X-ray standing waves reveal lack of OH termination at hydroxylated ZnO(0001) surfaces

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The vertical adsorption distances of the planar conjugated organic molecule 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) on hydroxylated ZnO(0001), determined with the x-ray standing wave technique (XSW), are at variance with adsorption geometries simulated with density functional theory for surface-structure models that consider terminating OH, whereas good agreement is found for PTCDI in direct contact with the topmost Zn layer. The consequential assignment of OH to subsurface sites is supported by additional, independent XSW and energy scanned photoelectron diffraction data and calls for a reconsideration of the prevalent surface models with important implications for the understanding of ZnO(0001) surfaces.

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The surface structure of zinc oxide (ZnO) exposed to water (H\textsubscript{2}O) and hydrogen (H, H\textsubscript{2}) is important not only for the understanding of heterogeneous catalytic processes \cite{1–5} but also because it controls the morphologies of condensed water \cite{6} and organic or metal adlayers \cite{7,8}, which are relevant for self-cleaning and (opto)electronic applications, respectively. Hydroxyl (OH) formation is generally found at the surfaces investigated in these SPM measurements is at variance with adsorption geometries simulated with density functional theory for surface-structure models that consider terminating OH, whereas good agreement is found for PTCDI in direct contact with the topmost Zn layer. The consequential assignment of OH to subsurface sites is supported by additional, independent XSW and energy scanned photoelectron diffraction data and calls for a reconsideration of the prevalent surface models with important implications for the understanding of ZnO(0001) surfaces.

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 technique [30,31] and compare these with the corresponding distances determined with density functional theory (DFT, see Ref. [29] for details) for clean Zn-ZnO (model $I$, implicitly limiting OH to subsurface sites) and OH-terminated Zn-ZnO. Because of the exclusive sensitivity to molecule-surface vertical distances in normal-incidence XSW (NIXSW) measurements presented later on, we test the least and most protruding OH configurations for OH-terminated Zn-ZnO, namely (2 × 1)-OH overlayers in fcc hollow [3,5,14,23,32] (model 2) and atop sites [1] (model 3) [cf. Figs. 1(b) and 1(c)].

The NIXSW analysis [29] of the partial photoelectron yield stemming from chemical species $X$ yields the coherent position $P_{H,X}$ and coherent fraction $f_{H,X}$ that quantify its location within the standing wave field and its positional disorder, respectively. The vertical distance between $X$ and an arbitrary reference species $Y$ can then be calculated according to $d_{X,Y} = d_{H} (n + P_{H,Y} - P_{H,X})$, where $d_{H}$ is the diffraction plane spacing of ZnO for $H = (0002)$ and $n = 0, 1, 2, \ldots$. is a free parameter that reflects the fact that XSW is only sensitive to the vertical position with respect to H modulo the period of the standing wave field. Importantly, several effects sensitively influence $f_{H}[30,33–35]$ and effects beyond the current theoretical description are indicated by observed $f_{H}$ variations between different chemical elements [33] and chemical species of the same element [34]. $P_{H}$ is a much more robust observable.

The O 1s core-level signal for oxygen in ZnO (OZnO) and OH (OOH) can be separately resolved by XPS [29], allowing us to determine the unknown location of OOH with respect to the substrate crystal structure, as is common XSW practice. In the current case, however, this approach suffers from two intricacies: Firstly, model $I$ does not explicitly include OH and does not permit a direct comparison with experiment. Secondly, due to the finite information depth of XPS, near-surface $d_{H}$ variations due to surface relaxation and surface preparation-induced effects have to be accounted for.

As we will show below, a convincing case based on precise $d_{O_{H\text{-}OOH}}$ values is nonetheless possible if also including XSW data obtained from a non specular reflection as well as energy scanned photoelectron diffraction (PhD) data. However, in order to increase the confidence in this assessment, we additionally followed an independent NIXSW-based approach: We deposit the planar π-conjugated organic molecule (COM) 3,4,9,10-perylene tetracarboxylic diimide [PTCDI, see Fig. 1(d)] and test whether PTCDI adsorbs on top of terminating OH and, in turn, whether the OOH location is above or below the topmost Zn layer. XSW would sense this (I) from OH acting as spacer layer between PTCDI and Zn-ZnO and (II) via the OOH–PTCDI distances. These additional measurements address both problems laid out above: First, approach (I) relies on distances between PTCDI and Zn-ZnO and an explicit knowledge of the OH location is not required, allowing to also test model $I$. Second, for an assumed OH termination, all OOH would be localized in the surface layer and directly in contact with PTCDI. Therefore, approach (II) is not affected by $d_{H}$ variations in the Zn-ZnO surface crystal structure. The Zn-ZnO surfaces were prepared according to three different recipes (labeled A–C) that represent the range of annealing temperatures employed in most previous Zn-ZnO surface studies [7,13,15,17,18,20,22,36,37] and also include H$_2$O exposure [37]. All crystals were hydrothermally grown (CrysTec, Berlin), annealed under atmospheric conditions (1000°C, 2 h) and in-situ (420°C, 10 min), and Ar$^{+}$ sputter-cleaned (0.5 keV, 15 min) [29]. Final annealing temperatures $T_{\text{ann.}}$ are included in Table I. For sample C, we monitored the OH fingerprint in the O 1s spectrum to elucidate the OH dynamics under UHV conditions and the effect of H$_2$O exposure. We could confirm complete OH desorption during annealing [29] and Fig. 2(a) shows a gradual re-formation of OH in the UHV environment as well as similar saturation OH intensities within the explored H$_2$O partial pressure range from $<3 \times 10^{-10}$ mbar (= UHV base pressure) to $5 \times 10^{-8}$ mbar.

Table I reports all relevant NIXSW results. As shown in Ref. [29], increasing $f_{H}$ when comparing samples A–C results from surface order being initially reduced by sputter-induced deprotonation $\text{OH}$.

![Diagram](image)

**FIG. 1.** (a) Calculated geometries for Zn-ZnO surface models 1–3 and protonated and deprotonated PTCDI using DFT [29]. The x-ray standing wave (XSW) is included to illustrate the ambiguity of the vertical adsorption distances determined with the XSW technique. The height of the O$_{\text{ZnO}}$ layer, used as reference in Table II and Figs. 2(b) and 3(a), is also indicated. (b), (c) Top view of models 2 and 3 that feature 0.5 ML OH in hollow and top sites, respectively. (d) PTCDI’s chemical structure and effect of deprotonation.

| Sample ($T_{\text{ann.}}$) | $A$ (420°C) | $B$ (600°C) | $C$ (700°C) |
|---------------------------|-------------|-------------|-------------|
|                            | $P_{H}$     | $f_{H}$     | $P_{H}$     | $f_{H}$     | $P_{H}$     | $f_{H}$     |
| O$_{\text{ZnO}}$         | 0.88±1      | 0.81±1      | 0.81±1      | 0.89±1      | 0.78±0.5    | 0.95±0.5    |
| O$_{\text{OH}}$         | 0.78±0.3    | 0.54±0.3    | 0.63±0.3    | 0.60±0.3    | 0.65±0.3    | 0.62±0.3    |
| Zn$_{\text{ZnO}}$       | 0.09±0.4    | 0.85±0.4    | 0.03±0.4    | 0.98±0.4    | 0.00±0.2    | 1.01±0.2    |
| N                        | 0.87±0.5    | 0.55±0.5    | 0.81±0.5    | 0.81±0.5    | 0.74±0.3    | 1.07±0.3    |
| C$_{\text{ZnO}}$        | 0.97±0.7    | 0.65±0.7    | 0.92±0.7    | 0.80±0.7    | 0.87±0.7    | 0.71±0.7    |
| C$_{\text{core}}$       | 0.11±0.2    | 0.28±0.2    | 0.15±0.2    | 0.35±0.2    | 1.00±0.5    | 0.55±0.5    |

$^{a}$Corrected for surface relaxation by +0.02 [29].
stopped. Horizontal lines show OH spectral weights directly after the NIXSW results better. To test these options further, we or a combination of adsorption sites would potentially fit OOH (orange) and the corresponding theoretical values for surface models 

![Diagram](image)

FIG. 2. (a) OH spectral contribution derived from O 1s core-level fits [29] as a function of time after the respective annealing was stopped. Horizontal lines show OH spectral weights directly after the indicated H2O doses and corresponding partial pressures. The vertical line indicates when PTCDI was deposited onto sample C. (b) Experimentally determined &Delta;P&subscript;H (referenced to O&subscript;ZnO) and &f&subscript;H for O&subscript;OH (orange) and the corresponding theoretical values for surface models 2 and 3 (red and blue). The data are presented by employing &Delta;P&subscript;H as angle and &f&subscript;H as radius. The star corresponds to sample C after H2O-dosing. The samples discussed in [29] are symbolized as thin circles (thin squares) if annealed at 420 °C (700 °C). Filled symbols show results for the (101) reflection. The three &f&subscript;H values for models 2 and 3 approximate the surface disorder of samples A–C (see text).

Table II. DFT-calculated vertical adsorption distances (in Å) of PTCDI and OH for models 1–3 and for protonated and deprotonated PTCDI, measured from the topmost oxygen layer of the ZnO crystal.

| Model (OH site) | I (subsurf.) | 2 (hollow) | 3 (atop) |
|-----------------|-------------|------------|----------|
| PTCIDI state    | Prot. Depr. | Prot. Depr. | Prot. Depr. |
| N               | 2.78 2.55   | 5.10 4.51  | 5.37 5.01 |
| C&subscript;O   | 2.86 2.81   | 5.09 4.69  | 5.38 5.17 |
| C&subscript;core| 3.21 3.45   | 5.20 5.26  | 5.48 5.50 |
| O&subscript;OH  | 1.93 1.92   | 2.43 2.43  | 2.43 2.43 |

damage/Ar-implantation and consecutively restored during annealing to a degree that depends on &T&subscript;anneal and the annealing duration. Vertical disorder in the topmost Zn layer additionally contributes. We derive &f&subscript;H = 0.7, 0.8, and 0.85 for the topmost Zn layer of samples A, B, and C, respectively. The respective lower &f&subscript;H,&subscript;O&subscript;OH indicates OH vertical disorder beyond that of the topmost Zn layer. The DFT-calculated vertical distances &d&subscript; are presented in Table II and can be converted into coherent positions via &d&subscript;/&d&subscript;0. The coherent position of another species can be selected as reference plane (denoted &P&subscript;H,)&subscript;X, converting &P&subscript;H,)&subscript;X to &Delta;P&subscript;H,)&subscript;X = &P&subscript;H,)&subscript;X – &P&subscript;H,)&subscript;Y. The Argand diagram [38] in Fig. 2(b) employs &X = O&subscript;OH and &Y = O&subscript;ZnO and thus &Delta;P&subscript;H,)&subscript;O&subscript;OH = 0 corresponds to O&subscript;OH at the same vertical position as O in the ZnO lattice. The presented comparison between experimental and theoretical values shows that model 2 is clearly at variance with experiment. In contrast, &d&subscript;OZnO.&subscript;O&subscript;OH predicted by model 3 is consistent with most of the NIXSW data if we additionally allow for a possible inward surface relaxation that we estimate as &P&subscript;H,relax, &lt; 0.04 (i.e., 0.1 Å) [29]. However, it seems that O&subscript;OH in bridge sites [23,32] or a combination of adsorption sites would potentially fit the NIXSW results better. To test these options further, we performed PhD to probe the local geometric structure of O&subscript;OH. Furthermore, we conducted XSW with &H = (101) as diffraction plane to gain access to O&subscript;OH’s in-plane atomic coordinates. The PhD results are presented in Ref. [29] and point to O&subscript;OH in O&subscript;ZnO-like sites, but with a higher degree of disorder. This site assignment excludes a significant abundance of OH in hollow (model 2) or bridge sites, leaving model 3 with its near O&subscript;ZnO-like atop site as the only realistic option for OH-terminated Zn-ZnO. However, in the XSW data for the (101) reflection that is included in Fig. 2(b), a very high degree of in-plane disorder is apparent from the low &f&subscript;H. This is not consistent with the notion of a single atop site dominating the OH population as would be the case for model 3. In addition, the atop configuration should be inherently unstable [3,5,14]. Indeed, in our DFT calculations we have to constrain the O&subscript;OH to stay on top of surface Zn atoms, because otherwise they relax into the energetically more favorable model 2 configuration. Therefore we suggest that OH, instead, substitutes subsurface oxygen sites, e.g., next to Zn vacancies and along the edges of surface reconstructions as suggested in Refs. [17,23] and Ref. [24], respectively. In this case, O&subscript;OH likely occupies a large variation of near O&subscript;ZnO-like sites, explaining also the in-plane disorder.

To substantiate these findings, we turn to the measurements that employ PTCDI as surface-structure probe. ZnO crystals have been probed by means of molecular adsorbates before: In a pioneering work, Staemmler et al. measured the binding energy of CO with thermal desorption spectroscopy and could successfully resolve several ZnO surface structures [39]. However, for hydroxylated Zn-ZnO surfaces, the authors could detect “no adsorption of CO [...] even at surface temperatures as low as 50 K,” leaving the OH location at Zn-ZnO surfaces an open question [5,24].

Our XSW-based approach differs from that of Staemmler et al. in two aspects: First, PTCDI is a much larger surface-structure probe than CO and adsorption at room temperature is guaranteed. On the other hand, the interaction with oxide surfaces is more complex for large COMs than for CO. XPS yields significant chemical shifts of PTCDI’s C 1s and N 1s core levels at the PTCDI/ZnO interface compared to bulklike PTCDI. From ultraviolet photoelectron spectroscopy (UPS), additional occupied density of states in the gap between highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) in the interface regime is apparent [27,29,40]. These observations are equivalent to those reported for PTCDI/TiO&subscript;2, for which a deprotonation reaction of PTCDI at the oxide surface was suggested as possible origin [41]. However, the same observations were also reported for C&subscript;2-PTCDI on ZnO [27], for which the N atoms are bound to butyl groups and a deprotonation reaction is not possible. Charge transfer rather than a change of PTCDI’s chemical structure was thus proposed to explain the chemical shifts [27,40]. To account for this uncertainty, we performed DFT calculations for models 1–3 for both protonated and deprotonated PTCDI, assume a coexistence of both states possible, and consider the adsorption distances between those resulting for protonated and deprotonated PTCDI as possibility space.

Second, the unclear concentration and type(s) of intrinsic dopants in ZnO yields large uncertainties for calculated COM...
carbonyl C (CC=O) and N (both representative of PTCDI’s Photoelectron yields could be separately resolved for PTCDI’s from our OH-vs-time analysis in Fig. 2(a), this marks enough had undergone their final annealing. As can be extrapolated cell onto samples ML coverage were deposited from a custom-built Knudsen representant of the Zn-ZnO surface structure.

These are important prerequisites for probing a large fraction of the surface area and arriving at results that are truly missing atoms, vacancies) but still small compared to most small Zn-ZnO surface openings (pits, rows and stripes of In addition, PTCDI’s footprint is too large to fit into the contrast, the time was reduced to only 30 min for sample C. To estimate that the surface of sample C has OH-depleted by 50% during PTCDI deposition compared to samples A and B. Photoelectron yields could be separately resolved for PTCDI’s carbonyl C (C C=O) and N (both representative of PTCDI’s functional groups) and all other C (C_cored, representative of its perylene core). PTCDI’s O_C=O has a core-level binding energy very similar to OOH and a XSW-analysis is not reliably possible [29]. As motivated above, we follow two different approaches, each employing an independent reference plane.

(i) Starting by first using O_{ZnO} as reference [Fig. 3(a)], a significant intramolecular bending is apparent for all three samples from the \Delta P_H differences between C_cored, C_{C=O}, and N. As can be seen in Fig. 1(a), this finding is in contrast to models 2 and 3 when assuming protonated PTCDI but approximately consistent with all other cases. However, when also considering the absolute \Delta P_H values, models 2 and 3 are clearly incompatible with the experimental data for C_cored and, to a smaller degree, C_{C=O}. In contrast, very good agreement between theory and experiment is achieved for model 1. Two aspects deserve special attention: First, the larger \Delta P_H for sample B than samples A and C can be rationalized by an increased intermolecular interaction at the larger PTCDI coverage in this case [29], a correlation that was reported for pentacene on Ag(111) [42]. In contrast, the OH depletions of the surface of sample C has no apparent effect on the adsorption distances that could, in turn, be related to terminating OH. Second, while the observed lower f_H for C_cored than for C_{C=O} and N is qualitatively consistent with bent molecules, experimental and theoretical f_H for C_cored do not agree within the error bars. A coexistence of different PTCDI chemical [41] or charge states [40], as indicated by two nitrogen species found from XPS [27,29,41], and a fraction of PTCDI in contact with H [16] or oxygen adatoms [21] are possible reasons for the relatively low f_H for C_cored.

(ii) From Fig. 3(b) it is clear that models 2 and 3 do not match the experiment also when using O_{OH} as reference. The discrepancy is least (most) pronounced for model 2 (3) due to a vertical (almost horizontal) OH bond orientation [cf. Fig. 1(a)].

Summarizing our conclusions from (i) and (ii), models 2 and 3 predict significantly too low adsorption heights, with the deviation for model 2 (3) being largest when referenced to O_{ZnO} (O_{OH}). Since our analysis covered the most and least protruding OH sites, this assessment also holds for intermediate terminating OH configurations like in bridge sites.

This is clear experimental evidence that an OH termination, even though predicted as thermodynamically most stable [5,14], does in fact not form upon Zn-ZnO hydroxylation in UHV. This suggests that kinetic barriers preserve the reconstructions that stabilize OH-free Zn-ZnO surfaces [13], as previously proposed by Valtiner et al. [24]. Since a comprehensive quantum-chemical description of the dynamic equilibrium of Zn-ZnO surface structures at realistic pressures and temperatures is still out of reach, only selected adsorption pathways [43,44] and surface configurations [32] have been tested. The present results demonstrate the importance of considering subsurface OH sites and modeling their formation and stabilization.

In conclusion, we have introduced a scheme to determine surface structures via the vertical adsorption distances of planar molecules and exploit this method to probe hydroxylated Zn-ZnO surfaces with PTCDI. The geometric structure prediction of PTCDI/Zn-ZnO warrants a sensitive comparison with experiment because the adsorption distances are primarily determined by the OH group configuration. Our results are not consistent with the common notion of OH-terminated Zn-ZnO surfaces but strongly hint towards OH in subsurface sites with significant in-plane disorder. This finding will have great implications for surface chemistry and heterogeneous catalysts and hopefully inspire increased incorporation of kinetic effects in theoretical modeling of surface structures, ultimately allowing their adequate description under realistic conditions.
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[29] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevMaterials.4.020602 for experimental and computational details as well as XPS, XSW, PhD, UPS, and LEED data [45–57].
