Geometry of $\alpha$-Cr$_2$O$_3$(0001) as a Function of H$_2$O Partial Pressure

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$^3$ Supporting Information

ABSTRACT: Surface X-ray diffraction has been employed to elucidate the surface structure of $\alpha$-Cr$_2$O$_3$(0001) as a function of water partial pressure at room temperature. In ultra high vacuum, following exposure to $\sim$2000 Langmuir of H$_2$O, the surface is found to be terminated by a partially occupied double layer of chromium atoms. No evidence of adsorbed OH/H$_2$O is found, which is likely due to either adsorption at minority sites, or X-ray induced desorption. At a water partial pressure of $\sim$30 mbar, a single OH/H$_2$O species is found to be bound atop each surface Cr atom. This adsorption geometry does not agree with that predicted by ab initio calculations, which may be a result of some differences between the experimental conditions and those modeled.

INTRODUCTION

The presence of a passive surface film is key to the exceptional corrosion resistance of stainless steel alloys.$^{1,2}$ Consequently, much effort has targeted the characterization and enhancement of this protective layer, which is often composed, at least partially, of chromia.$^{1,2}$ Such work includes fundamental studies of single crystal surfaces of $\alpha$-Cr$_2$O$_3$ to gain atomic scale insight into pertinent properties, e.g., refs 3$^−$10. To date, however, most of these measurements have been conducted in ultra high vacuum (UHV), limiting their relevance with regard to mechanistic understanding of corrosion performance in engineering environments. Targeting this omission, the current study is concerned with determining the surface structure of $\alpha$-Cr$_2$O$_3$(0001) in the presence of H$_2$O vapor through acquisition of surface X-ray diffraction (SXRD) data; water is an essential ingredient for many corrosion phenomena.

The structure of $\alpha$-Cr$_2$O$_3$(0001) as a function of both H$_2$O partial pressure and temperature has previously been explored by Costa et al. through ab initio modeling.$^6$ As a starting point for these calculations, a clean surface terminated by a single layer of 3-fold coordinated chromium atoms was assumed, as depicted in Figure 1A; this surface termination is labeled Cr$\rightarrow$Cr$\rightarrow$Cr on the basis of its first three atomic layers (the subscript indicates the average number of atoms in each 1 $\times$ 1 unit cell). Near room temperature, it was concluded that two other terminations become energetically favorable in the presence of H$_2$O. At lower H$_2$O partial pressures, dissociative adsorption was proposed to be the most likely scenario with each surface Cr becoming decorated with two hydroxyls (OH), i.e. Cr$\rightarrow$OH$\rightarrow$OH$\rightarrow$; a (OH)$\rightarrow$Cr$\rightarrow$OH$\rightarrow$ termination was found to be energetically unfavorable. Increasing the H$_2$O partial pressure resulted in the attachment of an intact H$_2$O molecule to each dihydroxylated Cr to form a new surface termination, i.e. Cr$\rightarrow$OH$\rightarrow$H$_2$O$\rightarrow$H$_2$O$\rightarrow$.

Parts B and C of Figure 1 illustrate the (OH)$\rightarrow$Cr$\rightarrow$OH$\rightarrow$ and (H$_2$O(OH)$_2$)$\rightarrow$Cr$\rightarrow$OH$\rightarrow$ adsorbate phases predicted in ref 6, including the location of the acidic hydrogen resulting from dissociative adsorption of H$_2$O. This moiety is bound to the topmost substrate oxygen atoms, forming a second distinct OH species. Hydrogen bonds formed between surface adsorbates (OH and H$_2$O) are also indicated in Figure 1, parts B and C. These theoretical structures are consistent with experimental characterization performed under UHV conditions of thin films of $\alpha$-Cr$_2$O$_3$(0001) exposed to H$_2$O, in that at room temperature, dissociative adsorption is evident.$^3,4$ Moreover, the existence of two distinct OH species, as well as interadsorbate hydrogen bonding, is apparent from vibrational data.$^8$
H2O partial pressure of single crystal

The H2O had been degassed through repeated freeze–thaw cycles. The sample was then transferred under vacuum to a static volume of H2O in UHV, the H2O partial pressure was ∼ 1000 mbar of H2O vapor. Prior to dosing, the H2O had been degassed through repeated freeze–thaw cycles. The sample was then transferred under vacuum to the beamline I07 for SXRD measurements. Initially, a systematic series of X-ray reflections was acquired from \( \alpha \)-Cr2O3–H2O.UHV. More specifically, for a given \((h,k,l)\)-integer, data were measured as a function of \( l \) to facilitate generation of so-called crystal truncation rods (CTRs); fractional-order rods (FORs) were also surveyed. \( h, k, l \) are the reciprocal lattice vectors, and are defined with reference to the real space \((1 \times 1)\) unit cell of the \( \alpha \)-Cr2O3\((0001) \) surface, described by lattice vectors \((a_1, a_2, a_3)\) which are parallel to the \([100], [010], [001] \) directions, respectively. The magnitudes of these lattice vectors are \( a_1 = a_2 = a = 4.957 \) Å, and \( a_3 = c = 13.592 \) Å, where \( a \) and \( c \) are the bulk lattice constants.

Subsequent to compiling surface diffraction data from Cr2O3–H2O.UHV in UHV, the H2O partial pressure was increased in a stepwise fashion by appropriate backfilling of the baby chamber with H2O. We note that above 1 \times 10^{-4} \text{ mbar} a static volume of H2O was employed rather than obtaining an equilibrium pressure through balancing the rates of H2O inflow and pumping, i.e. the baby chamber was no longer continuously pumped. For each H2O partial pressure, the intensity of the \((1, 0, 2.9)\) reflection was monitored to identify changes in the \( \alpha \)-Cr2O3\((0001) \) surface structure. Selection of this reflection was based upon its sensitivity to such variation as a function of O2 partial pressure. On the basis of these measurements (see below), a further systematic series of X-ray reflections was acquired from \( \alpha \)-Cr2O3\((0001) \) at a H2O partial pressure of ∼30 mbar; henceforth this surface will be referred to as \( \alpha \)-Cr2O3–H2O30mbar. It should be noted that as 30 mbar of H2O is equivalent to ∼100% relative humidity with the substrate at room temperature, one would expect the surface to be submerged beneath multiple monolayers of H2O in this environment.

To facilitate fully quantitative structure determination, the raw diffraction data acquired at UHV and \( p(\text{H}_2\text{O}) \sim 30 \text{ mbar} \) were integrated and corrected\(^\text{12} \) to enable plots of structure factor versus perpendicular momentum transfer for each CTR to be compiled. This procedure resulted in a total of 1054 \((1142)\) nonequivalent reflections from six CTRs for \( \text{Cr}_2\text{O}_3\sim\text{H}_2\text{O}_{30\text{mbar}} \). Concerning FORs, no evidence for any surface unit cell other than \( 1 \times 1 \) was found.

For surface structure determination, we adopted the usual approach of generating simulated SXRD data for a series of potential model structures, and iteratively refining structural (and nonstructural) parameters to find the overall best fit between experiment and theory. The ROD software was employed for this purpose.\(^\text{13} \) Reduced \( \chi^2 \) was used to evaluate the goodness of the fit; this is defined as follows:

\[
\chi^2 = \frac{1}{N - P} \sum_{i=1}^{N} \frac{|I_{\exp}(hkl) - I_{\text{calc}}(hkl)|^2}{\sigma_{\exp}^2(hkl)}
\]

where \( I_{\exp}(hkl) \) and \( I_{\text{calc}}(hkl) \) are the experimental and calculated intensities, respectively, \( N \) is the number of reflections, \( P \) is the number of parameters, and \( \sigma_{\exp}^2(hkl) \) is the estimated experimental error in the observed intensity. The goodness of the fit was determined by minimizing \( \chi^2 \) with respect to the parameters of the model hierarchy.

Here, the validity of the theoretical study of Costa et al.\(^\text{6} \) is explored experimentally. Analysis of SXRD data acquired at a H2O partial pressure of ∼30 mbar indicates that the \( \alpha \)-Cr2O3\((0001) \) surface is decorated by OH, but not exactly as predicted by Costa et al. at lower (B) and higher (C) H2O partial pressures. Hydrogen bonding is indicated by means of dashed lines; the smallest spheres are hydrogen atoms. The \( 1 \times 1 \) surface unit cell is indicated in the plan view in part A.


\[\text{Cr}_2\text{O}_3(0001)\]

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$N$ is the number of measured structure factors, $P$ the number of parameters optimized during fitting, and $F_{\exp}^{(hkl)}$ and $F_{\text{calc}}^{(hkl)}$ are the experimental and theoretically calculated structure factors, respectively. $\sigma_{\exp}^{(hkl)}$ is the uncertainty associated with $F_{\exp}^{(hkl)}$. $\chi^2$ behaves such that a value of 1 indicates that experiment and theory are essentially coincident, with agreement decreasing with increasing $\chi^2$. Values of $\chi^2$ significantly less than 1 suggest that the magnitudes of experimental uncertainties have been overestimated. The quoted precision of each fitted parameter is determined by systematically varying the parameter about its optimal value, and for each step optimizing all other parameters, until $\chi^2$ has increased by $1/(N-P)$ from its minimum value.\textsuperscript{14}

**RESULTS**

Figure 2 displays the intensity of the (1, 0, 2.9) reflection as a function of increasing H$_2$O partial pressure; please note, as described above, the sample had already been dosed with $\sim$2000 L of H$_2$O prior to acquisition of these data. Upon exposure of the sample to $\sim$30 mbar of H$_2$O vapor, there is an increase of $\sim$20% in the signal. This increase is fully reversible (i.e., there is an $\sim$20% decrease in intensity upon reducing the pressure down to $\sim$8 $\times$ 10$^{-7}$ mbar), which indicates that the change occurring at 30 mbar of H$_2$O is not maintained at lower vapor pressures. The inset in Figure 2 compares rocking scans acquired in UHV ($\sim$1 $\times$ 10$^{-9}$ mbar) and $\sim$30 mbar, demonstrating the significance of the variation in reflection intensity. Furthermore, this comparison shows that there is no appreciable variation in the width of the reflection, indicating that terrace size is not significantly influenced by the presence of H$_2$O. These data suggest that the presence of $\sim$30 mbar of H$_2$O vapor leads to a modification of the surface structure of $\alpha$-Cr$_2$O$_3$(0001). This supposition will be confirmed below, through analysis of the CTR data sets acquired from Cr$_2$O$_3$–H$_2$O$_{\text{UHV}}$ and Cr$_2$O$_3$–H$_2$O$_{30\text{mbar}}$.

Initially, attention was focused upon the diffraction data acquired from Cr$_2$O$_3$–H$_2$O$_{\text{UHV}}$. To begin the search for a structural solution, the clean surface structure (Cr$_2$O$_3$–clean$_{\text{UHV}}$) determined in recent quantitative LEED (LEED-IV)\textsuperscript{15} and SXRD\textsuperscript{7} studies was employed as a starting point. This surface exhibits a topmost partially occupied double layer of Cr atoms (Cr$_{0.61}$O$_{2.4}$ from LEED-IV\textsuperscript{15} and Cr$_{0.22}$O$_{1}$ from SXRD\textsuperscript{7}). Given that the current measurements were undertaken following exposure to $\sim$2000 L of H$_2$O, terminations with surface Cr atoms bonded to one or more OH/H$_2$O species were tested. It should be noted that H atoms were not explicitly included during generation of simulated SXRD data, due to their negligible X-ray scattering, i.e., only an oxygen atom was added for each OH/H$_2$O. Refinement of these OH/H$_2$O decorated structures, including atomic coordinates, site occupation, and a surface roughness parameter ($\beta$), resulted in $\chi^2$ values of 1.7, 2.1, and 1.8 for Cr atoms bound to one, two, or three OH/H$_2$O species, respectively. For completeness, a similar structural refinement was undertaken without any adsorbed OH/H$_2$O. Optimization of this structure resulted in a $\chi^2$ of 1.2, indicating that the SXRD data provide no substantive evidence for adsorbed OH/H$_2$O under the prevailing experimental conditions.

Figure 3 displays a comparison of the experimental CTRs acquired from Cr$_2$O$_3$–H$_2$O$_{\text{UHV}}$ with the best-fit theoretical simulations. To achieve this fit 41 parameters were optimized, i.e. 35 atomic coordinates, a scale factor, a surface roughness

![Figure 2](image1.png)

**Figure 2.** Plot of the intensity of the (1, 0, 2.9) reflection as a function of H$_2$O partial pressure; the $\alpha$-Cr$_2$O$_3$(0001) sample had been dosed with $\sim$2000 L of H$_2$O prior to acquisition of these data. Dashed line is a guide for the eye. Inset displays (1, 0, 2.9) rocking scans acquired at UHV (thin line) and $\sim$30 mbar of H$_2$O (bold line).

![Figure 3](image2.png)

**Figure 3.** Comparison of experimental CTR data (solid markers with error bars), acquired from $\alpha$-Cr$_2$O$_3$(0001) in UHV subsequent to exposure to $\sim$2000 L of H$_2$O (Cr$_2$O$_3$–H$_2$O$_{\text{UHV}}$), and theoretical best-fit simulations (solid red lines).
parameter, and fractional occupancy factors for Cr(1), Cr(2), O(1), and Cr(3) (these atoms are identified in Figure 4);

Debye–Waller factors for all atoms were maintained at bulk values, i.e., 0.5 Å². As may be expected for a χ² value of 1.2, there is a good level of agreement between theory and experiment. In a number of regions away from Bragg peaks, however, the uncertainty in the experimental structure factor is relatively large and can encompass zero. Given this situation, which may lead one to question the reliability of the optimum structure, a further structure refinement was undertaken excluding all data points where the error in the structure factor includes zero. Employing this more limited data set did not result in any significant changes in the structural solution, and so was not considered further.

The surface geometry emerging from analysis of the data acquired from Cr₂O₃–H₂O₃UV is illustrated in Figure 4. Corresponding atomic coordinates are listed in Table 1; all nearest neighbor Cr–O interatomic distances are physically reasonable. A topmost partially occupied Cr double layer is maintained in the optimized structure, although the fractional occupancies of both Cr sites are less than those determined previously for Cr₂O₃–clean₃UV⁷,¹⁵ layer occupancies determined from analysis of SXRD data from Cr₂O₃–H₂O₃UV (the present study) and Cr₂O₃–clean₃UV are indicated in Figure 4. Atomic layer spacings perpendicular to the α-Cr₂O₃(0001) surface derived from both the present results and the earlier measurements⁷,¹⁵ are listed in Table 2. As with the fractional occupancies, there are variations in these values, which are not negligible. As mentioned in ref ⁷, a plausible explanation for these discrepancies in surface structure is that they arise from small variations in sample preparation methods, e.g. anneal temperature. Furthermore, it should be remembered that the latest SXRD data were recorded after exposure to 2000 L of

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**Table 1. Optimized (x, y, z) Coordinates of Atoms Comprising the Cr₂O₃–H₂O₃UV Surface Derived from Analysis of the SXRD Data Presented in Figure 3⁷**

| atom                      | (x, y, z) coordinates (Å)       |
|---------------------------|--------------------------------|
| Cr₂O₃–clean₃UV            |                                |
| Cr(1) 0.0, 0.0, 0.0      | 3.31, 1.65, 22.65              |
| Cr(2) 0.0, 0.0, 22.27    | 0.00, 0.00, 22.81 ± 0.03       |
| O(1) 1.79, 165, 21.33    | 1.90 ± 0.04, 1.57 ± 0.05, 21.54 ± 0.05 |
| Cr₂O₃–H₂O₃UV             |                                |
| Cr(4) 3.31, 3.31, 20.39  | 1.65, 3.31, 20.55 ± 0.01       |
| O(2) 3.31, 20.00         | 1.68 ± 0.02, −0.14 ± 0.04, 18.89 ± 0.03 |
| Cr(5) 0.00, 0.00, 18.12  | 0.00, 0.00, 18.22 ± 0.01       |
| Cr(6) 1.65, 3.31, 17.74  | 1.65, 3.31, 17.86 ± 0.01       |
| O(3) 1.52, 16.80         | 1.53 ± 0.03, 1.56 ± 0.02, 16.90 ± 0.03 |
| Cr(7) 3.31, 15.86        | 3.31, 1.65, 15.96 ± 0.01       |
| Cr(8) 0.00, 0.00, 15.47  | 0.00, 0.00, 15.56 ± 0.01       |
| O(4) 1.79, 14.53         | 1.80 ± 0.03, 0.05 ± 0.02, 14.60 ± 0.03 |
| Cr(9) 1.65, 3.31, 13.93  | 1.65, 3.31, 13.64 ± 0.01       |
| Cr(10) 3.31, 16.51       | 3.31, 1.65, 13.26 ± 0.01       |
| O(5) 1.65, 19.21         | 1.62 ± 0.02, 1.74 ± 0.03, 12.17 ± 0.04 |
| Cr(11) 0.00, 0.00, 11.33 | 0.00, 0.00, 11.38 ± 0.01       |
| Cr(12) 1.65, 3.31, 10.94 | 1.65, 3.31, 10.97 ± 0.01       |
| O(6) 1.52, 0.00, 10.00   | 1.52, 0.00, 10.08 ± 0.03       |
| Cr(13) 3.31, 6.90        | 3.31, 1.65, 9.10 ± 0.01       |
| Cr(14) 0.00, 0.00, 8.68  | 0.00, 0.00, 8.81 ± 0.01       |
| O(7) 1.79, 16.50         | 1.79, 1.65, 7.74 ± 0.02       |
| Cr(15) 1.65, 3.31, 6.80  | 1.65, 3.31, 6.83 ± 0.01       |
| Cr(16) 3.31, 16.41       | 3.31, 1.65, 6.42 ± 0.01       |
| O(8) 1.65, −0.14, 5.47   | 1.65, −0.14, 5.47 ± 0.02       |
| Cr(17) 0.00, 0.00, 4.53  | 0.00, 0.00, 4.55 ± 0.01       |
| Cr(18) 1.65, 3.31, 4.15  | 1.65, 3.31, 4.16 ± 0.01       |
| O(9) 1.52, 1.52, 3.20    | 1.52, 1.52, 3.24 ± 0.03       |

*Fractional occupancy is indicated by a non-integer subscript in the ‘atom’ column; the overall occupancy of oxygen atoms in the layer containing O(1) is 1.11 ± 0.12, as there are three symmetry equivalent oxygen atoms per (1 × 1) unit cell. Atomic coordinates for the bulk-terminated Cr–Cr–O structure are also listed. Figure 4 provides a key to the identity of the atoms, and the axes x, y, and z. An asterisk (*) indicates that the parameter has been held constant during optimization. x and y coordinates not optimized due to symmetry constraints are italicized.

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H₂O, which may have induced surface modification, even though no clear evidence of surface bound OH/H₂O was found during analysis of the diffraction data. For example, a proportion of topmost oxygen atoms may in reality be OH’s due to reaction with the acidic hydrogen resulting from dissociative adsorption of H₂O. The optimum value of the surface roughness parameter ($\beta = 0.42$), along with lower fractional occupancies of surface layers, may also reflect surface modification induced by H₂O exposure; $\beta = 0.2$ was obtained during fitting of the SXRD data acquired from Cr₂O₃−H₂O_UHV in ref. 7. Greater surface roughness following H₂O exposure is apparently consistent with STM images acquired from a thin film of α-Cr₂O₃(0001), which suggest that H₂O induces geometric disordering within terraces.

Turning to Cr₂O₃−H₂O_Simbu structure determination commenced with refinement of the coordinates of the optimized Cr₂O₃−H₂O_UHV structure. A best-fit $\chi^2$ of 3.2 was obtained, suggesting that the presence of ~30 mbar H₂O results in surface modification beyond mere relaxation. Consequently, terminations of the optimum Cr₂O₃−H₂O_UHV structure, where surface Cr atoms are bound to one or more OH/H₂O species, were tested. Refinement of these OH/H₂O decorated structures, resulted in $\chi^2$ values of 1.1, 2.1, and 2.3 for Cr atoms bound to one, two, or three OH/H₂O species, respectively, i.e., a structure where each surface Cr is bound to a single OH/H₂O species is favored. More specifically, it is concluded that OH/H₂O is adsorbed atop Cr, at a distance of 2.09 Å, off atop adsorption was also tested, but found to increase $\chi^2$. A comparison of the experimental CTRs with the best-fit theoretical simulations is shown in Figure 5.

Figure 6 depicts the surface structural model employed to obtain the best-fit displayed in Figure 5, in which the oxygen atoms of adsorbed OH/H₂O species are labeled with 1', 2', 3', and 4'. As illustrated, the best fit was obtained with OH/H₂O (O(1') − O(4')) located atop Cr(1) and Cr(2), as well as above any Cr(3) and Cr(4) atoms available for bonding due to fractional occupation of the topmost oxygen layer (O(1')). It should be borne in mind that the presence of O(3') and O(4') does not result in unphysical interatomic distances, as the fractional occupancy of these atoms is governed by fractional occupancy of O(1'). Optimum atomic coordinates are listed in Table 3. Here, again, all nearest neighbor Cr−O interatomic distances are physically reasonable. During fitting 35 atomic coordinates were varied. In addition, as above, a scale factor, a surface roughness parameter, and fractional occupancy factors for Cr(1), Cr(2), O(1), and Cr(3) were also optimized. Debye−Waller factors for all atoms were again maintained at bulk values, i.e. 0.5 Å². The optimum surface roughness parameter, $\beta = 0.39$, is very similar to that obtained for Cr₂O₃−H₂O_UHV indicating that immersion in p(H₂O) ~ 30 mbar does not induce further surface roughening. Furthermore, it should be noted that the presence of O(1') and O(4') was constrained to have the same fractional occupancies as Cr(1) and Cr(2), respectively. Similarly, the fractional occupations of O(3') and O(4') were fixed to be equal to the fraction of available Cr(3) and Cr(4) atoms, respectively. Finally, all Cr−OH/H₂O bond lengths (i.e., Cr(1)−O(1'), Cr(2)−O(2'), Cr(3)−O(3'), and Cr(4)−

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**Table 2. Comparison of Atomic Layer Spacings ($d_l$) Perpendicular to the α-Cr₂O₃(0001) Surface Derived from Previous UHV LEED-IV⁷⁴ and SXRD⁵ Work and the Current UHV SXRD Measurements Acquired Following Exposure to ~2000 L of H₂O⁴¹**

| atomic layers | bulk-terminated | LEED-IV, ref 14 | SXRD, ref 7 | SXRD, this study |
|---------------|-----------------|-----------------|-------------|-----------------|
| Cr(1)/Cr(2)   | 0.38            | 0.27            | 0.22 ± 0.04 | 0.27 ± 0.05     |
| Cr(2)/O(1)    | 0.94            | 1.04            | 1.30 ± 0.03 | 1.27 ± 0.05     |
| O(1)/Cr(3)    | 0.94            | 0.96            | 0.68 ± 0.03 | 0.99 ± 0.05     |
| Cr(3)/Cr(4)   | 0.38            | 0.38            | 0.33 ± 0.01 | 0.56 ± 0.02     |
| Cr(4)/O(2)    | 0.94            | 0.93            | 0.64 ± 0.01 | 1.10 ± 0.02     |
| O(2)/Cr(5)    | 0.94            | not optimized   | 1.36 ± 0.01 | 0.67 ± 0.02     |

* Bulk terminated interlayer distances are also listed. Figure 4 indicates the identity of the atomic layers.

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**Figure 5. Comparison of experimental CTR data (solid markers with error bars), acquired from α-Cr₂O₃(0001) at p(H₂O) ~ 30 mbar (Cr₂O₃−H₂O_UHV), and theoretical best-fit simulations (solid red lines). Also included are theoretically simulated data (broken blue line) for optimum Cr₂O₃−H₂O_UHV geometry.**

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O(4′)) were constrained to have the same value during optimization.

**DISCUSSION**

Figure 7 summarizes the change in surface termination of α-Cr₂O₃(0001) determined through analysis of the SXRD data acquired from Cr₂O₃−H₂O_UHV and Cr₂O₃−H₂O₃_ambient. In the presence of ~30 mbar of H₂O, each under-coordinated surface Cr atom becomes decorated with a single atop OH/H₂O species. The lack of OH/H₂O on Cr₂O₃−H₂O_UHV is unexpected given that previous investigations of H₂O adsorption on α-Cr₂O₃(0001) have revealed the presence of adsorbed OH at room temperature even in UHV. The presence of OH/H₂O in these earlier studies were significantly lower than those employed in the present work. One possible explanation for this discrepancy is that the adsorbate X-ray beam could induce adsorbate desorption. Such a process would still occur at p(H₂O) ~ 30 mbar, but the OH/H₂O overlayer would be dynamically maintained due to the continuous flux of surface impinging H₂O molecules. Alternatively, it may be that under UHV conditions the surface coverage of OH/H₂O species is simply significantly lower than at 30 mbar (e.g., OH/H₂O may only be located at specific defect sites), and so the diffraction data are not sensitive to their presence. This possibility seems to contradict the previous studies, which suggest that adsorption is not restricted to minority sites at room temperature in UHV. However, it should be noted that these studies were undertaken on thin films of α-Cr₂O₃(0001), rather than a suitably oriented single crystal. It could very well be that this difference in substrate leads to variation in H₂O adsorption, i.e., thin films of α-Cr₂O₃(0001) may display significant

| atom | (x, y, z) coordinates (Å) |
|------|--------------------------|
| Cr(11) | 0.00, 0.00, 11.33 | 0.00, 0.00, 11.39 ± 0.01 |
| Cr(12) | 1.65, 3.31, 10.94 | 1.65, 3.31, 11.02 ± 0.01 |
| O(6) | 1.52, 0.00, 10.06 | 1.52, 0.00, 10.06 ± 0.01 |
| Cr(13) | 3.31, 1.65, 9.06 | 3.31, 1.65, 9.12 ± 0.01 |
| Cr(14) | 0.00, 0.00, 8.68 | 0.00, 0.00, 8.72 ± 0.01 |
| O(7) | 1.79, 1.65, 5.77 | 1.79, 1.65, 5.78 ± 0.01 |
| Cr(15) | 1.65, 3.31, 6.80 | 1.65, 3.31, 6.55 ± 0.01 |
| Cr(16) | 3.31, 1.65, 6.41 | 3.31, 1.65, 6.45 ± 0.01 |
| O(8) | 1.65, −0.14, 5.47 | 1.65, −0.14, 5.50 ± 0.01 |
| Cr(17) | 0.00, 0.00, 4.83 | 0.00, 0.00, 4.85 ± 0.01 |
| Cr(18) | 1.65, 3.31, 4.15 | 1.65, 3.31, 4.16 ± 0.01 |
| O(9) | 1.52 ± 0.12, 3.20 | 1.52 ± 0.14, 3.22 ± 0.03 |

Fractional occupancy is indicated by a non-integer subscript in the “atom” column; the overall occupancy of oxygen atoms in the layer containing O(1) is 1.2 ± 0.09, as there are three symmetry equivalent oxygen atoms per (1 x 1) unit cell. Atomic coordinates for the bulk-terminated Cr−Cr−O-structure are also listed. Figure 6 provides a key to the identity of the atoms. An asterisk (*) indicates that the parameter has been held constant during optimization. x and y coordinates not optimized due to symmetry constraints are italicized.
concentrations of sites active for dissociative adsorption of H₂O that are not present to any significant extent on the single crystal substrate. Finally, it is concluded in ref 4 that surface-bound OH is expected to slowly desorb from α-Cr₂O₃(0001) at around room temperature. Such loss of OH, if it occurs, would likely result in SXRD data being acquired in UHV from a surface with a coverage of OH well below saturation. However, this desorption process is probably not the origin of the observed lack of adsorbed OH/H₂O on Cr₂O₃−H₂O$_{\text{UHV}}$. If it were, one might expect an OH/H₂O overlayer closer to saturation coverage to be maintained on the surface at H₂O partial pressures well below 30 mbar, which is not reflected by the plot in Figure 2, i.e., would expect increase in diffracted signal to occur at lower p(H₂O).

Concerning the structure determined at p(H₂O) ~ 30 mbar, it can be seen that it is inconsistent with the predictions emerging from the calculations of Costa et al. They conclude that a (OH)−Cr−O−termination is energetically unfavorable, contradicting our experimental structure determination. It may be argued that this discrepancy is again due to the influence of the X-ray beam. However, in our opinion, that the X-ray beam would selectively desorb OH/H₂O species from each surface Cr leaving one remaining is doubtful. One more plausible reason for this difference, as stated in the Experimental Methods, is that the SXRD data have been acquired from a surface submerged beneath multiple monolayers of H₂O, due to the relative humidity being ~100%. In contrast, Costa et al. do not explicitly include multiple layers of water in their modeling, which may be the origin of the variation in interfacial structure. An alternative explanation for the divergence between the ab initio predictions and experiment is that the initial clean substrate termination used for the calculations is significantly different to that determined by diffraction. It could be that the more disordered surface found in the experiment hinders the formation of an extended network of OH/H₂O hydrogen bonding, which emerges from the first-principles modeling, resulting in Cr binding to multiple OH/H₂O species becoming energetically unfavorable. Another possible reason for the difference is that there is a significant energy barrier to the attachment of additional OH/H₂O to each Cr, and so cannot be realized with the substrate at room temperature. Further ab initio modeling, which more closely mimics both the experimentally determined α-Cr₂O₃(0001) termination and the measurement environment, is required to test these hypotheses. For example, ab initio molecular dynamics could be employed to better simulate the submerged substrate.

Regarding the precise nature of the adsorbed species at 30 mbar of H₂O, only the Cr−(OH/H₂O) interatomic distances (i.e., Cr(1)−O(1′), Cr(2)−O(2′), Cr(3)−O(3′), and Cr(4)−O(4′)) provides any direct insight. As indicated above, a value of 2.09 Å, with an error bar ranging from ±0.01 Å for Cr(3)−O(3′) and Cr(4)−O(4′) to ±0.07 Å for Cr(1)−O(1′), has been obtained for this parameter; the spread in the magnitude of the errors is a result of the variation in fractional occupancies (lower occupancy leads to a larger error). Costa et al. predict that the Cr−O bond length for a surface bound OH moiety should be 1.97 Å, increasing to 2.1 Å for adsorbed H₂O. On this basis, one might propose that at 30 mbar of H₂O, Cr₂O₃(0001) is decorated with adsorbed molecular H₂O rather than OH. However, this deduction must be regarded with caution due to the approach employed for fitting the diffraction data, i.e. to limit the number of parameters optimized, the possibility for each substrate atom to adopt more than one location was not incorporated, even where there were variations in local environment. For example, regarding the Cr₂O₃−H₂O$_{\text{UHV}}$ data, this approach results in employing only two atoms (Cr(3) and Cr(4)) to describe the first subsurface double layer ofCr atoms, even though some are bound to O(1) and others to O(3′) or O(4′) atoms. Given that this change in local coordination is likely to lead to somewhat different atomic coordinates, the Cr−(OH/H₂O) inter atomic distance (2.09 Å) is less well-defined than indicated above. Consequently, we conclude that it is not possible to uniquely identify the adsorbate (OH or H₂O) present on Cr₂O₃−H₂O$_{\text{UHV}}$ from the current SXRD data set. However, the weight of other evidence5,6 suggests that dissociative adsorption is more likely, i.e. the adsorbate is OH.

Comparing the present results to those obtained for the interaction of H₂O with other (0001) surfaces of corundum-type metal oxides, of particular interest are near ambient pressure photoemission data from α-Fe₂O₃(0001). In that study, it was concluded that as the partial pressure of H₂O increases, the surface becomes increasingly decorated with surface OH, attaining a maximum coverage of ~1 monolayer at ~10⁻⁷ mbar. Adsorbed H₂O is also observed, suggested to be located above the OH layer, i.e. a three layer Fe₂O₃(0001)/OH/H₂O interface is formed. One might also expect similar layering on α-Cr₂O₃(0001) at 30 mbar of H₂O, but only a single OH/H₂O layer is evident from analysis of the SXRD data. However, it should be remembered that SXRD is sensitive to adsorbed layers displaying order both parallel and perpendicular to the surface plane of the substrate. Hence, the analysis presented here should not be interpreted as indicating that only a single layer of OH/H₂O is present on Cr₂O₃(0001) at 30 mbar H₂O, but that only this layer is sufficiently ordered to be apparent in SXRD. Again, 30 mbar of H₂O is equivalent to ~100% relative humidity with the substrate at room temperature, and so the surface is expected to be submerged beneath multiple monolayers of H₂O.

Another result worthy of mention is the local adsorption geometry of OH obtained from photoelectron diffraction (PhD) measurements in UHV performed following exposure of V₂O₃(0001) to H₂O. In contrast to the current study, no evidence for OH atop surface V atoms was found. Instead, only the surface oxygen atoms (equivalent to O(1) in Figures 4 and 6) are hydroxylated through attachment of H, presumably derived from H₂O dissociation; the location of the dissociated OH fragment is not identified. This difference may be due to the initial V₂O₃(0001) surface being terminated by vanadyl groups (V═O), rather than under-coordinated V atoms.

Of further interest is a brief consideration of the previous SXRD study probing the surface structure α-Cr₂O₃(0001) as a function of oxygen partial pressure. It is pleasing to note that away from UHV (p(H₂O) ~ 30 mbar (current study), and p(O₂) = 1 × 10⁻⁴ mbar) the optimum surface structures are not identical, i.e. data have not simply been acquired from similarly contaminated surfaces due to extrinsic components of the ambient environment. For both H₂O and O₂, adsorption occurs atop under-coordinated surface Cr atoms, but the Cr−O bond distance is significantly shorter in the presence of O₂ (1.57 ± 0.03 Å). This shorter Cr−O distance is consistent with the formation of surface chromyl (Cr═O) groups. Furthermore, unlike H₂O/OH decorated α-Cr₂O₃(0001), the chromyl terminated surface remains intact following reduction of the O₂ partial pressure.
To summarize, SXRD data have been acquired from \(\alpha-Cr_2O_3\)(0001) as a function of \(H_2O\) partial pressure. In UHV, after exposure to \(\sim2000\) L of \(H_2O\), the surface is terminated by a partially ordered double layer of chromium atoms; the lack of adsorbed \(OH/H_2O\) is concluded to be most likely a result of either adsorption only at defects, or X-ray induced desorption. This surface geometry is largely consistent with those determined in recent LEED-IV \(^{15}\) and SXRD \(^{7}\) studies of clean \(\alpha-Cr_2O_3(0001)\) in UHV, although there are differences in the values of atomic coordinates and fractional layer occupancies. At \(\sim30\) mbar of \(H_2O\), a single \(OH/H_2O\) species is bound atop each surface Cr. This result is not consistent with the \textit{ab initio} calculations of Costa et al. \(^{6}\) which predict that surface termination evolves as a function of \(H_2O\) partial pressure at around room temperature as \(Cr-O_\text{ad} \rightarrow (OH)_2-Cr-O_\text{ad} \rightarrow (H_2O(OH))_\text{ad}-Cr-O_\text{ad}\). One possible explanation for this discrepancy between theory and experiment is that the calculations do not explicitly take into account multiple layers of interfacial \(H_2O\), which is the expected SXRD measurement environment, as the relative humidity is \(\sim100\%\).

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b04607.

LEED and Auger data acquired from \(\alpha-Cr_2O_3(0001)\) substrate (PDF)

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Notes
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