Characterization and Optimization of Photoelectrode Surfaces for Solar-to-chemical Fuel Conversion

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June 10, 2010

Project ID# PD058

Overview

Timeline
- Start: March 2010
- End: February 2011
- Percent complete: 20%

Barriers
- Photoelectrochemical Materials Efficiency
- Photoelectrochemical Materials Durability

Budget
Total project funding
- DOE $100K
- Contractor $140K

(5% of PI, 100% of postdoc)

Funding for FY09: N/A

Funding for FY10:
- 240K FY10

Partners
NREL (J. Turner)

UNLV (C. Heske)

Relevance

- Objectives
  - Understand underlying mechanism of surface corrosion of semiconductor-based photoelectrochemical cells
  - Understand dynamics of water dissociation and hydrogen evolution at the water-photoelectrode interface
  - Understand electronic properties of the water-electrode interface
  - Understand relationship between corrosion and catalysis
- Relevance to H_2 program
  - Inform experimental efforts to increase durability of photocatalyst
  - Inform experimental efforts to increase catalytic efficiency

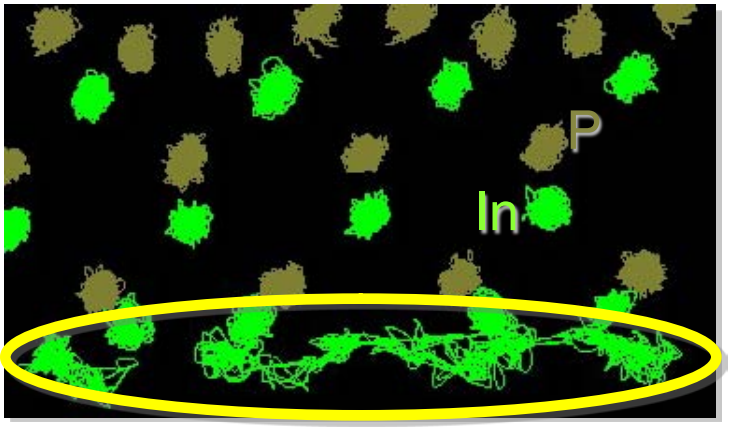
Technical Approach

- Perform large-scale interfacial simulations of III-V semiconductor surfaces in contact with water
  - Use quantum molecular dynamics (Density Functional Theory, DFT) for accurate interfacial modeling
  - Electronic structure data permits materials characterization and experimental interpretation
- Examine different surface treatments, geometries, and solution chemistries
- Correlate surface degradation with atomistic surface structure, chemistry, and dynamics
- Relate interfacial water dissociation with tested surface morphology

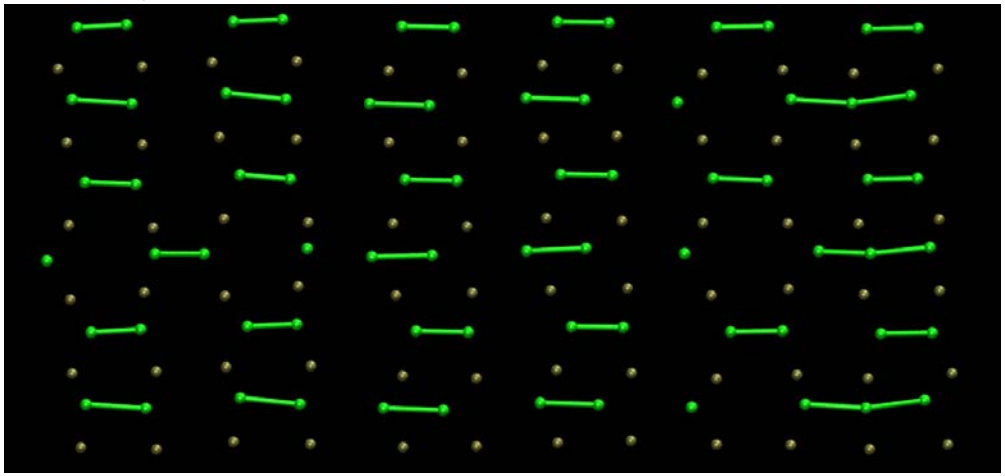
Milestones and Deliverables

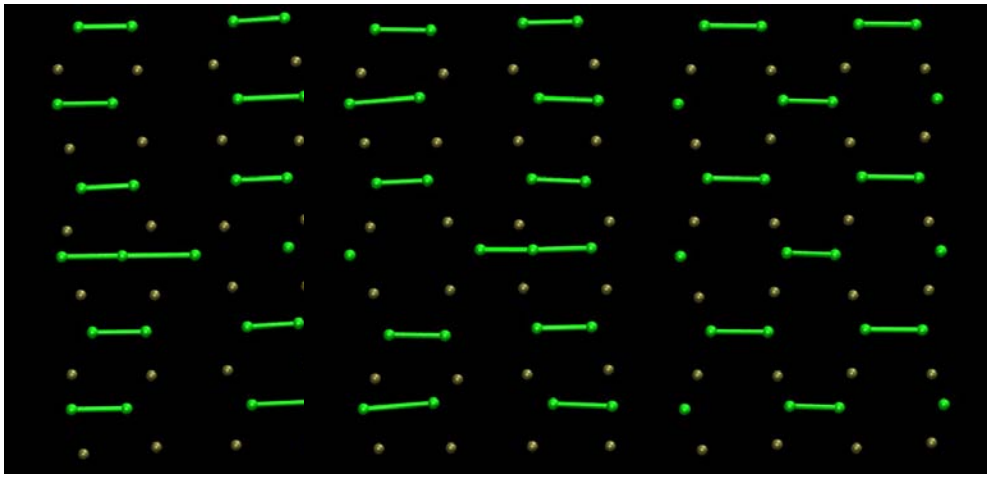
Milestone	Description	% Completed
1	Perform simulations on InP, GaP, $GaInP_2$	30
2	Examine effects of ions and nitrogen additives in solution	5
3	Investigate precursor states for surface photocorrosion processes	10
4	Study mechanisms of dissociative adsorption of water as a first step in photo-induced hydrogen evolution	20
5	Formulate representative model to deliver simulated spectra to experimental collaborators	0

Technical Accomplishment – Structure and stability



Dynamics of bare (In-terminated) InP(001)





Dynamical surface structure leads to dynamical electronic structure

Technical Accomplishment – Structure and stability

- Oxide is key to understanding corrosion, could also have relevance for reactivity (Heller, *Science* 223, 1141 [1984])
- Tested stability of various oxides:

Site	InP (eV)	InP+N (eV)	GaP (eV)	GaP+N (eV)	(In/Ga-O-In/Ga)
Bridge x (1)	0	0.04	0.32	1.24	0
Bridge x (2)			0.41	0.29	0
Bridge y	1.05	0.47	0.67	0.63	1
Atop (1)	0.51	0	0	0	0.75
Atop (2)	0.46	0.67	0.06	0.86	0.75
Atop (3)	0.56	0.38	0.28	0.75	0.5
Hollow (1)	0.31	0.54	0.59	1.41	0
Hollow (2)	0.46	0.61	0.78	1.56	0

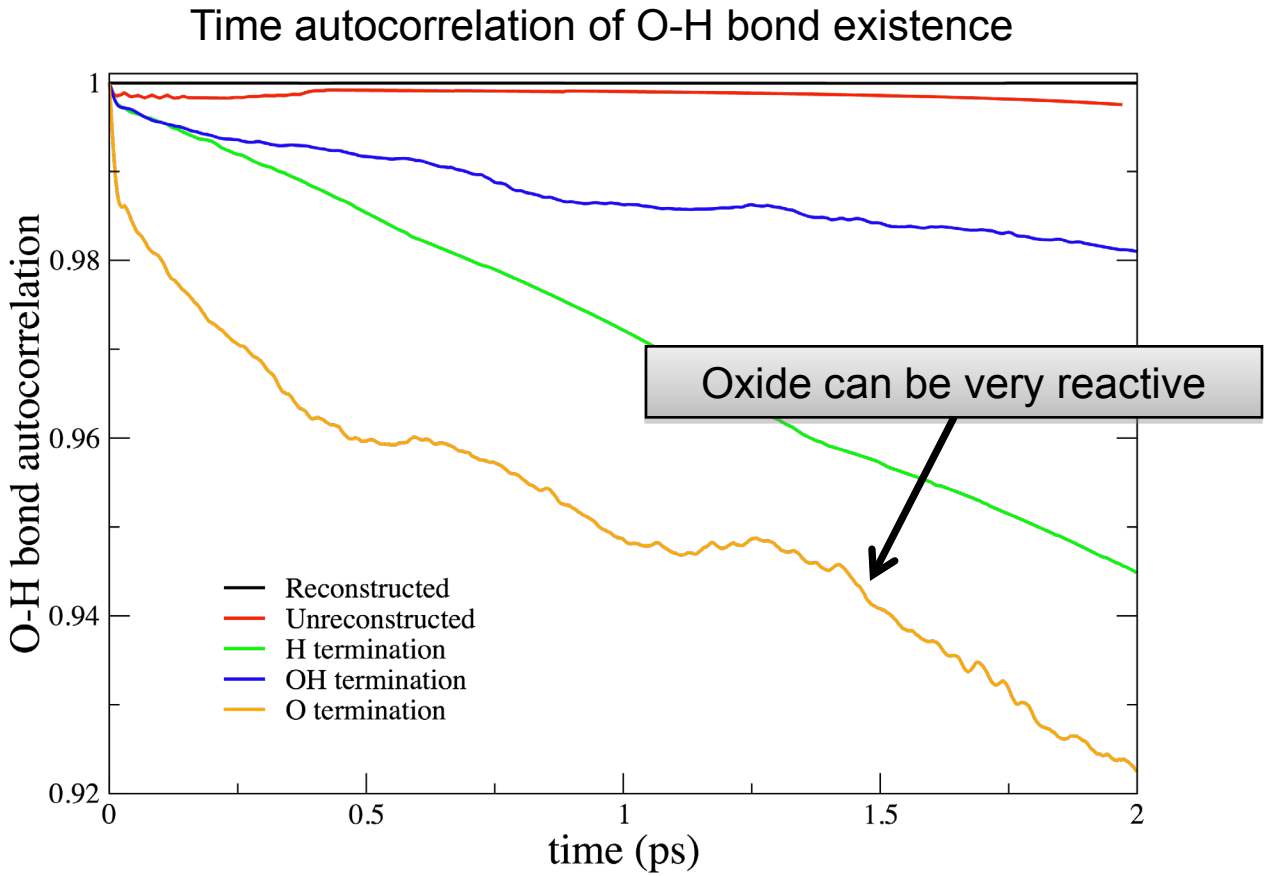
Subsurface oxides **Surface oxides**

Both surface and subsurface oxides should be considered

Technical Accomplishment – Structure and reactivity

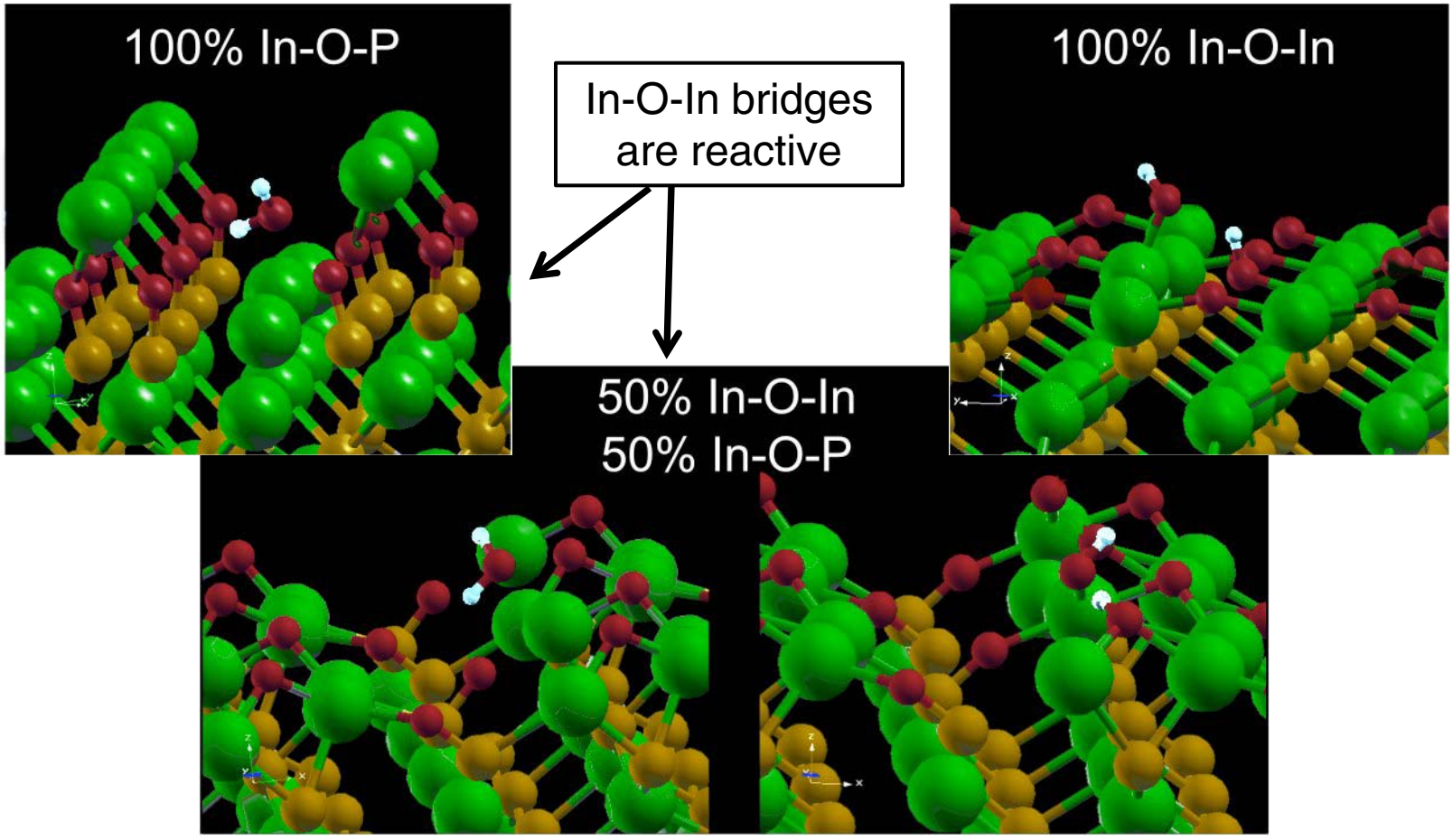
- Photoexcitation is difficult to simulate, but we can look for precursors to photolysis

- "Inner-sphere" electron transfer: look for dissociative adsorption of water as precursor



Dynamics show evidence of dissociative adsorption

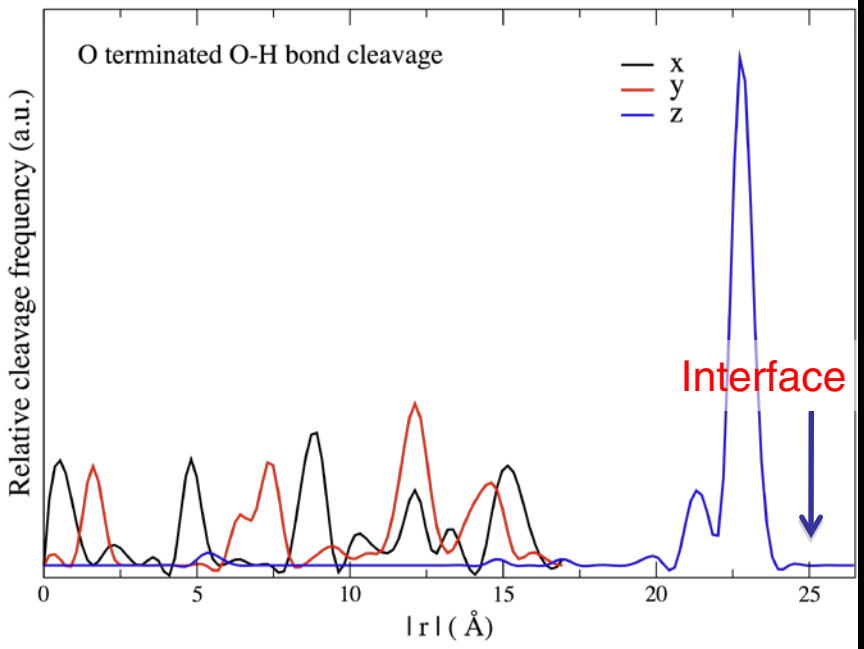
Technical Accomplishment – Surface oxides of InP(001)

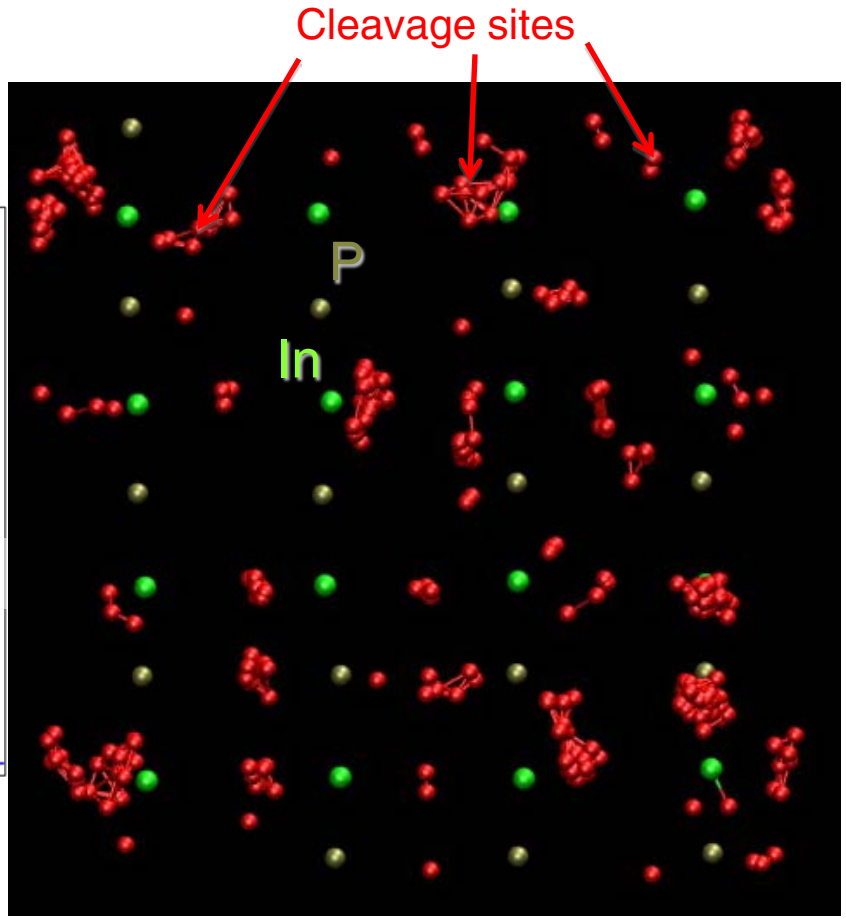


Oxide reactivity can be categorized according to O bond topology

Technical Accomplishment – Surface oxides of InP(001)

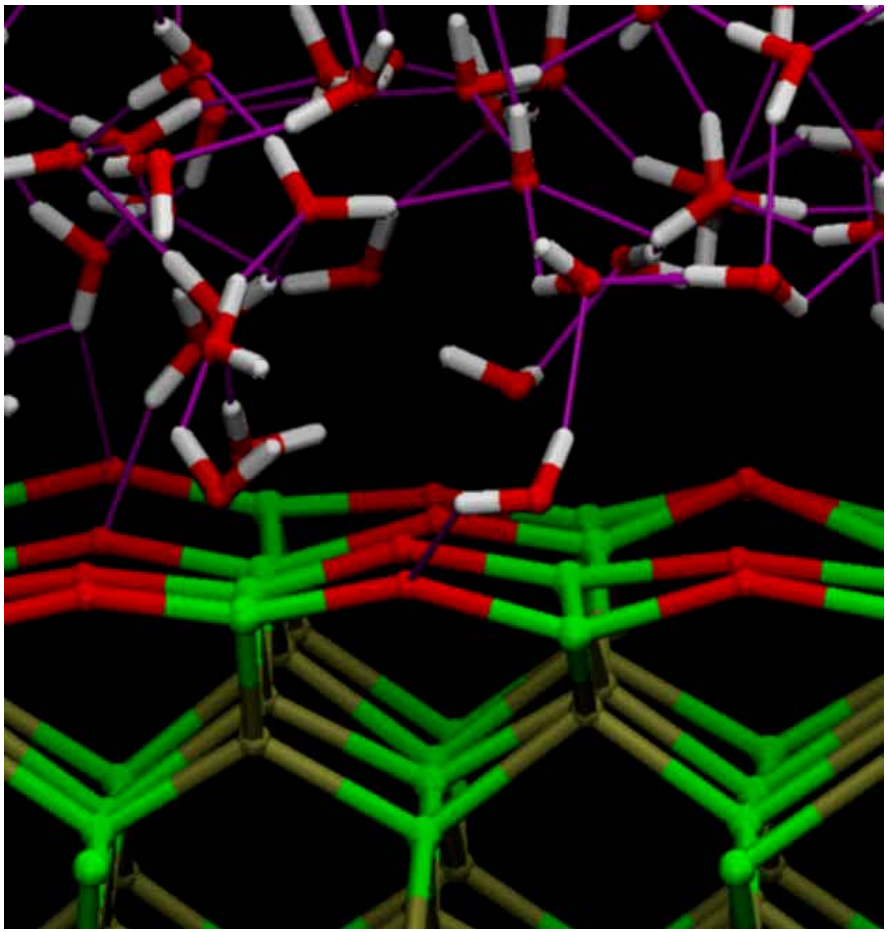
Locations of water cleavage for O-terminated InP(001)



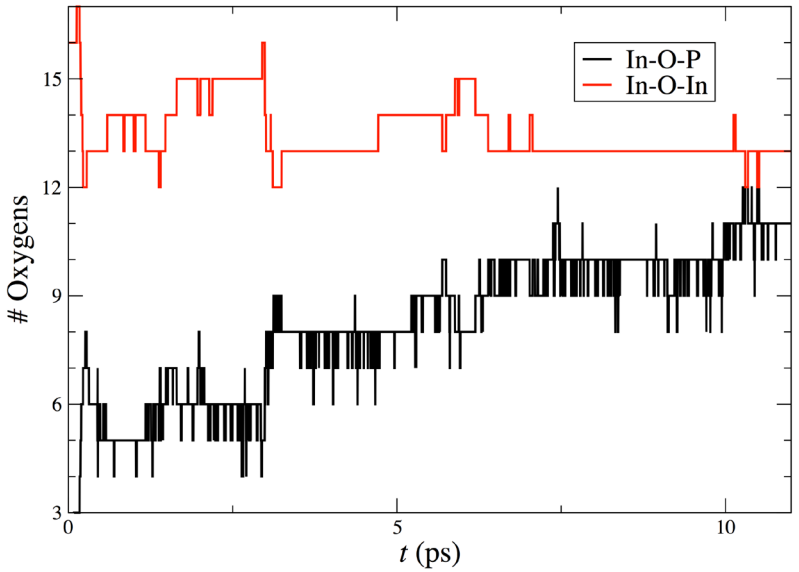


Preferred reaction sites correlate with surface structure

Technical Accomplishment – Surface oxides of InP(001)

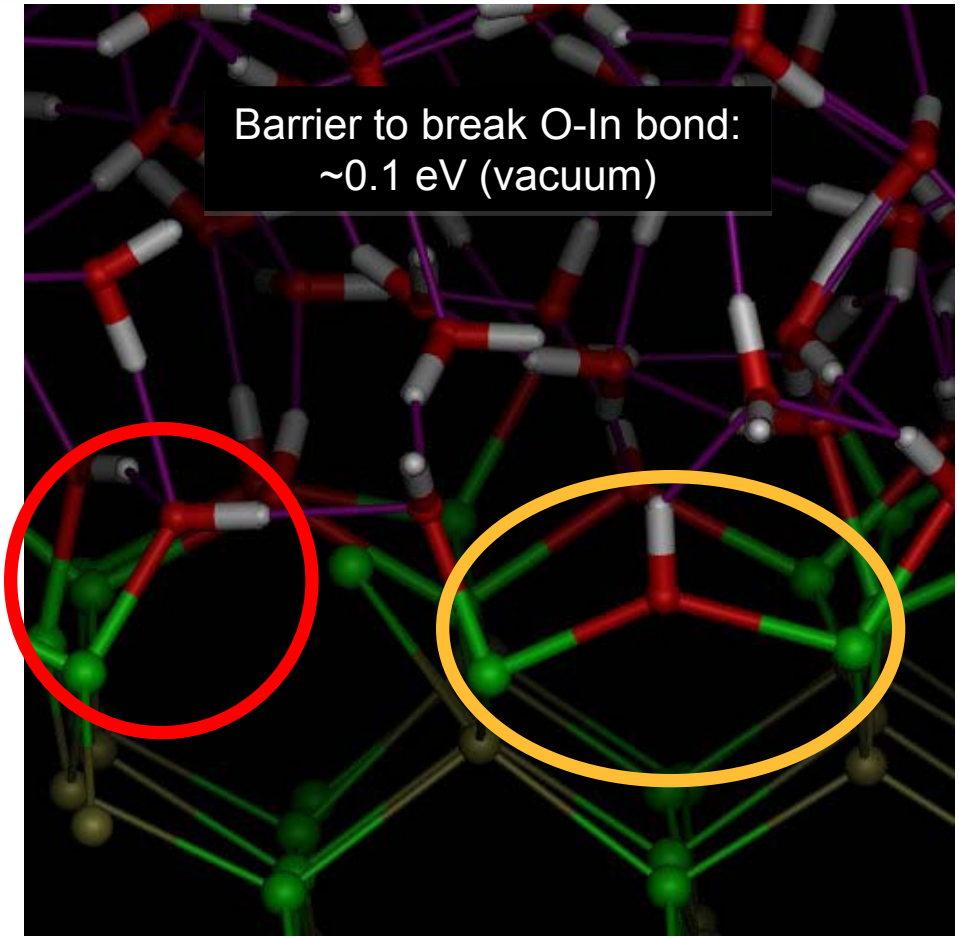


1) Formation of In-OH_2 bond
2) Transfer of H to neighboring O in In-O-In bridge
3) In-O-In bond cleavage
4) Optional formation of In-OH-P bond

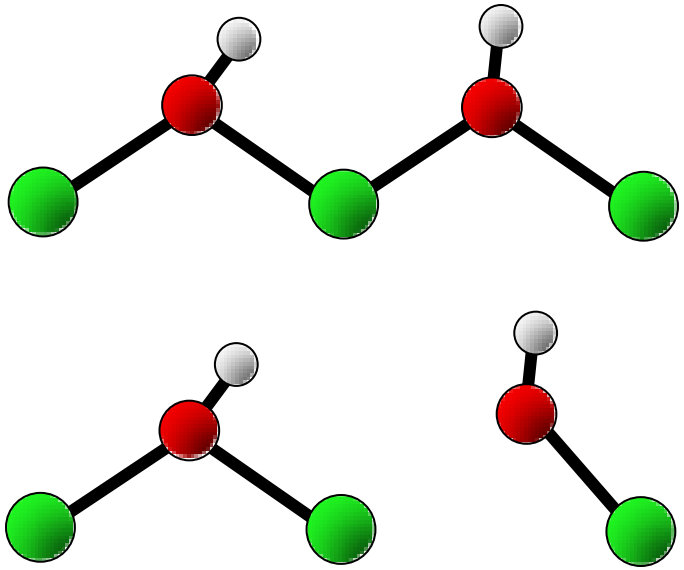


Mechanism of dissociative adsorption of water on In-O-In bridge

Technical Accomplishment – Surface hydroxides of InP(001)



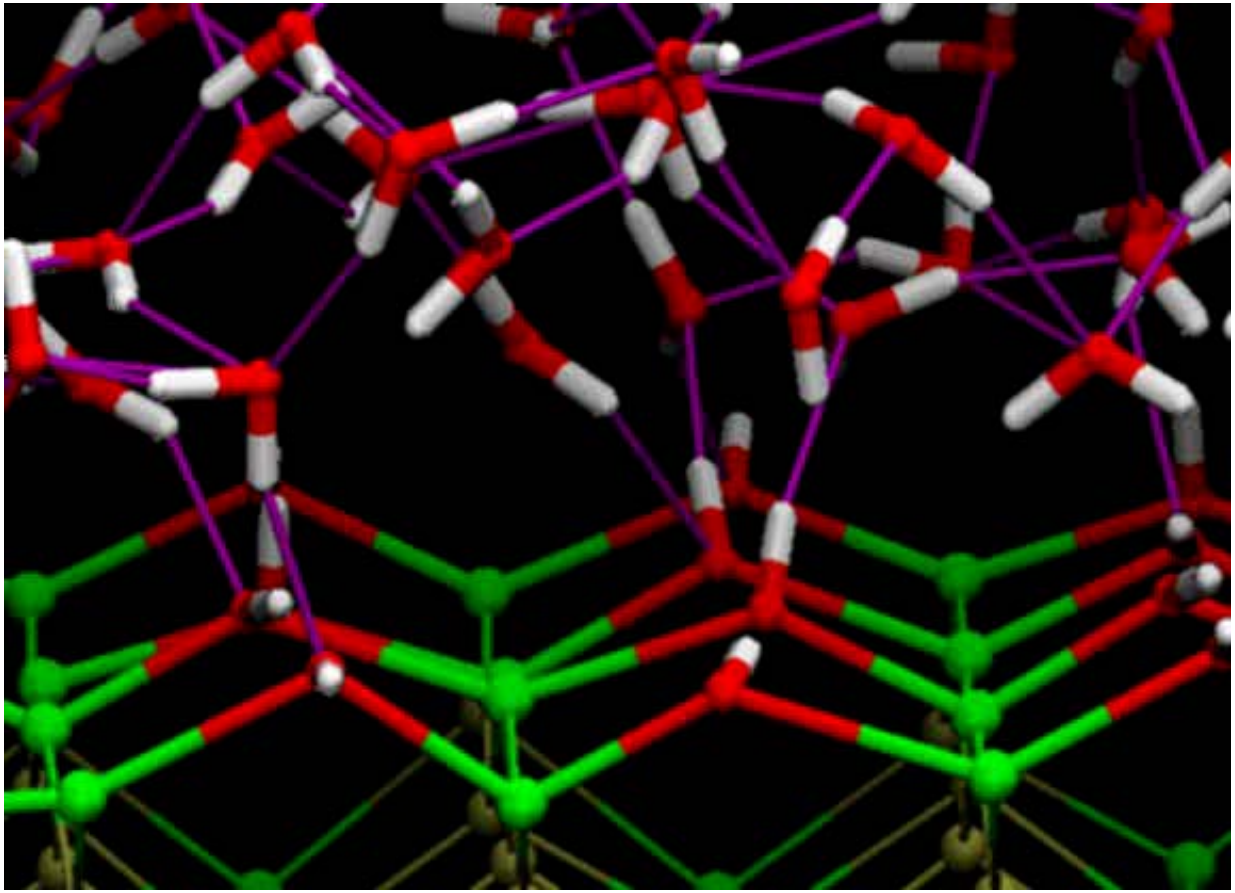
Barrier is lowered by hydrogen bonding with surrounding water



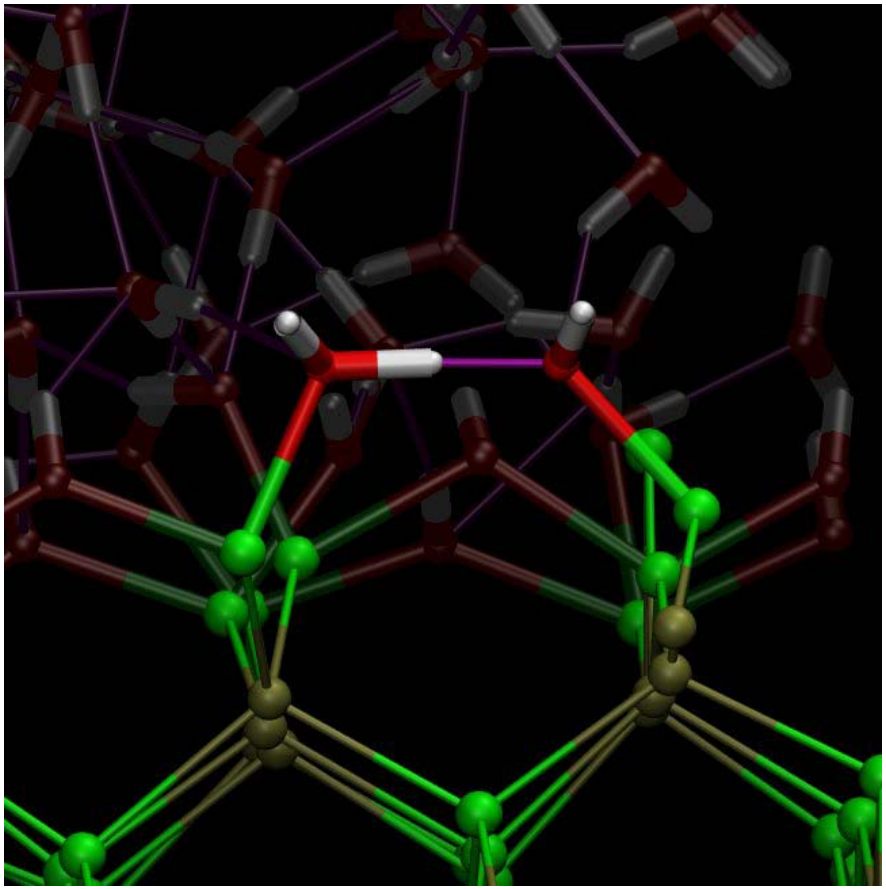
Hydroxide bridge is most stable, but conversion to atop is facile

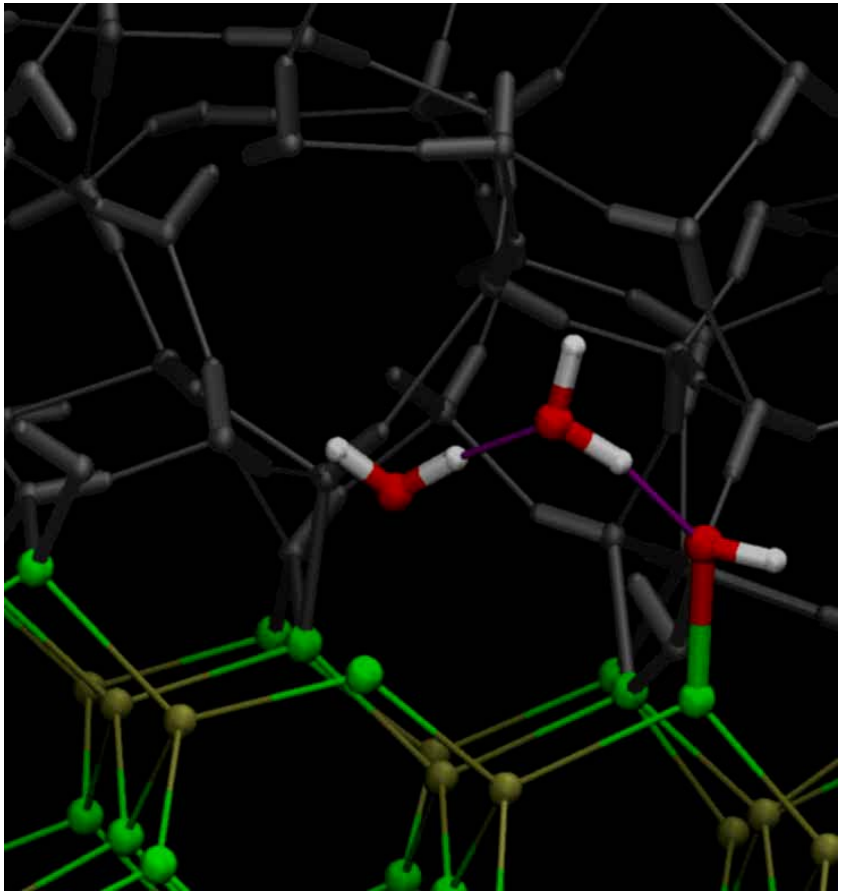
Technical Accomplishment – Surface hydroxides of InP(001)

Dynamic equilibrium between atop and bridge hydroxide configurations



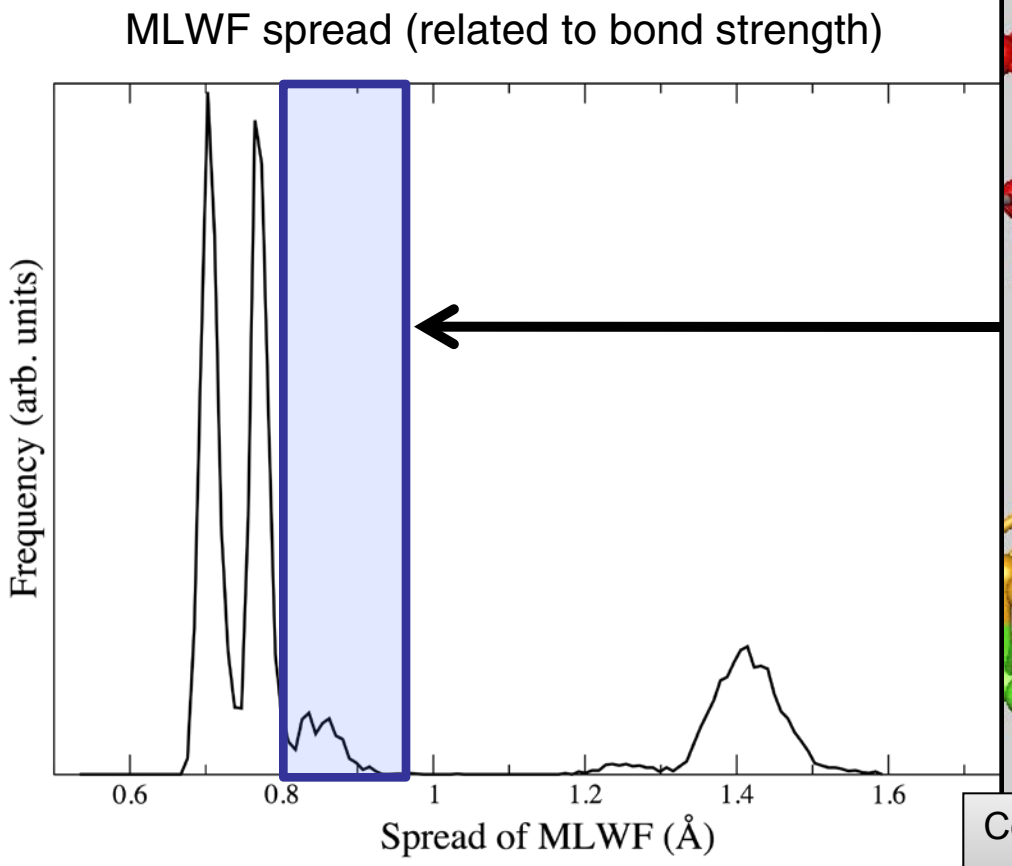
Technical Accomplishment – Surface hydroxides of InP(001)

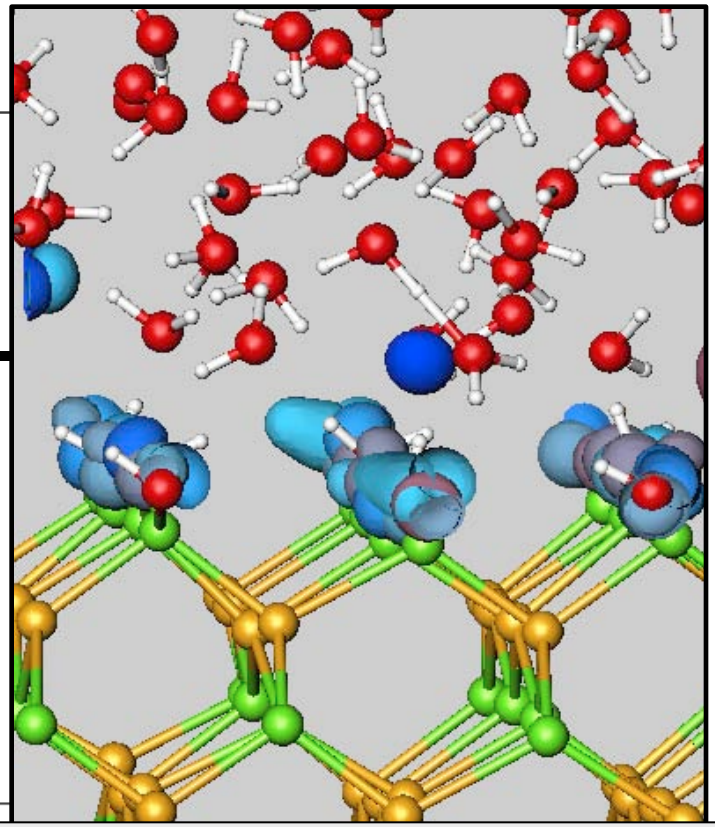




Metastable H-bond bridges facilitate water dissociation and hydrogen transport

Technical Accomplishment – Surface hydroxides of InP(001)



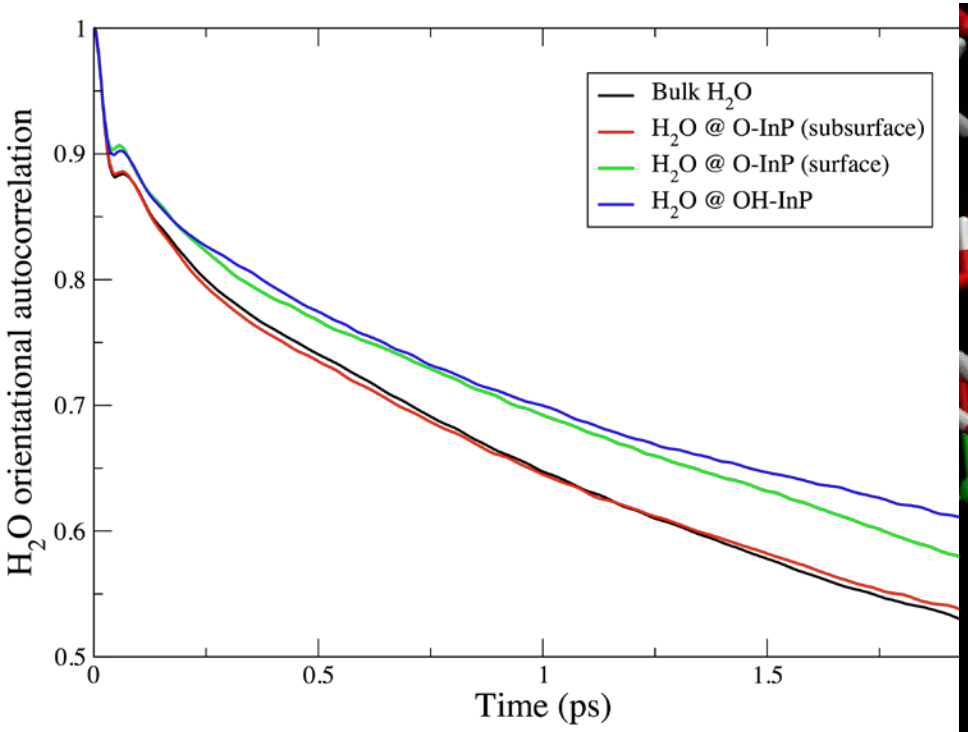


Code developed by J.L. Fattebert under DOE SciDAC grant DE-FC02-06ER46262

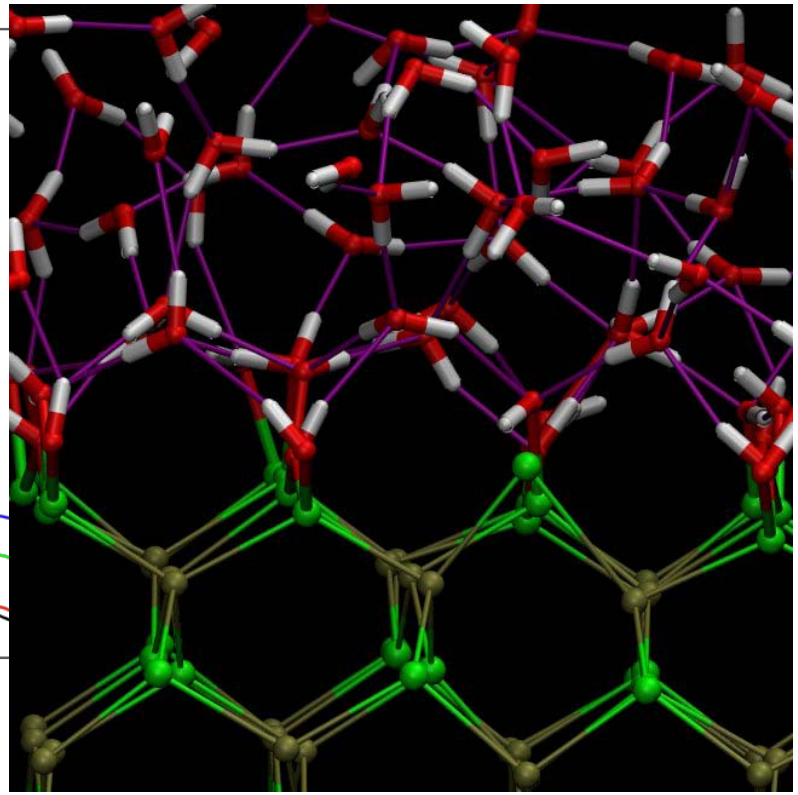
Can use maximally localized Wannier functions to examine bonding

Technical Accomplishment – Structure of interfacial H_2O

Time autocorrelation of H_2O orientation



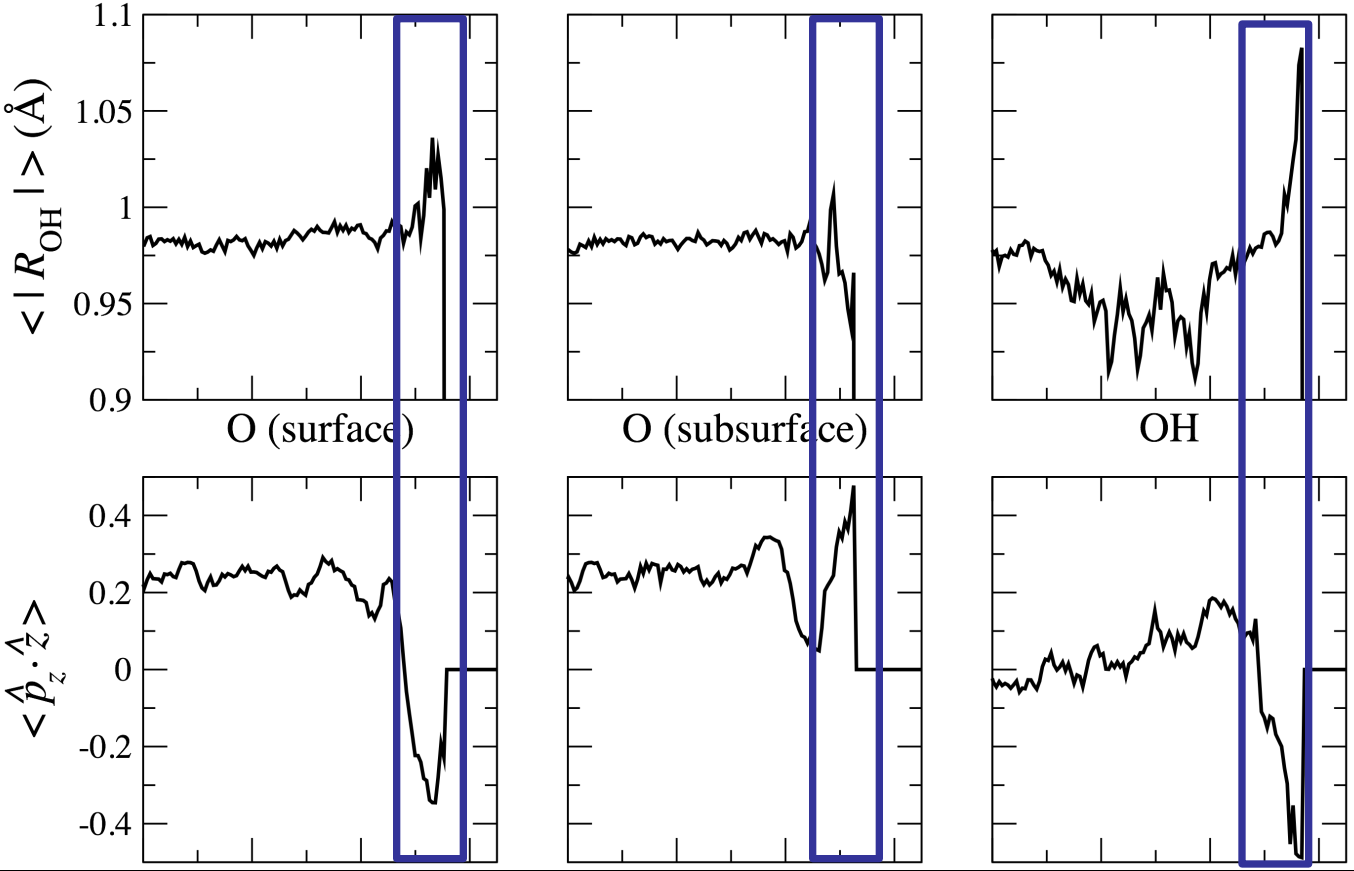
Structure of water near OH-terminated surface



Water orientation is less dynamic near interface with reactive surface

Technical Accomplishment – Structure of interfacial H_2O

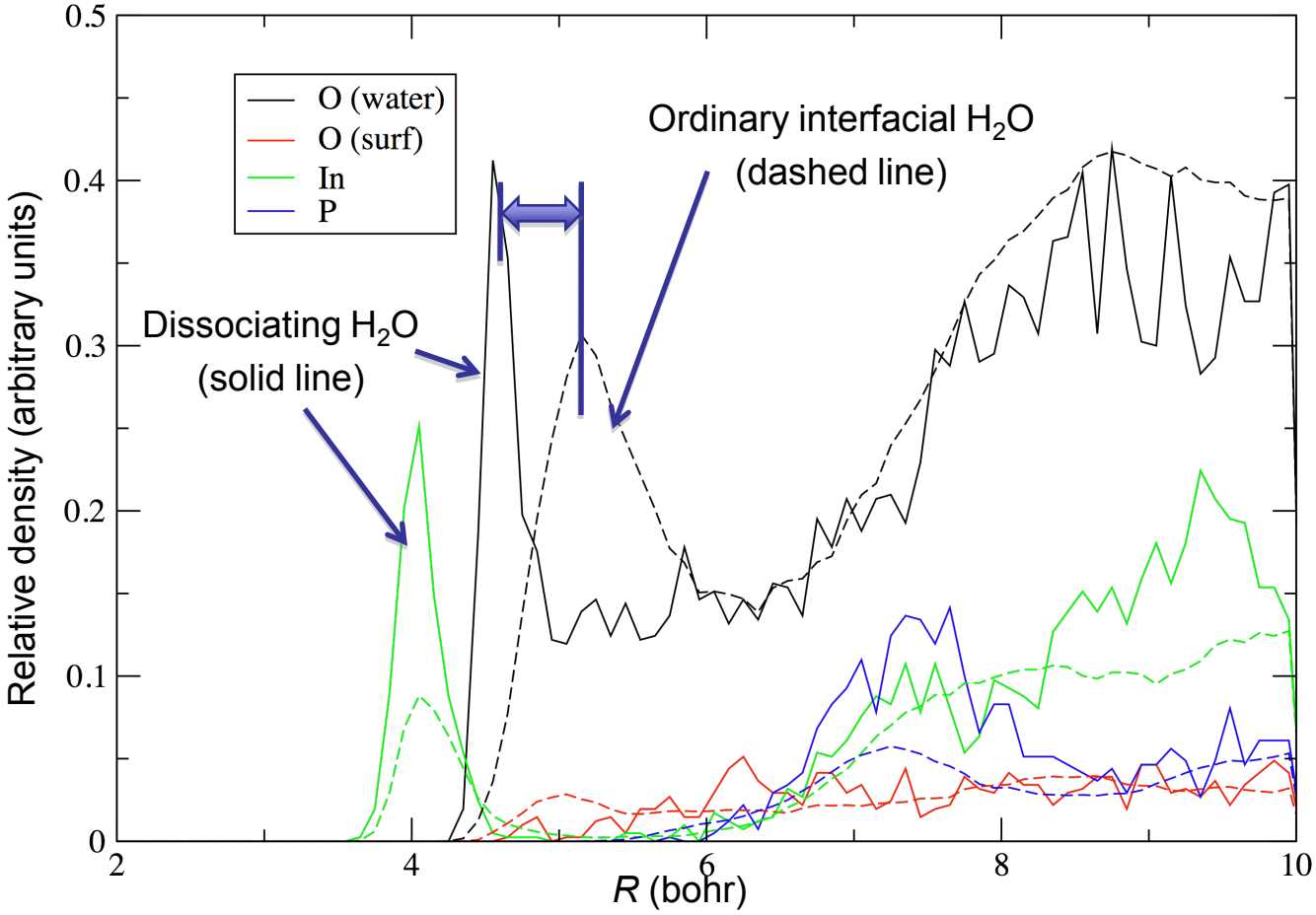
Average O-H bond length and dipole component perpendicular to the surface for water near interface

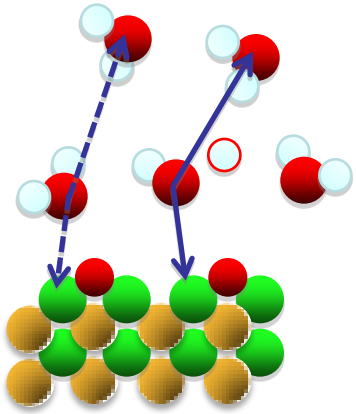


Water near interface has preferred orientation and different dipole strength

Technical Accomplishment – Structure of interfacial H_2O

Radial distribution of atoms surrounding interfacial H_2O (for InP + oxide)





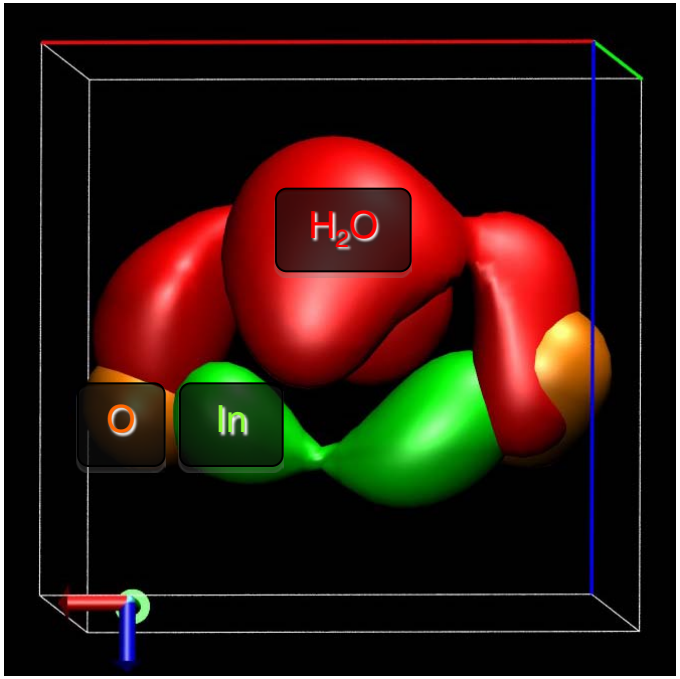
Surrounding water molecules are closer upon dissociation

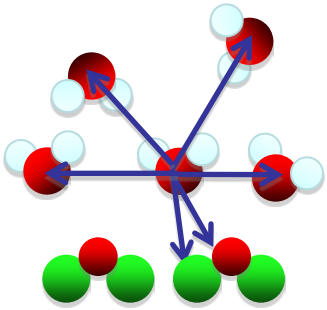
Technical Accomplishment – Structure of interfacial H_2O

Surrounding water molecules more structured upon dissociation

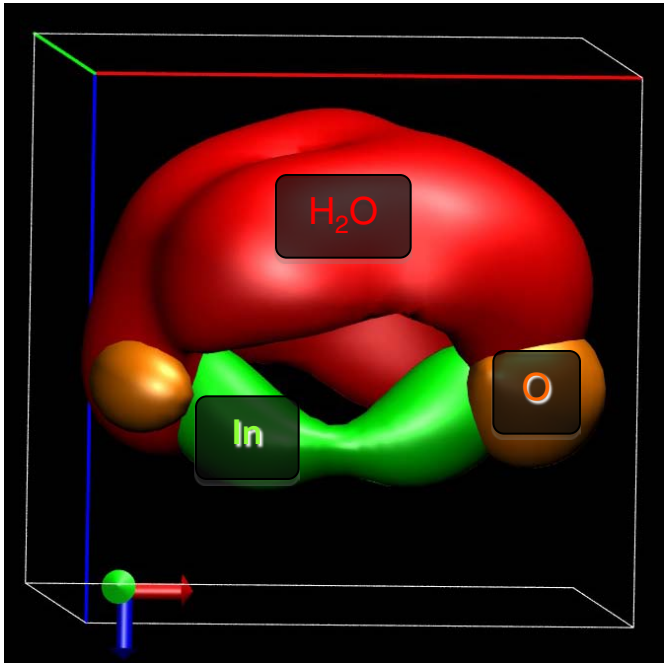
Angular distribution of atoms surrounding interfacial H_2O (for InP + oxide)

Dissociating H_2O



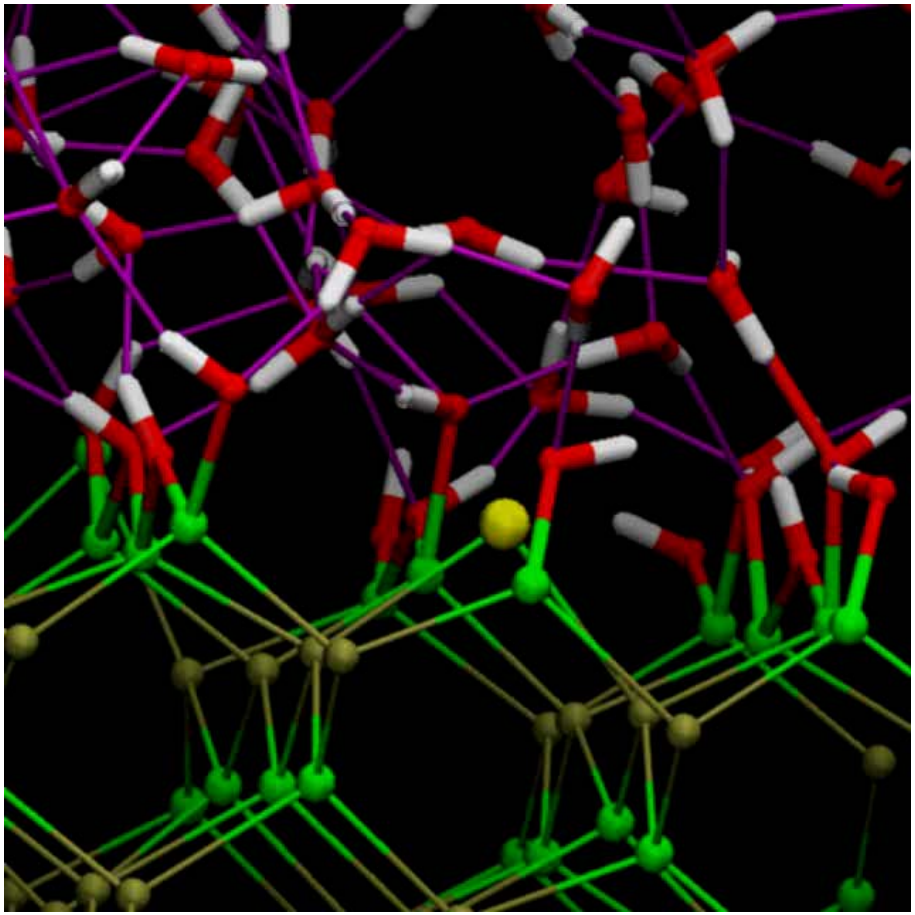


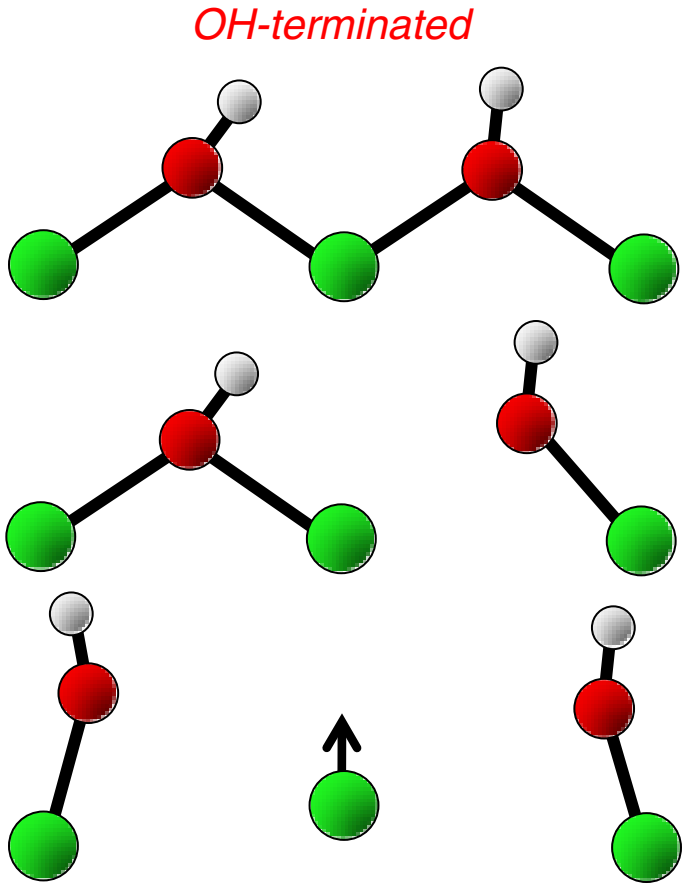
Ordinary interfacial H_2O



Interfacial water structure is correlated with surface activity

Technical Accomplishment – Surface instability





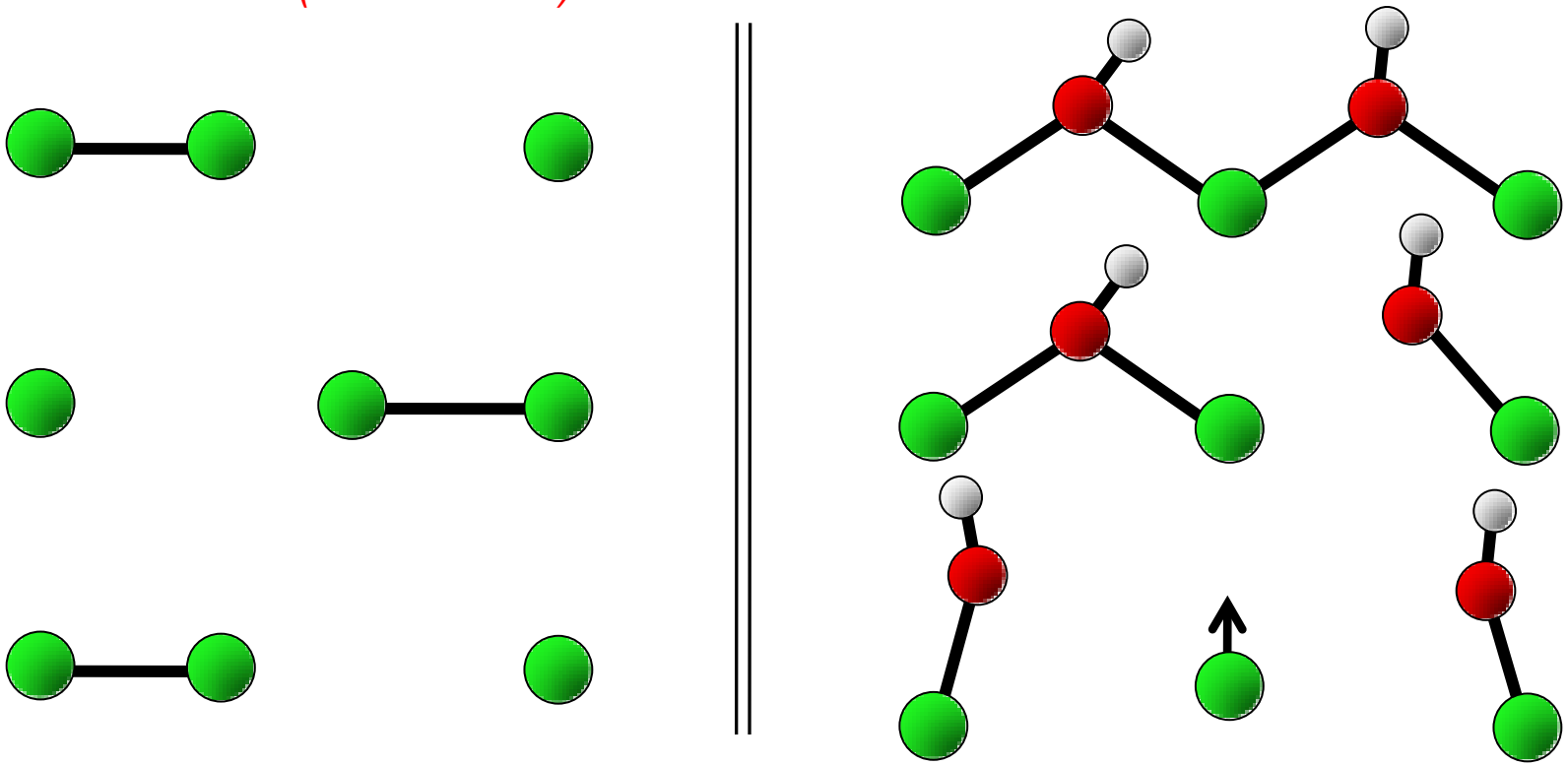
Broken hydroxide bridge provides possible motivation for In dissolution

Technical Accomplishment – Surface instability

Why don't we see dissolution of In for the bare surface?

Bare surface (In-terminated)

OH-terminated



Exposed surface indium stabilizes through In-In dimerization, but dimerization is inhibited in InP+O by presence of oxide bridge

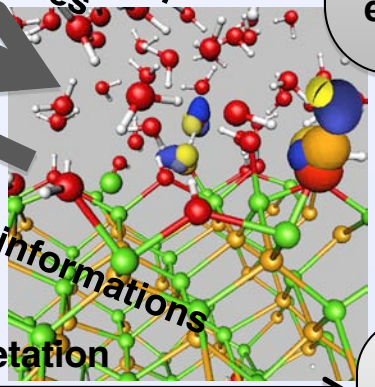
Collaborations: Theory-experiment feedback cycle for accelerating development of efficient & robust electrode

NREL experiments: (DOE lab)
- J. Turner & T. Deutsche
- DOE H_2 program
- Synthesize electrode materials
- Assemble device
- Analyze H_2 production performance and corrosion resistance

NREL theory: (DOE lab)
- K. Kim & W. Ih Choi
- DOE H_2 program
- Ab initio surface simulations (mostly static)
- Gas phase reaction energetics

Basic information on electrodes

Detailed microscopic informations



Sample

Choice of surface

X-ray interpretation

UNLV experiments: (University)
- C. Heske & G. Kyle
- DOE H_2 program
- Hi-fidelity (in-situ) characterization of water-electrode interface using X-ray spectroscopy

LBNL theory: (DOE lab)
- D. Prendergast
- Not in H_2 program
- X-ray spectrum simulations

LLNL theory: (DOE lab)
- B. Wood & T. Ogitsu
- DOE H_2 program
- Large scale ab-initio MD of water-electrode interface

Proposed future work

Milestone	Description	% Completed
1	Perform simulations on InP, GaP, $GaInP_2$	30
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3	Investigate precursor states for surface photocorrosion processes	10
4	Study mechanisms of dissociative adsorption of water as a first step in photo-induced hydrogen evolution	20
5	Formulate representative model to deliver simulated spectra to experimental collaborators	0

Complete the rest of simulations and analysis. In particular, focus on the collaborations with the experimental groups (UNLV & NREL) to investigate on the photo induced hydrogen evolution reaction and the corrosion.

Summary

- We have performed the quantum MDs of water-electrode interfaces
  - At ambient condition, surface structure of InP dynamically changes, which affects on the dynamics of water
  - A few stable surface oxide morphologies were identified, which correlate with chemical activities
  - Upon a H_2O dissociation, surrounding H_2Os evolve cooperatively
- The electronic excitation spectrum of a realistic water-electrode model can be calculated
  - X-ray spectroscopic information (eg. XAS) can be directly compared between theory and experiments
  - Precise information on the nature of hydrogen evolution and the electrode corrosion will be obtained
  - Such an information will be used in finding a good electrode material or in an appropriate surface treatment