phase, localization of the holes following an electronic excitation is a *fait accompli* and the molecule may dissociate via a Coulomb explosion.⁶ Further generalization of the ASD process is suggested by recent work reporting O^+ desorption from a thin oxide layer on Cr(110) as a result of Cr core-level excitation.⁷ Since the Cr oxide layer is not in its maximal valency state, this suggests that the maximal valency condition is not necessarily required in the PSD of oxides.

In this work we present PSD results for OH on Ti and Cr which clearly reveal the dissociation of a molecular adsorbate (OH) resulting in the desorption of positive fragment ions (H^+) as a result of metal core-level excitation. This is an example of the Coulomb explosion of a molecular adsorbate arising from excitation of a core level on a metal substrate atom that is not in its maximal valency state. As such, this is a further generalization of the ASD process. Although PSD of H^+ ions has been observed previously at metal core levels [e.g., from H_2O/TiO_2 ,⁸ H_2O/Ti ,⁹ and $(H_2, H_2O)/Ta$ and $(H_2, H_2O)/Nb$, Ref. 10], in all but one case⁹ it was suggested that the H^+ ions came from H-M bonds and not from the OH species. Our results also reveal an ion yield which is sensitive to the electronic configuration

of the metal core-hole state that subsequently undergoes the Auger decay. It rules out the possibility that the metal core-hole contribution could result from an indirect process, namely, secondary electrons arising from photoexcitation processes, as recently proposed.¹¹ Such an x-ray-induced electron stimulated desorption (XESD) process¹¹ would clearly not be sensitive to the electronic configuration of the core-hole state.

A double-pass cylindrical mirror electrostatic analyzer was used for the ion (PSD) and electron [ultraviolet photoelectron spectroscopy (UPS)] analyses.⁹ Photons for these experiments from the U.S. National Bureau of Standards (NBS) synchrotron light source [Synchrotron Ultraviolet Radiation Facility II (SURF-II)] were monochromatized by either a grazing-incidence (25–75 eV) or normal-incidence (12–30 eV) monochromator.⁹ Sample cleaning was performed by repeated Ar sputtering and heating cycles. Residual surface hydrogen on Ti could be removed by oxygen exposure and subsequent heating at 750°C. All experiments for Ti were done at 300 K. The Cr surface was dosed with H_2O at 80 K followed by heating to 200 K. Evidence that H_2O is dissociated on the Ti(001) and Cr(110) surfaces is obtained from the characteristic UPS spectrum for OH.^{9,12} The PSD measurements on Cr were made at 80 K. It should be emphasized that parallel ESD data in which mass analysis was performed (time of flight) indicated no positive ions other than H^+ ions were desorbed in significant amounts from the surface; also, hydrogen-dosed surfaces did not produce a measurable H^+ PSD ion signal. Thus, the observed H^+ ion yield is definitely associated with the adsorbed OH. The PSD for OH/Ti has been reported previously;⁹ the results for OH/Cr and for bulk H_2O were obtained in this work. Bulk H_2O films ≥ 50 Å thick were prepared by adsorbing H_2O at 80 K.

The PSD H^+ yield curve for bulk H_2O in Fig. 1(c) is in substantial agreement with that previously reported in a more narrow energy range, for $h\nu$ below 35 eV.¹³ A detailed comparison¹⁴ of the PSD H^+ yield from bulk H_2O with photodissociation in the gas phase has revealed that the peak below 35 eV arises from valence ionization plus shake-up producing the two-hole-one-electron ($2h-1e$) excitations $1b_1^{-1}3a_1^{-1}4a_1$ and $1b_1^{-2}4a_1$. Therefore, this contribution can be termed an intramolecular valence excitation. Note that a similar feature is present in the H^+ PSD spectra of OH adsorbed on the Ti and Cr surfaces. This suggests

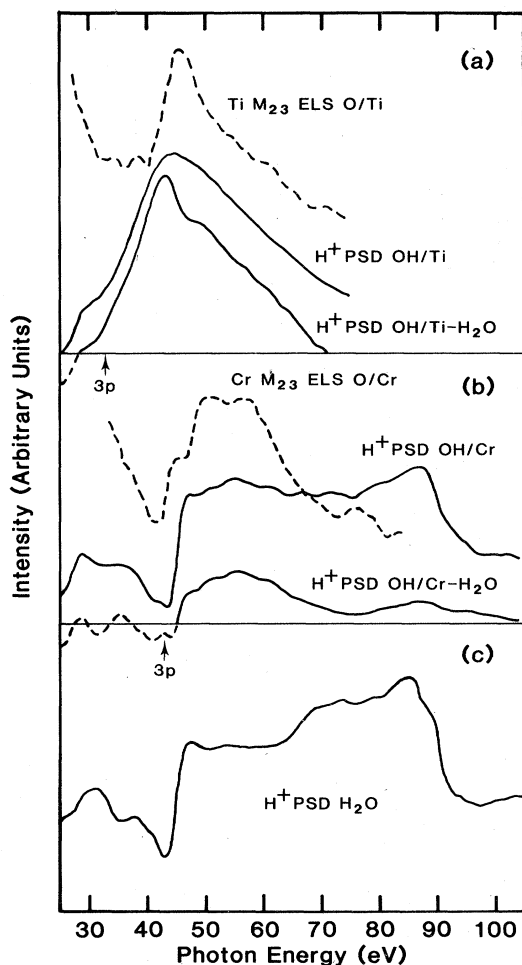


FIG. 1. (a) Comparison of the H⁺ PSD spectrum from OH/Ti and the Ti M_{23} EELS spectrum from O/Ti (Ref. 19). Also shown is a difference spectrum equal to the H⁺ PSD yield from OH/Ti minus the yield from bulk water [shown in panel (c) below]. The metallic 3*p* and 3*s* binding energies in each metal are indicated by the arrows. (b) Comparison of the H⁺ PSD spectrum for OH/Cr, the difference spectrum (obtained as described above) for OH/Cr, and the Cr M_{23} EELS spectrum from O/Cr (Ref. 7). (c) The PSD H⁺ yield from bulk solid water (~ 50 -Å-thick H₂O film).

strongly that the intramolecular excitations in chemisorbed OH are similar to those in bulk solid water as might be expected from the similarity in the potential curves for H₂O and OH.¹⁴ The H⁺ contributions above 42 eV in the H₂O films [Fig. 1(c)] are believed to arise from valence ionization plus shakeoff producing two-hole (2*h*) excitations and a resultant Coulomb explosion of the H₂O molecule. A similar contribution has been seen in the gas phase above 45 eV.¹⁴ The ~ 3 -eV shift in the 2*h* threshold between the gas and solid is comparable to the 2.3-eV change in the Auger parameter for these same systems and arises from intermolecular screening of the two holes in the solid.¹⁵ We assume that the H⁺ ion yield above $h\nu = 40$ eV arises in part from similar 2*h* excitations in chemisorbed OH [Figs. 1(a) and 1(b)].

Visual inspection of the OH/*M* spectra in Figs. 1(a) and 1(b) reveals dramatic differences and clearly suggests that

not all H⁺ contributions come from intramolecular OH excitations. Previously, comparison of the OH/Ti spectrum with the gas phase photodissociation spectrum indicated the principal H⁺ contribution with threshold around 32 eV could arise from the OH $2\sigma^{-1}$ excitation.¹⁴ However, a similar H⁺ contribution around 32 eV is not present for OH/Cr ruling this possibility out. A large H⁺ contribution for each metal appears just above the metallic 3*p* binding energy (shown by the arrows in Fig. 1) suggesting the presence of a metal core-level ASD contribution.

The presence of the 2*h*-1*e* contributions in all three PSD spectra suggests the possibility of subtracting out the intramolecular PSD contributions from the metal core-level contributions. The validity of this subtraction requires that the spectral shape of the intramolecular contribution to the OH PSD spectrum be the same as that of the bulk H₂O spectrum. Although this similarity is suggested above, we note that various processes such as differential neutralization of the many 2*h* final states could alter the spectral line shape of the intramolecular contribution from one metal to another, but the data in Figs. 1(a) and 1(b) indicate that this is not occurring to a large extent. The difference spectrum, $I(\text{H}^+(\text{OH}/M)) - aI(\text{H}^+(\text{H}_2\text{O}))$, is shown for each metal, where the constant factor *a* has been chosen to make the difference average to zero in the 24–45-eV region. The remainder in this region (indicated by the dashed lines) can be related to the uncertainty in the OH/*M* spectrum. We believe that these difference spectra are a good approximation to the metal core-level PSD contributions. However, the effect of core-level excitations is quite obvious even in the raw data of OH/Ti, without subtracting the bulk water H⁺ yield spectra. Nevertheless, the difference spectrum is useful to assess the core-level contribution to the H⁺ PSD yield particularly from OH/Cr, since in this case the Cr 3*p* threshold coincides with the 2*h* threshold of bulk water.

The metal core-level ASD contribution for each metal is compared in Fig. 1 with a spectrum that reflects the 3*p* photoabsorption cross section. Comparison of spectra with bulk systems or with metal surfaces heavily dosed with oxygen should be utilized because similar spectra for OH/*M* would primarily reflect the 3*p* cross section of the bulk metal and not of the local surface hydroxide. For each metal, the M_{23} electron-energy-loss spectrum (EELS) for O/*M* (Refs. 7 and 19) is shown. It should be mentioned that the secondary electron yield shows the same spectral shape as the electron-energy-loss spectra at the 3*p* threshold in both metals¹⁶ and oxides. This is not true for the H⁺ PSD yield observed in this study. While thresholds and peak energies are closely related to the EELS spectra, there are differences in the detailed near edge structure. Deviations of the H⁺ yield from the electron-energy-loss intensity are also observed at higher energies. This indicates that the core-level-induced H⁺ yield cannot be explained by secondary electron stimulated ion desorption.¹¹ In addition, the onset of the H⁺ ion yield is seen to occur at 25-eV excitation energy. The number of secondary electrons with kinetic energy higher than 25 eV created by photons of energy ranging between 35 and 85 eV is negligible. Therefore, for the XESD mechanism to produce the observed yields at the 3*p* thresholds for Ti and Cr would require unrealistically high ESD cross sections. Consequently, an intrinsic mechanism for H⁺ desorption from OH groups bonded to a core-hole-excited metal atom is proposed. Similar differences in the near edge structure between EELS and PSD of O⁺ from

O/Cr have been seen earlier where they were interpreted as arising from the near threshold and the higher core-hole states decaying to final states with different probabilities for subsequent desorption.⁷

Just below the Fermi level, UPS data reveal valence bands^{9,12} which we shall group into the metallic ν_0 and bonding ν_1 bands with electron density,

$$\begin{aligned} \nu_0 &= c(3d) \quad , \\ \nu_1 &= g(3d) + b(\text{O}_{2p}\text{H}) \quad . \end{aligned} \quad (1)$$

Normal Auger decay of the metal core hole creates the valence-band holes ν_0^{-2} , $\nu_0\nu_1$, and ν_1^{-2} with the relative intensity c^2 , gc , and g^2 . These relative intensities assume that the intra-atomic Auger process dominates the Auger decay;¹⁷ interatomic Auger processes which have been ignored in almost all quantitative theoretical Auger line-shape interpretations are consistent with this assumption.¹⁸

The core excited states near the $3p$ threshold and up to 10 eV beyond are quite localized $3d$ -like states but heavily mixed with the degenerate continuum which is indicated in the following the symbol $\bar{3}\epsilon d$.⁷ The possible final states resulting from decay of the $3p^{-1}\bar{3}\epsilon d$ core-hole states depend on whether the excited electron remains as a spectator ($\nu^{-2}\bar{3}\epsilon d$), participates in (ν^{-1}), or escapes (ν^{-2}) before the Auger process. The localized nature of the $\bar{3}\epsilon d$ resonances suggest that the ν^{-1} final state is an important decay mode (ν here is either ν_0 or ν_1).^{7,19} However, owing to the mixing with continuum states, ν^{-2} or $\nu^{-2}\bar{3}\epsilon d$ final states will also be significant. The one hole ν^{-1} final states ($\nu = \nu_0$ or ν_1) do not produce desorption; the ν^{-2} and $\nu^{-2}\bar{3}\epsilon d$ final

states may produce desorption because the two-hole final states have significantly longer lifetimes.²⁰ It is expected that the ν^{-2} and $\nu^{-2}\bar{3}\epsilon d$ final states will facilitate desorption only when $\nu = \nu_1$ (i.e., when the valence holes have some occupation of the OH adsorbate); thus, ν_0^{-2} , $\nu_0^{-1}\nu_1^{-1}$, $\nu_0^{-2}\bar{3}\epsilon d$, and $\nu_0^{-1}\nu_1^{-1}\bar{3}\epsilon d$ states are not expected to be active in desorption.

It should be noted that the ν_1^{-2} final state primarily responsible for the H^+ desorption is localized primarily on the OH adsorbate (i.e., $g \ll b$), although the probability for excitation is determined by the electron density on the metal substrate atom (i.e., g^2). The strong localization on the OH adsorbate provides for a sufficiently long lifetime; indeed, OH dissociation probably proceeds after the Auger process similar to the way it does following the intramolecular excitation of the $2h$ state. The ratio $g^2/(c^2+gc)$ [see Eq. (1)] decreases with the ionicity from Ti to Cr and explains why the $3p^{-1}\bar{3}\epsilon d$ contribution relative to the intramolecular contributions is much larger for Ti than for Cr.

In summary, we have established a further generalization of the Auger Stimulated Desorption (ASD) process involving photon stimulated desorption (PSD) of H^+ from OH on Ti and Cr. We have shown that molecular adsorbate dissociation arises from a metal substrate intra-atomic Auger process. The adsorbate dissociation results from a $2h$ covalent antibonding state and the metal atom does not have to be in its maximal valency state.

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