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# Reexamination of the fundamental interactions of water with uranium

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## Abstract

Interactions of  $D_2O$  with uranium metal at 85 and 300 K have been examined using surface specific techniques of thermal desorption mass spectroscopy (TDMS), ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectroscopy (SSIMS). At low temperatures (85 K),  $D_2O$  adsorbs dissociatively at low exposures ( $\leq 0.5$  L) forming a mixture of surface-bound OD, O and D species while at higher exposures both molecular and dissociative adsorption is observed. The OD species are relatively stable up to  $\sim 200$  K, above this temperature their concentration rapidly decreases (undetectable at  $T \geq 400$  K). Three  $D_2$  desorption states are observed upon annealing a  $D_2O$  layer(s) on uranium prepared at 85 K: deuterium atoms recombining directly from dissociating OD/ $D_2O$  groups between 120 and 300 K; recombination of deuterium adsorbed directly on the metal surface at  $\sim 395$  K ( $\leq 1.2$  L); and deuterium atoms that interact with the metal and recombine and desorb in the presence of an oxygen layer at  $\sim 435$  K ( $\geq 1.2$  L). At 300 K, adsorption is primarily dissociative with the formation of OD groups at higher exposures ( $\geq 3.0$  L). Similar to the 85 K adsorption, three  $D_2$  desorption states are observed in the TDMS spectra when  $D_2O$  is adsorbed at 300 K. The origin of these peaks is the same as for the 85 K except that the desorption temperature for the last peak is notably higher. This difference in  $T_{max}$  for the high-temperature peak when dosing at 300 K is attributed to thicker oxide/oxygen layer obtained when exposing the surface to  $D_2O$  at 300 K. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The interactions of  $H_2$ ,  $O_2$ , and  $H_2O$  at actinide and actinide oxide surfaces have a profound influence in the ultimate safe and stable disposition of such materials. A number of reaction scenarios present undesired consequences in the storage and stabilization of actinides. As an example, residual adsorbed water and subsequent radiolysis events can lead to undesired gas generation and pressure buildup. In addition, the concentrations of  $H_2$  and  $O_2$  arising from radiolytic or thermal events may give rise for concern with respect to their chemical incompatibility. From this background information it is a simple progression to see how these fundamental interactions pragmatically underpin an enormous number of

containment and design strategies for safe storage of actinide materials. Given the importance of these interactions, it might be anticipated that a significant investment has been made in understanding the science behind safe storage of actinide materials.

Despite the extreme relevance of these interactions, only a limited number of surface studies [1–3] have appeared that address the molecular scale chemistry of water interactions occurring at uranium and oxidized surfaces of uranium; however, there have been a fair number of scientific studies published that address these issues from engineering, historical and programmatic standpoints [4,5]. In a recent publication by Balooch and Hamza [3], the fundamental interactions of hydrogen and water on uranium metal were examined using the combined techniques of molecular beam scattering, thermal desorption mass spectroscopy (TDMS) and atomic force microscopy. In examining this publication, we were intrigued by the interpretation of the thermal

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chemistry monitored by TDMS of H<sub>2</sub> following water exposure at 300 K. Hydrogen was observed to desorb in three states from uranium following H<sub>2</sub>O exposure with the first feature at 360 K being attributed to recombination of adsorbed H atoms from a clean U surface and the higher temperature feature seen desorbing at 490 K being attributed to decomposition of surface hydroxyls. A noticeable shoulder was also observed following the largest exposures on the low-temperature side of the 490 K feature and was assigned to the decomposition of bulk UH<sub>3</sub>. In some of our recent work using the molecular level probes of ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectroscopy (SSIMS), we were able to follow the interfacial growth of surface hydroxyls following water exposure to UNb alloys [21]. Furthermore, the thermal conversion of surface hydroxyls to oxide with concomitant release of H<sub>2</sub> (or D<sub>2</sub>) was also monitored and appeared to be opposite that suggested to be occurring at U surfaces [3]. In light of this inconsistency, we have reexamined the fundamental interaction of water at uranium metal surfaces using the combined techniques of TDMS, SSIMS, UPS and XPS, and suggest a different interpretation for hydrogen desorption following water exposure at uranium surfaces.

## 2. Experimental procedures

Experiments were performed in an ultra-high vacuum (UHV) chamber with base pressures of less than  $4 \times 10^{-8}$  Pa acquired by a combination of turbomolecular, ion and titanium sublimation pumps. The UHV chamber contains instrumentation to obtain XPS, UPS, TDMS and SIMS measurements. The XPS data were taken using a MgK $\alpha$  source ( $h\nu = 1253.6$  eV) with an incident X-ray power of 200 W. The UPS data were collected using the radiation from the HeI resonance line ( $h\nu = 21.2$  eV). Photoelectrons emitted from the sample were energy selected using a commercial hemispherical analyzer (Physical Electronics, Eden Prairie, MN, Omnicfocus 3 Analyzer) with the pass energies for the XPS and UPS measurements being 47 and 3 eV, respectively. All XP and UP spectra reported herein are given in terms of binding energy (BE). TDMS measurements were acquired with a quadrupole mass spectrometer (Leybold, Model SSM 200) that was able to monitor multiple masses simultaneously. The ramp rate (3 K/s) was controlled by a Eurotherm temperature controller. Static SIMS measurements were acquired using a differentially pumped 3 keV Ar<sup>+</sup> ion beam passed through a Wien filter rastered over a  $2 \times 2$  mm<sup>2</sup> area. Ion beam doses were kept below a level necessary for noticeable disruption of the surface concentration of adsorbate.

The polycrystalline sample was mechanically polished to a mirror finish. Purity of the bulk uranium was

99.97% with the major impurity being C at 300 ppm. Tantalum wires (0.010 in. dia.) were spot-welded to opposite ends of the sample mounted on a holder that permitted resistive heating and liquid nitrogen cooling to a base temperature of 85 K. Temperatures were measured using a type K thermocouple spot welded to the edge of the foil. Initial cleaning was achieved by alternate hot (675 K) and cold (298 K) sputtering cycles using 5 keV Ar<sup>+</sup> ions until no trace of oxygen or carbon could be detected by XPS.

The D<sub>2</sub>O used in this study was purchased from Aldrich and reported to have 99.9 at.% deuterium. Before using, D<sub>2</sub>O was degassed by multiple freeze pump thaw cycles prior to exposure to the uranium metal. A directional gas doser of conventional design [7] was used in this study with an enhancement factor determined previously to be  $\sim 100$  [6]. Deuterium (99.98 at.% D) was acquired from Matheson and used without further purification. For all spectra, exposures are reported in Langmuir ( $1.33 \times 10^{-4}$  Pa s<sup>-1</sup>) which includes the enhancement factor for the directional doser.

## 3. Results

Fig. 1 illustrates the TDMS traces monitoring desorption of D<sub>2</sub>O ( $m/e = 20$ ) after exposing a clean uranium surface to D<sub>2</sub>O at 85 K. For low exposures of D<sub>2</sub>O (0.5 and 0.7 L), there are essentially no desorption features in the  $m/e = 20$  channel. Therefore, at these coverages, D<sub>2</sub>O primarily undergoes dissociation. This finding is consistent with that for water molecules on many clean metal surfaces [8]. We only detected significant quantities of D<sub>2</sub> desorbing from the surface at these coverages (illustrated below). Therefore, there is no recombination of atomic deuterium and oxygen at

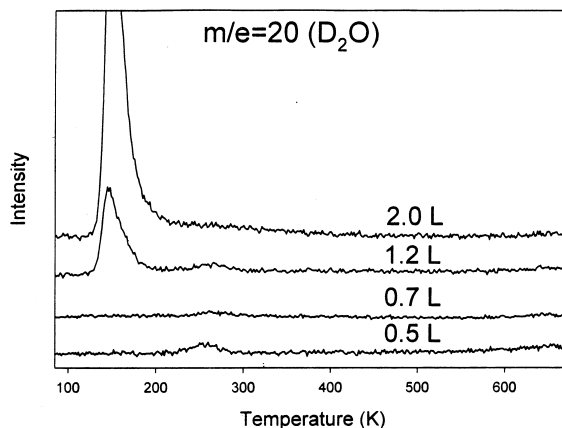


Fig. 1. Thermal desorption mass spectra monitoring the  $m/e = 20$  (D<sub>2</sub>O) channel after dosing increasing amounts of D<sub>2</sub>O at 85 K on a clean uranium surface.

higher temperatures to form  $D_2O$ . Apparently, all oxygen from dissociated  $D_2O$  became irreversibly bound to the metal at these temperatures. There is a very small feature at  $\sim 250$  K which may point to a strongly chemisorbed state of  $D_2O$ <sup>1</sup> [9]. It is also possible that observed  $D_2O$  at this temperature could be due to desorption from areas other than the prepared surface (e.g. sides of the uranium sample or the sample holder).<sup>2</sup> Because the overall intensity suggests that the amount of  $D_2O$  is very small, we do not consider it further.

For exposures exceeding one monolayer (1.2 and 2.0 L) there is a significant desorption feature at  $\sim 155$  K, which does not reach saturation. The low desorption peak temperature indicates that  $D_2O$  in this state arises from the sublimation of ice and is only weakly bound [8,10]. Because, this is the only significant desorption feature of  $D_2O$  at any exposure, it might be rationalized that the desorption kinetics of  $D_2O$  in direct contact with the metal might be degenerate with the desorption kinetics of the ice multilayers. Reference again to the desorption traces performed at lower exposures reveals this not to be the case: the  $D_2O$  layer in direct contact with the surface undergoes dissociation. As will be shown below, a significant amount of dissociation occurs upon adsorption at 85 K. It can be concluded that the feature at  $\sim 155$  K arises from  $D_2O$  not interacting with the surface but instead with a tightly bound  $D_2O/OD/O$  layer in direct contact with the surface. One desorption peak for large exposures of water to clean uranium at low temperatures was observed by Winer et al. [1,2] as well. They also claimed that this feature arises from water that is not interacting directly with the surface; however, their desorption temperature was approximately  $45^\circ$  higher (200 K) than what we observed. Such a high desorption temperature is indicative of a state that is interacting directly with the metal surface [8].

Fig. 2 illustrates the TDMS traces monitoring  $m/e=4$  after exposing  $D_2O$  at 85 K. At all exposures there is a low-temperature feature centered at approximately 180 K, which increases in intensity with coverage. Interestingly, this peak is extremely broad having significant intensity for nearly  $200^\circ$  (100–300 K). Previous studies have shown that hydrogen on a clean uranium surface recombines and desorbs above 300 K [3,11]. Therefore, this feature must arise from dissociation of  $D_2O$  and/or OD and not surface-bound deuterium at-

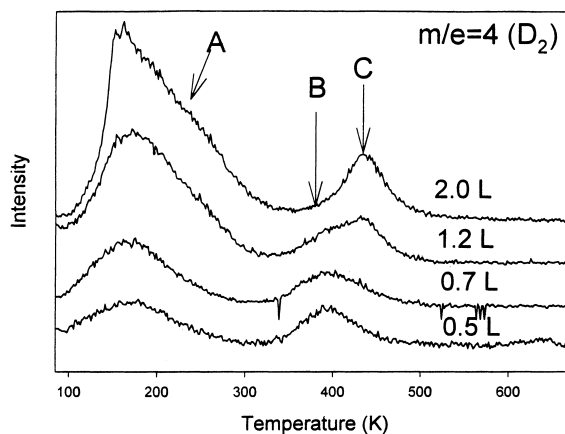


Fig. 2. Thermal desorption mass spectra monitoring the  $m/e=4$  ( $D_2$ ) channel after dosing increasing amounts of  $D_2O$  at 85 K on a clean uranium surface.

oms (addressed in Section 4). For the highest exposure (2.0 L) there is an extra component in this feature at the low-temperature side. This is attributed to a cracking fragment of  $D_2O$ , which desorbs from the multilayer at this temperature (Fig. 1, top trace). Two higher desorption features are observed above 300 K, which are labeled as peaks B and C. At low coverages (0.5 and 0.7 L), there is only one desorption feature at  $\sim 395$  K. The desorption temperature is consistent with desorption of hydrogen from a clean uranium surface [3,11]. The trace for an exposure 1.2 L exhibits two unresolved peaks at  $\sim 395$  and 435 K. After an exposure of 2.0 L, only the 435 K feature is present. The nature of these two desorption peaks will be addressed thoroughly in Section 4.

UP spectra were taken prior to each temperature ramp for the exposures in Fig. 2 to detect species present on the surface at 85 K (Fig. 3). The bottom spectrum is characteristic of a clean U surface [12,13]. There is an intense emission feature near the Fermi-level that is attributed mainly to the U 5f states. A weak feature also exists at 2.3 eV due to the U 6d states of the clean metal.

An exposure of 0.5 L  $D_2O$  at 85 K to the clean uranium surface produces two new emission features at  $\sim 6.3$  and 10.1 eV. This two-peak pattern provides strong evidence for the formation of hydroxyls on the surface at these exposures [14,15]. The two valence levels responsible for these photoelectron peaks are the  $1\pi$  (6.3 eV) and the  $3\sigma$  (10.1 eV) orbitals. Dissociative adsorption of  $D_2O$  at low coverages has also been observed on other clean metal surfaces [16–19]. As discussed below, it is likely that dissociation results in a mixture of hydrogen-, oxygen- and hydroxyl-bound species. Lack of ice photoemission data at these exposures is consistent with the TDMS data, which show no multilayer formation (lack of desorption feature at  $\sim 155$  K).

<sup>1</sup> The desorption temperature is too low to indicate recombination of atomic hydrogen and oxygen. Expected temperatures for this occurrence usually exceed 250 K.

<sup>2</sup> Careful positioning of the uranium surface with respect to the entrance cone of the mass spectrometer greatly reduces the amount of desorbing species detected that do not arise from the prepared surface.

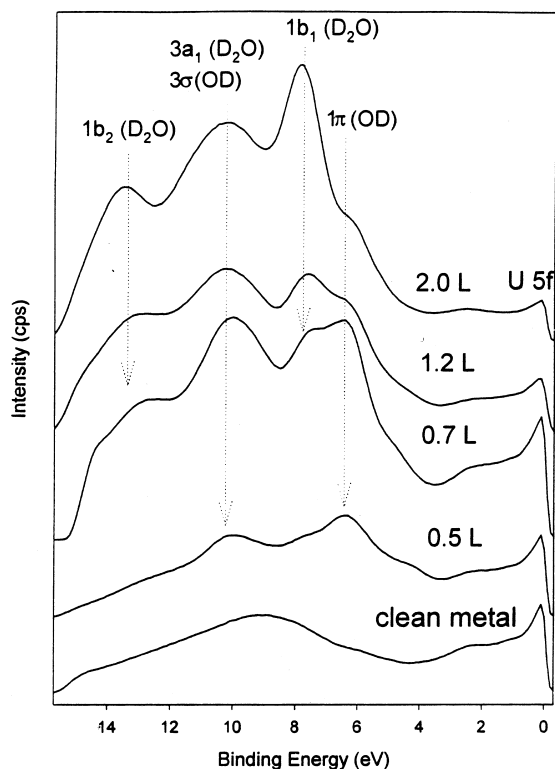


Fig. 3. Ultraviolet photoelectron spectra collected using the HeI resonance line after dosing increasing amounts of  $D_2O$  at 85 K on a clean uranium surface.

There are significant changes in the UP spectrum after an exposure of 0.7 L  $D_2O$ . First, emission features from surface-bound hydroxyls appear to increase, now being located at  $\sim 6.5$  and  $10.1$  eV. The second noticeable difference is that there are new features growing in at  $\sim 7.5$  and  $12.7$  eV. Thus, not only is the concentration of hydroxyls increasing but also there is an appearance of a new surface-bound species which is assigned to molecularly adsorbed  $D_2O$ . A three-peak pattern is expected for the molecular adsorption of water arising from the  $1b_1$ ,  $3a_1$  and  $1b_2$  orbitals [15]. Characteristic positions for these photoelectron peaks are  $5.5$ – $7.5$ ,  $8$ – $10$  and  $12$ – $14$  eV, respectively [8,15]. We do not observe a new emission feature from the  $3a_1$  orbital since it is close to the energy of the  $3\sigma$  orbital of hydroxyl. Even though molecularly adsorbed  $D_2O$  is observed at this exposure, no desorption of  $D_2O$  is observed in the TDMS spectrum (Fig. 2). Thus, all molecularly adsorbed water (and OD) at this coverage (0.7 L) must undergo complete dissociation at higher temperatures to leave surface-bound oxygen and desorb deuterium.

With increasing exposures (1.2 and 2.0 L), the photoelectron peaks due to molecularly adsorbed water

increase without much variation in position.<sup>3</sup> At these exposures, there is desorption in the  $m/e = 20$  channel ( $D_2O$ ) at  $\sim 155$  K due to ice sublimation. Once again, the data strongly suggest that  $D_2O$  desorption only occurs from multilayers residing on a  $D_2O/OD/D$  layer interacting directly with the surface. Significant intensity remaining near the Fermi-level after dosing 2.0 L  $D_2O$  indicates that there is only a thin layer of bound species at this exposure.

The existence of hydroxyl groups on the surface after dosing with  $D_2O$  was confirmed by SSIMS following the negative ions. Fig. 4 illustrates these spectra after dosing 2 L  $D_2O$  on a clean uranium surface at 85 K and annealing to increasing temperatures. Significant intensity is only observed in the  $m/e = 4$ ,  $m/e = 16$  and  $m/e = 18$  channels corresponding to the mass fragments  $D^-$ ,  $O^-$  and  $OD^-$ , respectively. Since this is above the exposure required to create multilayers at 85 K, we expect that the intensity in the  $m/e = 18$  channel ( $OD^-$ ) before annealing primarily arises from a combination of molecularly adsorbed  $D_2O$  (of which OD is a cracking fragment) and adsorbed hydroxyl groups. Similarly,  $D^-$  is due to cracking fragments of  $D_2O$  and hydroxyls as well as from deuterium directly adsorbed on the metal.

Annealing to 175 K, however, either removes molecularly bound  $D_2O$  or causes it to thermolytically dissociate. Therefore, the signal in the  $OD^-$  channel primarily arises from hydroxyls residing on the surface. It is also possible that sputtered deuterium and oxygen atoms recombine in the gas phase to form  $OD^-$ ; however, the probability of this is very low because to the low flux of atoms inherent in the SSIMS experiment [20]. If recombination were a significant pathway, intensity in the  $OD^-$  channel should be significant until hydrogen desorbs. The data in Fig. 1 illustrated that hydrogen desorbs at temperatures exceeding 350 K [3,11], whereas it is observed in the spectra that the  $OD^-$  signal greatly attenuates before this temperature. The intensity in the  $OD^-$  channel is the greatest after annealing to 175 K but this does not necessarily indicate that there are more surface-bound hydroxyl groups than at 85 K. At 85 K, there is a layer(s) of  $D_2O$  residing on the species that are in direct contact with the surface. Sputtering at this temperature preferentially removes the outer molecular layer(s) of  $D_2O$ . It is possible that there are more hydroxyl species present on the surface at 85 K and that a certain fraction dissociates upon annealing to 175 K. Other studies (shown below) reveal that only a small percentage, at most, of the hydroxyls dissociate upon annealing to 175 K. Therefore, we can state that the 175 K spectrum is a fair indication of the maximum fractional coverage of hydroxyls possible when dosing at 85 K. Unfortunately,

<sup>3</sup> At higher multilayer coverages, the peak positions should shift closer to values expected for gas-phase  $D_2O$ .

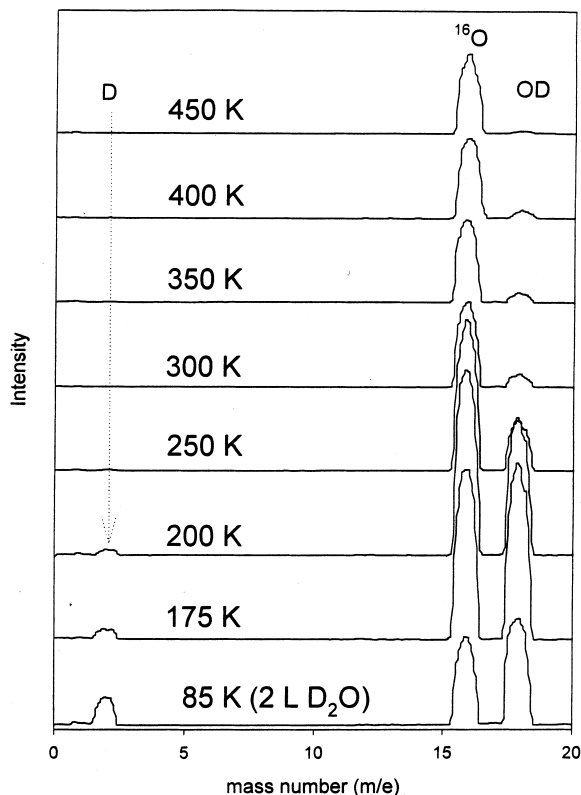


Fig. 4. Static secondary ion mass spectroscopy (negative ions) collected after exposing a clean uranium surface to 2 L  $D_2O$  at 85 K and annealing to progressively higher temperatures. The  $m/z$  region spans from 0 to 20 amu.

with the available data we are not able to calculate the fractional coverage of OD on the surface. From related work, we believe that the surface hydroxyl concentration (OD/O) may be as high as 0.3 [21].

Annealing to higher temperatures attenuates the signal observed in the  $m/e = 18$  channel. By 250 K, the signal is only about 25% of that observed in the 175 K spectrum. The intensity drops drastically at 300 K and is nearly gone after annealing to 400 K. It is interesting to note that there are small amounts of hydroxyls present on the surface at temperatures as high as 400 K. Significant intensity in the  $m/e = 16$  ( $O^-$ ) channel is observed even after annealing to 450 K due to surface-bound oxygen.

In order to accurately explore the temperature-dependent behavior of surface-bound hydroxyl groups, a small amount of  $D_2O$  (0.5 L, below the onset of molecular adsorption) was dosed on clean uranium surface (Fig. 5). For comparison, the spectrum obtained after exposing a clean uranium surface to 500 L  $O_2$  at 500 K is shown; it was illustrated previously that this procedure produces a thin film of stoichiometric  $UO_{2.0}$  [6,11,21]. Since the oxide thickness is greater than the inelastic mean free path for photoelectrons created by ultraviolet

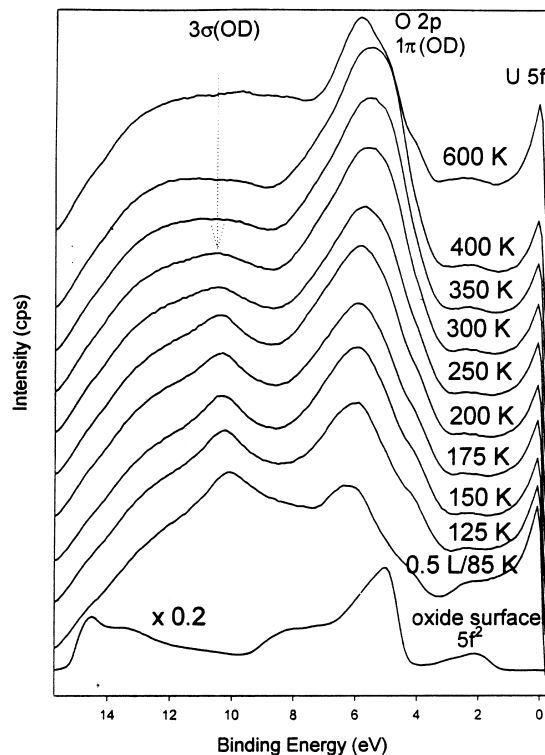


Fig. 5. Ultraviolet photoelectron spectra collected using the HeI resonance line after dosing 0.5 L  $D_2O$  at 85 K and annealing to progressively higher temperatures.

radiation (HeI resonance line), there is no intensity near the Fermi-level arising primarily from the U 5f states. Below 14 eV, there are two emission features at 2.1 and 5.0 eV due to the localized U  $5f^2$  band and the O 2p level of uranium oxide, respectively. The shape and position of these photoelectron peaks are very similar to those found for  $UO_2$  [12,22].

Similar to Fig. 3, there are two features at 6.2 and 10.1 eV after a dose of 0.5 L  $D_2O$  at 85 K due to the  $1\pi$  and  $3\sigma$  orbitals of surface-bound hydroxyl groups. Annealing the surface up to 175 K produces very little change in the UPS spectra – the emission features shift position slightly to 5.9 and 10.4 eV. There is, however, a significant change in the relative intensities of the two peaks after annealing to temperatures up to 175 K. The feature near 6 eV appears to be increasing measurably, whereas the feature near 10 eV changes only slightly. This could be due to a slight conversion of hydroxyls to surface-bound oxygen and deuterium between 85 and 175 K; judging from the loss in intensity of the 10 eV feature, the conversion must be small. The noticeable change in intensity for the emission feature at 6 eV could be due to a significantly larger cross section for photoelectron creation of a surface-bound oxygen relative to a hydroxyl species.

Annealing to temperatures greater than 175 K, attenuates the signal near 10 eV while increasing the signal near 6 eV (this signal shifts to  $\sim 5.5$  eV upon annealing to 400 K). In agreement with the previous SSIMS data this is due to a conversion of hydroxyls to surface-bound oxygen and deuterium. There is no observable intensity due to hydroxyl species after annealing the surface to 400 K. Even though at temperatures near 400 K there is only surface-bound oxygen (small amounts of deuterium could be present), the position and shape of the O 2p photoelectron peak does not resemble that for  $\text{UO}_2$ . Additionally, there is not a significant emission peak near 2.0 eV from the localized U 5f<sup>2</sup> level. The almost symmetrical shape of the O 2p photoelectron peak is more indicative of chemisorbed oxygen [23]. Evidently, these exposures are not high enough to create a uranium oxide surface. Evidence for a very small concentration of oxygen on the surface is also provided by the small reduction in intensity near the Fermi-level and the near-surface region still appears to be largely metallic. As will be shown shortly, at higher temperatures and exposures the transformation from a chemisorbed oxygen surface species to an uranium oxide film can be achieved.

Annealing to 600 K reduces the intensity of the peak near 6 eV which is due to the O 2p photoelectrons. This is due to increased mobility of the anion (diffusing further into the surface). XPS measurements (data not shown) showed increased uranium metal after annealing to this temperature.

As shown above only the layer of adsorbates in direct contact with the uranium metal remain on the surface when  $\text{D}_2\text{O}$  is adsorbed at 85 K and annealed. In order to understand in more detail the nature of the dissociated fragments of  $\text{D}_2\text{O}$ , we exposed clean uranium to  $\text{D}_2\text{O}$  at room temperature (300 K) and acquired TDMS and UPS measurements. When exposures are made at this temperature, the spectra (especially the UP spectra) will not be dominated by features from adsorbed water because the ice sublimation layers desorb at much lower temperatures ( $<200$  K). Additionally, exposing the surface to  $\text{D}_2\text{O}$  at this temperature should increase the surface coverage of adsorbates.

Figs. 6 and 7 illustrate the TDMS and UPS measurements taken after exposing a clean uranium surface to  $\text{D}_2\text{O}$  at 300 K. For exposures between 0.2 and 1.5 L, there is only one desorption feature in the  $m/e = 4$  ( $\text{D}_2$ ) channel at approximately 395 K. We assign this peak to recombination of surface-bound deuterium. Similar desorption temperatures were seen when only  $\text{D}_2$  was adsorbed on a clean metal surface [3,11]. The TDMS lineshapes change very little with exposures up to 1.5 L: there is only one desorption feature at  $\sim 400$  K that increases in intensity. At these exposures (0.2–1.5 L), the UP spectra (Fig. 7) exhibit only one photoelectron peak between 5.9 and 5.7 eV due to the O 2p level of adsorbed oxygen. The shape and position of this emission feature

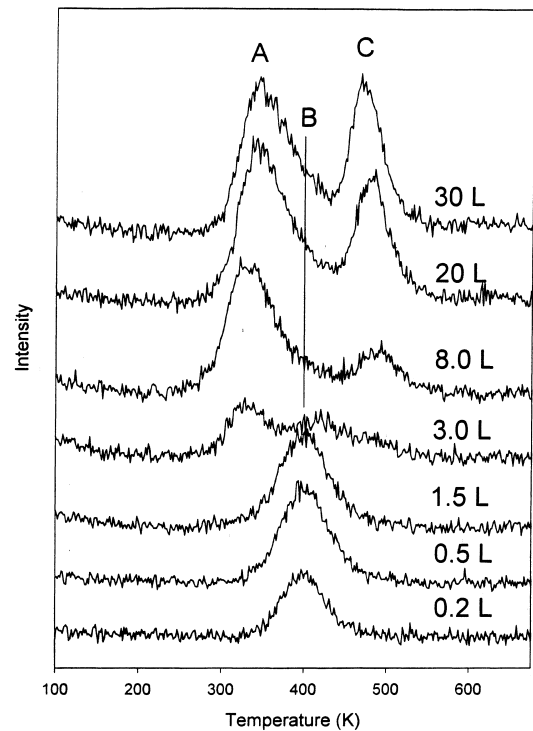


Fig. 6. Thermal desorption mass spectra monitoring the  $m/e = 4$  ( $\text{D}_2$ ) channel after dosing increasing amount of  $\text{D}_2\text{O}$  at 300 K on a clean uranium surface.

indicates that the surface-bound oxygen is largely chemisorbed [23]; as shown below, however, the nature of the surface-bound oxygen changes with increasing exposures. Interestingly, there is no evidence for hydroxyl species present on the surface below a coverage of 1.5 L. Therefore, all deuterium must be bound directly to the surface at these coverages which confirms our assignment made previously.

At exposures of 3.0 L or greater, the TDMS traces monitoring  $\text{D}_2$  desorption change significantly. Two desorption features due to the recombination of surface-bound deuterium replace the single desorption feature. The peak temperatures in the 3.0 L trace are at  $\sim 340$  and 420 K. Dosing the surface with 8.0 L  $\text{D}_2\text{O}$  at 300 K produces two desorption features at  $\sim 340$  and 490 K. While there is little change in the position or intensity of the low-temperature feature for exposures beyond 8 L, the amount of  $\text{D}_2$  desorbing at  $\sim 490$  K appears to increase substantially up to 30 L. Complimentary UPS measurements at these exposures allowed us to understand the origin of the two desorption features in the TDMS traces. Starting at an exposure of 3.0 L (and especially noticeable at 8 L) there is an additional feature at  $\sim 10.5$  eV, shifting to  $\sim 10.7$  eV with higher exposures. As discussed previously, this emission feature arises from the  $3\sigma$  orbital of adsorbed hydroxyls [14,15]. It cannot be due

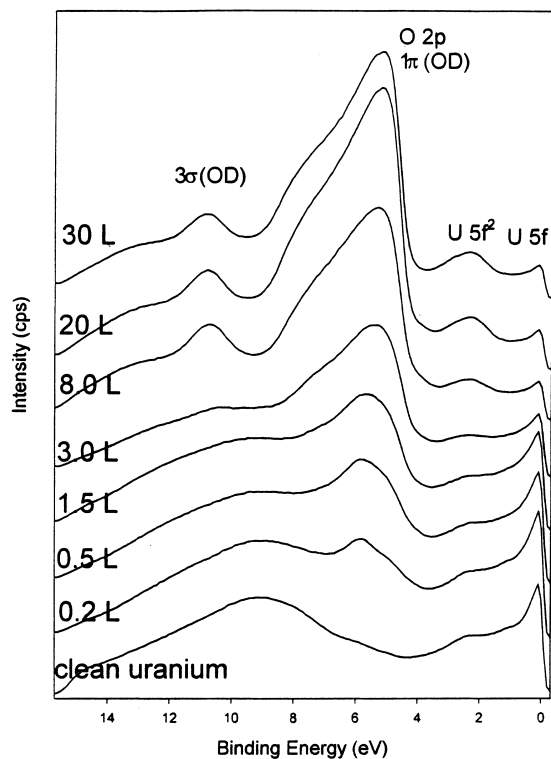


Fig. 7. Ultraviolet photoelectron spectra collected using the HeI resonance line after dosing increasing amounts of  $D_2O$  at 300 K on a clean uranium surface.

to adsorbed  $D_2O$  for two reasons: molecular  $D_2O$  is not stable on the surface at this temperature; and a photoelectron peak at  $\sim 12.5$  eV, which would arise from the orbital of  $1b_2$   $D_2O$ , is not present [15]. Annealing the surface to 400 K removes any adsorbed hydroxyl groups as indicated by the loss of the emission feature at  $\sim 10.7$  eV (data not shown). With this information, we can assign the desorption feature at  $\sim 340$  K to the recombination of deuterium atoms from dissociating hydroxyl groups present on the surface. It is also worthwhile to observe that the intensities of the 10.7 eV emission feature (in the UP spectra) and the 340 K desorption feature (in the TDMS data) do not increase between 8 and 30 L. Therefore, a saturation coverage of adsorbed hydroxyl groups must be attained at after 8 L exposure. The high-temperature  $D_2$  desorption feature at  $\sim 490$  K is assigned to recombination of surface-bound deuterium. Our assignment contradicts that previously proposed by Balooch and Hamza [3]. They assigned the low-temperature desorption feature to recombination of surface-bound hydrogen and the high-temperature feature to dissociating hydroxyl groups. The nature of the adsorbed species on the surface at 300 K is discussed below.

The UP spectra collected at higher exposures of  $D_2O$  strongly suggest the formation of a uranium oxide film.

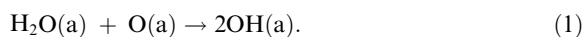
Direct evidence for this is found by examining the two emission features at 2.3 and 5.2 eV observed at exposures of 8.0 L or greater. The position and shape of the feature at 5.2 eV, having a shoulder on the high BE side, is similar to that observed for the O 2p states of  $UO_2$  [13,22]. Additionally, the peak at 2.3 eV arises from photoelectrons from the localized U  $5f^2$  level of uranium oxide [13]. Significant intensity remaining near the Fermi-level indicates that the amount of uranium oxide near the surface region is small even at 30 L exposure. XPS measurements shown in Fig. 8 confirm that the amount of oxide near the surface relative to uranium metal is very small. <sup>4</sup> Oxide growth is indicated by the photoelectron peaks from the U  $4f_{7/2}$  and  $4f_{5/2}$  core levels at  $\sim 381$  and 392 eV, respectively [1,2,24–26]. As can be seen the amount of oxide growth near the surface region is very small relative to surface prepared with 150 L  $O_2$  at 300 K (in this spectrum there is no indication of uranium metal).

#### 4. Discussion

The studies described above have provided additional insight into the reactivity of  $D_2O$  on clean uranium and the adsorbed species present as a function of temperature and exposure. In our opinion, the combined data [1–3] collected previously were not complete, thereby preventing an adequate description of the uranium- $D_2O$  interaction. Accordingly, we have performed these studies as well as those reported elsewhere [21]. Below, we describe in more detail the important findings from our work together with the insights provided by the studies performed previously [1–3,6,27,28].

##### 4.1. Water adsorbed on clean uranium at low temperatures (85 K)

At low exposures on uranium,  $D_2O$  was observed to undergo dissociation to form surface-bound hydroxyl groups. Dissociation of  $D_2O$  at low temperatures to form hydroxyl groups has also been observed on a limited number of other clean metal surfaces [17–19]. On a larger number of metal surfaces, however, formation of hydroxyl groups at low temperatures was observed in the presence of surface-bound oxygen at low exposures by the mechanism shown below after molecular adsorption occurred on the clean surface [10,14,29–35].



<sup>4</sup> The inelastic mean free path for photoelectrons for XPS is greater than that for UPS. Nevertheless, the measurement does indicate the small amount of uranium oxidation.

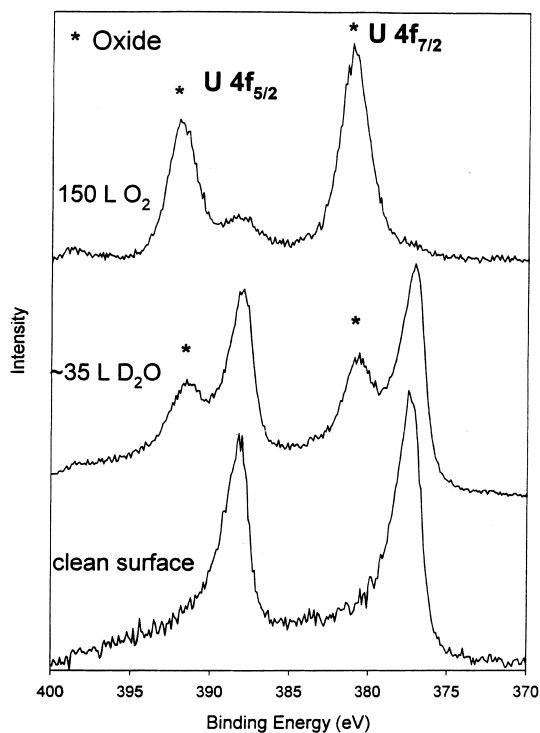
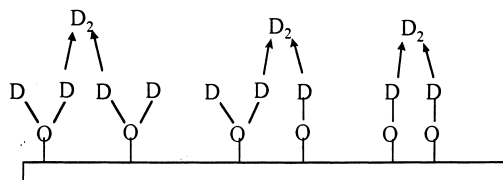


Fig. 8. The U 4f phototoelectron spectra after the following treatments to a clean uranium surface: clean surface; 35 L D<sub>2</sub>O at 300 K; and 150 L O<sub>2</sub> at 300 K.

We believe that a similar reactivity pattern is occurring on the uranium surface. That is, at extremely low exposures of D<sub>2</sub>O complete dissociation occurs leaving surface-bound oxygen atoms, which subsequently react with adsorbed water to form hydroxyl groups. In fact, our UPS data (not shown) suggest that there are no hydroxyl groups for exposures below 0.2 L D<sub>2</sub>O. Studies by Kumar et al. of H<sub>2</sub>O chemisorption on lanthanum suggested that only oxide and hydride formed at low exposures with hydroxide formation beginning only after ~35 L exposure [36]. They obtained a saturation OH/H ratio of ~0.4 from integrating the respective OH and O components of the O 1s photoelectron peak (from XPS measurements). Undesirable signal-to-noise levels precluded such a quantification of the components in the O 1s photoelectron peak in our XP spectra. At exposures where the component from the hydroxyl is evident the signal intensity is very low, while at higher exposures the signal from the ice sublimation layer dominates the O 1s photoelectron peak making quantification of the different components impossible. We have, however, obtained a OH/H ratio of ~0.35 for the similar U6Nb surface after saturation with D<sub>2</sub>O at 175 K [21].

Significant dissociation occurs at temperatures below 200 K after annealing a surface-bound layer of D<sub>2</sub>O and

OD groups (Fig. 2). Even at low exposures, where it was shown by UPS that only adsorbed hydroxyl species exist (along with adsorbed oxygen and deuterium), there is a fair amount of D<sub>2</sub> desorbing upon annealing at low temperatures. We believe that D<sub>2</sub> desorption at these temperature results from direct recombination of deuterium atoms from dissociating D<sub>2</sub>O/OD groups as shown below.

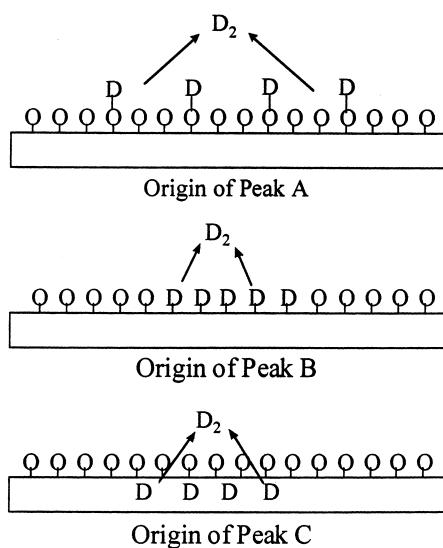


Two observations support this conclusion. First, if the deuterium became directly bound to the surface it would desorb at a much higher temperature, as was illustrated when D<sub>2</sub> was directly adsorbed on a clean metal surface [3,6]. The second piece of information was provided by an experiment in which a small amount of H<sub>2</sub>O was dosed at 85 K followed by a large dose of D<sub>2</sub> (data not shown) [34]. If desorption was occurring from surface-bound H (or D) species there should be significant intensity for the HD and D<sub>2</sub> channels at low temperatures whereas significant amounts of HD or D<sub>2</sub> only desorbed at temperatures above 300 K. Direct recombination of deuterium from dissociating D<sub>2</sub>O/OD groups also suggests that these groups must be in close proximity even at low coverages. Hydrogen-bonded clusters have been observed on metal surfaces at temperatures as low as 20 K even for very small coverages [8,37].

High-temperature desorption (>350 K) of D<sub>2</sub> after adsorbing D<sub>2</sub>O at 85 K also indicates that a certain fraction of deuterium atoms become bound to the surface. Thus, there are two pathways for deuterium upon dissociation of adsorbed D<sub>2</sub>O/OD groups; either the atoms recombine directly (low-temperature desorption feature as shown in Scheme 1) or they become adsorbed on the metal surface (high-temperature desorption feature). The high-temperature desorption is somewhat complicated, however, because of the presence of two D<sub>2</sub> desorption features at 395 and 435 K (peak B and C, respectively). Peak B is present only at doses below 2.0 L while peak C is only manifested after an exposure of at least 0.7 L. In order to understand the origin of these two desorption features, it is first necessary to qualitatively characterize the nature of the surface as a function of exposure. At the two lowest exposures (0.5 and 0.7 L), lack of desorption from the ice sublimation layer (Fig. 1) indicates that only a submonolayer of adsorbates are on the surface. Annealing produces an incomplete layer of surface-bound



oxygen with areas/patches of uranium/uranium hydride (H or D atoms) still exposed to vacuum. At higher coverages, a more complete monolayer of surface-bound adsorbates is formed (as indicated by multilayer desorption at  $\sim 155$  K).<sup>5</sup> In contrast to submonolayer exposures, annealing such a coverage probably produce a near complete surface-bound oxygen layer. It was shown in complimentary studies that a layer of oxygen atoms will reside near the surface while the hydrogen/deuterium atoms will reside below this surface-bound oxygen layer(s) [11]. Therefore, hydrogen or deuterium present on the surface should not prevent the formation of surface-bound oxygen layers. For low exposures (below multilayer formation), deuterium atoms recombine and desorb from the uranium surface that is not covered with oxygen (peak B). The temperatures for desorption ( $\sim 395$  K) agree well with those when deuterium is adsorbed on a clean uranium metal surface at 85 K. Peak C is attributed to deuterium atoms that recombine and desorb in the presence of a near complete or complete surface-bound oxygen layer. Evidently, the presence of this oxygen layer provides an energetic barrier to the desorption of deuterium/hydrogen. Co-adsorption of deuterium and oxygen showed similar results [11]. In these studies a large amount of  $D_2$  was exposed to a clean uranium surface followed by carefully controlled exposures of oxygen. This experimental procedure produced an oxide layer coexisting with metal-bound deuterium. Deuterium desorption temperatures increased in proportionally with the coverage of the oxide layer. Temperatures for  $D_2$  desorption ranged from  $\sim 390$  to 580 K, with 390 K corresponding to a clean surface and 580 K from a surface with a corresponding oxide layer thickness of 60 Å [11]. In contrast to this, only a single layer of surface-bound oxygen is produced from any exposure of  $D_2O$  at 85 K since all  $D_2O$  desorbs that is not in direct contact with the surface. The difference in desorption temperature appears to be directly related to thicknesses of the surface-bound oxygen layers produced by adsorbing  $D_2O$  or oxygen. As shown below,



a thicker oxide layer can be prepared by dosing with  $D_2O$  at higher temperatures causing a shift to higher temperatures of the  $D_2$  desorption feature.

#### 4.2. Water adsorbed on clean uranium at high temperatures (300 K)

Insights gained from the studies performed when water ( $D_2O$ ) was exposed to a clean uranium metal surface at 85 K helped in understanding the information in the TDMS/UPS measurements when  $D_2O$  was exposed at 300 K to the clean surface. Following low exposures of  $D_2O$  (300 K), there is a single  $D_2$  desorption feature at approximately 400 K. Because of similarities in the spectra for low-temperature exposures, this feature (peak B) can be assigned to recombination and desorption of deuterium from a metal surface with an incomplete layer of surface-bound oxygen. At higher exposures two peaks develop on the high- and low-temperature side of the original peak at 400 K. As discussed above, the low-temperature peak (peak A) is due to deuterium atoms that recombine directly from dissociating hydroxyl (OD) groups. The high-temperature peak (peak C, starting at  $\sim 430$  K and shifting to  $\sim 490$  K) is assigned to deuterium atoms that recombine and desorb in the presence of a layer(s) of surface-bound oxygen/oxide. The increase in desorption temperature of peak C indicates that a thicker surface-bound oxygen/oxide layer must be present for large exposures of  $D_2O$  on uranium at 300 K than are produced by annealing a multilayer of  $D_2O$  from 85 K. UP spectra support this conclusion: the relative intensity of the O 2p level is much greater after a large exposure of  $D_2O$  at 300 K. If the above argument is true, peak C should grow and

<sup>5</sup> It is also possible that multilayer formation commences before saturation of the first layer. Even though this probably occurs to a small extent, we believe that the first layer is close to saturation before the multilayer formation for the following reasons:  $D_2$  desorption increases only slightly (ignoring the cracking fragment of  $D_2O$  desorbing from the multilayer) upon increasing the exposure from 1.2 L to 2.0 L; and the heat of adsorption for  $D_2O$  on the clean uranium metal is probably significantly greater than intermolecular bonding since it dissociates at low temperatures (a certain fraction below 85 K).

shift to higher temperature with larger exposure as the oxide layer increases. For the exposures shown in this study, peak C does not shift; however, for much larger exposures (>500 L), however, peak C does shift to higher temperatures with a proportional increase in its intensity.

In some aspects, our data are similar to that reported by Balooch and Hamza [3]. They also adsorbed D<sub>2</sub>O on a clean uranium surface at 300 K and monitored D<sub>2</sub> desorption, but never observed one desorption feature for D<sub>2</sub> at ~400 K. Instead, their lowest exposure spectrum appeared similar to our highest exposure spectrum. Evidently, their exposures were too high to observe desorption of D<sub>2</sub> from a surface with an incomplete layer of surface-bound oxygen. The assignments by Balooch and Hamza also differ somewhat from the ones that we have proposed. It was suggested in their study that peak A originated from surface-bound deuterium (or hydrogen in their case) while peak C originated from dissociating hydroxyl groups. We believe that the assignments made by Balooch and Hamza are incorrect primarily due to the lack of low-coverage data. The deuterium/hydrogen desorption feature arising from uncovered uranium surface (with respect to surface-bound oxygen) was never actually identified. Additionally, our UPS data clearly show that any hydroxyls present on the surface at 300 K are gone after annealing to 400 K. Therefore, the dissociation of these species could not produce the feature exceeding this temperature. A more thorough comparison of our data and that from Balooch and Hamza will follow in a subsequent publication.

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