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Nature of Lone-Pair−Surface Bonds and Their Scaling Relations

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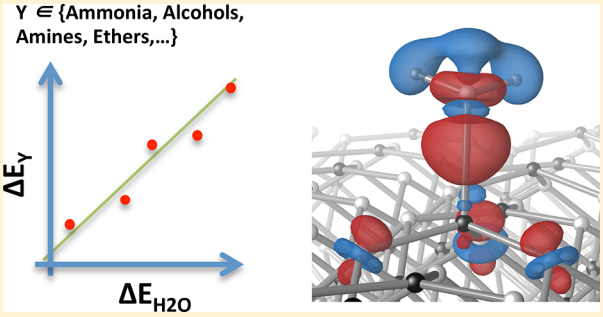
Supporting Information

ABSTRACT: We investigate the (surface) bonding of a class of industrially and biologically important molecules in which the chemically active orbital is a 2*p* electron lone pair located on an N or O atom bound via single bonds to H or alkyl groups. This class includes water, ammonia, alcohols, ethers, and amines. Using extensive density functional theory (DFT) calculations, we discover scaling relations (correlations) among molecular binding energies of different members of this class: the bonding energetics of a single member can be used as a descriptor for other members. We investigate the bonding mechanism for a representative (H_2O) and find the most important physical surface properties that dictate the strength and nature of the bonding through a combination of covalent and noncovalent electrostatic effects. We describe the importance of surface intrinsic electrostatic, geometric, and mechanical properties in determining the extent of the lone-pair−surface interactions. We study systems including ionic materials in which the surface positive and negative centers create strong local surface electric fields, which polarize the dangling lone pair and lead to a strong "electrostatically driven bond". We emphasize the importance of noncovalent electrostatic effects and discuss why a fully covalent picture, common in the current first-principles literature on surface bonding of these molecules, is not adequate to correctly describe the bonding mechanism and energy trends. By pointing out a completely different mechanism (charge transfer) as the major factor for binding N- and O-containing unsaturated (radical) adsorbates, we explain why their binding energies can be tuned independently from those of the aforementioned species, having potential implications in scaling-driven catalyst discovery.



INTRODUCTION

Scaling relations or linear correlations among binding energies (BEs) of adsorbates are at the heart of computational catalyst design.[1−3] The many-dimensional search space for the optimum catalyst can be significantly reduced to a low-dimensional space of a few descriptors due to such relations.[4−8] Most literature on scalings has focused on relations among open-shell unsaturated intermediates (eg., O*, OH*, OOH*). However, a similar understanding of closed-shell adsorbates is lacking. Here, we show broadly applicable, material-independent scaling relations among a class of closed-shell molecules, whose chemically active orbital (HOMO) is an N or O 2*p* lone pair,[9] in which the N or O is bound to neighboring atoms and groups in the molecule via single bonds. This class includes water, ammonia, alcohols, ethers, and amines, which find use in medical, biological, pharmaceutical, fertilizer, and fuel industries.[10−13] While there are studies that calculate BEs of these molecules[14−30] on specific surfaces, here we obtain a generalized understanding of their binding mechanisms and BE trends on a wide range of materials. The application of this descriptor-based approach[31−34] goes beyond merely predicting BEs, also implying the existence of a common lone-pair−surface bonding mechanism. We pick H_2O as a representative of the class, study its bonding, and shed light on this common mechanism.

Our choice of H_2O stems from the essential role of water−surface interactions in a wide range of fields, from catalysis, electrocatalysis, and surface wetting to corrosion of solids.[35−39] Water binding to transition metal (TM) surfaces has been extensively studied, especially in the context of water layer structures at the solid interface.[40−43] Here, we first introduce a simple electronic structure descriptor that models the water−TM interaction as a covalent interaction between the water HOMO and the surface empty bands. The interaction between water and clean TM surfaces[44] leads to a weak binding.[45−47] In

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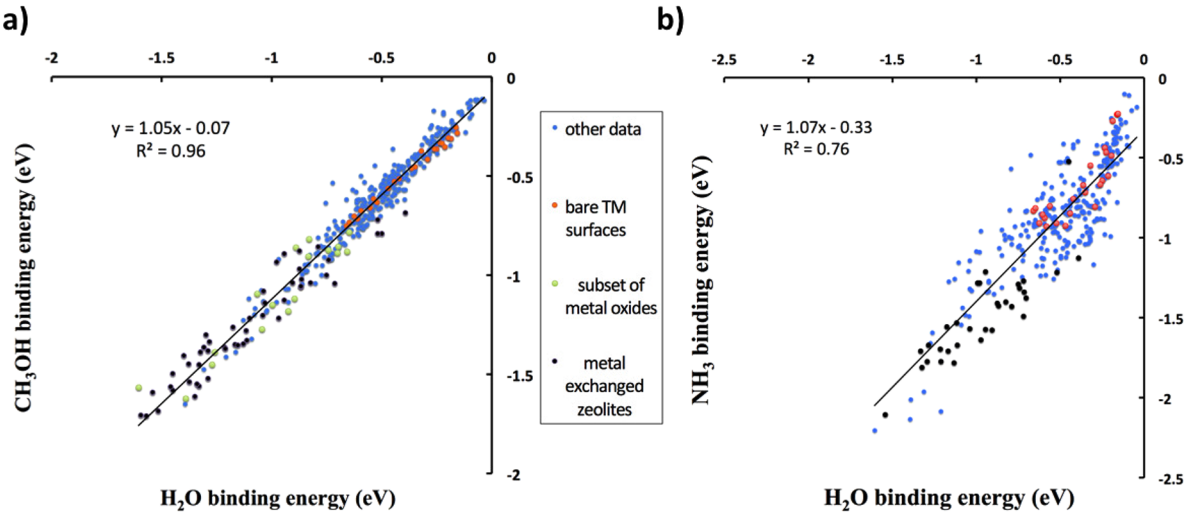

Figure 1. Scaling relations between BEs of (a) CH_3OH vs H_2O and (b) NH_3 vs H_2O.

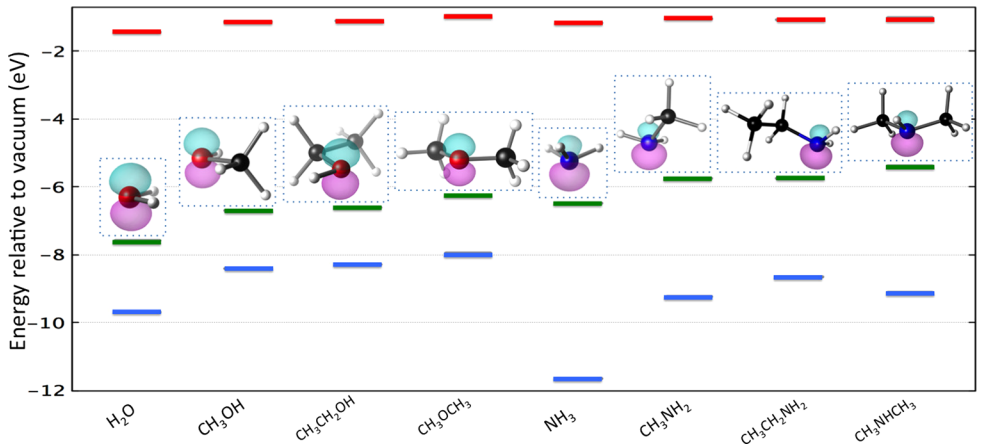

Figure 2. DFT-derived MOs for some molecular species with O or N 2*p* lone pairs. The lines indicated in green show the HOMO, blue indicates the HOMO-1, and red denotes the LUMO. For the HOMO, we have graphically shown the MO by plotting the wave function: magenta and cyan show different signs of the wave function.

contrast, on more ionic systems including oxides, several studies observe much stronger BEs.[48] This sizable span of BEs from a few tenths of an electronvolt on TMs[44,49] to more than 1 eV on some oxide surfaces[48,50] combined with variations within the class of oxides[48] leads us to discover what dictates the strength of lone-pair−surface interactions. By extending our covalent model for H_2O binding on clean TM surfaces to other surfaces, we disentangle the covalent and noncovalent contributions to the BEs. We show how noncovalent interactions become important and sometimes dominate when departing from bare TM surfaces. Noncovalent lone-pair interactions[51−62] have been discussed previously in the molecular chemistry literature: e.g., lone-pair−π interactions.[63−67] We show that intrinsic surface electrostatics can polarize the dangling water HOMO and greatly stabilize its molecular bonding. The polarized lone pair[68] then acts as an enhanced (induced) dipole that interacts with the local electrostatic potential well[69] created by the surface positive and negative centers. We explain the role of formal charges, geometry, and surface electronic and mechanical properties on the BEs. Such knowledge can then be used to predict the water interaction with a wide range of surfaces and has applications in electrocatalysis and electrochemistry,[70−72] surface wetting,[73−77] solid−water interfaces beyond TMs,[78−85] solids corrosion,[38,86,87] biological systems,[88,89] etc. As a consequence of the material-independent scaling relations we find between the N and O 2p lone-pair species, such knowledge is transferrable to other molecules in this class.

RESULTS AND DISCUSSION

Material-Independent Lone-Pair Scaling Relations. We conducted DFT calculations to study molecular (intact) lone-pair bonding on a large and diverse set of surfaces (a complete list is given in section 24 of the Supporting Information). Figure 1a shows that the H_2O and CH_3OH BEs scale broadly. We also investigated the scaling between O 2*p* and N 2*p* lone pairs through H_2O and NH_3 (Figure 1b).

In order to understand these correlations, we plot the DFT-derived molecular orbitals (MOs) and their energies in Figure 2. Details on the level alignments are in section 1 of the Supporting Information. The broadly observed scaling relations imply a similar surface bonding mechanism and therefore require similarities in the electronic structure.[1,3] Clearly, for these species, the character of the chemically active orbital (HOMO) is similar (O or N 2*p* lone pair). Since we have already observed a correlation among BEs of H_2O, CH_3OH,

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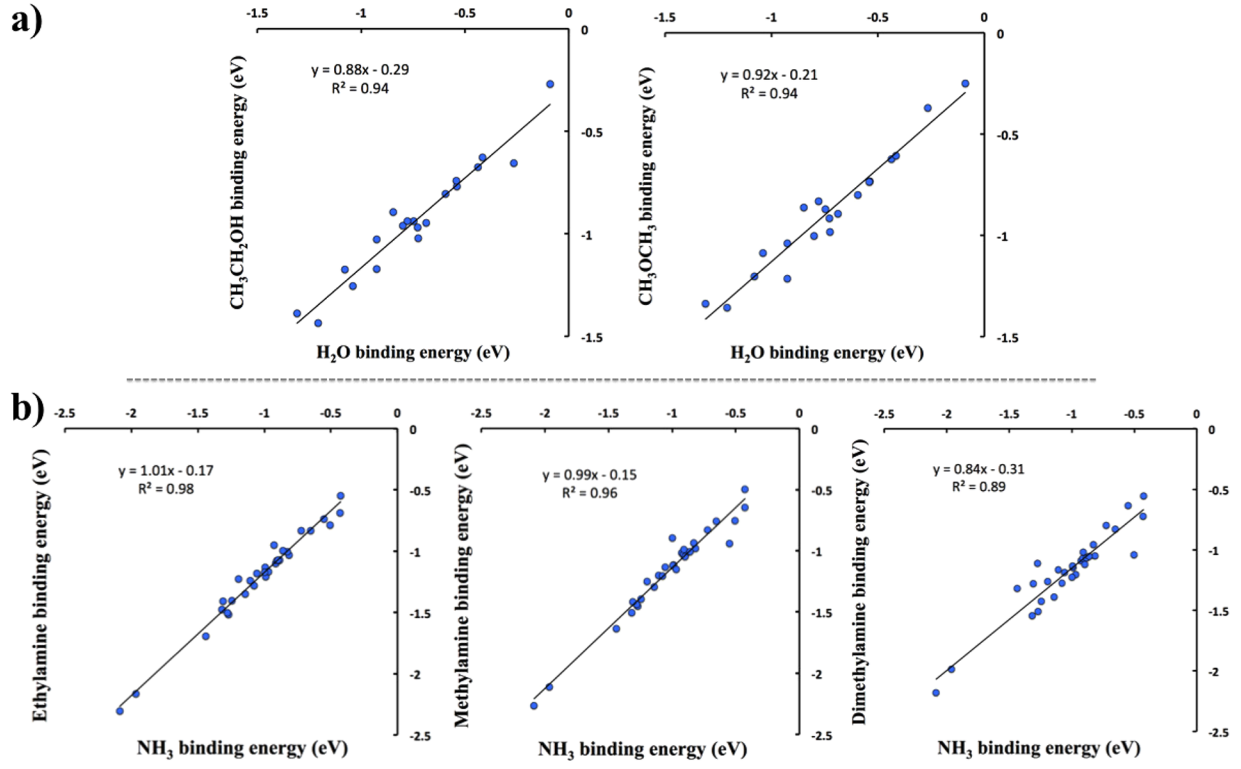

Figure 3. Scaling relations among (a) ethanol, dimethyl ether, and water and (b) ethylamine, methylamine, dimethylamine, and ammonia.

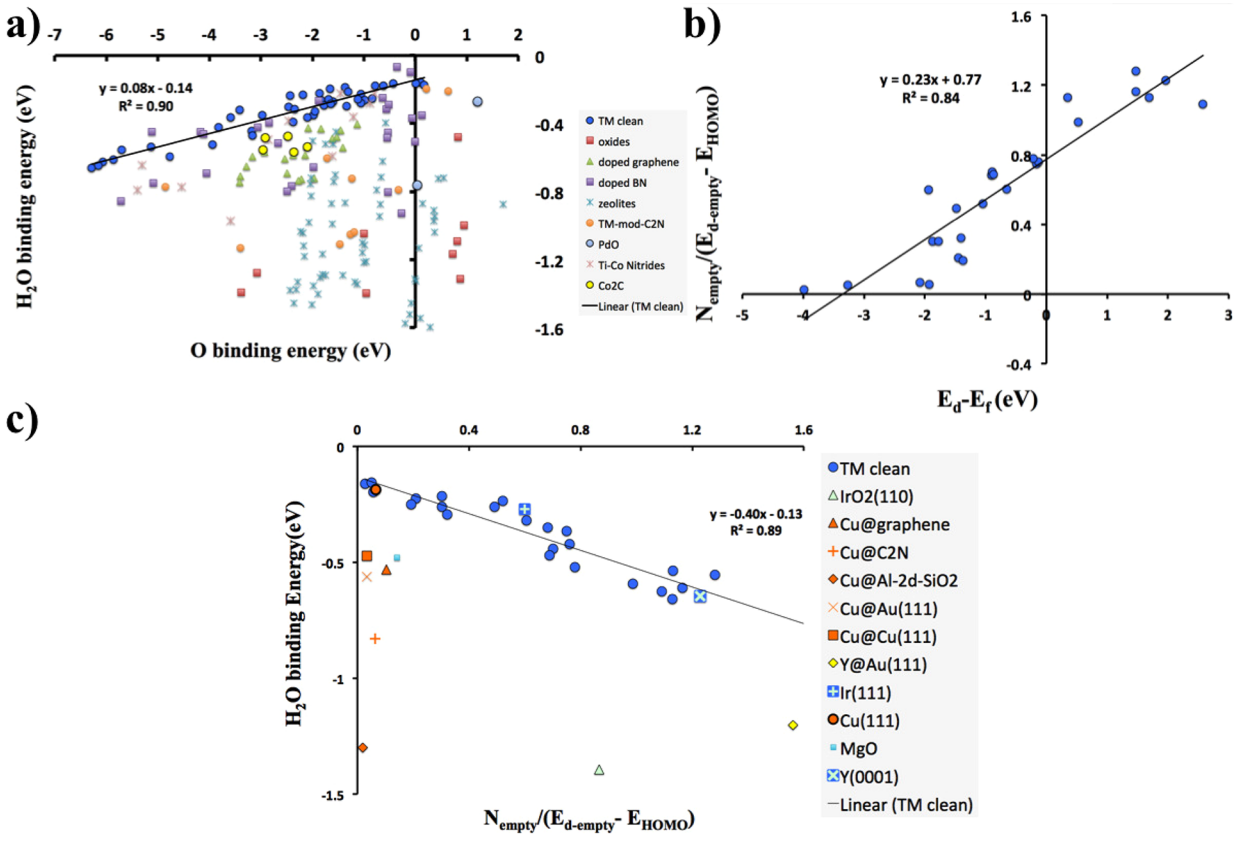

Figure 4. (a) H_2O BE versus O on a number of TMs, oxides, nitrides, carbides, and single-site systems. (b) The new descriptor $N_{empty}/(E_{d\text{-empty}} - E_{HOMO})$ scaling with the previously used descriptor for adsorbates binding to TM surfaces $E_d - E_f$ (center of d band relative to Fermi energy). (c) H_2O BE scaling with $N_{empty}/(E_{d\text{-empty}} - E_{HOMO})$ for TM surfaces but not for other systems. O BE is relative to 1/2 O_2, while H_2O binding is relative to H_2O under vacuum.

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and NH_3, we expect that there should be similar relationships among all the considered molecules. In Figure 3 we show the correlations based on BE calculations on a diverse subset of materials (see section 24.3 of the Supporting Information). The coefficients of determination are very high in all cases: we are able to predict the BE for any of these molecules by knowing only the BE of one of them.

Comparing Figure 1b with the other plots in Figures 1 and 3, we notice a greater scatter when we compare species with O versus N 2*p*. For example, the mean absolute error (MAE) is 0.05 eV in Figure 1a and 0.15 eV in Figure 1b. Both MAEs are significantly smaller than the range of variations in BEs of the species across different materials (>2 eV). Thus, the correlation in Figure 1b is meaningful and strong enough to indicate a common bonding mechanism across both the O and N 2*p* lone-pair species discussed here (an explicit comparison is given in section 20 of the Supporting Information).

Lone Pair−Surface Bond on Clean Transition-Metal Surfaces. Due to the aforementioned scalings, we will focus primarily on the water−surface interaction as the class descriptor. Abild-Pedersen et al.[1] have described scaling relations between BEs of hydrogen-containing adsorbates on TM surfaces. The BE of hydrogenated species AH_x is linked to that of the central atom A via

$$E_{ads}(AH_x) = \gamma E_{ads}(A) + \xi \quad (1)$$

$$\gamma = \frac{x_{max} - x}{x_{max}} \quad (2)$$

where x_{max} is the maximum number of H atoms that can bond to A to form a stable gas-phase molecule (e.g., 2 for O and 3 for N). The largest contribution to the bonding of AH_x ($x < x_{max}$) species on TMs come from hybridization and charge transfer from the metal *sp* states.[1,90] This is approximately constant among TMs, and the variation among different metals comes from a smaller contribution caused by the metal *d* states (ΔE_d).[1,90] When $x = x_{max}$, e.g., $x = 4$ in CH_4, the H atoms bonded to the central atom provide it with the optimum charge density and, according to eq 2, the scaling parameter $\gamma = 0$.

Here, we investigate the relation among H_2O and O BEs for a diverse set of materials (Figure 4a). For clean TM surfaces, the binding geometry is characterized by an almost flat on-top geometry (the normal to the H_2O plane being almost parallel to the surface normal and the oxygen on top of the surface metal), consistent with the literature.[15,16,44,86,91−93] On clean TM surfaces H_2O BE scales with O with a nonzero slope and *y* intercept of $\gamma \approx 0.08$ and $\xi \approx -0.14$ eV. Below we describe the physics behind this nonzero γ.

The H_2O HOMO is a dangling filled O 2*p* state perpendicular to the H_2O plane (Figure 2) denoted as a $1b_1$ MO.[94−96] Such a filled orbital can, in principle, interact with the unoccupied part of the surface conduction band and lower its energy.[97−99] In a view of the projected density of states (PDOS) plots,[100−102] this is manifested as an increased broadening of the adsorbed H_2O HOMO and an increased mixing between H_2O and metal states (Figure 5). For details see section 2 of the Supporting Information.

Unlike the bond between AH_x ($x < x_{max}$) species and TM surfaces, dominated by electron transfer to the adsorbate states,[1,90] the aforementioned bond is not associated with electron transfer from the surface to the closed-shell molecule. Some of the adsorbates with $x = x_{max}$ such as H_2O and NH_3 have dipole moments which can induce a dipole moment in the

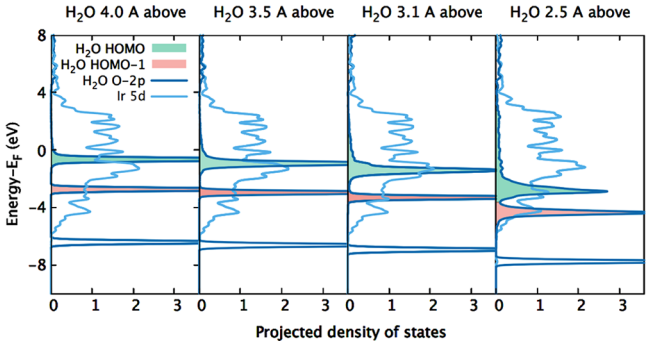

Figure 5. PDOS for H_2O adsorption on the Ir(111) surface.

metal[103] (i.e., induced image charges in the metal[104]). The induced dipole further polarizes the molecule[19,103,105] and further stabilizes the lone-pair−surface bond.[44,45,104,106] This interaction shows up in PDOS plots as a gradual energy downshift of the center of the H_2O HOMO as it approaches the surface (Figure 5). There are also van der Waals (vdW) interactions that further stabilize the bonding.[107−109] Theoretical surveys find the magnitude of the vdW interaction to be $\lesssim$0.2 eV per H_2O molecule.[107,110−112] Despite the large number of factors that might affect the surface−water bonding, we find that a simple model in which the water HOMO interacts with the empty part of the *d* band (above E_f) captures the variations in water BE among different TMs.

First, we turn to the Newns−Anderson (NA) model. As pointed out by Bligaard and Nørskov,[113] in the limit of small surface−adsorbate coupling $|V_{ad}| \ll E_d - E_a$, the bond energy between a completely filled state $|a\rangle$ and a partially filled state $|d\rangle$ (with filling *f*) is given by

$$\delta E \propto \frac{1 - f}{E_d - E_a} V_{ad}^2 \quad (3)$$

$$1 - f \propto N_{empty} \quad (4)$$

Here N_{empty} is the total number of states above the Fermi energy for the surface chemically active $|d\rangle$ orbital. If we take the adsorbate filled state $|a\rangle$ to be the water HOMO, then for a constant coupling constant V_{ad}

$$\delta E \propto \frac{N_{empty}}{E_d - E_{HOMO}} \quad (5)$$

We find that, for clean TM surfaces, the right-hand side of eq 5 correlates extremely well with a new descriptor in which E_d (center of the *d* band) is substituted by $E_{d\text{-empty}}$, the center of the empty fraction of the *d* band:

$$\frac{N_{empty}}{E_d - E_{HOMO}} \propto \frac{N_{empty}}{E_{d\text{-empty}} - E_{HOMO}} \quad (6)$$

The right-hand side of eq 6, to which we refer as empty band descriptor (EBD), correlates with the center of the *d* band, which is the more frequently used descriptor[114−116] for radical adsorbate (including O) interactions with TM surfaces (Figure 4b). We find that H_2O BEs on TM clean surfaces correlate with the EBD (Figure 4c) and consequently the center of the *d* band. This is the underlying reason for the scaling between H_2O and O on clean TM surfaces (Figure 4a).

Choosing EBD as a descriptor means that we model the H_2O molecular bonding as a chemical bond between the O 2*p* lone-

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pair (HOMO) and center of the empty part of the surface *d* band. This useful correlation between H_2O BE on clean TM surfaces and EBD is quantified by the simple relation

$$E_{bind}(H_2O{-}TM_{clean}) = E_{bind}^{covalent}(H_2O) \approx -0.39\ (eV)^2 \frac{N_{empty}}{E_{d\text{-empty}} - E_{HOMO}} - 0.13\ (eV) \quad (7)$$

Equation 7 can be extended beyond the simple case of transition metals (section 3 in the Supporting Information) to separate the covalent contribution to the lone-pair−surface bonding from noncovalent contributions that will be discussed later in this article.

Understanding the Role of Intrinsic Surface Electrostatics in Water−Surface Bonding. As shown above, the interaction between water and clean TM surfaces is understood on the basis of a *d*-band model. We now turn our attention to other materials where a simple covalent model fails. We find the noncovalent interactions originating from intrinsic surface electrostatics (ISE) to be the dominant interaction. Positive centers (surrounded by negative centers) which form as a result of electron transfer from more electropositive (e.g., metals) to more electronegative constituents of the solid (e.g., O or N in oxides or nitrides, respectively) create strong local electrostatic potential (ESP) wells and strong and inhomogeneous local surface electric fields. These then stabilize the dangling HOMO of H_2O and lead to an "electrostatic bond".

To elucidate this electrostatic effect, we perform a gedankenexperiment. We embed a Cu atom in different host structures, departing gradually from the behavior of clean TMs, and we calculate the oxidation state of the Cu in each structure using Bader charge analysis (BCA).[117,118] From the data shown in Table 1, the formation of a partial positive charge on the Cu increases the H_2O BE. First we look at a Cu atom added on Cu(111) and Au(111), denoted by Cu@Cu(111) and Cu@Au(111), respectively. Here, the partial positive charge is formed due to the loss of metal coordination and relative destabilization of the Cu valence orbitals that lead to electron migration to the Fermi energy (the electron sea located on surrounding more coordinated copper atoms). There is a greater partial charge on Cu adsorbed on Au(111), since in addition to the aforementioned effect, there is also a difference in electronegativity that drives electrons from Cu to the Au(111) bed.[119,120] The greatest partial charge is noticeable on the system in which Cu bonds to electronegative O atoms, denoted by Cu@Al@2*d*-silica (similar to Cu-exchanged zeolites[121,122]). Figure 6 shows how the partial positive charge creates an ESP well.

Table 1. H_2O and O BEs on a Cu Atom in Different Host Structures[a]

system	Cu oxidation state	O binding energy (eV)	H_2O binding energy (eV)
Cu(111)	+0.0	−1.36	−0.19
Cu@Cu(111)	+0.11	−1.10	−0.47
Cu@Au(111)	+0.30	−0.05	−0.56
Cu@Al@2*d*-silica	+0.78	0.87	−1.30

[a]The oxidation state (without adsorbates) is calculated using Bader charge analysis (BCA). O binding is relative to 1/2 O_2, while H_2O binding is relative to H_2O in vacuum.

To understand how the partial positive charge and the associated ESP well enhance H_2O bonding, we analyze the bonding mechanism on Cu@Au(111). As per Figure 7, we bring down the H_2O from a larger distance in vacuum to its equilibrium bonding distance. It is seen that as H_2O approaches the surface Cu atom, it feels the ESP well and the strong nonuniform electric field associated with it and its HOMO (depicted in Figure 2) polarizes,[103,124,125] leading to more electron density on the side facing the surface. The fact that H_2O can redistribute its electrons on the side facing the ESP well further stabilizes its bonding, as even more electrons can lower their potential energy in the ESP well. The gradual energy downshift of the H_2O HOMO is evident in Figure 7e. (Some details on the geometry and charge redistribution shown in Figure 7 are given in of the section 4 of the Supporting Information.)

Having a simple covalent model (eq 7) constructed for H_2O on clean TM surfaces allows us to disentangle the covalent effect from the electrostatic effect for H_2O binding to Cu@Au(111). Here, unlike the case of clean TM surfaces, there is an additional contribution to the BE. Thus, the right side of eq 7 does not yield the whole BE, but only the covalent contribution. As seen in Figure 4c, for all surfaces in Table 1, the same covalent contribution to the BE is predicted (the same EBD). Therefore, the difference in H_2O BE for these compounds, from −0.19 for Cu(111) to −1.30 eV for Cu@Al@2*d*-SiO_2, is due to the difference in ISE.

The fact that H_2O BE scales with EBD and the center of the *d* band on clean TM surfaces (Figure 4) is the reason for the H_2O−O scaling on these materials (Figures 4a and 8a). As seen in Figure 8a, the H_2O−O scaling for TM surfaces even holds for calculations done on TM monolayers with only small deviations. The ISE breaks the scaling between the *d*-band center and H_2O binding by introducing a more important bonding mechanism. By enhancing ISE, one gets a more pronounced deviation from H_2O−O scaling line on TM-based materials. We designed a numerical experiment to test the effect of extreme ISE using TM-only materials: we took two TMs with extreme electronegativity difference, namely Y and Au,[120] and put a single Y atom on top of a Au(111) bed (Figure 8c). BCA shows that the Y acquires a charge of +1.6 e, much greater than Cu partial charge on Cu@Cu(111) and Cu@Au(111). As predicted, Y@Au(111) has the largest deviation from the scaling lines for clean TM surfaces in both Figure 8a and Figure 4c, a direct result of its sizable ISE. Another set of numerical experiments was carried out on TM dimers, stripes, and clusters on clean facets to elucidate the importance of electrostatics and how it creates deviation from the scaling line in Figure 8a. Details on this are given in section 5 of the Supporting Information.

Looking at the results presented in Table 1, we note the different trends for O and H_2O binding. This is due to two different mechanisms of bonding. For O, we have charge transfer from metallic delocalized *sp* states, while for H_2O, we have HOMO polarization under ISE and an interaction strength depending on the depth of the ESP well. Thus, among systems presented in Table 1, Cu(111) has a relatively strong O binding as (i) it is a conductor with delocalized *sp* states at the Fermi level and (ii) it has a small enough work function so that these electrons pour into and stabilize the O 2*p* states. Conversely, Cu@Al@2*d*-SiO_2 is an ionic solid with a band gap and has a very weak O binding. Nevertheless, it is exactly due to this ionic nature that it has a significant ISE and a

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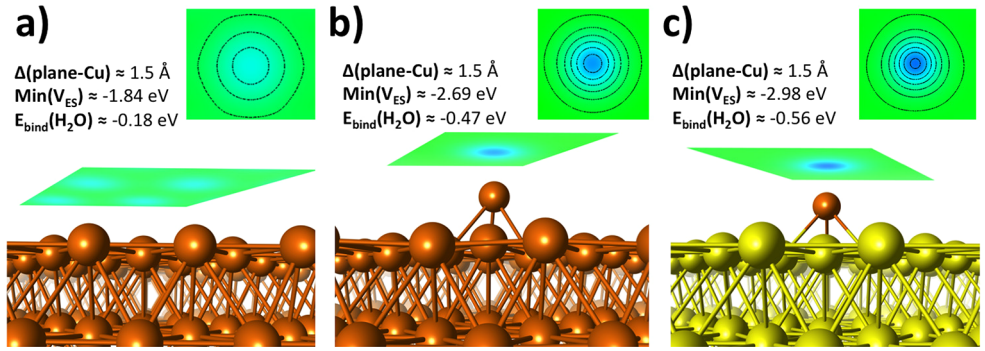

Figure 6. Partial positive charge on Cu in Cu@Cu(111) and Cu@Au(111) leading to the creation of an ESP well above the Cu. The plane at which the ESP is mapped is chosen to be 1.5 Å above the Cu. Min(V_{ES}) shows the depth of the ESP well. The 2D heat maps show the ESP on a red−green−blue (RGB) coloring scheme where blue shows the minimum of the ESP.

strong affinity for H_2O, while Cu(111) has no ISE and very weak affinity for H_2O. The general lack of correlation between H_2O and O binding (beyond clean TM surfaces) is evident in Figure 4a. To reemphasize, all four systems in Table 1 have the same EBD (according to Figure 4c) and thus the same contribution from covalency; therefore, one sees clearly how HOMO polarization and stabilization in an ISE-generated ESP well is the dominant effect in H_2O bonding. (A discussion on why embedding the same atom in different environments leads to a larger or smaller change in EBD and H_2O binding is given in section 6 of the Supporting Information.)

Lone-Pair Bonding beyond Transition-Metal Surfaces. The best starting point for understanding water bonding to ionic materials is a metallic system with considerable ionic nature: e.g., rutile IrO_2(110) comprised of Ir^{4+} cations and O^{2-} anions. Due to the large positive formal charge on Ir, IrO_2(110) has a significant ISE, deep ESP wells, and large H_2O BE (−1.39 eV for intact molecular binding). This is a general feature among the rutile XO_2 surfaces for molecular binding of H_2O and molecules which scale with it.[20,48,98,126] The difference between a simple on-top and a more complicated geometry with more significant hydrogen bonding is negligible (see section 7 of the Supporting Information). Hence, below we restrict ourselves to on-top binding (with a BE value of −1.34 eV as opposed to −1.39 eV) to focus on major electrostatic effects.

In Figure 9 we look at changes in the electron density distribution as water approaches the metal cation on IrO_2(110). As H_2O begins to feel the ESP well, its HOMO begins to polarize and stabilize (downshift in energy evident in Figure 9e). The broadening of the H_2O HOMO is more significant on IrO_2(110) than on Cu@Au(111) (compare Figure 9e to Figure 7e), and this suggests a greater covalent contribution to the BE. This is also confirmed by using eq 7 and the corresponding EBD values (Figure 4c) for the two systems. The EBD value for IrO_2(110) yields a value of ∼−0.5 eV as the covalent contribution (using eq 7); thus, the remainder of the −1.34 eV BE is attributed to the noncovalent electrostatic effect. The covalent contribution is read off from Figure 4c by drawing a vertical line from the point for IrO_2(110) and finding its intersection with the scaling line. One also observes (Figures 9a−d) that, as the H_2O approaches the surface, in order (i) to minimize the electron−electron repulsion between filled H_2O states and surface states and (ii) to create a surface dipole that further enhances the H_2O binding,[103] electrons on Ir redistribute (among hybridized states close to E_f) and some migrate to the O below. IrO_2(110) is a metallic surface that has a strong H_2O binding along with a reasonable affinity for O. A side by side analysis which contrasts the charge transfer and covalent nature for O and OH with an electrostatic nature for H_2O bonding on IrO_2(110) is given in section 9 of the Supporting Information.

Role of Geometry in Lone-Pair Bonding. As can be understood from the example of IrO_2(110) and comparison with Cu@Cu(111) and Cu@Au(111), a greater ISE leads to stronger H_2O binding. Nevertheless, ISE does not guarantee a strong interaction with H_2O, as the surface geometry also matters. To elucidate the role of geometry and how it changes the depth of local ESP wells near the surface, we consider Figure 10. The BE we calculate for H_2O on MgO(001) is −0.5 eV (that in experiment is −0.7 eV[48]). For ZnO(10$\bar{1}$0) our DFT value is −1.00 eV (in good agreement with computational literature[50,127−129]), while that in the experiment is −1.17 eV.[48] For IrO_2 our calculated value is −1.4 eV. We note that although our DFT-calculated values for MgO and ZnO were underestimated by ∼0.2 eV in comparison to experiment (most probably due to underestimation of the vdW interaction[107,112,130,131]), the difference in H_2O BE for the two is almost in perfect match with experiment: yet another example of DFT capturing BE trends better than it captures their absolute values.[132,133]

Comparing our values of −0.5, −1.0, and −1.4 eV for MgO(001), ZnO(10$\bar{1}$0), and IrO_2(110), respectively, we ask: what determines this hierarchy of the BEs? All three have strong ionic nature, and so ISE effects are present for all. We argue that this difference can be understood by considering (i) the cation formal charges and (ii) the geometry in which the surface cations and anions are arranged. These factors determine the depth of the ESP well above the surface, which is the major factor for determining H_2O BE. Comparing Figures 10a,b, one sees the effect of cation formal charge. On both IrO_2(110) and MgO(001) the cation is surrounded by four O^{2-} in a (almost) planar geometry. We see a deep ESP well and a strong H_2O binding in IrO_2(110), but not in MgO(001), a difference ascribed to the cation formal charges (Mg^{2+} vs Ir^{4+}). Comparing Figure 10b,c, one observes a deeper ESP well on ZnO (relative to MgO), which causes it to bind H_2O more strongly. ZnO and MgO have the same (+2) cation formal charge: what causes the difference is the different geometry in which the cations and anions are arranged. In ZnO(10$\bar{1}$0), each Zn^{2+} is surrounded by three O^{2-} and arranged in a geometry in which the Zn sticks out from the plane of the neighboring oxygens, while for MgO(001) each Mg^{2+} is surrounded by four O^{2-} in a planar geometry, so that

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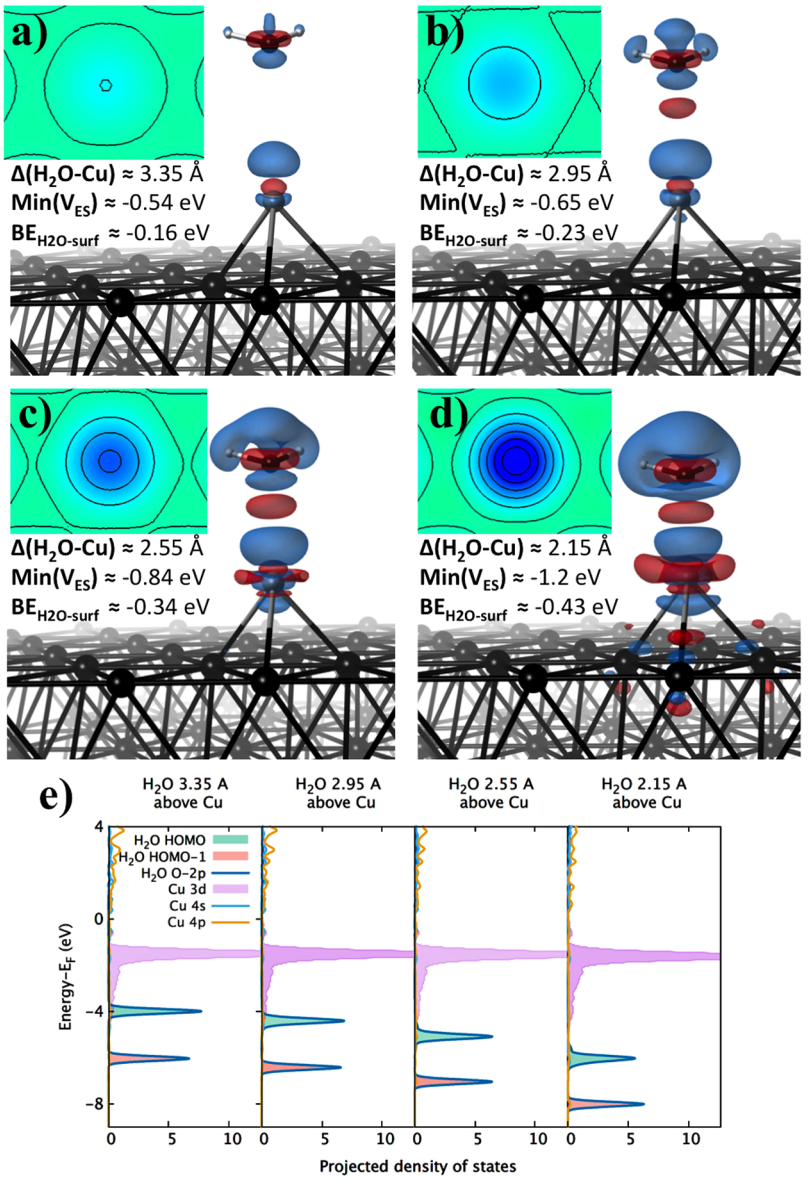

Figure 7. (a)−(d) Electron density redistribution ($\rho_{\text{with water}}-\rho_{\text{water}}-\rho_{\text{without water}}$) as a function of H_2O distance as it approaches the Cu from vacuum to its equilibrium bonding distance on Cu@Au(111). The dangling H_2O HOMO polarizes in response to the ESP well. In the 3D electron redistribution plots,[123] red (blue) shows the regions populated (depopulated) by electrons, for the same isovalue. The 2D heat maps show the ESP on an RGB coloring scheme in which blue shows the minimum of the ESP. (e) PDOS. To generate this figure, we first relax the surface geometry with adsorbed molecule (shown in (d)). We then rigidly displace the H_2O in the z direction with no further relaxation and perform self-consistent field calculations to obtain the electron density and density of states.

the proximity of more anions creates a shallower ESP well. One should also note that, as depicted in Figure 10d and consistent with the electrostatics-driven water binding, the H_2O binding geometry to the ZnO(10$\bar{1}$0) surface is angled in such a way that the (polarized) HOMO falls into the minimum of the surface ESP well.

The cation formal charge has a determining role for H_2O binding to the surface. The anion formal charge is also important. As an example, we have calculated the H_2O BE on MgF_2(110) to be ∼−1.0 eV, which should be compared to −0.5 eV on MgO(001). In both cases, H_2O binds in an on-top geometry to Mg^{2+}, but for rutile structure MgF_2(110), Mg^{2+} is surrounded by four F^-, while for MgO(001), Mg^{2+} is surrounded by four O^{2-}. Naturally the ESP well is deeper and H_2O BE is larger in magnitude on Mg^{2+} in MgF_2(110). More examples of the effect of geometry on lone-pair bonding (on α- and γ-alumina and fluorides) are given in section 10 of the Supporting Information.

For confirmation that the above differences, e.g. between H_2O binding on MgO(001) and IrO_2(110), are mostly due to the difference in ISE rather than the difference in covalency (see section 11 of the Supporting Information).

Role of Surface Mechanical Properties in Lone-Pair Bonding. Having discussed the role of geometry and formal charges, we now move to the effect of surface mechanical properties. They dictate how the surface geometry changes in the presence of the molecular species and how this effects the BEs.

As seen in Figure 11 (in agreement with both theory and experiment[135−138]), adsorption of molecular H_2O on Al^{3+} on α-

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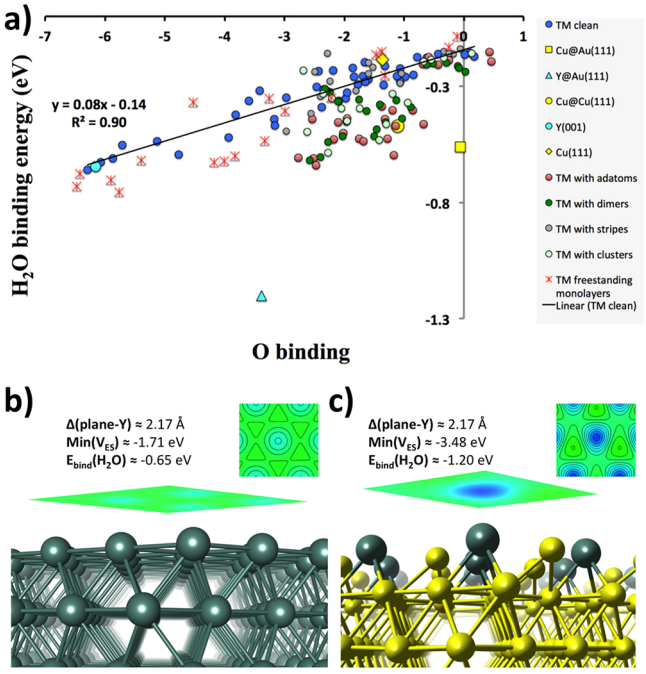

Figure 8. (a) Illustration of how most of the points that deviate from H_2O−O scaling line are adsorbed adatoms, dimers, or clusters of TM on clean TM surfaces. Increasing the ISE by depositing a (relatively) electropositive TM atom on a (relatively) electronegative TM bed leads to a greater deviation from the scaling line. Illustration showing for (b) Y(0001) and (c) Y@Au(111) the creation of extreme ISE, H_2O binding, and ESP well on Y@Au(111) due to the extreme electronegativity difference among the two elements. This greatly enhances H_2O binding on Y@Au(111) relative to clean Y(0001). On Y@Au(111), major surface reconstructions drag one Au per unit cell out of the plane.

Al_2O_3(0001) leads to an upward shift of the Al^{3+} cation. Why does the interaction of a stable closed-shell molecule such as water with Al-terminated α-Al_2O_3(0001) surface create such a large surface distortion? In brief, Al^{3+} movement increases the depth of the ESP well (Figure 11) and the electrostatic interaction with the water HOMO. The stabilization gained by this increased interaction is greater than the mechanical energy cost for the distortion.

Figure 12 shows the interaction and polarization of the H_2O HOMO in the ESP well enhanced by the outward Al^{3+} movement. In Figure 12d, we see accumulation of electrons between Al^{3+} and H_2O, which can be interpreted as a bond formed by the H_2O HOMO becoming polarized[103] and its electrons being accumulated on the side facing the surface in response to the strong local electric field generated by the protruding Al^{3+}. BCA reveals that the charge transfer from water to the surface is almost negligible ($\lesssim$0.01 e) and all of the electrons, although polarized and shifted toward the surface-facing side of H_2O plane, still remain within the boundary of H_2O oxygen. This is a sign of a relatively small covalent effect and an electrostatically driven bond, as also confirmed by the PDOS plot in Figure 12e, in which the water HOMO and HOMO-1 preserve their relatively sharp molecular nature with just an energy downshift dictated by the ISE and the ESP well it generates. For more details on interpreting Figure 12e, see section 12 of the Supporting Information.

As an example of how different surface mechanical properties lead to different affinities for binding O and N 2*p* lone-pair closed shell species, we investigated the effect of doping boron (B) into the α-Al_2O_3(0001) surface: one surface Al out of four in a 2 × 2 cell is replaced by a B. Although B and Al share the same number of valence electrons, B is much smaller.[134] Thus, doping a B in place of an Al leads to stretched and stiffer metal−O bonds which changes the surface's ability to distort. These stiffer B−O bonds are partially responsible for the weaker H_2O BE on B@α-Al_2O_3(0001) of ∼−0.2 eV (compare this to ∼−1.1 eV on α-Al_2O_3(0001) without B doping). More details are given in section 13 of the Supporting Information.

We observe that this type of mechanical distortion, in which the surface cation moves away from the plane of the anions to enhance H_2O BE, is a general behavior[139] for surfaces exposed to water (and other molecules with lone-pair interactions). Some such distortions are 0.14 Å for MgO(001), 0.06 Å for IrO_2(110), and 0.01 Å for both Cu@Cu(111) and Cu@Au(111). This "adsorbate-induced lifting" has also been reported in the literature for a number of molecules discussed in this paper including H_2O[137] and CH_3OH.[139] Even for nonionic surfaces, such a lifting destabilizes the valence orbitals on the "lifted" atoms relative to its neighbors and leads to creation of a partial positive charge on that atom which can stabilize the lone-pair bonding. There is a mechanical cost to create this distortion, but there is a gain by enhancing the lone-pair−surface bonding. The interplay of these positive and negative terms determines the exact amount of lifting for each specific case.

As mentioned earlier, rutile structure XO_2 compounds have a strong affinity for lone-pair bonding. Nevertheless, there is a hierarchy among rutile metal oxides.[48] This can also be related to the different surface mechanical properties (details are given in section 14 of the Supporting Information).

More Details on Material Independence of the Lone-Pair Scaling Relations. Why is there a material-independent scaling relation for the BEs of N and O 2*p* lone pair species discussed here? We describe some conjectures below.

There are some common features among this class of molecules: the chemically active part of the molecule (for surface adsorption) is the O (N) atom where the high energy (thus potentially chemically active) and dangling occupied orbitals are located. Also, the HOMOs of this class of molecules are nonbonding MOs dominated by 2*p* character around the N^{3-} or O^{2-} core and are energetically in close proximity (Figure 2) and thus should share similar polarizabilities. Therefore, from the point of view of the surface, these molecules are very similar. The different sizes of these molecules can lead to different (size-dependent) vdW interactions with the surface.[140−143] Nevertheless, this discrepancy can be adsorbed in the *y* intercept of the scaling.

Another common feature in the class is the fully saturated N^{3-} and O^{2-} atoms: the molecules are not in need of any charge transfer from the surface. They only "see" the surface locally through the depth of the ESP well and the center of the empty part of the surface bands. Their binding is not strongly affected by the surface conductivity or the availability of an electron reservoir. This differs from unsaturated (e.g., OH_x (x < 2)) species. A gedankenexperiment which contrasts the nearsightedness of molecular H_2O binding with more delocalized atomic binding mechanism for O is presented in section 15 of the Supporting Information. The effect of this nearsightedness is also evident once one considers the coverage dependence for H_2O binding to surfaces (sections 16 and 17 of the Supporting Information).

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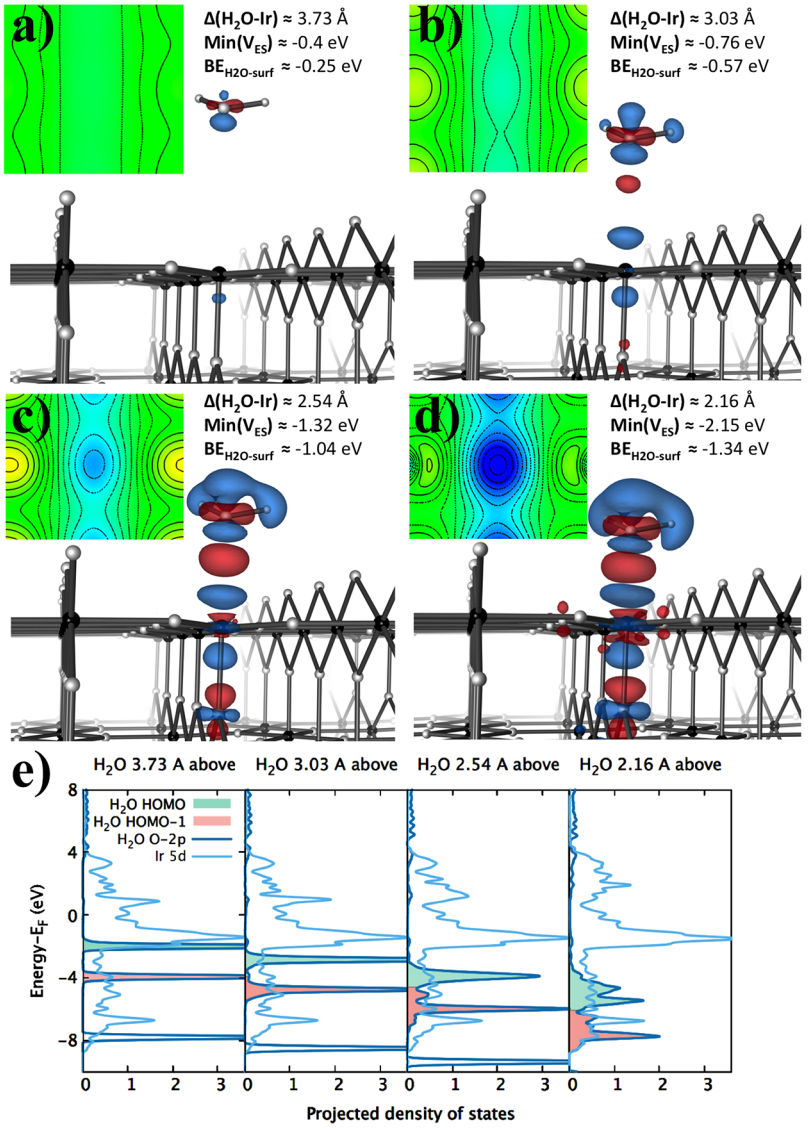

Figure 9. (a)−(d) Electron density redistribution as a function of displacing H_2O in the z direction from vacuum to its equilibrium bonding distance on IrO_2(110). In the 3D electron redistribution plots red (blue) shows the regions populated (depopulated) by electrons. The 2D heat maps depict the ESP. The lattice oxygens are shown by the small white balls. (e) PDOS.

For the molecules discussed here, the O or N (on which the lone pair is located) is bound via single bonds to neighboring atoms and groups. One might initially think that a molecule such as formaldehyde (CH_2O) in which the HOMO has significant O 2p character[144] is also a member of the class of molecules discussed here and scales with the others. This is not the case due to the double bond between C and O (see section 18 of the Supporting Information for more details).

A discussion on the possible role of steric hindrance and interaction with multiple sites for the case of larger molecules on corrugated surfaces are given in section 19 of the Supporting Information.

Dissociative versus Intact Binding. Throughout this work, we have focused on molecular (as opposed to dissociated) surface binding of closed-shell species. On some surfaces, the molecular binding mode is not the global energy minimum and the molecule prefers to dissociate. This can happen on some metallic compounds with strong affinity for O and OH binding[145,146] or on some ionic insulators.[147−150] Nevertheless, in almost all of these cases, a molecular (intact) binding mode exists as a stable local minimum. An interesting question is as follows: when is the dissociated binding more energetically favorable than the intact (molecular) mode? Currently, we do not have a complete answer to this question, but this can be an interesting venue for future research. Below we discuss some conjectures and, taking water as an example, make some connections to the literature on dissociative binding of these closed-shell molecules.

On metallic systems due to the existence of an electron sea at the Fermi level, the driving force for water dissociation is the charge transfer to dissociation products. Here, the affinity for water dissociation will naturally be correlated with O and OH BE, and for example on clean TM surfaces such affinity increases from the right to the left of the periodic table.[145,151] A recent experimental work by Kiawi et al. on cationic Fe_n^+ (n = 6−15) clusters shows a size-dependent water dissociation.[152] This can be partially due to the size-dependent availability of mobile charges. As we showed earlier, on a clean TM surface H_2O molecular binding scales with O (and OH) BE; consequently, one can find the energy ordering between

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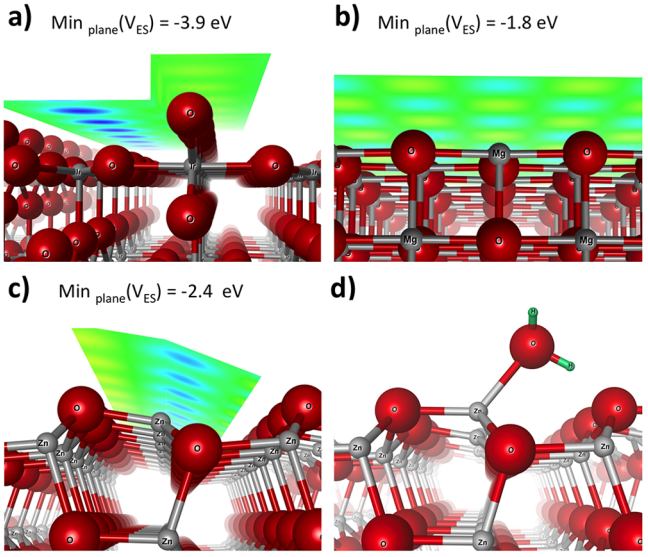

Figure 10. Local ESP wells on the surfaces of (a) $IrO_2(110)$, (b) MgO(001), and (c) $ZnO(10\bar{1}0)$. The planes at which the ESP is plotted are chosen to be 1 Å + cation ionic radius[134] away from the surface. (d) H_2O binding geometry on $ZnO(10\bar{1}0)$. Color code: O (red) and metal cation (gray).

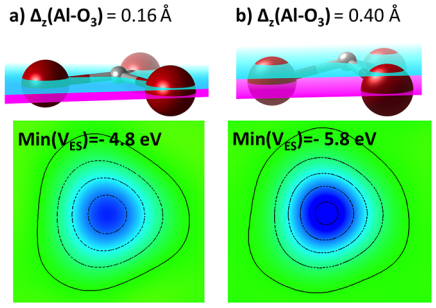

Figure 11. Mechanical distortion of the surface of α-$Al_2O_3(0001)$ upon H_2O adsorption: (a) Al^{3+} cation in its fully relaxed position; (b) Al^{3+} cation moving up in the presence of H_2O^*. The separation between Al^{3+} and the O plane is denoted by $\Delta_z(Al-O_3)$. The planes at which the ESP is plotted are chosen to be 1 Å + cation ionic radius[134] away from the surface. The minimum of ESP at the plane is denoted by Min(V_{ES}).

dissociative and intact binding modes. In addition, the intact water BE can give us the molecular desorption barrier. By comparing this barrier to the dissociation barrier (scales with water dissociative BE), one can also take into account the kinetics. As a result, one can find the borderline at which the surface becomes active toward water dissociation. This border is known in the literature to be Ru(001).[145] For metallic systems in which ISE is present, e.g. ionic metals such as $IrO_2(110)$, the simple scaling between H_2O and O (and OH) breaks down; thus, finding a universal borderline for dissociative versus intact binding is not a trivial task, even on metallic systems. Nevertheless, one might be able to develop several materials-class-dependent scalings with associated borderlines.

In contrast to metals, on insulators charge transfer from the surface is not the mechanism behind water dissociation. On those ionic insulators on which water dissociation is more energetically favorable (e.g., clean Al-term α-$Al_2O_3(0001)$[147,153−156]), the dissociation process can be envisaged as follows. (i) Water first adsorbs molecularly; the strong electric field created by the positive surface cation significantly polarizes the HOMO, dragging its charge density to one side of the molecule and closer to the surface cation, and such a state is a local energy minimum (metastable). (ii) A rare event (associated with an energy barrier) can then move the system from this metastable state by reshaping the electron cloud even further such that the whole electron density is taken from the water H atom, forming an OH^- and a H^+, with H^+ possessing a momentum component moving it away from the local attraction field created by OH^-; the H^+ ejection will then be further facilitated by the strong repelling electric field created by the surface cation and the attractive field of the nearby anion. (iii) The ejected H^+ becomes attached to the neighboring surface anion. The whole process is a heterolytic bond cleavage. The H^+ attached to the surface anion is also attracted (via Coulomb interaction) to its OH^- pair on the neighboring surface cation: this can lead to large energy costs to further separate them.[157,158] This is also known in the literature as acid−base stabilization.[159,160] The most important interactions for such a dissociated binding mode can be thought of as (i) the OH^-−surface cation, (ii) the H^+−surface anion, and (iii) the H^+−OH^- interaction. The question of which binding mode (intact versus dissociative) is more stable then reduces to this: when is the collective effect of the three aforementioned interactions stronger than the H_2O lone-pair−surface bond? We conjecture that the OH^-−surface cation interaction in such systems can, in principle, scale with the molecular H_2O BE on these surfaces, as an OH^- is isoelectronic with H_2O. This scaling can create a correlation between H_2O molecular and dissociative binding modes on ionic insulators.

As mentioned before, there is a subset of ionic systems which are metallic or have metallic states in their immediate neighborhood. An interesting observation is that such metallic states can further stabilize the dissociation mode on these materials. A few examples include enhancement of water dissociation on (i) metallic[161] (CaO terminated) $Ca_3Ru_2O_7(001)$ relative to the insulator CaO(001),[162] on (ii) MgO ultrathin layers on metallic supports (with or without interfacial defects),[163−165] and on (iii) (polarization-driven) charge-doped ferroelectric oxide surfaces, e.g. $PbTiO_3(001)$.[166]

Lewis Acid and Base Concepts Revisited for Surface Chemistry. We have introduced scaling relations between molecules which interact with the surface through their 2*p* lone pairs. In molecular chemistry, these are categorized as Lewis bases (LBs). Similarly, the surface sites which bind these molecules are Lewis acids (LAs). In a standard Lewis acid−base interaction (LABI), it is often assumed that the HOMO of the LB covalently interacts with the LUMO of the LA to create a lower energy level for the electron pair to occupy. Since this lower energy state is a mixture of LB HOMO and LA LUMO, this leads to an effective charge transfer from the LB to the LA.

In 1982 Stair applied the Lewis acid and base concept to the study of surface chemical phenomena.[167] Using the perturbational molecular orbital theory of acid−base interactions developed by Klopman[168] and extended by Jensen,[169] the perturbation energy ΔE^{pert} is

$$\Delta E^{pert} = \Delta E^{ch} + \Delta E^{orb} + \Delta E^{repl} \quad (8)$$

Here, ΔE^{repl} is a repulsive term due to the electron−electron repulsion between the filled orbitals. ΔE^{orb} is an attractive term describing the covalent interaction between the LB HOMO and the LA LUMO, similar in nature to the bond energy

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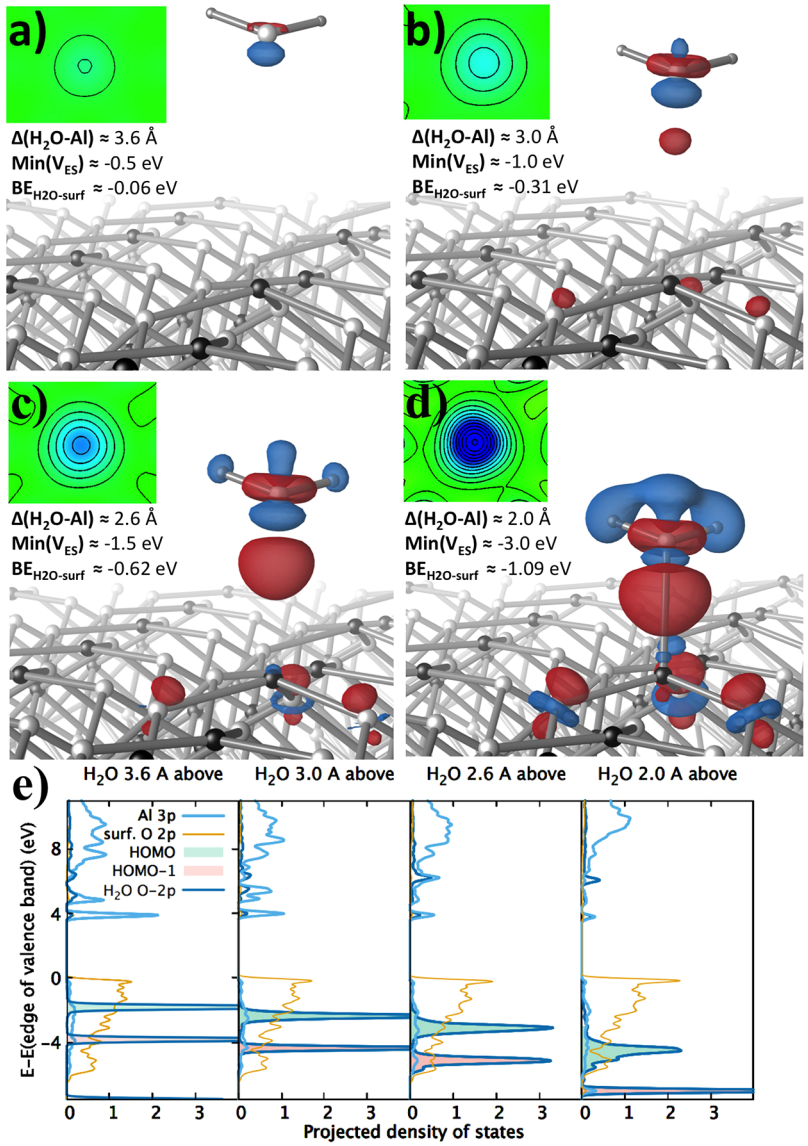

Figure 12. (a)−(d) Electron density redistribution as a function of displacing H_2O from vacuum to its equilibrium bonding distance on α-Al_2O_3(0001). In the 3D electron redistribution plots red (blue) shows the regions populated (depopulated) by electrons plotted for the same isovalue. The 2D heat maps depict the ESP. (e) PDOS.

predicted by the Newns−Anderson Model (eqs 3 and 7). ΔE^{ch} describes the Coulomb attraction between cation acids and anion bases: for gas-phase species it includes permanent dipole, charge-induced dipole, and polarization in addition to charge−charge interactions. According to Stair, this electrostatic interaction is expected to be very weak for neutral acid−base adducts such as molecules bonded to a surface; thus, the electron transfer via covalent bonding accounts for the LABI in surface chemistry. Some of the surface phenomena discussed in this work agree with this fully covalent picture, but most require modifications to it.

The natural redefinition of a LUMO for surface chemistry is the empty part of the surface chemically active band (SCAB); for TMs this is the empty part of the *d* band. For TM surfaces, we showed that the surface−water interaction is captured by a simple covalent model (eq 7). According to the mutual scalings between water and the other molecules in the class, similar models can be made for the rest of them. The picture of a fully covalent interaction works well for clean TM surfaces. Looking at Figure 1 and the scaling equations, one notices that generally $|BE(H_2O)| < |BE(CH_3OH)| < |BE(NH_3)|$; this can be rationalized by a fully covalent LABI picture considering the HOMO alignment of these molecules (Figure 2), $E_{HOMO}(H_2O) < E_{HOMO}(CH_3OH) < E_{HOMO}(NH_3)$. A higher HOMO energy means a stronger covalent interaction with the surface, as the HOMO gets closer to the empty part of the SCAB. Although this BE trend can be justified within a fully covalent picture, there is yet another contributing phenomenon working in the same direction that has an electrostatic rather than covalent origin: a higher energy HOMO is easier to polarize and responds better to the surface ESP well. An example investigating NH_3 binding to an oxide surface, illustrating its similarities and differences in comparison to the H_2O binding, is given in section 20 of the Supporting Information.

Another qualitative agreement with a fully covalent LABI picture is our prediction of the surface active sites for lone-pair bonding. The LB species prefer to bond to surface atoms that dominate the empty part of the SCAB: i.e., the surface LA site,

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the atom with a higher electropositivity.[29] In a standard fully covalent LABI picture, this causes a better overlap between filled LB and empty LA orbitals. Another reason, on the basis of results and discussions in our work, is that these types of sites have some partial positive charge leading to an ESP well which electrostatically polarizes and stabilizes the HOMO. On the basis of our calculations, the class of closed-shell molecules discussed here always bind preferably to the most electropositive surface constituent even when the difference of electronegativity is small[170−174] (examples are given in section 21 of the Supporting Information).

Beyond the simple case of clean TM surfaces, the simple fully covalent LABI picture is insufficient to describe the lone-pair−surface bonding. Taking Cu as an example, we showed (Figure 4c) how creation of ISE changes the lone-pair BE to the surface without changing the EBD (eq 7): with the same covalent contribution; a positive center creates an ESP well, polarizes the dangling HOMO, and creates a stronger lone-pair−surface bond. This is not a chemical bond, as it is not associated with considerable mixing among surface and adsorbate states, nor is there a considerable charge transfer from the molecule to the surface. As indicated by BCA, the HOMO polarization which results in electron accumulation between H_2O and the surface site does not involve any sizable charge transfer to the surface LA site: the lone-pair electrons polarize but remain within the H_2O. The small numbers reported in this work (a few hundredths of an electron) for charge transfer from LB to surface LA site are a result of the covalent interaction of LB HOMO and surface LA LUMO (empty part of surface effective band), not the HOMO polarization. Our work on TM adatoms on TM clean surfaces and oxides shows that the extent of the effect of ISE-driven HOMO polarization and stabilization can be larger than the covalent contribution. Thus, on many surfaces with strong affinity for lone-pair (molecular) bonding, the bond is characterized as a strong physical (electrostatic) rather than a chemical (covalent) bond: the attractive contribution of ΔE^{ch} in eq 8 is significant.

The surface binding of the class of closed-shell molecules discussed in this work has been frequently named in the literature as a dative bond.[21,127,137,175−189] Throughout this work, we intentionally refrained from using this term, as a dative bond is a type of covalent bond, while our results show that the covalent effect does not, in general, fully capture the nature of the lone-pair−surface bonds.

Taking into account both electrostatic and covalent contributions to the BEs also allows for rationalization of the lone pair−surface binding geometries (section 22 of the Supporting Information).

OUTLOOK AND CONCLUSIONS

Scaling relations among the binding energies (BEs) of AH_x ($x < x_{max}$) species have been shown to exist[1,190,191] and have become a cornerstone of theoretical catalyst design.[2,192−194] We have expanded the reaches of this approach, by demonstrating material-independent scaling relations among some species with $x = x_{max}$, such as H_2O and NH_3, and other similar closed-shell lone-pair species including alcohols, ethers and amines. We showed, in general, a lack of correlation between the molecular BEs of these saturated x_{max} species (e.g., H_2O) and those of their open-shell relatives (e.g., O), except for special cases such as binding to clean TM surfaces. Electron transfer from the surface to the adsorbate is the major contributor for effective binding of AH_x ($x < x_{max}$) species. This mechanism is nonexistent for closed-shell lone-pair species discussed here. Hence, one has the freedom to engineer the materials properties and tune these two types of BEs independently. For instance, a metallic TM surface is active toward O and inert toward intact molecular adsorption of H_2O, while an insulating ionic system can be active toward H_2O and inert toward O. The illustration of this apparent lack of correlation between the surface chemistry of closed-shell molecules and their radical dehydrogenated relatives provides new ideas and insights for catalytic materials design. One possible application is designing hybrid systems with sites that are active toward radicals but inert toward closed shells and vice versa.

Having identified material-independent correlations among this class of closed-shell molecules, we described the bonding mechanism for H_2O, the findings of which are generalizable to the other molecules. We explained the critical role of intrinsic surface electrostatics (ISE) in creating local electrostatic potential wells which polarize and stabilize the dangling lone pair (HOMO) of these molecules. For cases of strong bonding, this electrostatic effect was shown to be the dominant interaction. The role of surface electronic structure, geometry, formal charges, and mechanical properties in dictating the strength of the lone-pair−surface bond were also investigated. This fundamental understanding was used to explain the wide span of the BEs both experimentally and computationally observed on different categories of materials.[44,48] For instance, we discussed why lone-pair molecular binding is generally weaker on clean transition metals and stronger on ionic oxides or why there is a hierarchy even within an ionic materials class.[48] Other experimental observations including adsorbate-induced lifting of surface cations in ionic solids[135−139] were also elucidated. We have also related our findings on solid-state systems to the general Lewis acid−base interactions in the context of molecular chemistry. The insights garnered here let us expand the scaling-driven catalyst discovery approach[2,3,195,196] to include an important class of closed-shell molecules.

COMPUTATIONAL METHODS

We performed calculations using density functional theory (DFT)[197,198] with plane wave basis sets, mostly using the Quantum Espresso software package.[199] The Bayesian error-estimation functional with van der Waals interactions (BEEF-vdW)[133] was used as the exchange correlation functional. Details on convergence parameters and pseudopotentials used in different sets of our calculations are given in section 23 of the Supporting Information. The convention for the sign of the BEs is that an exothermic process corresponds to a negative adsorption energy. For instance, water BEs are defined as

$$\begin{aligned} \mathrm{BE}(H_2O) &= E_{\mathrm{bind}}(H_2O) \\ &= E(\text{surface with } H_2O) - E(\text{bare surface}) \\ &\quad - E(H_2O \text{ molecule}) \end{aligned}$$

ASSOCIATED CONTENT

Supporting Information

The Supporting Information document associated with this article contains The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00902.

Details as described in the text and a list of materials and BEs used in this work (PDF)

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Notes

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ABBREVIATIONS

DFT, density functional theory; BE, binding energy; MO, molecular orbital; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; TM, transition metal; EBD, empty band descriptor; SCAB, surface chemically active band; ISE, intrinsic surface electrostatics; PDOS, projected density of states; ESP, electrostatic potential; BCA, Bader charge analysis; LABI, Lewis acid−base interaction; LA, Lewis acid; LB, Lewis base

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