X-RAY PHOTOELECTRON STUDY OF THE REACTION OF WATER WITH CERIUM

B E KOEL*, G PRALINE, H -I LEE** and J M WHITE***

Department of Chemistry, University of Texas, Austin, Texas 78712 (USA)

R L HANCE

Department of Chemistry, Abilene Christian University, Abilene, Texas 79601 (USA)

(First received 5 March 1980, in final form 7 April 1980)

ABSTRACT

The interaction of D₂O with a polycrystalline cerium surface, successfully cleaned by heavy Ar⁺ bombardment and annealing, was studied at 120 and 300 K using XPS. At 300 K, O(1s) states were observed at BE 530.3 (Ce₂O₃) and 532.7 eV (adsorbed OD). When clean Ce at 120 K was exposed to D₂O, the O(1s) spectra were initially dominated by transitions at 532.7 and 534.9 eV (adsorbed D₂O). For exposures greater than 10 Langmuir (L), a multilayer of ice grows and the O(1s) spectra become dominated by a peak at 536.0 eV. Ce(3d) spectra are also presented.

The results of interaction with D₂O are compared with oxidation by O₂. The significant differences are (1) the absence of Ce(IV) when oxidation is performed with D₂O at 300 K, (2) the relatively small extent of oxidation that occurs when Ce is exposed to D₂O at 120 K, and (3) the larger chemical shift of the Ce(III)-derived species upon exposure to D₂O at 300 K.

INTRODUCTION

Water is known to play an active role in the oxidation of metals [1], by influencing either the composition of the passivation layer or the kinetics of oxidation, or both. Thus, it is of interest to characterize the surface species present when clean metals are exposed to controlled amounts of water.

X-Ray photoelectron spectroscopy (XPS) can distinguish between various forms of oxygen—chemisorbed, chemically combined, or in different chemical environments in molecules [2]. It can also be used to determine the

* NSF Trainee
** Present address Department of Chemical Technology, College of Engineering, Seoul National University, Seoul, Korea
*** Author to whom correspondence should be sent
valence state of a metal [3] Thus, XPS is a powerful tool for the study of the surface-reaction products, or surface species, formed by the interaction of water with a metal. This utility has already been demonstrated in studies of the reaction of O$_2$ and H$_2$O with a variety of metals, including heavy lanthanides [4], transition metals [5, 6, 7], and non-transition metals [6, 8].

Using XPS, we have focused on the identification of the surface species that are formed when D$_2$O interacts at 120 and 300 K with a Ce foil which has first been bombarded with Ar$^+$ ions. This work extends typical chemisorption studies to a very reactive metal, provides for an interesting comparison with the oxidation of Ce by O$_2$ [9], and extends studies on the oxidation of the heavier, less reactive lanthanides (terbium to lutetium [4]).

**EXPERIMENTAL**

**Instrumental details**

An ion-pumped Physical Electronics (PHI) Model 548 electron spectrometer was used in these measurements. The base pressure after bakeout was less than 1 x 10$^{-10}$ torr, and was $\sim$2 x 10$^{-10}$ torr during experiments. After high-pressure (4 x 10$^{-3}$ torr) Ar$^+$-sputtering, the pressure remained in the mid 10$^{-9}$-torr regime for some time, but mainly resulted from the presence of Ar and He. A double-pass, cylindrical-mirror analyzer (CMA) was used in the retarding mode for XPS, at a pass energy ($E_p$) of 50 or 100 eV, for a constant analyzer-resolution of 0.8 or 1.6 eV, respectively. The data for XPS were recorded digitally using signal-averaged pulse-counting techniques. The results were stored on magnetic tape for subsequent reduction on a CDC 6600 computer, using programming written in this laboratory. Data reduction consisted of smoothing of the raw data (using a choice of the order of a polynomial routine and number of points to be smoothed) and curve synthesis using Gaussian peak-shapes.

Mg K\(\alpha\) X-rays (h\(\omega\) = 1253.6 eV) were used in XPS. The X-ray source was aligned in a plane perpendicular to the CMA axis, and made a 67° angle with the sample-surface normal. The sample surface was inclined so that its normal vector made an angle of 30° with the CMA axis. Angle-integrated collection allowed for the detection of near-normal ($\sim$12°) through grazing-angle ($\sim$72°) photoelectrons, where the integrated average for the take-off angle with respect to the surface normal was 50°. The full width at half-maximum (FWHM) of the Au(4f$_{7/2}$) line excited by Mg K\(\alpha\) photons was 2.5 and 1.6 eV for $E_p$ = 100 and $E_p$ = 50 eV, respectively. All of the high-resolution spectra shown in this work were obtained using $E_p$ = 50 eV.

For Auger electron spectroscopy (AES), the electron gun was internal to the CMA and collinear with the CMA axis. The beam voltage was 3 kV and the beam current was 10 \(\mu\)A. The CMA was used in the non-retarding mode, and the spectra were recorded in the d\(N(E)/dE\) mode using 1-V peak-to-peak modulation and phase-sensitive detection.
A gold foil was mounted beside the sample, and the spectrometer work-function was assumed so that the Au(4f\(_{7/2}\)) line occurred at BE 83.8 eV. This was consistent with the Fermi edge of Ce at BE 0.0 eV and the Ce(3d\(_{5/2}\)) line at BE 883.2 eV. For each set of experiments, the Ce(3d) lines for clean Ce were recorded to check for drift in the voltage scale and for changes of multiplier gain.

The position of the Ce Fermi level, \(E_F\) (half-intensity of the low-BE side of the valence-band edge), was determined by actual measurement of the valence-band spectra. This procedure is possible for Ce since the 4f photoelectron peak and its Mg \(K\alpha_{3,4}\) satellite are well separated from the valence-band edge. All reported binding-energies are referenced to the Ce Fermi level.

The dose vapor was D\(_2\)O (99.8% D, from SCI-GRAPHICS) and was used after repeated cycles of successive freezing, pumping and thawing. Exposures were accomplished using a dynamically-pumped doser-system which had a multi-channel array as the nozzle [8]. This allowed the exposure pressure to be as high as \(10^{-7}\) torr while the system pressure out of the beam path remained in the low \(10^{-9}\)-torr regime.

The doser calibration was provided by comparing the oxygen signals on exposure to O\(_2\) obtained using the doser with those from back-fill of the UHV chamber. Correction for the molecular weights and ion-gauge sensitivities of the different gases was made.

**Sample preparation**

The sample (area 1 cm\(^2\), thickness 0.25 mm) of 99.9%-pure Ce foil (Ventron, Alfa Products, shipped from the supplier in mineral oil) was spot-welded to a larger Ta foil and mounted on a manipulator so that it could be heated (button heater. Model E292 purchased from Spectra-Mat, Inc., Watsonville, CA 95076) and cooled (liquid nitrogen). The sample temperature was monitored using a chromel-alumel thermocouple. Preparation and cleaning of the sample were accomplished as follows. The sample was degreased by ultrasonic cleaning in acetone, and, while under ethanol, was spot-welded along its edges to a thin Ta foil that could be easily mounted on the button heater. The front face of the sample was mechanically polished to a metallic luster with fine-grain sandpaper wetted with acetone. The sample was immediately placed in vacuum and the system was then baked for two days at 150\(^\circ\)C. Further cleaning was done by Ar\(^+\) sputtering at an Ar pressure of \(4 \times 10^{-5}\) torr, with the ion-gun defocused and operated at 5 kV and 20 mA. The ion-current density at the sample was 150 \(\mu A\) cm\(^{-2}\). Initially the principal impurity detected by AES was oxygen, but, after 8 h of sputtering, its level was reduced well below that of carbon. Detectable amounts of chlorine and nitrogen were also present. Further sputtering at 300 K did little to reduce these levels. Spectra (XPS and AES) for the cleanest surfaces are discussed in the following section. Heating the sample to 600 K caused segregation of carbon to the surface, and, after 4 h of sputtering at this temperature, the carbon signal was reduced to a low level. Routine cleaning of
the sample during experiments involved sputtering for 10 min at the experimental temperature under the same ion-beam conditions as described above. Periodically the sample was checked by AES to verify the effectiveness of the cleaning and to confirm that no carbon build-up had occurred. A similar cleaning technique was used successfully for Ce foil by Chamberlain and Baun [10], who eliminated all impurities except O and Zr, the latter impurity was not observed in the present study.

RESULTS AND DISCUSSION

Spectra of clean cerium

The AES spectrum of Ce, after cleaning using the procedure described above, is shown in Fig 1a. No additional structure was observed at kinetic energies greater than 1000 eV, and chlorine, carbon, nitrogen, and oxygen remained as detectable impurities. Using relative-sensitivity factors for AES [11], we estimate the surface impurity concentrations to be 1% Cl, 9% C, 3% N, and 2% O, assuming all of the impurities are in the first surface-layer.

![AES spectrum of Ce](image)

![XPS spectrum of Ce](image)

Fig 1 (a) The AES spectrum of cerium foil heavily bombarded with Ar⁺ ions (b) The XPS spectrum (Mg Kα) of the same foil
Since a very high sputtering-rate was used for cleaning, it is probable that these impurities are distributed uniformly throughout the bulk of the sample, but rapid surface-segregation at the measurement temperature could lead to increases in their surface concentrations. When the sample was cooled to 120 K and sputtered while cooling, AES showed no detectable C(KVV) signal, with Cl, N, and O signals about the same as described above.

Figure 1b shows the XPS spectrum, using Mg Kα₁,₂ photons, of Ar⁺-cleaned Ce. The spectrum is characterized by intense 3d peaks and two strong series of Auger transitions. At lower intensity, 4p and 4d transitions are observed, the latter being somewhat stronger. Transitions from 5p electrons can also be observed, at 18 eV. Features arising from the 4f level and the conduction-band (5d6s) electrons [12] are not observed above the background, although they appear at very low BE when multiple scans are added together. The peak at BE 434.2 eV is due to the the Cu(Lα) “ghost” of the Ce(4d) parent-line; the Cu(Lα) photons arise from Cu showing through the Mg anode in the X-ray source [13]. A simple calculation shows that similar “ghost” lines do not affect other parts of the spectra.

**Exposure to D₂O at 300 K**

The reaction of D₂O with Ce foil, as characterized by O(1s) spectra, is shown in Fig. 2. Two binding energies dominate BE 530.3 eV, peak 2, and BE 532.7 eV, peak 3. Table 1 summarizes these and other O(1s) results obtained following reactions with D₂O and O₂. The O(1s) peak at BE 530.3 eV is identical to that found for the reaction of O₂ with Ce [9]. From this comparison, work on the heavier lanthanides [4], and arguments presented below, we assign this feature to a Ce(III) species, probably Ce₂O₃. Similarly we assign peak 3 as OD with contributions from OD(a) and CeO(OD) [and perhaps some small contribution from Ce(OH)₃]. Based on calculations of overlayer thickness, discussed below, the intensity of peak 3 indicates that more than one monolayer of OD is present for exposures greater than ~20 L.

**TABLE 1**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temp (K)</th>
<th>BE (ev) of O(1s) peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak 1 (CeO₂)</td>
</tr>
<tr>
<td>O₂ₐ</td>
<td>300</td>
<td>529.6</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>529.6</td>
</tr>
<tr>
<td>D₂O</td>
<td>300</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>—</td>
</tr>
</tbody>
</table>

---

Fig 2 O(1s) Spectra for various exposures of Ce to D$_2$O at 300 K. Peak 3 is assigned to OD(a) and peak 2 to Ce$_2$O$_3$

The presence of some contribution from CeO(OD) is also consistent with Ce(3d) data described later. The low-BE peak at ~522 eV (Fig 2) is from a satellite of the X-ray source.

Initially (at exposures ≤ 3.5 L) only peak 2 appears in the O(1s) spectrum, at BE 530.3 eV, as shown in Fig 2. With further exposure, this peak increases in intensity, and peak 3 appears at BE 532.7 eV. Peak 3 grows faster with continuing exposure than does peak 2, and has one-half of the intensity of peak 2 at saturation. As determined by Gaussian fitting (see inset in Fig 4), both peaks grow with a constant FWHM of 1.9 eV and constant BE, within experimental error, indicating sample-charging to be a negligible problem. No intensity can be assigned with certainty to a low-BE species (peak 1, CeO$_2$ in Table 1) which appears during exposure to D$_2$O. In the case of a 3.5-L exposure to D$_2$O, the O(1s) peak is asymmetric on the low-BE side, and could indicate an unmeasurable amount of Ce(IV) (as CeO$_2$) during all
Fig 3 O(1s) Peak areas as a function of D$_2$O exposure at 300 K, (a) total area, (b) oxide, and (c) OD(a) The spectra used to obtain these results were similar to those shown in Fig 2. The decomposition into oxide and hydroxide is described in the text, and shown for one case in the inset to Fig 4.

of the subsequent exposures. The Ce(3d) spectra discussed below confirm that Ce(IV) is not present to a significant extent.

The variation in O(1s) peak area with D$_2$O exposure is shown in Fig 3. Curve (a) shows the total peak area in the O(1s) region, and indicates a high initial sticking-coefficient ($S_0 \approx 0.4$). The peak area approaches saturation between 70- and 100-L D$_2$O. Curves (b) and (c) show the areas for peaks 2 and 3, respectively. Peak 2 increases more rapidly at first, and reaches saturation at 45-L D$_2$O. Peak 3 is present early (\(~5\) L) and continues to grow slowly to saturation at \(~110\)-L D$_2$O. The small increase in intensity of this peak at high exposure has little effect on the total O(1s) intensity.

Curves (b) and (c) in Fig 3 were obtained by empirically synthesizing the O(1s) intensity with a sum of two Gaussian peaks, using a Tektronix video terminal. An example of the synthesis for 150-L D$_2$O is shown in the inset to Fig 4. Three synthesized curves are produced: peak 2, peak 3, and their

Fig 4 Hydroxide/oxide ratio as a function of exposure, from the data of Fig 3. The inset shows how the experimental spectrum was modeled by using the sum of the Gaussian peaks for the two components.
The experimental spectrum illustrates the background noise of the raw data, and the error commonly incurred in the fitting procedure. The scatter in the uptake data (Fig 3) is due largely to the latter source of error. As compared with results for O₂ [9], the total O(1s) intensity at saturation and 300 K is lower by ~10% for D₂O. Throughout the course of the exposure to D₂O, the part of the spectra (Fig 3) characteristic of the oxide increases in intensity at one-half of the rate found during exposure to O₂.

Figure 4 shows the ratio of the area of peak 3 to that of peak 2 as a function of D₂O exposure at 300 K. Even though the scatter is fairly large, it is clear that peak 3 gradually increases in intensity relative to peak 2 until the ratio saturates at 0.5. This result is in excellent agreement with work on the heavier lanthanides [4].

The Ce(3d) spectra for various exposures to D₂O at 300 K are shown in Fig 5. The clean surface gives two principal peaks, namely, the 3d₅/₂ (BE 883.2 eV) and 3d₃/₂ (BE 901.7 eV) spin–orbit doublet, with the 3d₅/₂ peak at lower BE and the most intense. Satellites due to multiplet splitting...

![Fig 5 Ce(3d) XPS Spectra for various exposures of Ce to D₂O at 300 K](image-url)
also appear at \(\sim 9\)-eV higher binding energy from the parent photoelectron peaks [14]. New features are clear after as little as 5 L exposure, and these continue to grow as the exposure increases. Compared to the spectrum for 0-L exposure, the new features appear at 2.9-eV and 1.1-eV lower BE. We assign the higher-BE peak as the parent ionization of Ce(II1) in Ce\(_2\)O\(_3\) or a mixed oxide—hydroxide, and the lower-BE peak as a shake-down charge-transfer satellite. With this assignment, Ce metal does not contribute measurably to the spectra after a 50-L exposure. Using an attenuation length of 8 Å, Ce(3d) spectra such as those shown in Fig 5 indicate an oxide thickness of 4 and 12 Å after D\(_2\)O exposure of 10 and 20 L, respectively. These values are 50% of those observed for identical O\(_2\) exposures at 300 K, and are fully consistent with the rates at which O(1s) peaks grow (see Fig 2).

These results follow closely those obtained for oxidation by O\(_2\), but there are differences. One is that high exposures to D\(_2\)O do not give rise to a feature at 916.6 eV which is characteristic of Ce(IV) [15, 16]. We conclude that, under the conditions used here, oxidation by water terminates at Ce(II1). This is consistent with the O(1s) spectra of Fig 2. A further indication that the peaks in Fig 5 are properly assigned to Ce(II1) is their similarity to those from bulk Ce(tmhd)\(_3\) [16]* and Pr\(_2\)O\(_3\) [16]. We find the satellite/parent intensity ratio to be 0.78, which is somewhat higher than for Ce(tmhd)\(_3\) [16]. Another distinction between the spectra for O\(_2\) and D\(_2\)O exposures is the splitting of the peaks associated with each component of the spin—orbit doublet. In the case of O\(_2\) [9], this splitting is 3.7 ± 0.1 eV, while for D\(_2\)O, it is 4.0 ± 0.1 eV. With respect to transitions in the clean metal, the major difference is in the position of the higher-BE component, which is shifted up by 2.9 eV in the case of D\(_2\)O but only by 2.6 eV for O\(_2\) exposure. The lower-BE component is shifted down by 1.1 eV in both cases. This difference is consistent with the formation of a mixed oxide—hydroxide Ce(II1) species in the case of D\(_2\)O oxidation.

The Ce 3d XPS spectra of Ce(OH)\(_3\) have been reported [17]. Transitions at 881.7 and 888.0 eV were found in the 3d\(_{5/2}\) region and were assigned as the parent and a charge-transfer shake-up satellite of a Ce(III) species, respectively. However, because of the strong similarity of this Ce(OH)\(_3\) spectrum to Ce(IV) spectra [9, 15, 16] and the dissimilarity to Ce(II1) spectra, we believe that their sample had a surface layer dominated by Ce(IV). This is not unexpected, since air-passivation [16] and controlled exposure to O\(_2\) [9] both lead to a surface layer that is rich in metal of the higher oxidation state.

We also recorded the X-ray-excited Auger spectra (XAES) of the MNN Auger transitions of cerium for kinetic energies (KE) between 600 and 700 eV. The clean-surface spectrum contains a very broad peak with a maximum at KE 655 eV. As the exposure to D\(_2\)O is increased, significant shape-changes

* tmhd = 2, 2, 6, 6-tetramethyl-3, 5-dionatoheptane
occur, with the notable growth of a new peak at KE 670 eV. The first-derivative AES (electron-excited) spectra of these surfaces (discussed below) also show these effects, the spectra are almost identical to those reported earlier for O₂ exposure [9]. With the current success [18–21] in deconvoluting AES and XAES spectra for solids and adsorbed molecules, the deconvolution of the Ce(MNN) spectra for the clean and oxidized surface should show interesting details that will contribute to the identification of the surface species formed during oxidation and to the description of electronic changes in cerium during oxidation.

The possibility of hydride formation must also be considered, since lanthanides do react with water to form hydrides [22]. Under UHV conditions, this reaction does not occur to a significant extent, as evidenced by the rapid appearance and growth of oxide upon exposure to D₂O. This is not surprising, since the mechanism for CeH₃ formation is simply filling of the octahedral sites in the Ce lattice with hydrogen [23], and, under the low partial pressures of H₂ in a UHV chamber, this should not be observable.

Exposure to D₂O at 120 K

Figure 6 shows the O(1s) region for D₂O exposures at 120 K. Four peaks can be identified and assigned: peak 2 at BE 530.3 eV to Ce₂O₃, peak 3 at BE 532.7 eV to OD(a), peak 4 at BE 534.9 eV to D₂O(a), and peak 5 at BE 536.0 eV to D₂O(s) (multilayer ice). These are listed in Table 1. The features at lower BE in this Figure arise from X-ray-source satellites. Unlike the OD distribution at 300 K, at 120 K the OD species are confined to the surface (see below).

At low exposures, the spectra are characterized by the growth of peak 3 at BE 532.7 eV. Some intensity should be assigned to peak 2 at BE 530.3 eV, but it contributes only a small amount to the total O(1s) intensity. It is difficult to discern whether or not the growth of this peak with exposure is due to the overlap of the peak of higher intensity (peak 3), but we believe that it remains of low intensity up to saturation. This is supported by the Ce(3d) spectra shown below.

When exposure to D₂O reaches 5 L, a higher-BE peak at 534.9 eV (peak 4) becomes apparent, and continues to grow with larger exposures. This peak is rapidly overshadowed by the growth of peak 5 at BE 536.0 eV. Peak 5 becomes the only resolvable feature in the O(1s) spectrum near saturation. Its position does not change up to at least 180-L D₂O. Moreover, sample-charging is negligible, since biasing the sample (by −3 V) produces a uniform shift and no broadening. This peak (5) is clearly from a multilayer of D₂O, since the Ce features (see below) are severely attenuated. The feature at 534.9 eV is sensibly assigned to chemisorbed water. Compared to the multilayer, interaction of the D₂O with Ce in a monolayer should shift the position of the O(1s) peak to lower BE due to enhanced electrostatic screening of the core hole. This final-state is accompanied by an initial-state effect.
Fig 6 O(1s) XPS Spectra for various exposures of Ce to D₂O at 120 K. Features at BE ~527 eV are X-ray-source satellites Peak 2, Ce₂O₃, peak 3, OD(a), peak 4, D₂O(a), and peak 5, D₂O(s)

Involving the interaction of the oxygen lone-pair with cerium. A Gaussian synthesis of the O(1s) spectrum obtained after a 10-L D₂O exposure (Fig. 6) gives 2.6 eV for the FWHM of D₂O(a), while ice gives 2.1 eV. This narrowing is attributed to two effects: (1) isolation of the water molecules from the heterogeneous region of the sputtered cerium-surface, and (2) increased core-hole lifetime in the multilayer.

Within experimental error, the initial slopes of the curves for D₂O uptake at 310 and 120 K are the same [monitored by O(1s) peak area, as in Fig 3]. The curves diverge at ~20 L, due to the chemisorption and condensation of D₂O at 120 K. However, the oxygen-containing species are not distributed in the same manner at these two temperatures, as shown by comparing Figs 6 and 2.

The intensity variation in the various O(1s) peaks with D₂O exposure at
Fig 7 Variation of O(1s) peak areas for (a) hydroxide, (b) adsorbed water, and (c) total oxygen, as a function of exposure to D₂O at 120 K

120 K is shown in Fig 7. Curve (c) shows the total intensity of oxygen-containing species, while curves (a) and (b) show the intensity of OD(a) and D₂O(a), respectively. Referring to Figs 6 and 7, the initial adsorption of D₂O causes the appearance and growth of peak 3, followed by a steady growth of peaks 4 and 5. This is accompanied by a decline in the intensity of peak 3, which begins at ~10 L D₂O. Peak 3, OD(a), is not observable at exposures greater than 100 L D₂O, because it is attenuated by a thick layer of solid D₂O.

The O(1s) binding energies reported in Table 1 are in excellent accord with the results of Padalia et al. [4] For exposure to water at 300 K, they found peaks at 531.0 ± 0.5 eV and 533.0 ± 0.5 eV, assigned to oxide and hydroxide, respectively, for each of the seven heavy lanthanides, Tb–Lu. At low temperatures, they found additional features at 534.8 ± 0.4 and 535.7 ± 0.2 eV which were assigned as chemisorbed water and ice, respectively. They concluded that the adsorption of water at 300 K produces a relatively thick layer of oxide terminated by a monolayer of hydroxide. To within experimental error, our results are identical, and follow the same temperature-dependence. The assignment of the feature at 532.7 eV (Fig 6) as hydroxide is further confirmed by the XPS results obtained for Pt by Norton [24], who found an O(1s) feature at 533 ± 0.5 eV when H₂ is added to an oxygen-covered surface at low temperature. Further confirmation is provided by the work on Al of Rogers [25] and Fuggle et al. [26], who found O(1s) peaks for OH(a) and condensed water near 533 and 536 eV, respectively. One distinction between Ce and the heavier lanthanides is the possibility of generating Ce(IV) in addition to Ce(III) species. Evidently, the presence of a surface layer of hydroxide stabilizes Ce(III), and kinetically inhibits the formation of the thermodynamically more stable Ce(IV).

Evidence supporting this conclusion comes from the following experiment.
A clean Ce surface was exposed at 300 K to 50-L D$_2$O followed by 100-L O$_2$. The O(1s) and Ce(3d) spectra both changed upon exposure to O$_2$. The Ce(IV) satellite appeared, but at low intensity, while the O(1s) total area increased by 18% and its intensity distribution reflects consumption of 50% of the hydroxide and formation of the higher oxide. The Ce(IV) component of the 3d spectrum is equivalent to an O$_2$ exposure of less than 50 L.

As shown in Fig. 8, the Ce(3d) peaks for low-temperature exposure to D$_2$O do not show the structure observed at 300 K. Both the 3d$_{5/2}$ and 3d$_{3/2}$ peaks broaden considerably. For example, a 20-L D$_2$O exposure gives rise to shoulders on the high-BE side of each of the 3d metal peaks, indicating some oxidation, but no splitting is observed. Moreover, the peak maximum does not shift as a function of D$_2$O exposure. The main effect of 100-L D$_2$O at 120 K is to reduce the 3d peak intensity to ~10% of its value in clean-surface spectra, with very little oxidation of the surface. This is in contrast to low-temperature O$_2$ exposure, where oxide formation occurs readily [9].

Comparison of Figs. 5 and 8 indicates that a 5-L D$_2$O exposure at 300 K gives the same broadening as a 30–100-L D$_2$O exposure at 120 K. Comparing this to Fig. 7 indicates that the small amount of dissociative chemisorption of water
(into mainly hydroxide) which occurs in the early stages of the exposure is responsible for oxidation of the outermost layer of cerium.

Assuming the hydroxide is confined to the outermost layer and that the main effect of the exposure to water is the formation of a uniform overlayer of ice, several calculations of layer thicknesses may be made. For example, from Fig 7, the OD(a) intensity reaches a maximum at an exposure of 10 L, and at this exposure the Ce(3d) attenuation (based on a scattering-length of 8 Å) gives an effective overlayer thickness of 1.90 Å. This is consistent with a distribution comprised of one-half of a monolayer each of OD(a) (thickness \(\approx 1.01 \text{ Å}\)) and D\(_2\)O(a) (thickness \(\approx 2.75 \text{ Å}\), based on O–O distance in ice) as indicated in Fig 6. At exposures greater than 10 L, the attenuation of the OD(a) and the Ce(3d) features are self-consistent. The data for a 100-L D\(_2\)O exposure indicate an effective overlayer thickness of 13.3 Å if a scattering length of 8 Å is used. On this basis, the sticking coefficient is 0.2. These calculations must be viewed cautiously, since the scattering length is based on a compilation of results obtained on various solids [27] and not on any specific measurements on Ce or D\(_2\)O overlayers thereon. Upper bounds of 13.0 Å for the overlayer thickness and 8.0 Å for the escape depth can be set, using a sticking coefficient of unity and assuming cubic-lattice ice is formed.

---

**Fig 9** O(1s) XPS Spectra for a surface prepared by 50-L exposure to D\(_2\)O at 120 K, spectrum (a), followed by heating to 240 K (b), and then to 300 K (c).
Figure 9 shows the effects of heating a surface that has been exposed to 150-L D$_2$O at 120 K. Warming the sample to ~240 K (curve b) causes the loss of D$_2$O(a) by evaporation, and the conversion of a significant amount of hydroxyl to oxide. The distribution, however, is quite different from that obtained from exposure to D$_2$O at 300 K (inset to Fig 4), where the oxide peak has twice the intensity of that for the hydroxide. As shown in Fig 9, upon warming to 240 K, the distribution is reversed [I(OH) = 2I(O)]. Interestingly, this low-temperature distribution is the same as that found by Barr [16] in his study of air-passivation of cerium at higher temperatures. Upon heating the sample to 300 K (curve c), extensive reduction to the oxide occurs, and the oxide-to-hydroxide ratio increases to 2, as for a saturation exposure at 300 K. The total O(1s) intensity decreases by 10% upon warming from 240 to 300 K. Accompanying changes in the Ce(3d) region also indicate oxidation. Both spectra are equivalent to those obtained from 15-L D$_2$O at 300 K.

SUMMARY

The XPS studies of the interaction of D$_2$O with Ce reported here may be summarized as follows:

1. Exposure at 300 K gives rise to O(1s) features characteristic of oxide and hydroxide, while the Ce(3d) spectra indicate Ce(III), but no Ce(IV) as observed when O$_2$ is used.

2. Exposure at 120 K gives O(1s) features characteristic of adsorbed OD, chemisorbed D$_2$O, a multilayer of ice, and a small amount of oxide. This is confirmed by the Ce(3d) spectra, which are characteristic of clean Ce except for slight broadening.

3. Exposure at 120 K followed by warming to 240 and 300 K gives spectra characteristic of hydroxide and oxide surface-species. Between 240 and 300 K, hydroxide converts into oxide with a 10% loss of O(1s) intensity.

4. At 300 K, a relatively thick layer of oxide forms, and after an exposure of 50 L the features characteristic of metallic Ce are no longer observable.

5. As compared to the case for O$_2$, exposure to D$_2$O gives rise to different satellite-splittings in the Ce(3d) spectra, suggesting that different electronic structures involving Ce(III) are formed in the two cases.

6. The spectra observed for Ce exposed to D$_2$O are in excellent accord with those found for the heavier lanthanides [4].

ACKNOWLEDGEMENTS

This research was supported in part by the National Science Foundation (J M.W.) and by the Robert A. Welch Foundation (R.L.H. and J M.W.)
REFERENCES

8. J W Rogers, Jr, Thesis, University of Texas at Austin, Austin, TX, 1979
13. S Evans and E Raftery, J Electron Spectrosc Relat Phenom, 17 (1979) 137
14. See ref 9, and references cited therein
17. K Tatsumi, M Tsutsui, G W Beall, D F Mullica and W O Milligan, J Electron Spectrosc Relat Phenom, 16 (1979) 113
20. P H Holloway, T E Madey, C T Campbell, R R Rye and J E Houston, Surf Sci, 88 (1979) 121
25. J W Rogers, Jr, Ph.D dissertation, University of Texas, 1979