

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

PI: Tadashi Ogitsu

Presenter: Brandon C. Wood

Lawrence Livermore National Laboratory

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)



U.S. DEPARTMENT OF
ENERGY

UNLV
UNIVERSITY OF NEVADA LAS VEGAS



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 H₂ program
 - Inform experimental efforts to increase durability of photocatalyst
 - Inform experimental efforts to increase catalytic efficiency



Technical Approach

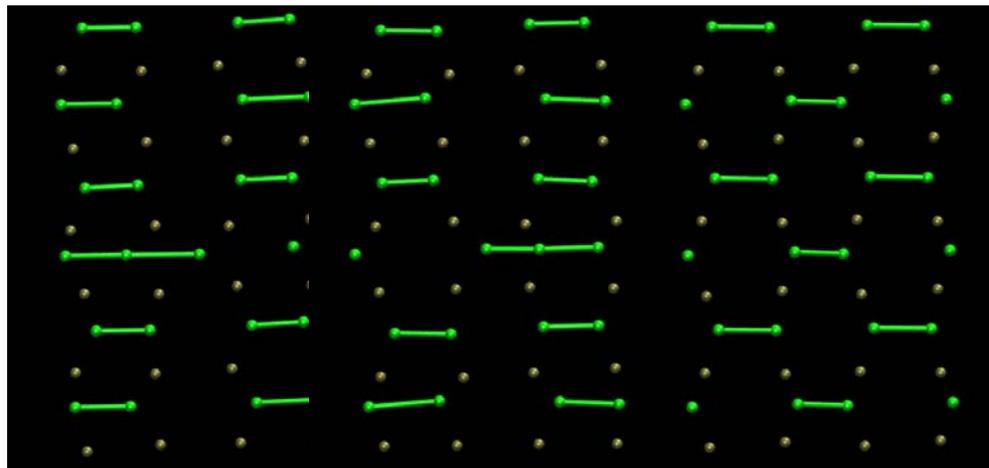
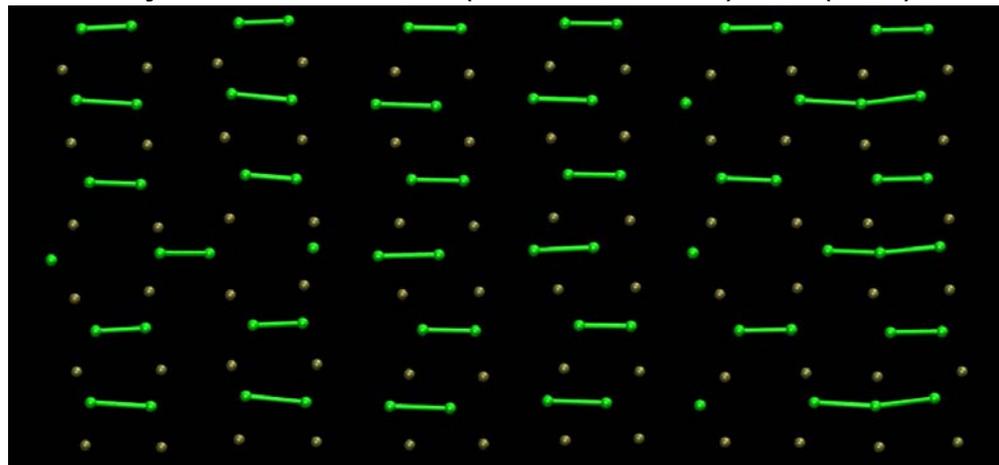
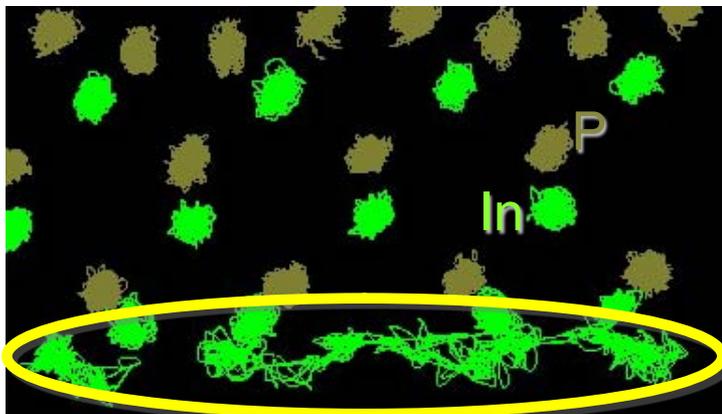
- Perform large-scale interfacial simulations of III-V semiconductor surfaces in contact with water
 - Use quantum molecular dynamics (Density Functional Theory, DFT) for accurate interfacial modeling
 - Electronic structure data permits materials characterization and experimental interpretation
- Examine 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)

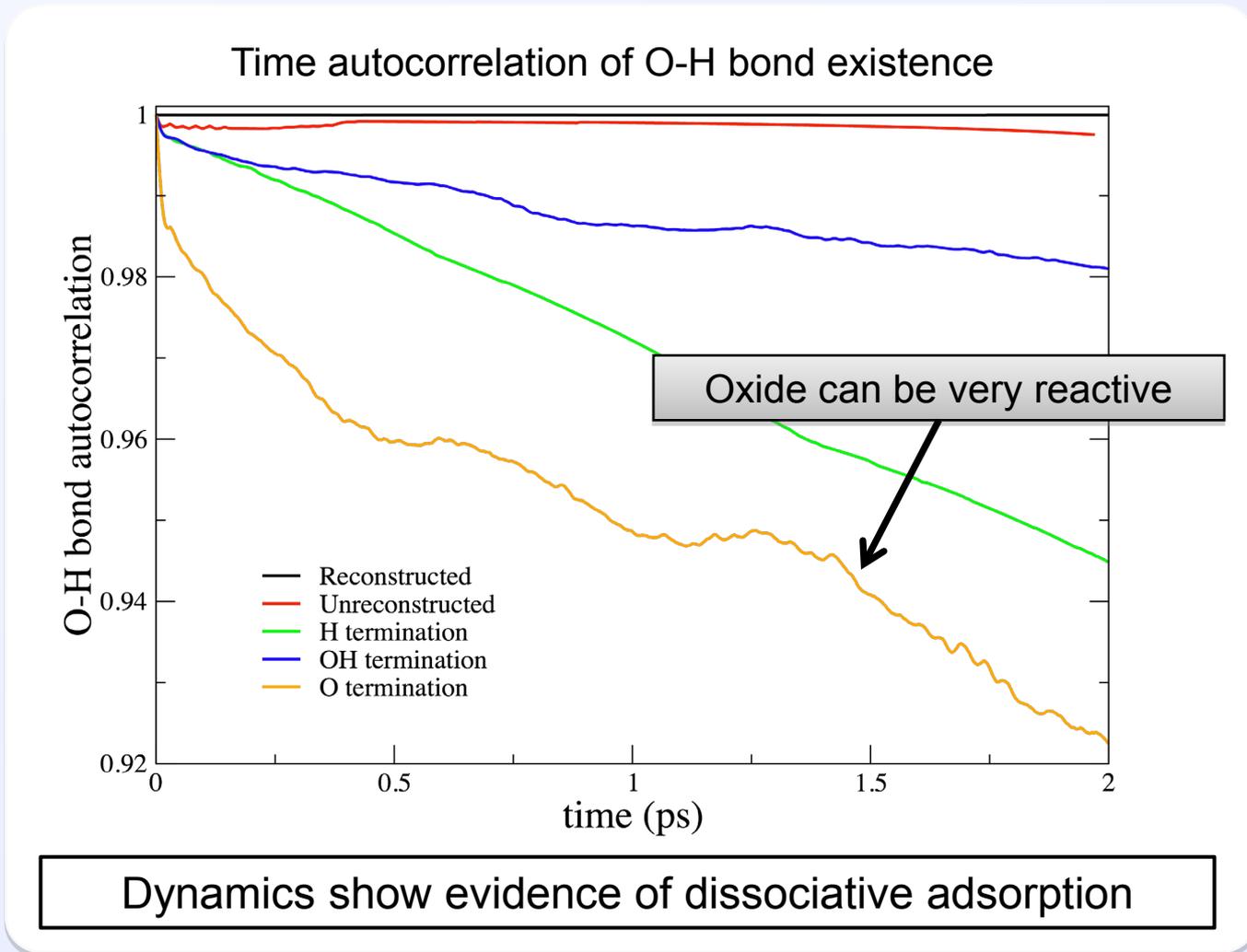


Dynamical surface structure
leads to dynamical
electronic structure

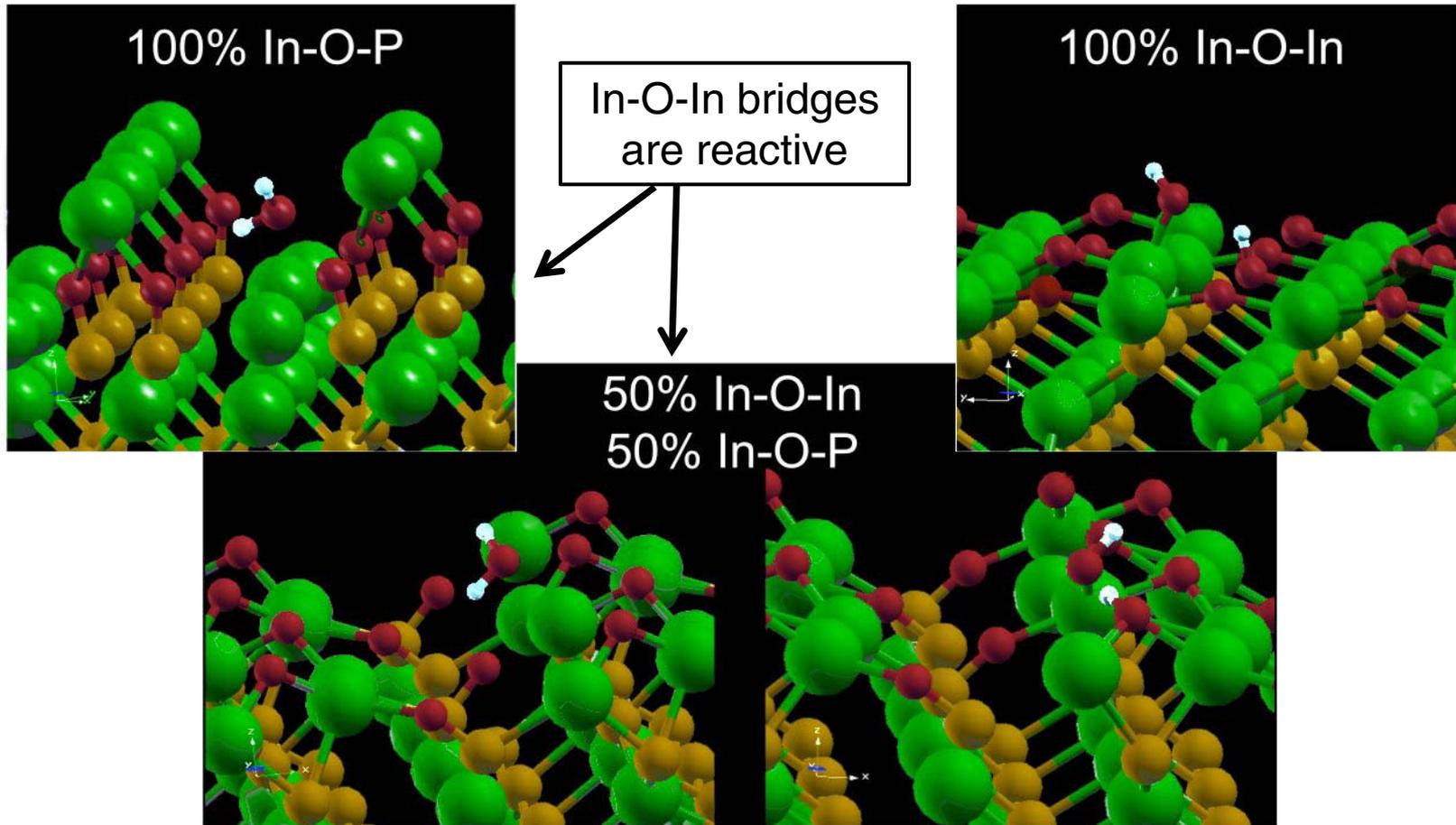
Technical Accomplishment – Structure and reactivity

- 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



Technical Accomplishment – Surface oxides of InP(001)

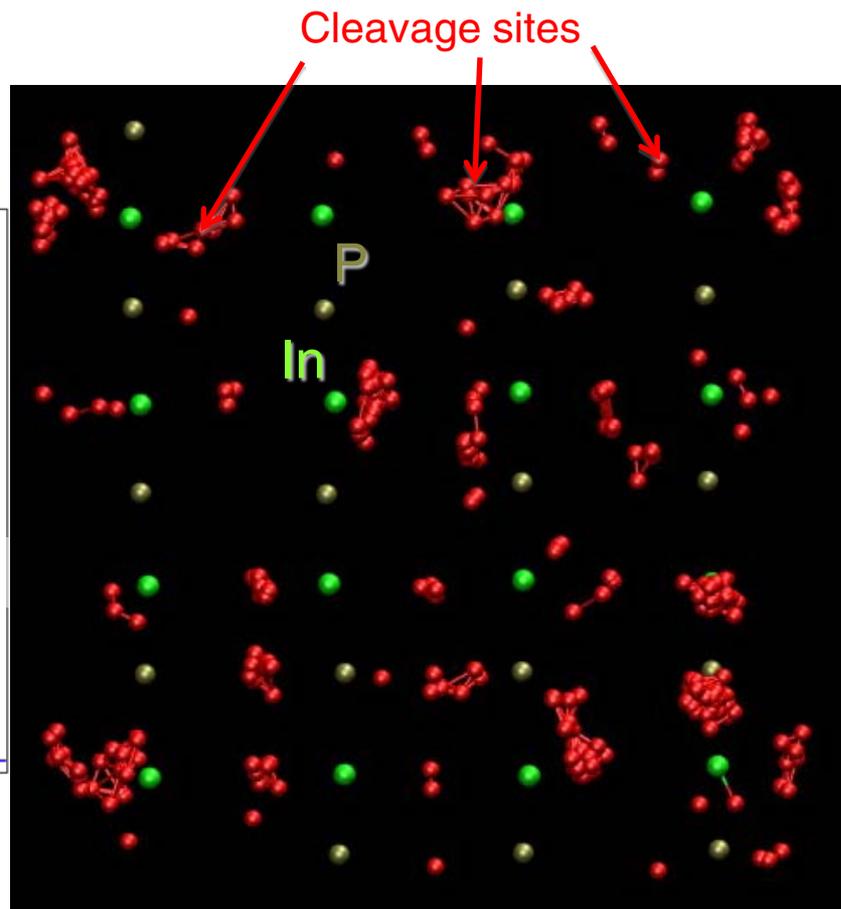
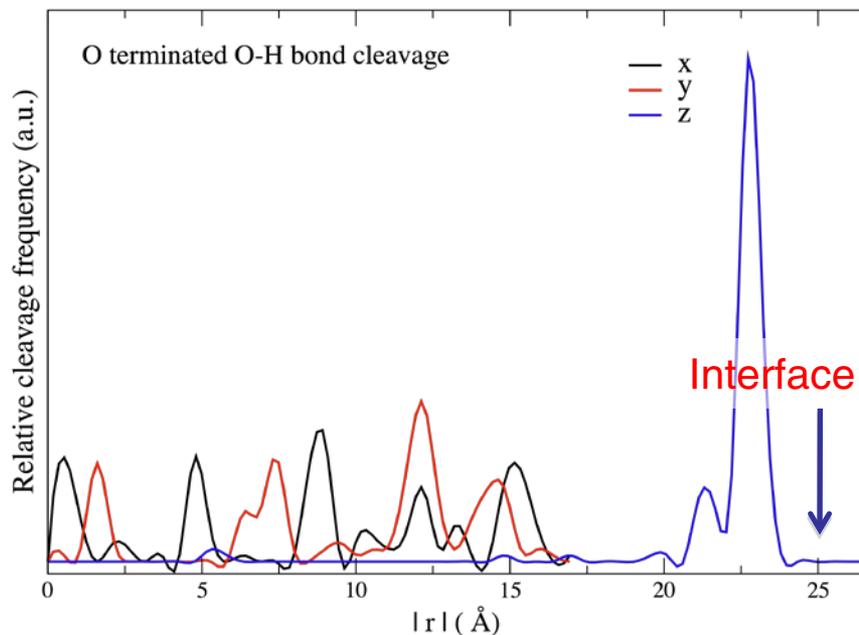


Oxide reactivity can be categorized according to O bond topology



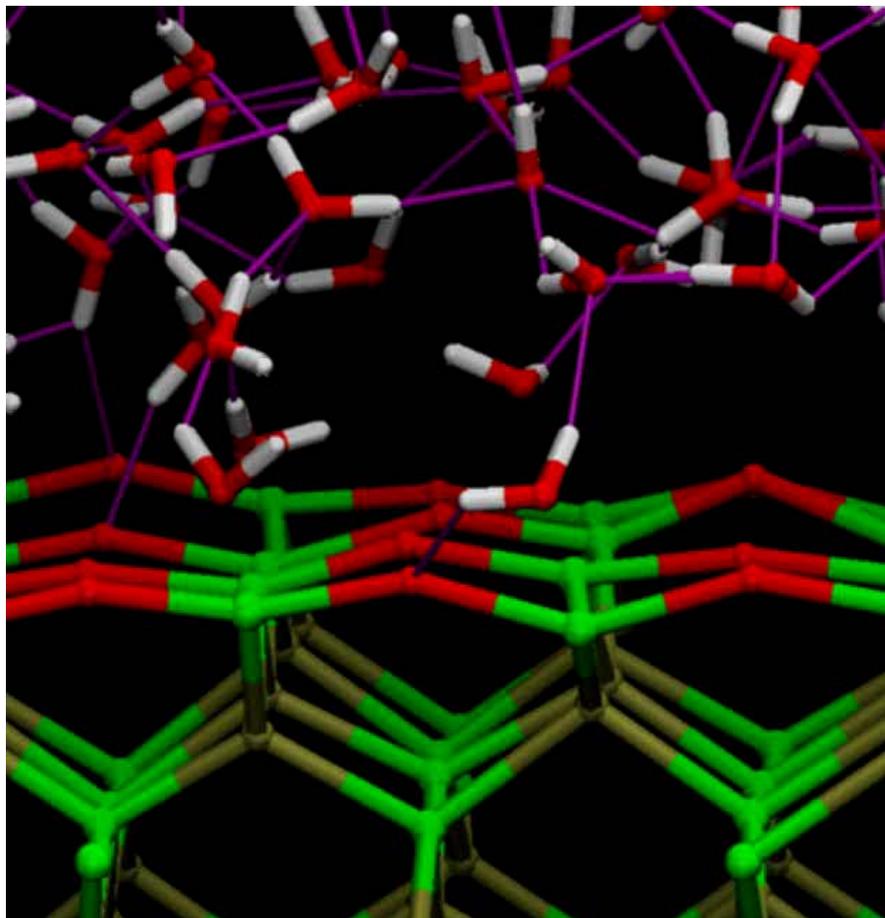
Technical Accomplishment – Surface oxides of InP(001)

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

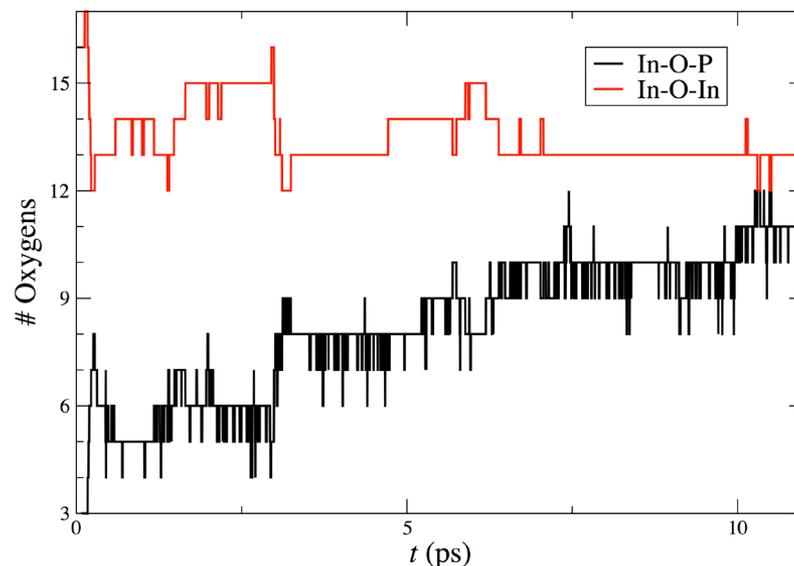


Preferred reaction sites correlate with surface structure

Technical Accomplishment – Surface oxides of InP(001)



- 1) Formation of In-OH₂ 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



U.S. DEPARTMENT OF
ENERGY

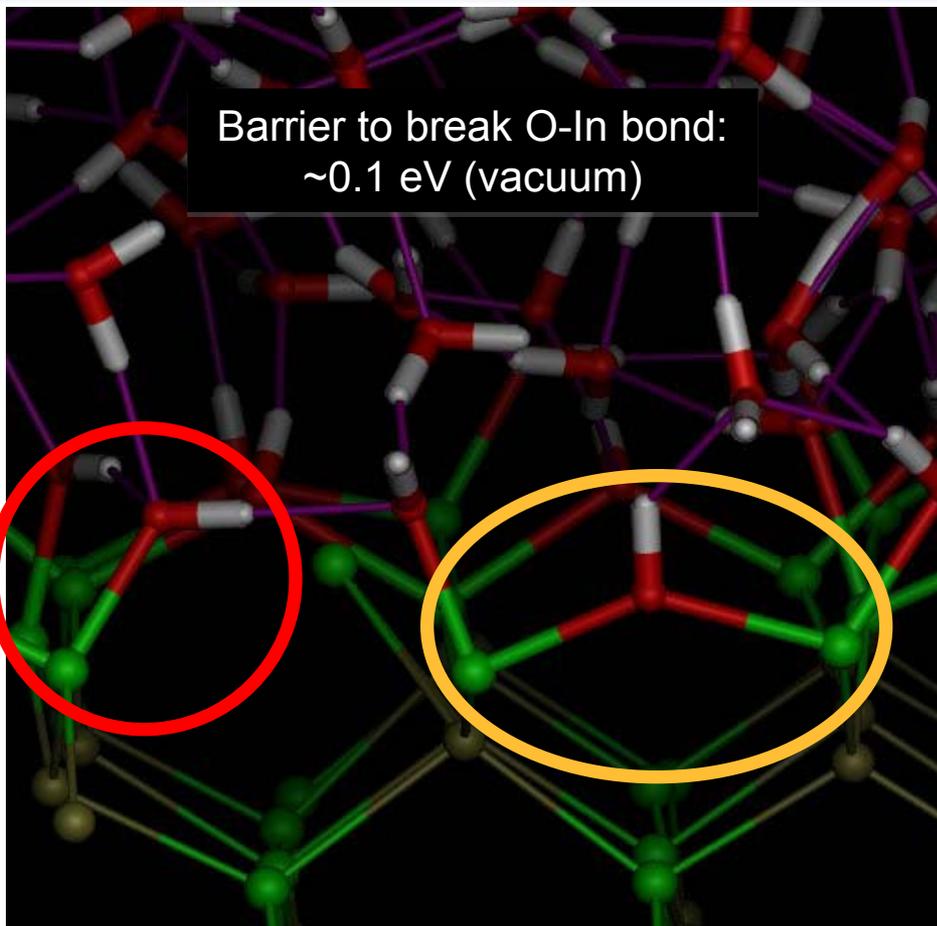
UNLV
UNIVERSITY OF NEVADA LAS VEGAS



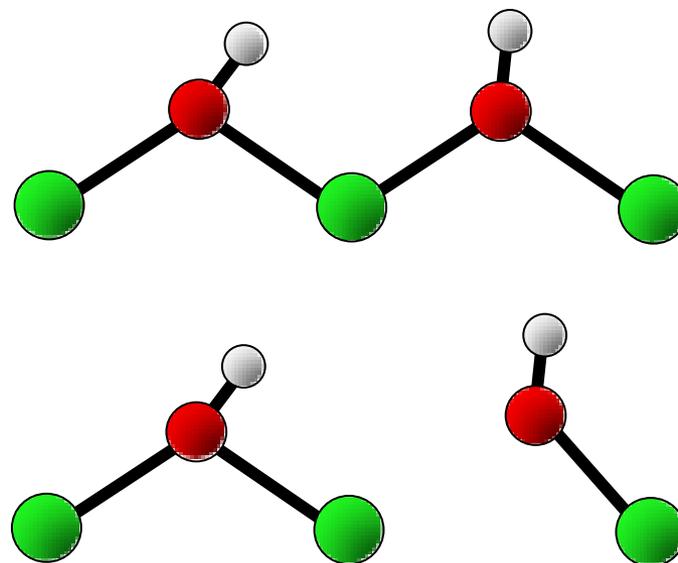
DOE Hydrogen Program Annual Merit Review



Technical Accomplishment – Surface hydroxides of InP(001)



Barrier is lowered by hydrogen bonding with surrounding water

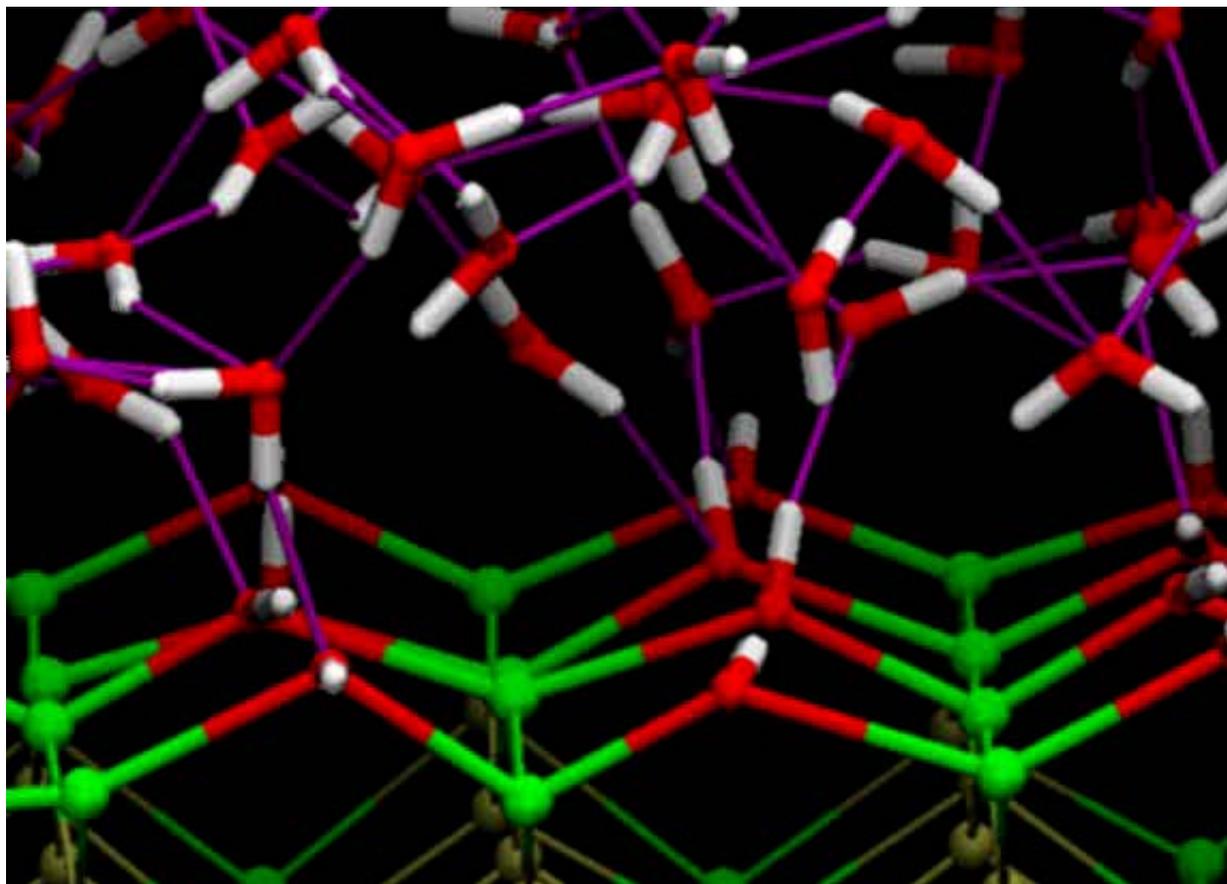


Hydroxide bridge is most stable, but conversion to atop is facile

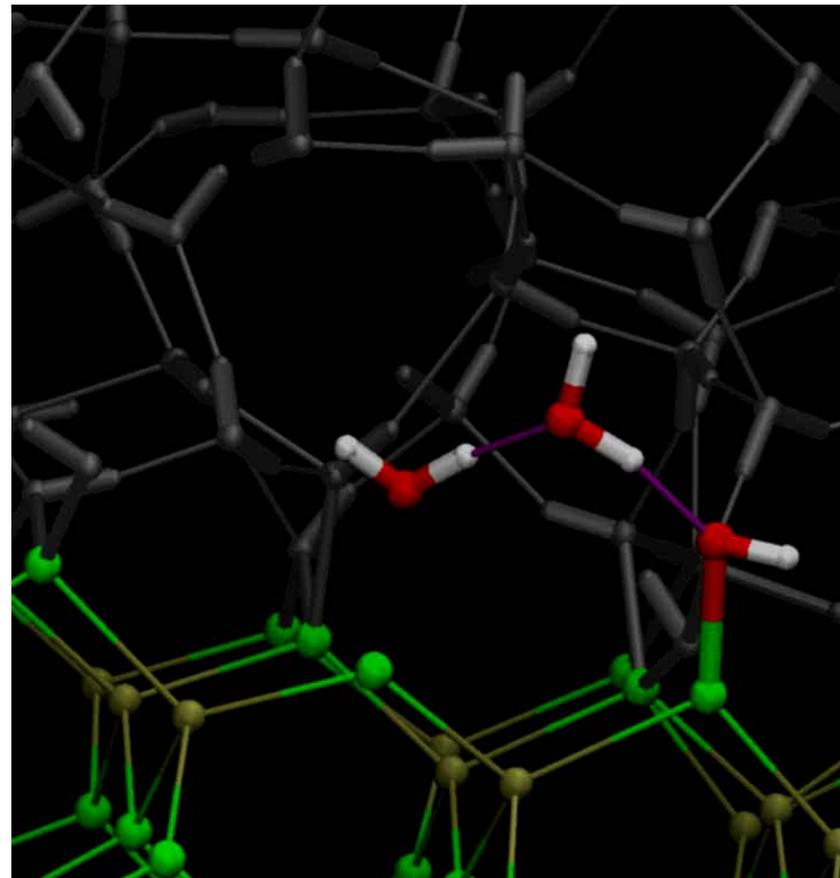
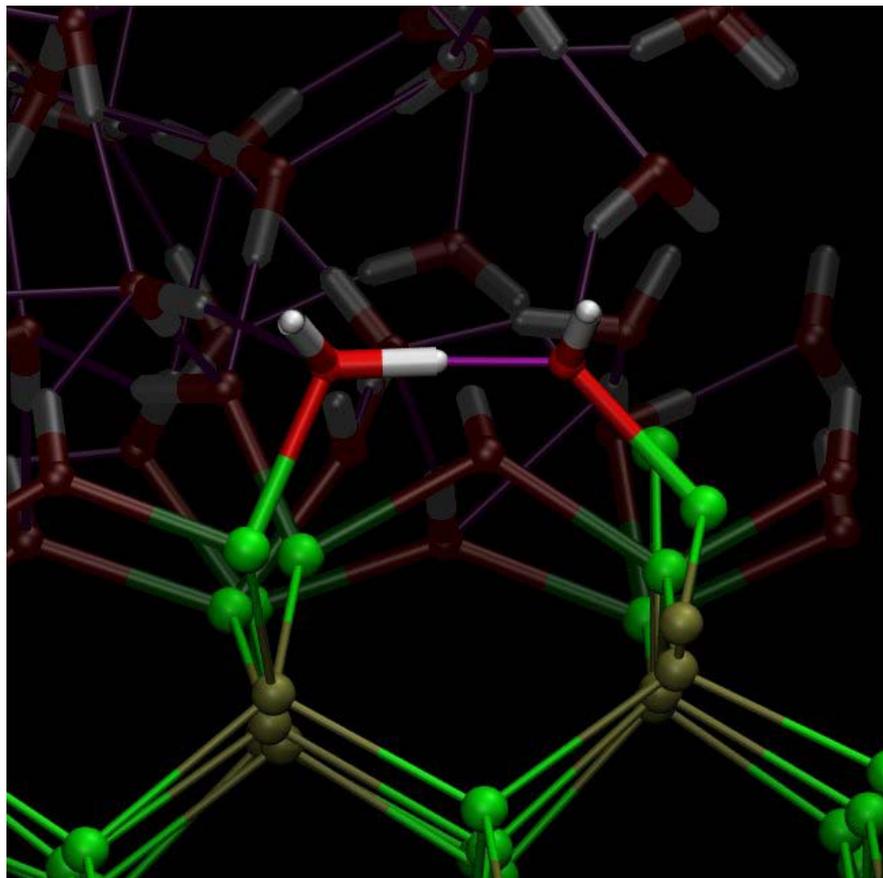


Technical Accomplishment – Surface hydroxides of InP(001)

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



U.S. DEPARTMENT OF
ENERGY

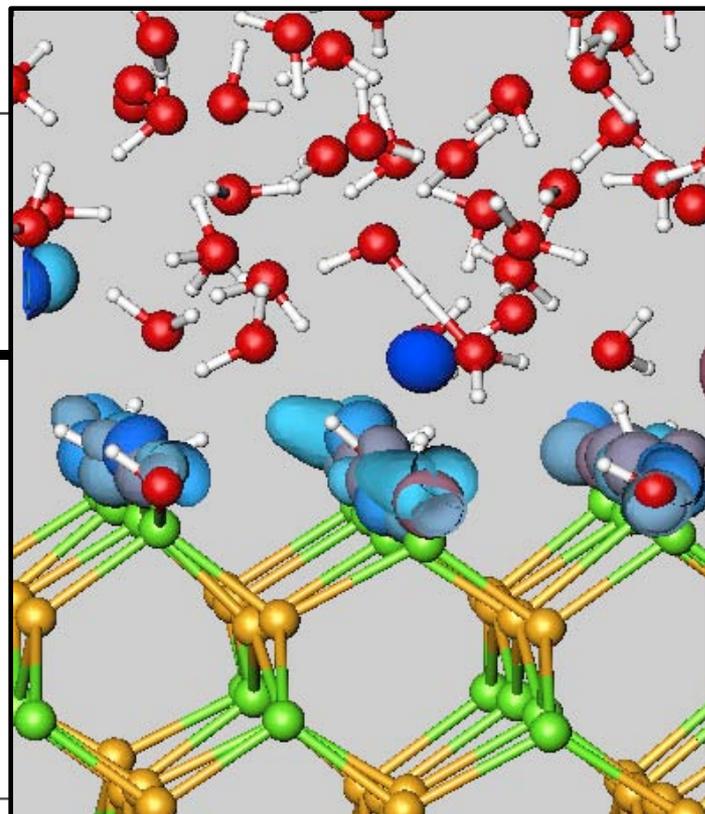
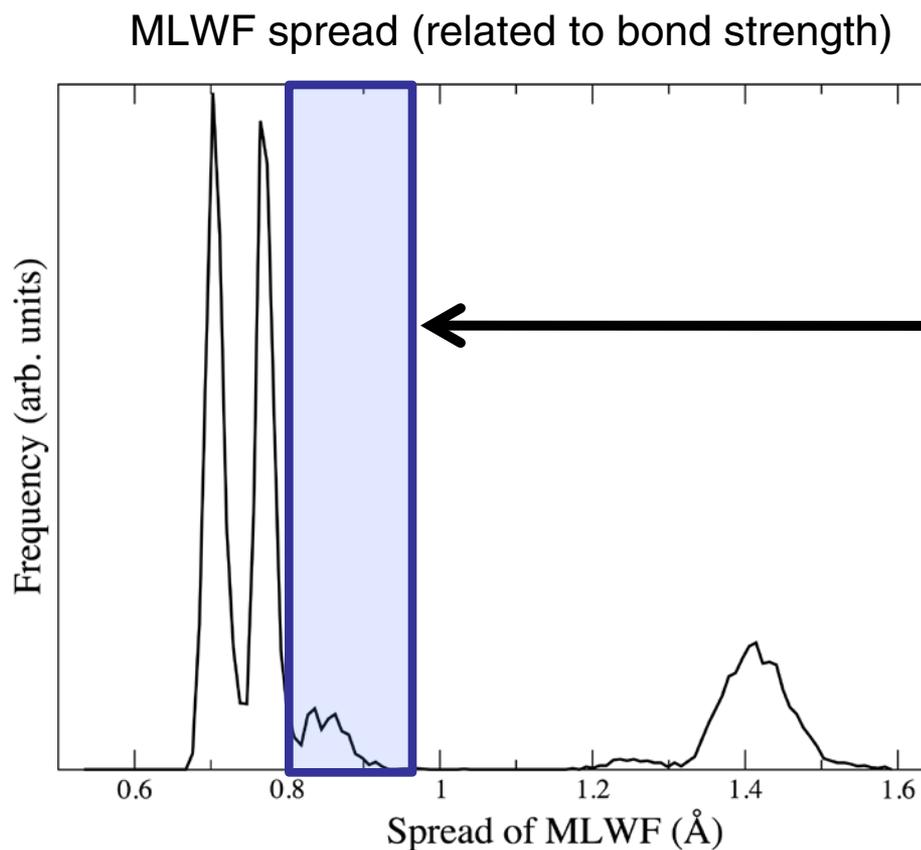
UNLV
UNIVERSITY OF NEVADA LAS VEGAS



DOE Hydrogen Program Annual Merit Review



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



U.S. DEPARTMENT OF
ENERGY

UNLV
UNIVERSITY OF NEVADA LAS VEGAS

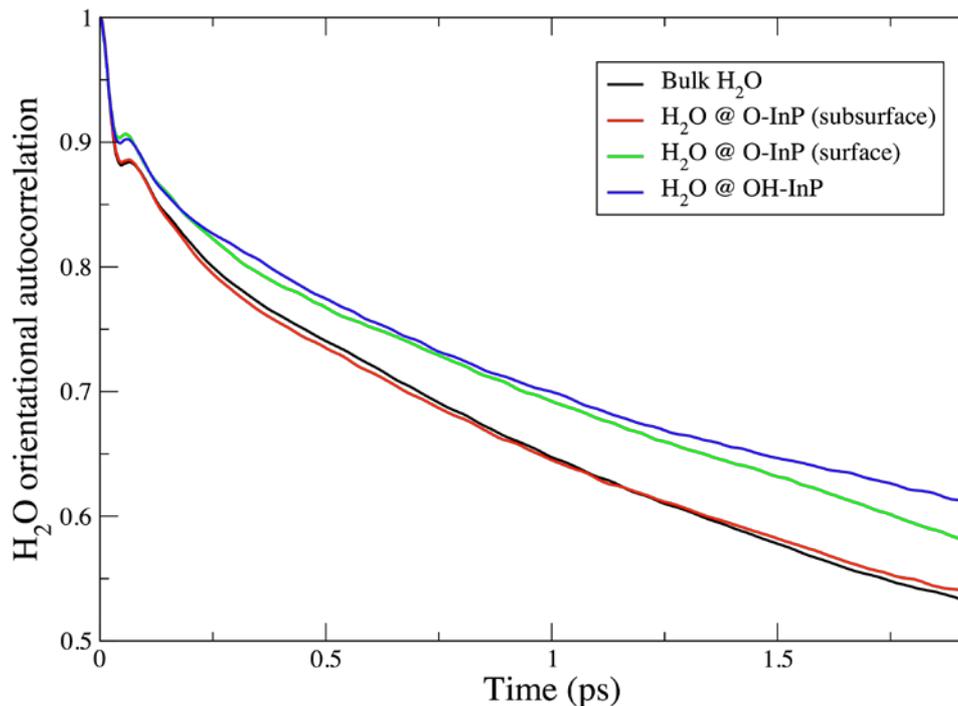


DOE Hydrogen Program Annual Merit Review

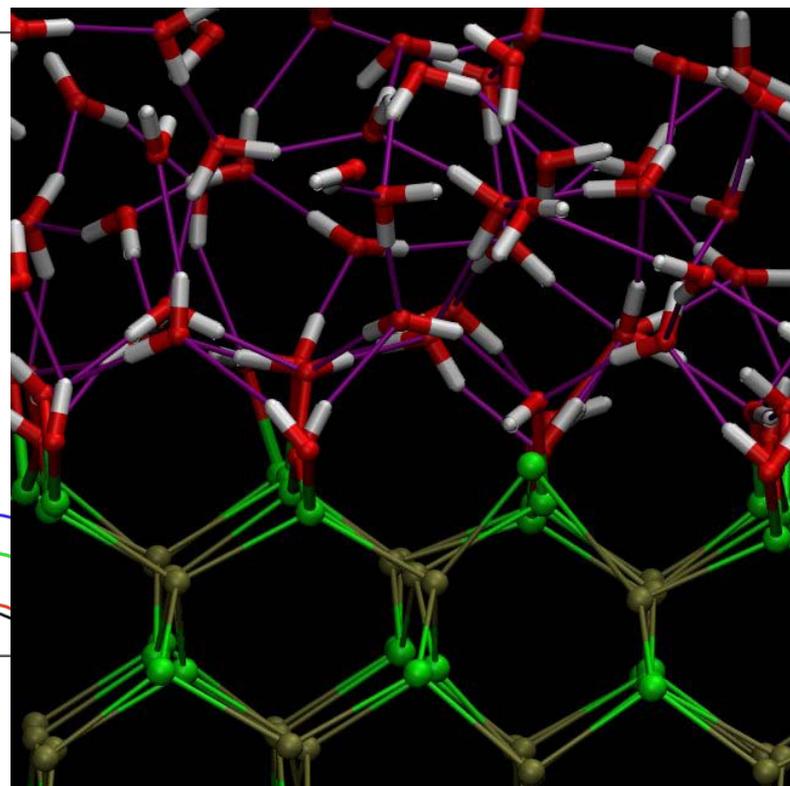


Technical Accomplishment – Structure of interfacial H₂O

Time autocorrelation of H₂O orientation



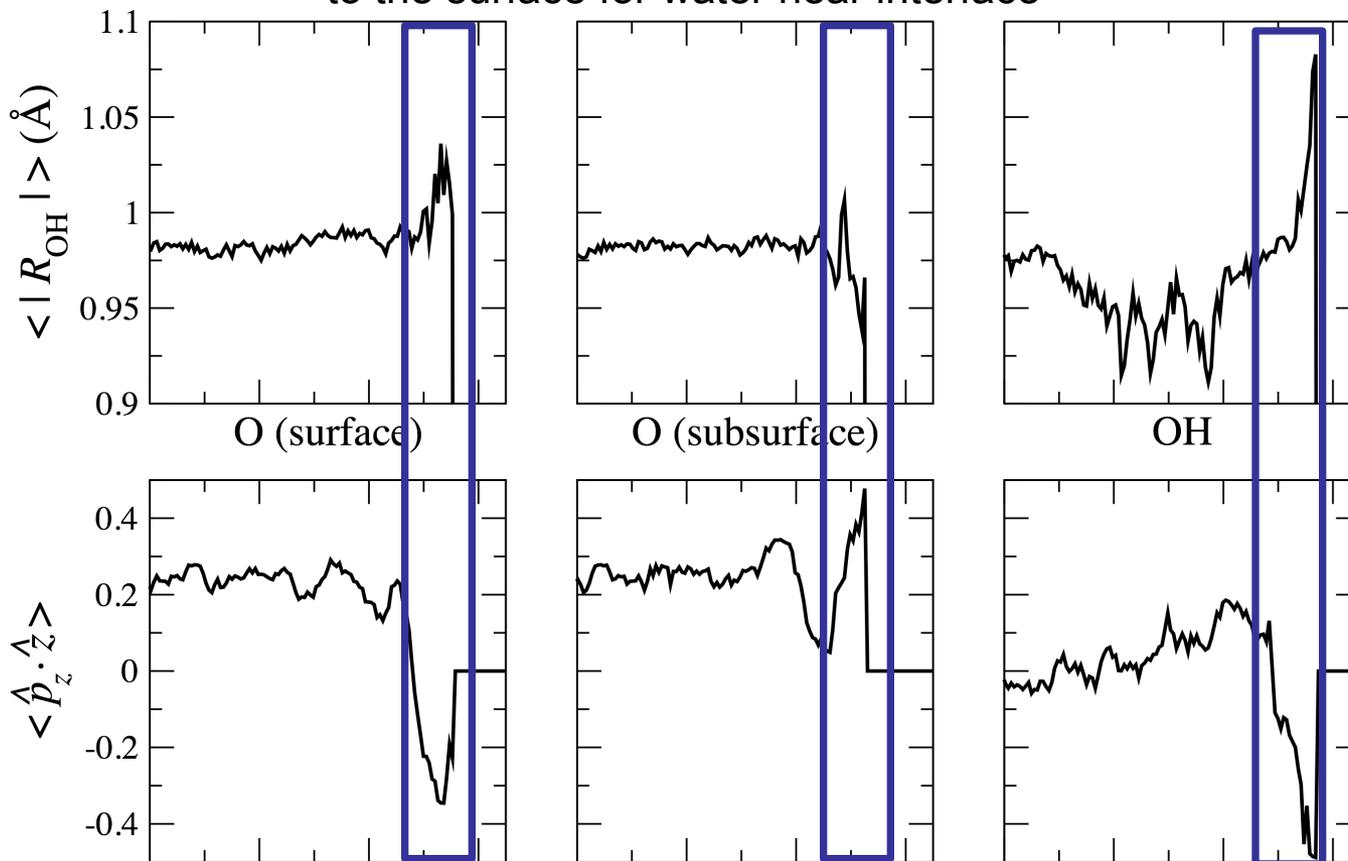
Structure of water near OH-terminated surface



Water orientation is less dynamic near interface with reactive surface

Technical Accomplishment – Structure of interfacial H₂O

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



U.S. DEPARTMENT OF
ENERGY

UNLV
UNIVERSITY OF NEVADA LAS VEGAS

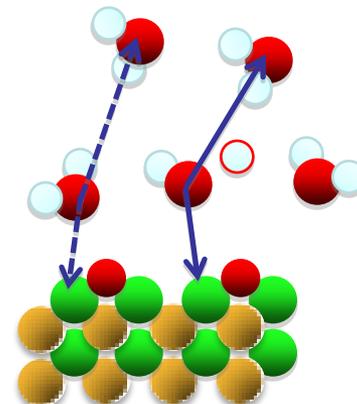
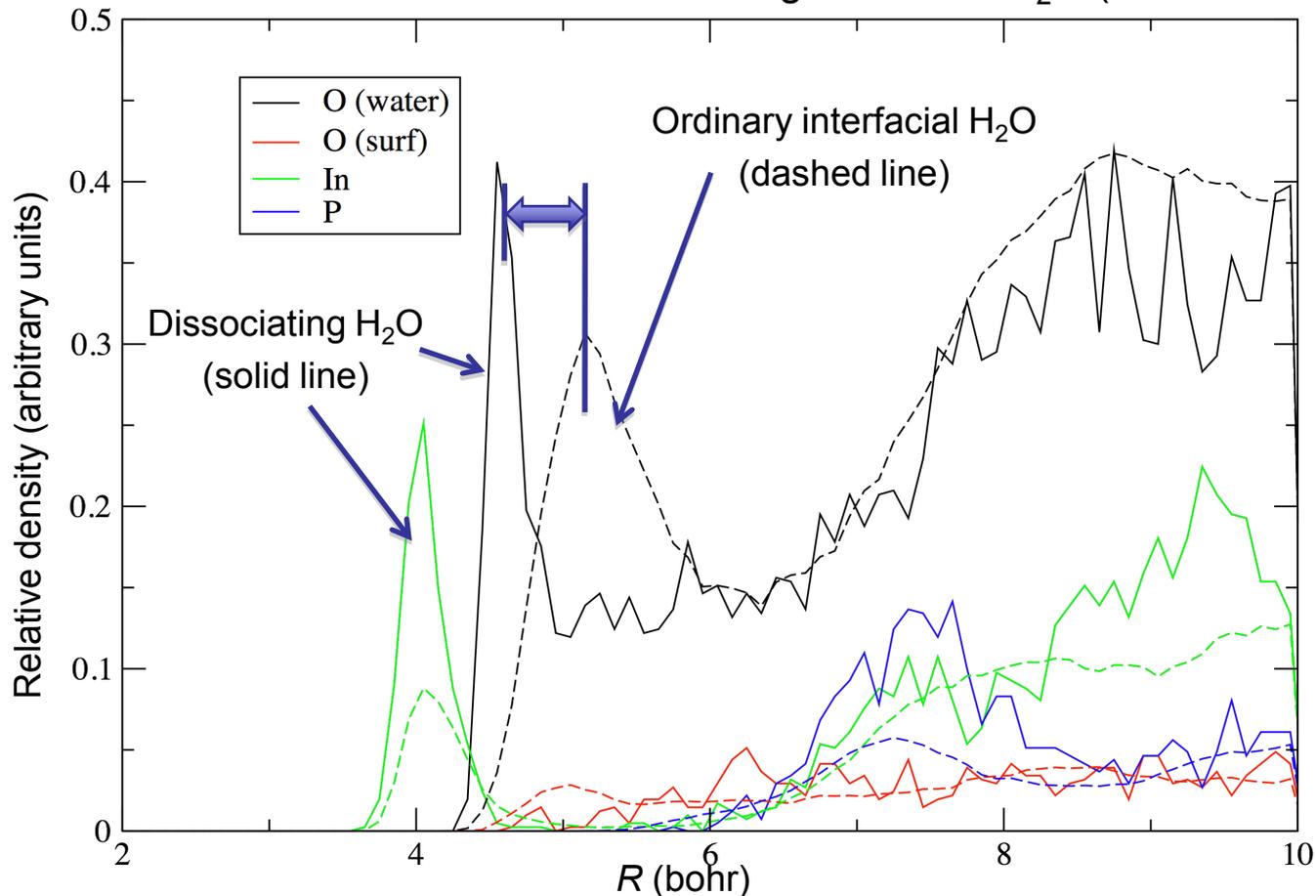


DOE Hydrogen Program Annual Merit Review



Technical Accomplishment – Structure of interfacial H₂O

Radial distribution of atoms surrounding interfacial H₂O (for InP + oxide)



Surrounding water molecules are closer upon dissociation

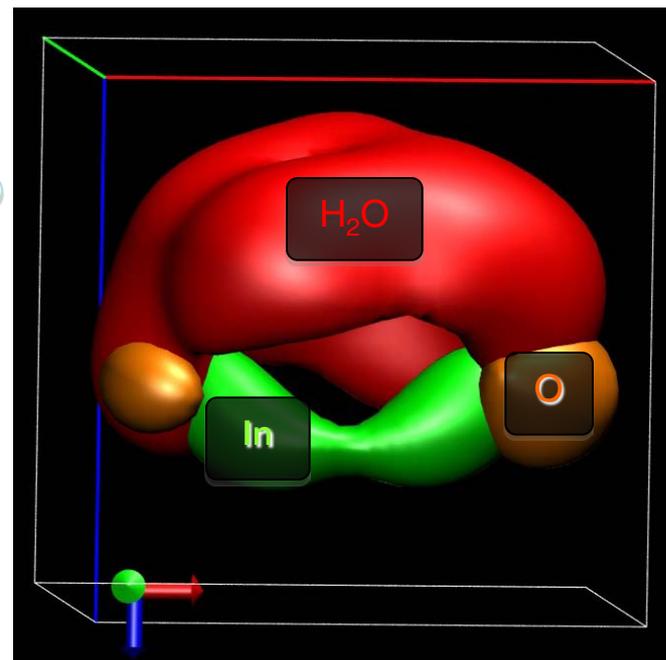
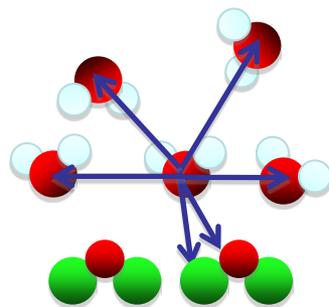
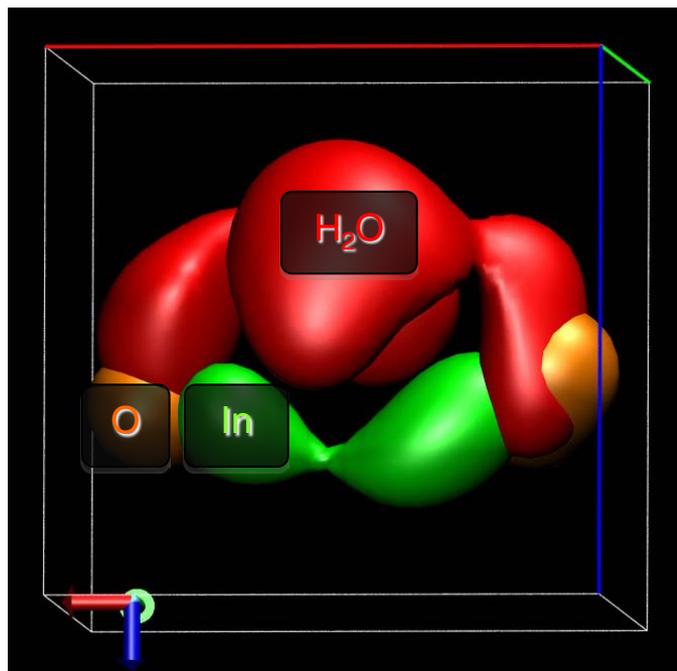
Technical Accomplishment – Structure of interfacial H₂O

Surrounding water molecules more structured upon dissociation

Angular distribution of atoms surrounding interfacial H₂O (for InP + oxide)

Dissociating H₂O

Ordinary interfacial H₂O



Interfacial water structure is correlated with surface activity



U.S. DEPARTMENT OF
ENERGY

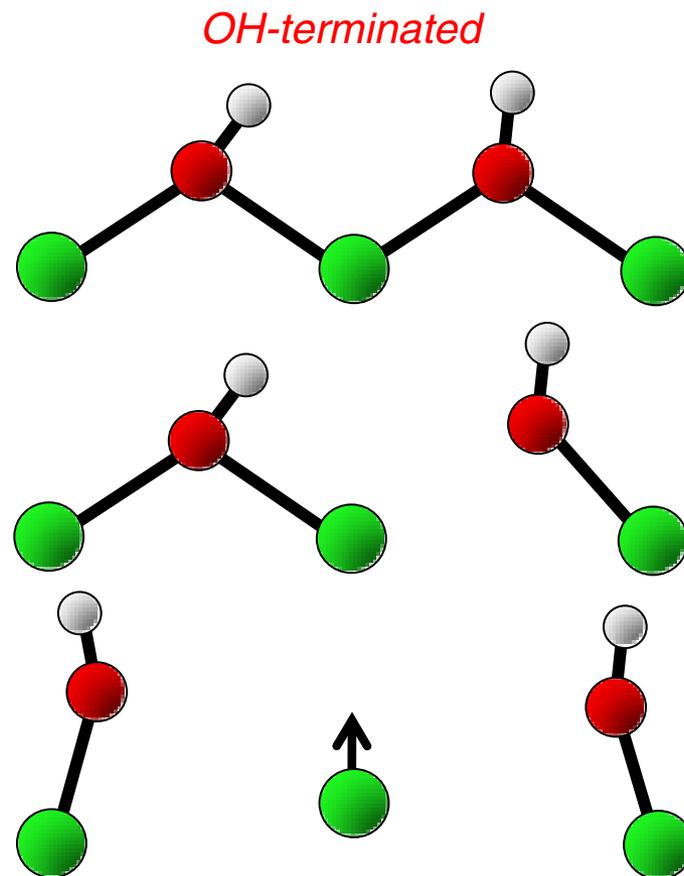
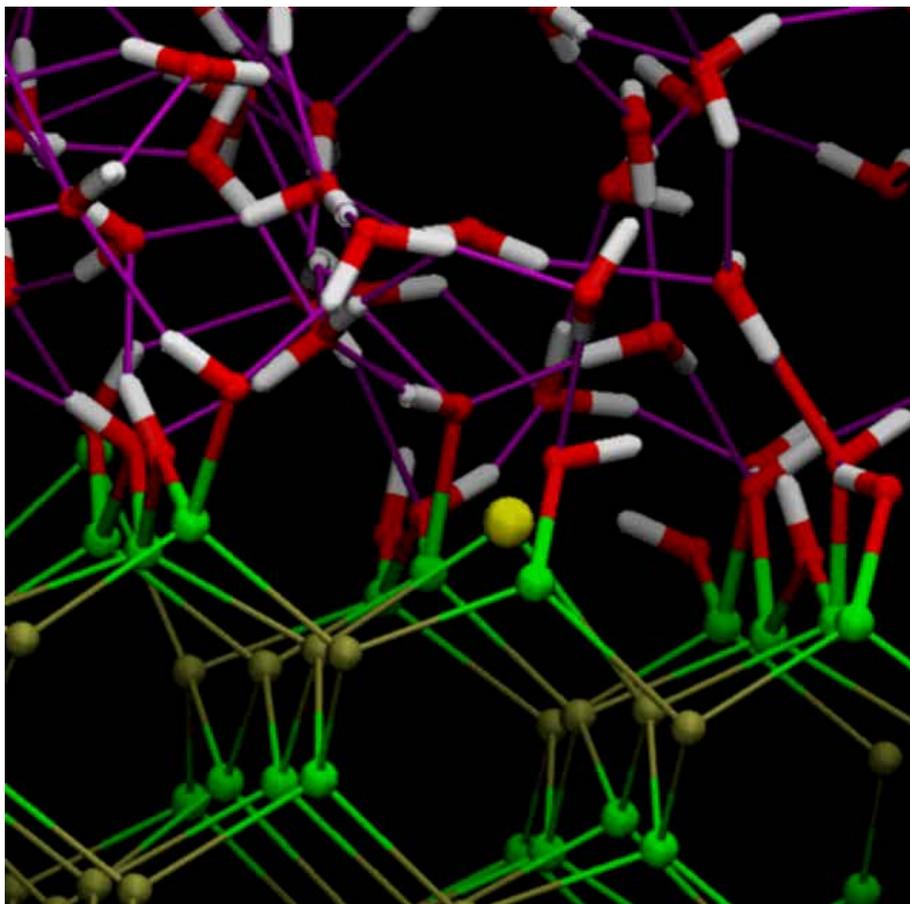
UNLV
UNIVERSITY OF NEVADA LAS VEGAS



DOE Hydrogen Program Annual Merit Review



Technical Accomplishment – Surface instability



Broken hydroxide bridge provides possible motivation for In dissolution



U.S. DEPARTMENT OF
ENERGY

UNLV
UNIVERSITY OF NEVADA LAS VEGAS



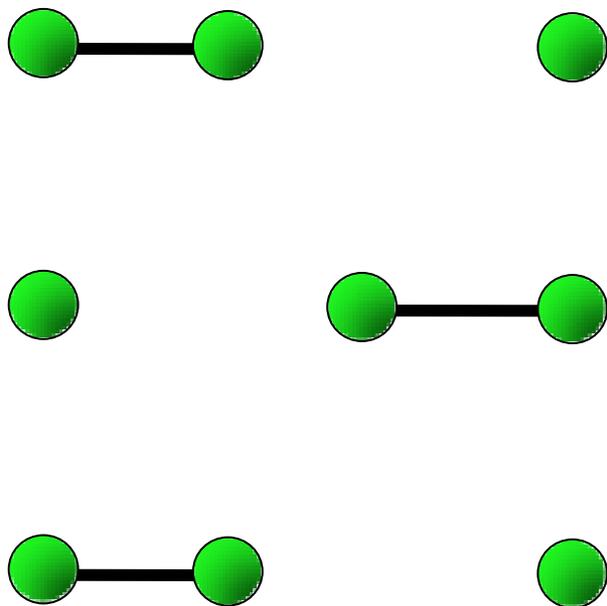
DOE Hydrogen Program Annual Merit Review



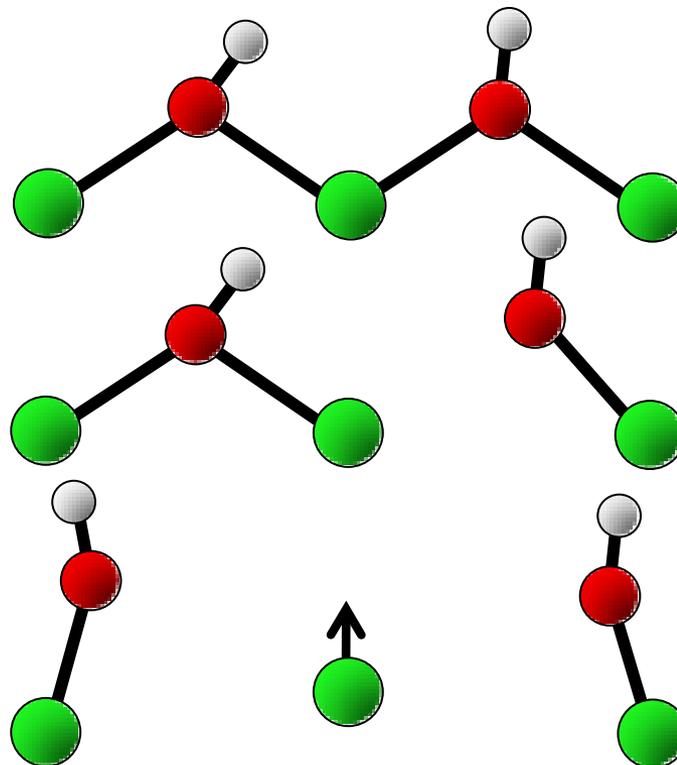
Technical Accomplishment – Surface instability

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

Bare surface (In-terminated)



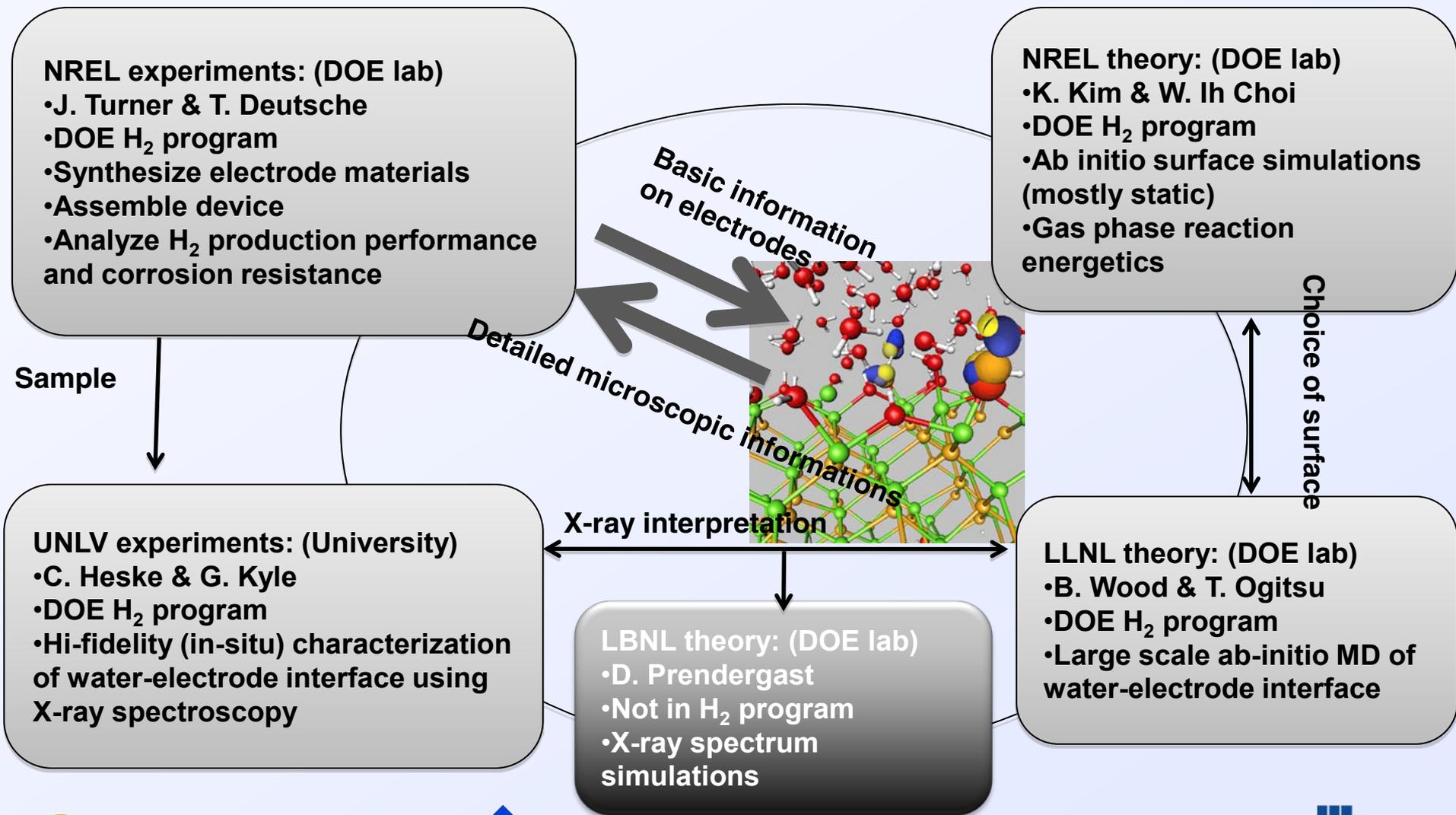
OH-terminated



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



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



Proposed future work

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

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 H₂O dissociation, surrounding H₂O molecules 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

