Water on Metal Oxide Surfaces

$\text{H}_2\text{O}/\text{ZnO}(10\overline{1}0)$

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Water adsorption at oxide surfaces:

- H-bonding between H$_2$O and H$_2$O
- H-bonding between H$_2$O and O$_{\text{surface}}$
- very dynamical system

ZnO (10\overline{1}0)
ZnO:  

**Wurtzite Structure**  
Tetrahedral Coordination  
Hexagonal Packing (AbaBAb..)  

Cutting perpendicular to c-Ache ('basal plane') gives two very different surfaces:  

- Zn-terminated (0001) Surface  
- O-terminated (0001) Surface  

→ "polare" surfaces  

'mixed terminated' (non-polar) surfaces (1010), (1120)  

**ZnO Samples:**  

- High exciton binding energy, ~60meV  
- Wide bandgap semiconductor, ~3.3 eV  

Sn-doped  

Prism face  

Zn- side  

polar (0001)-Zn and (0001)-O surfaces;  
non-polar (1010) and (1120) surfaces
Clean ZnO(1010):
(wurtzite structure)

Zn-O dimers:

STM (experimental)

STM (calculated)

ZnO (1010)
Clean ZnO(10\bar{1}0):

empty-states STM
(sputtered & annealed, 970 K)

300 Å x 300 Å, V_{sample} = +1.5 V, 3.6 nA

Not a reducible material
no point defects visible
two kinds of defects:

full layer deep holes and half layer deep holes

Water/ZnO(10\bar{1}0):
(2x1) overlayer

Helium Atom Scattering
(Helium Atom Scattering)

LEED
T = 300 K

**Water/ZnO(10\{1\}0): calculations**
(B. Meyer)

**DFT:**
- gradient-corrected PBE functional
- Vanderbilt ultrasoft pseudopotentials
- plane wave cutoff 25 Ryd (tests with 30 Ryd)
- periodic slabs, 6 to 8 ZnO layers
- dipole correction to suppress artificial interactions between the slabs
- (6x4x1) Monkhorst-Pack k-point mesh
- Full atomic relaxations of all configurations
- tested with coupled cluster-type calculations

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**Isolated water molecule:**

0.94 eV

**Full Monolayer:**

1.03 eV

'key-lock' configuration

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**Water/ZnO(10\{1\}0): calculations**
(B. Meyer)

**Car-Parrinello Molecular Dynamics:**
- some of the water molecules dissociate
- partially dissociated structure remains stable

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**Isolated water molecule:**

**Full Monolayer: half-dissociated**

1.13 eV

Second water molecule triggers dissociation:
**Water/ZnO(10\(\bar{1}\)0): (2x1) overlayer**

**STM (empty states)**

- many small domains, narrow
- weak coupling between neighboring rows
- domain boundaries not 2\(\times\)1
Water/ZnO(10\overline{1}0):

STM (room temperature)

- For a full ML of water, domains with a (1x1) structure are observed (ca. 10%) in addition to (2x1)

- Another structure with (2x1) periodicity, but a much smaller corrugation appears as well (?)!

high mobility around defects
Water/ZnO(10\bar{1}0): STM (room temperature)

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1.

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**Water/ZnO(10\overline{1}0):**

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**The 'intermediate' structure: hypothesis**

- small energy difference, small barrier
- water overlayer constantly dissociates/associates at room temperature
- potentially triggered by loosely bound water/H at the defects
- 'intermediate' structure in STM is time average between two energy minima

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**Molecular (1x1)**

**Half-dissociated (2x1)**

\[ kT = 26 \text{ meV} \]
MD calculations, simulated STM images
(B. Meyer)


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Water adsorption at the ZnO(10\bar{1}0) surface:

- Water forms a very stable 2x1 overlayer
- Strong attractive interaction - 2 dim clustering
- Half the water molecules are dissociated (mediated by water-water interaction)
- Fully molecular layer almost degenerate in energy
- Water is loosely bound around observable defects
- The overlayer appears to be quite dynamic in STM - dissociation/association at RT, induced by H from defects?