Center for Interface Science: Solar Electric Materials

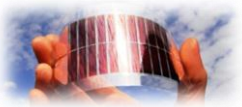
Molecular Orientation of Phosphonic Acids on Transparent Conductive Oxides

Lingzi Sang[1], Matthew C. Schalnat[1], Jeanne E. Pemberton[1], Matthew Gliboff[2], Kristina Knesting[2], David Ginger[2], Ajaya Sigdel[3], Joseph Berry[3], Anthony Giordano[4], Sergio Paniagua[4], Seth Marder[4], Hong Li[4], Jean-Luc Brédas[4]

[1]Department of Chemistry and Biochemistry, University of Arizona
[2]Department of Chemistry, University of Washington
[3]National Renewable Energy Laboratory
[4]Department of Chemistry and Biochemistry, Georgia Institute of Technology

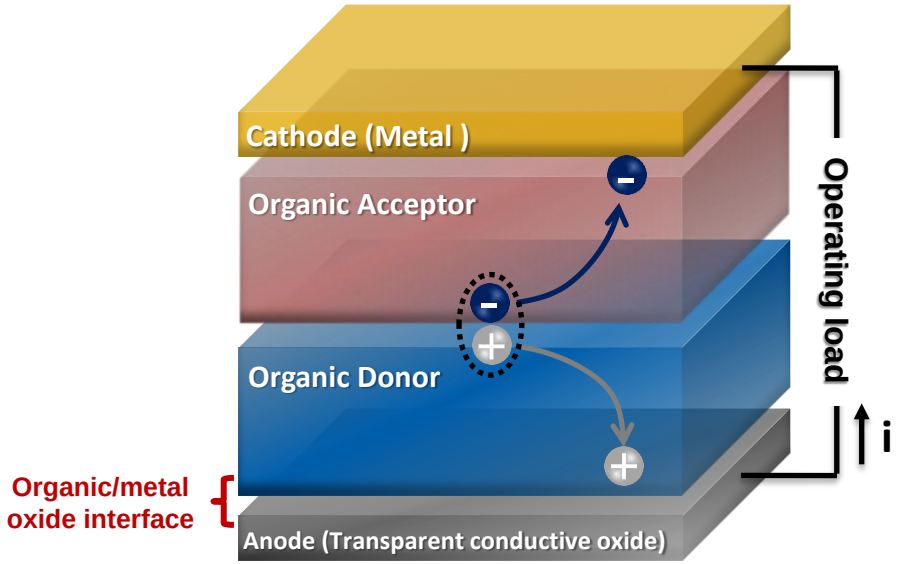
Research supported as part of the Center for Interface Science: Solar Electric Materials (CISSEM), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001084

Organic Photovoltaic Cells (OPVs)



Process of solar energy conversion:

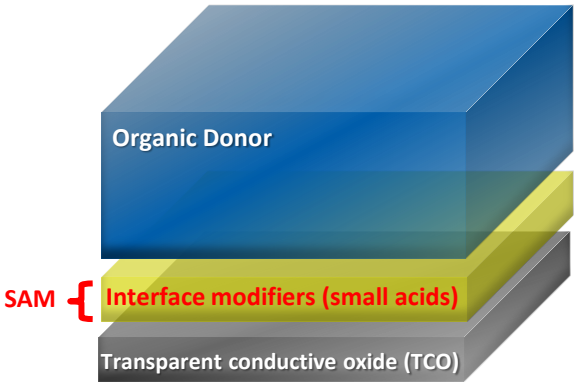
1. **Light absorbed and exciton generated**
   (Best light absorber molecules?)
2. **Exciton diffusion**
   (Exciton diffusion length? How to improve?)
3. **Charge separation**
   (How to eliminate charge recombination?)
4. **Charge carrier transport to electrodes**
   (How to improve charge transfer efficiency?)
5. **Charge collection at electrodes**

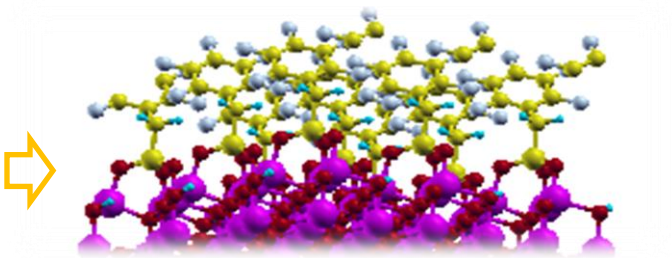


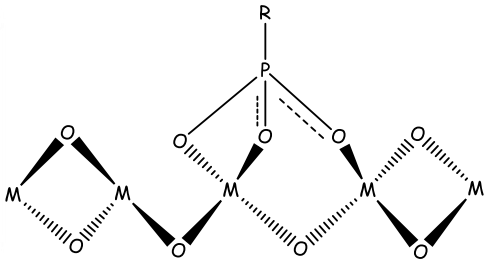
Key: Heterogeneity at the interface

Interface Chemistry

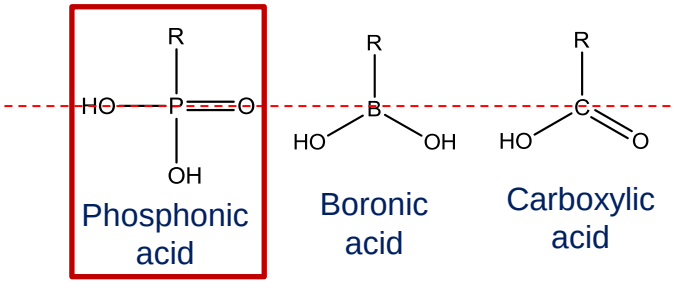
Organic/Metal Oxide Interface







Small acid SAMs



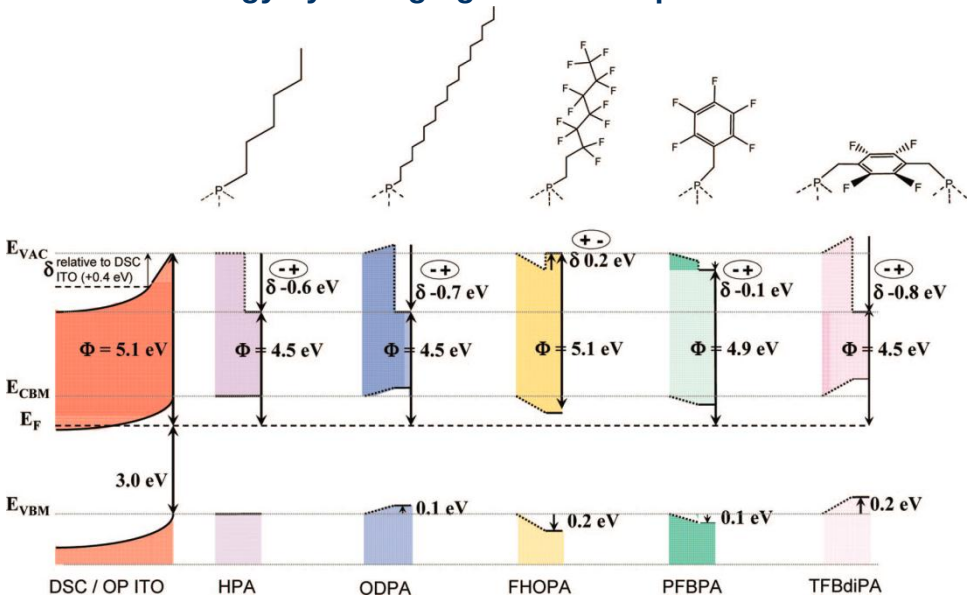
Hydrophobic (better contact with Donor)

Chemically bond to TCO

Improvement of interface compatibility

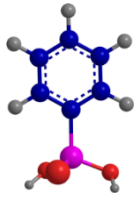
Orientation of Phosphonic Acids (PAs)

Tune surface work function and match the surface energy by changing interface dipole[1]



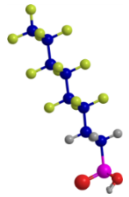
Phosphonic acid models

Octylphosphonic Acid (OPA)

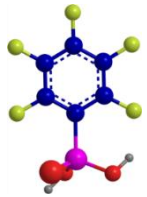


Phenylphosphonic Acid (PPA)

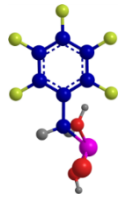
Benzylphosphonic Acid (BnPA)



F_{13}-octylphosphonic Acid (F_{13}-OPA)

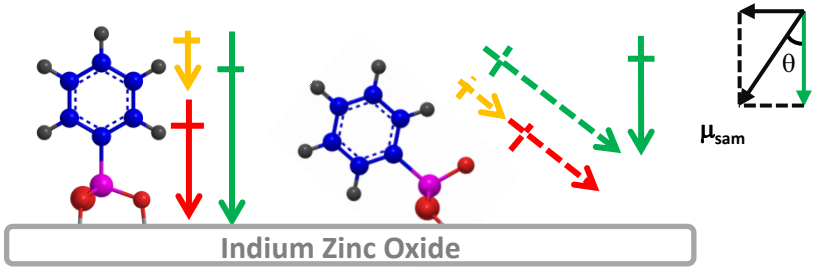


F_5-phenylphosphonic Acid (F_5-PPA)



F_5-Benzylphosphonic Acid (F_5BnPA)

Molecular orientation affects net interface dipole



[1] Sergio A. Paniagua,Peter J. Hotchkiss,| Simon C. Jones,et.al, J. Phys. Chem. C, Vol. 112, No. 21, 2008

Collaborative Research on Molecular Orientation of PPA

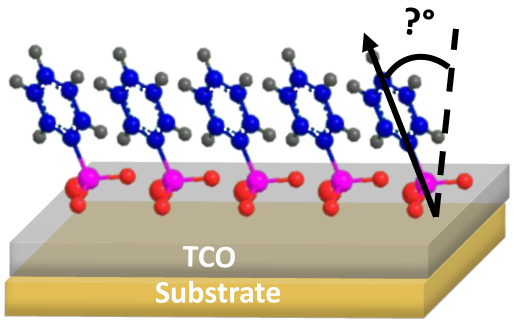
Phosphonic acids synthesis
Marder Group

Georgia Institute of Technology

NREL NATIONAL RENEWABLE ENERGY LABORATORY **Substrate preparation**

Sputtered
(70:30 (wt%) In_2O_3:ZnO)

Vary with techniques



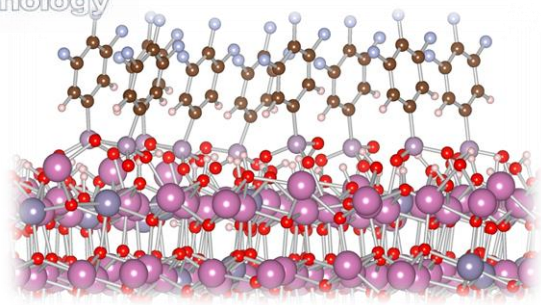
Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS)

THE UNIVERSITY OF ARIZONA

PM-IRRAS instrument at Pemberton Lab (UA)

Density Functional Theory (DFT) Calculations

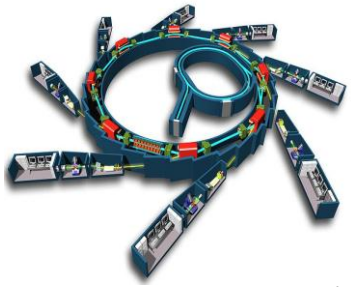
Georgia Institute of Technology

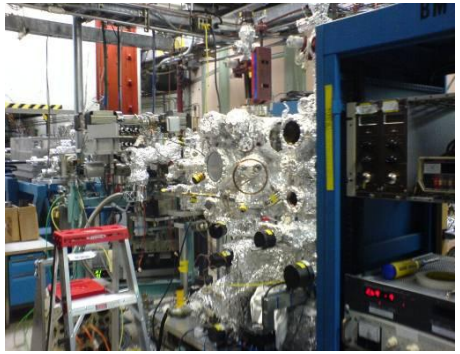


(Image courtesy of the Brédas group)

Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

UNIVERSITY OF WASHINGTON SLAC





Beamlines at SLAC (left), and NEXAFS instrument (right)
Work with Ginger group

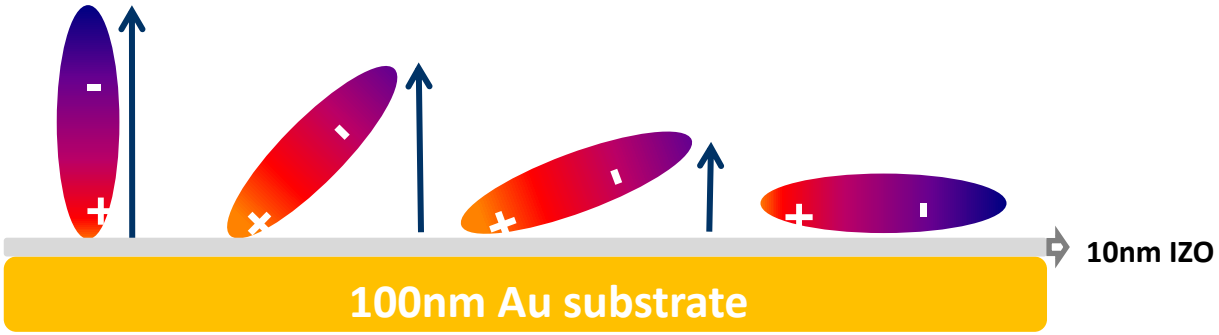
CIS:SEM

ARIZONA Georgia Tech NREL NATIONAL RENEWABLE ENERGY LABORATORY PRINCETON UNIVERSITY UNIVERSITY of WASHINGTON

PM-IRRAS Surface Selection Rules

PM-IRRAS Instrument

THE UNIVERSITY OF ARIZONA.



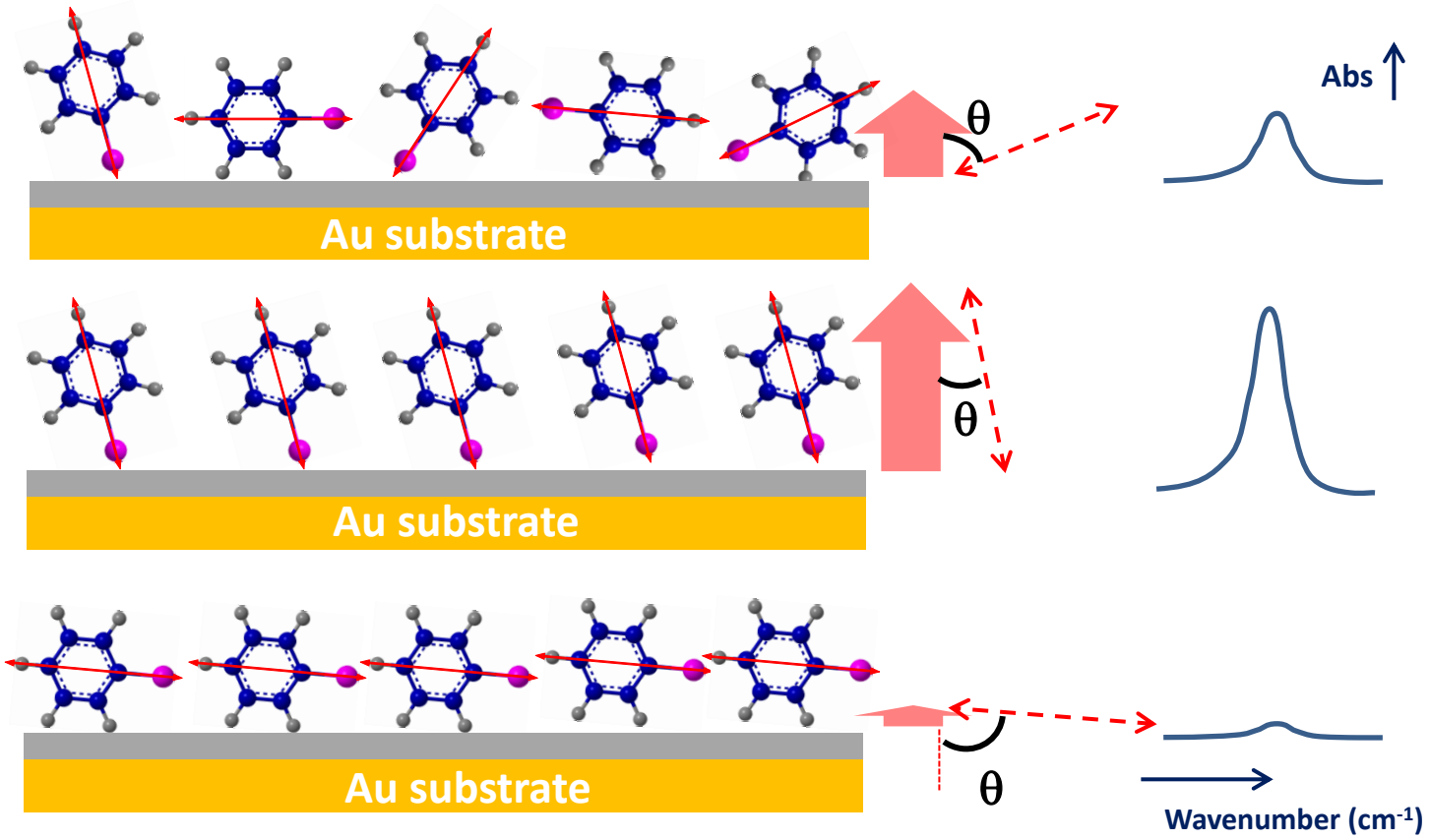
Surface selection rules:

1. Only p component of the incident light can interact with surface species

2. Only the perpendicular component of transition dipole moment can be detected

PM-IRRAS: Mathematically cancels out isotropic signal; improve surface sensitivity

Quantitatively Determine Molecular Orientation via PM-IRRAS



$$Abs \propto \cos^2\theta$$

Experimentally:

$$\frac{Abs_{monolayer}}{3 \times Abs_{isotropic}} = \cos^2\theta$$

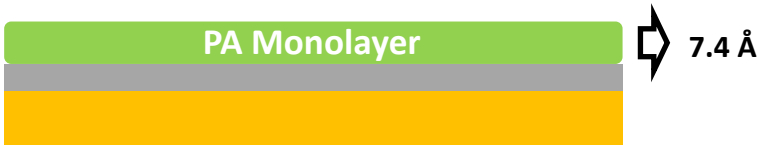
θ is tilt angle the angle of a specific transition dipole moment with respect to the surface normal

Quantitatively Determine Molecular Orientation via PM-IRRAS

Transmission IR experiment

Accurate concentration of PPA^{2-} salt in KBr pellet with measurable thickness

PM-IRRAS



Monolayer of PPA with theoretically calculated surface coverage on IZO/Au substrate

Salt concentration

Thickness of KBr pellet

No effect of substrate on Abs. signal

Isotropic molecules

Factors that affect Abs values

Surface coverage

Monolayer thickness

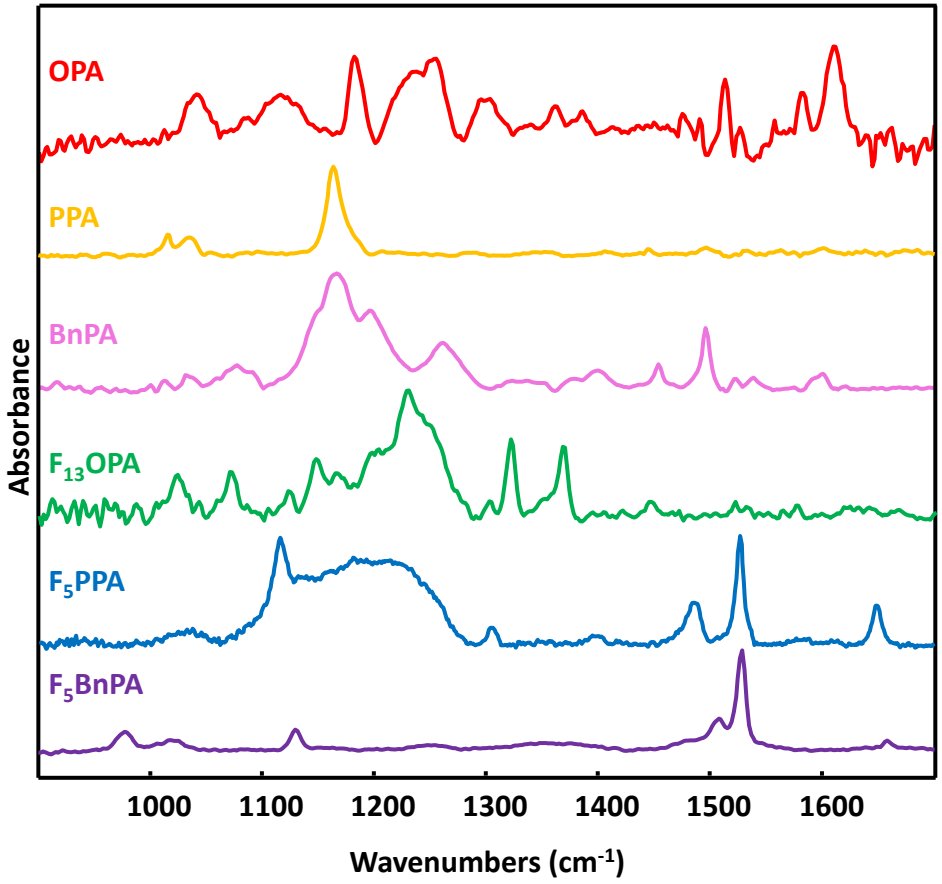
Optical constants affect Abs. signal of monolayer

Molecules with preferred specific orientation

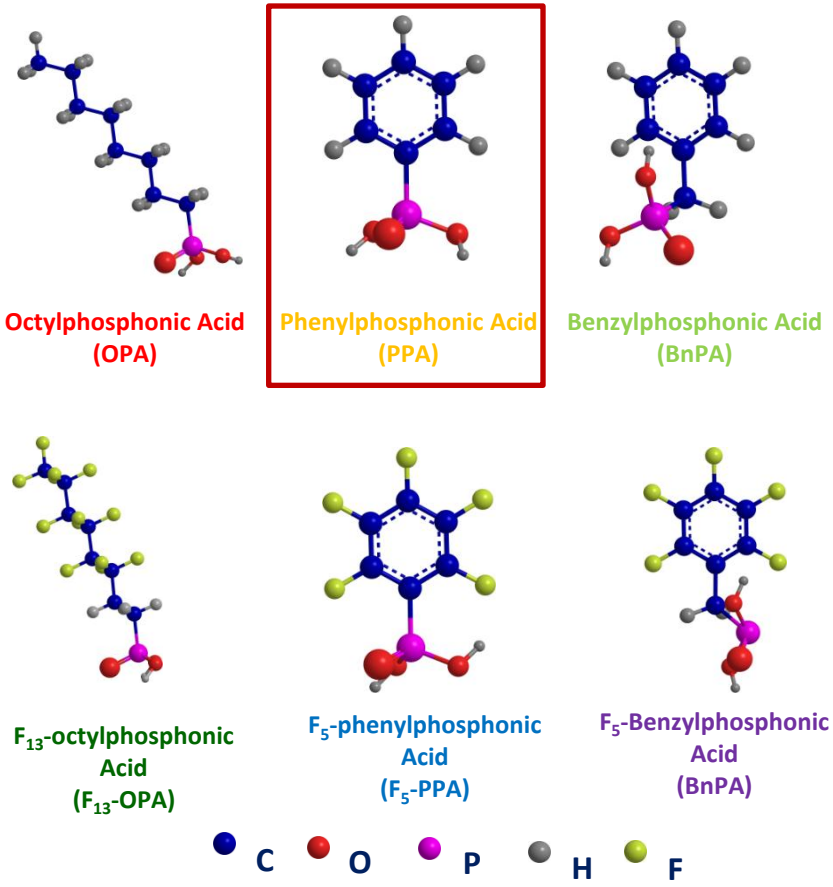
Key: Simulate transmission IR spectra for same conditions as monolayer; compare intensity differences due to molecular orientation

PM-IRRAS of Phosphonic Acids (PAs)

PM-IRRAS of PA-modified IZO

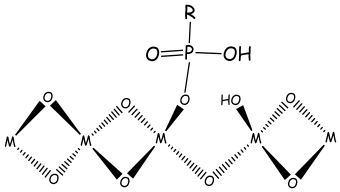


Phosphonic acid models



Spectral Interpretation for Aryl-Containing PAs

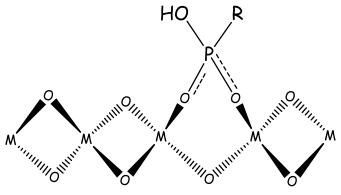
Four possible binding modes and their vibrational signatures for phosphonic acids on metal oxide surfaces



Monodentate

$\nu(P{=}O_{free})$ ~ 1200 cm^{-1}

$\nu(P\text{-}OH)$ ~ 950 cm^{-1}

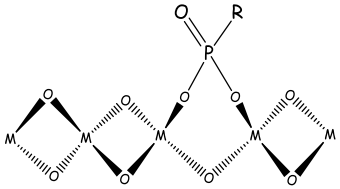


Bidentate w/free -OH

$\nu(P\text{-}OH)$~ 950 cm^{-1}

$\nu_{as}(PO_3)$ ~ 1050 cm^{-1}

$\nu_{s}(PO_3)$ ~ 1020 cm^{-1}

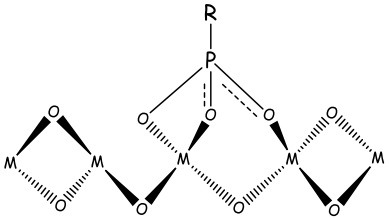


Bidentate w/free P=O

$\nu(P{=}O_{free})$ ~ 1200 cm^{-1}

$\nu_{as}(PO_3)$ ~ 1050 cm^{-1}

$\nu_{s}(PO_3)$ ~ 1020 cm^{-1}

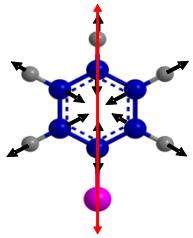


Tridentate

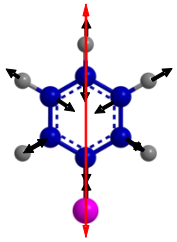
$\nu_{as}(PO_3)$ ~ 1050 cm^{-1}

$\nu_{s}(PO_3)$ ~ 1020 cm^{-1}

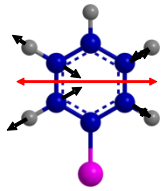
Vibrational modes of phenyl ring and phosphonic acid groups used for molecular orientation determination



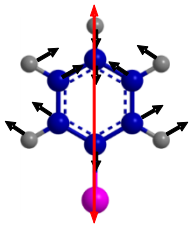
ν_2
3050 cm^{-1}



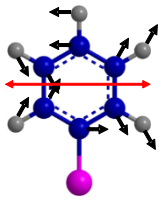
ν_{20a}
3020 cm^{-1}



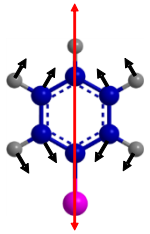
ν_{20b}
3080 cm^{-1}



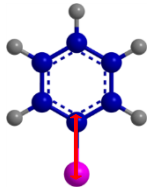
ν_{19a}
1498 cm^{-1}



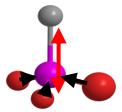
ν_{19b}
1440cm^{-1}



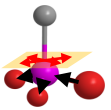
ν_{8a}
1597cm^{-1}



$\nu_{(C\text{-}P)}$
1148 cm^{-1}

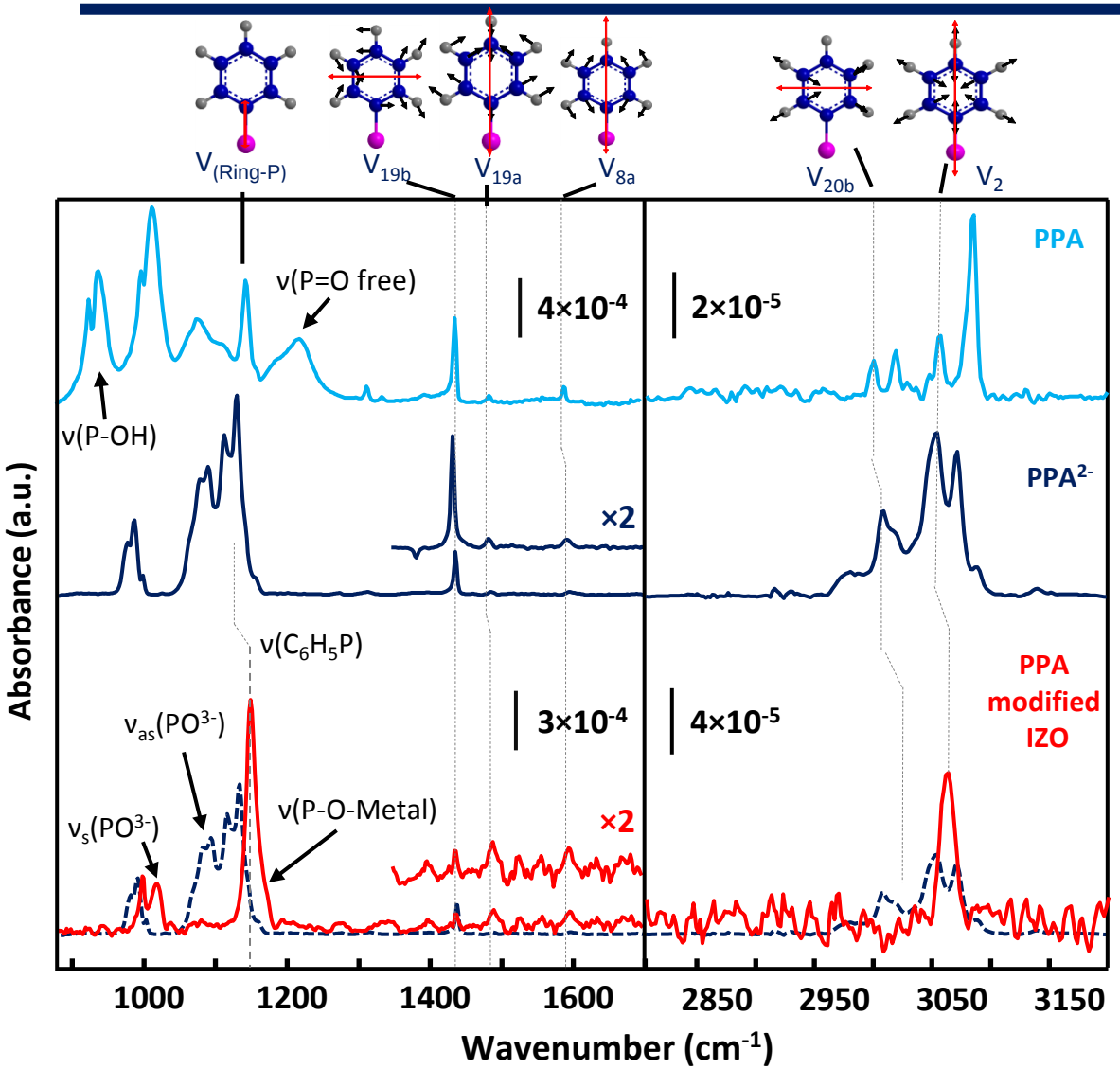


$\nu_s(PO_3)$
1018 cm^{-1}



$\nu_{as}(PO_3)$
1040 cm^{-1}

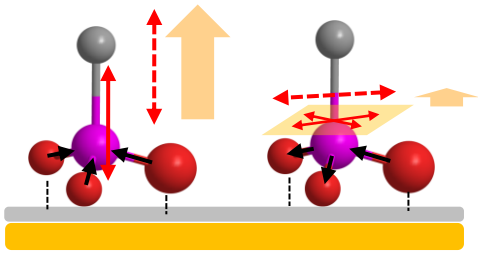
Binding and Molecular Orientation of PPA by PM-IRRAS



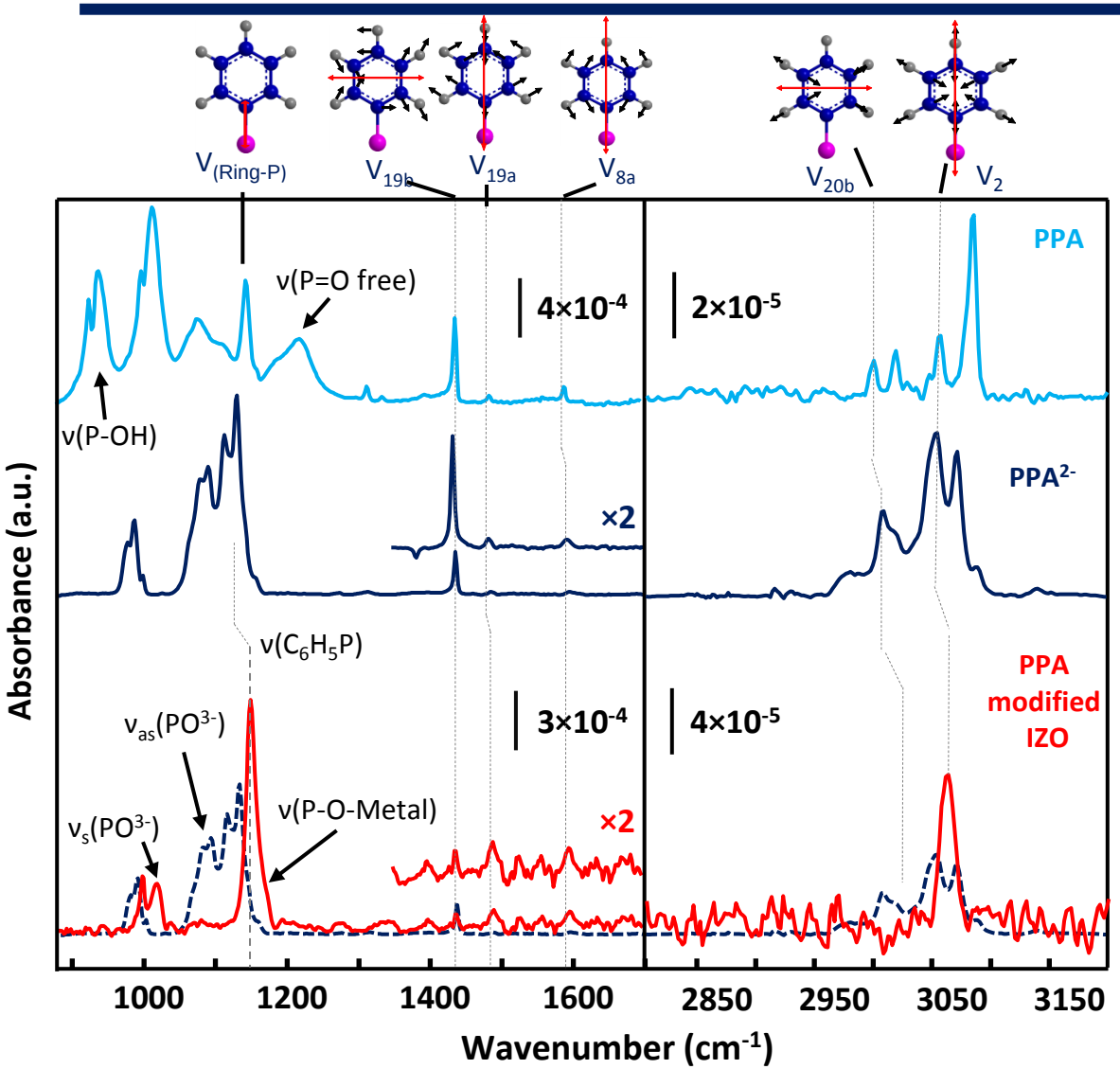
Binding modes:

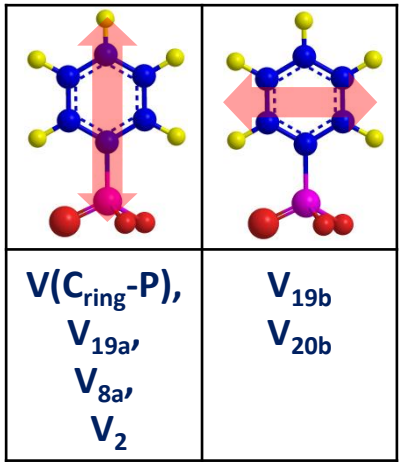
1. The absence of v(P-OH) at 920 to 950 cm^{-1} and v(P=O free) at 1200 cm^{-1} and the appearance of v(P-O-metal) at 1166 cm^{-1} suggest P=O and two P-OH groups are all bonded to oxide surface

2. Significant decrease of $v_{as}(PO^{3-})$ compare to $v_s(PO^{3-})$ suggests the PO^{3-} group is mostly perpendicular to the surface.



Binding and Molecular Orientation of PPA by PM-IRRAS



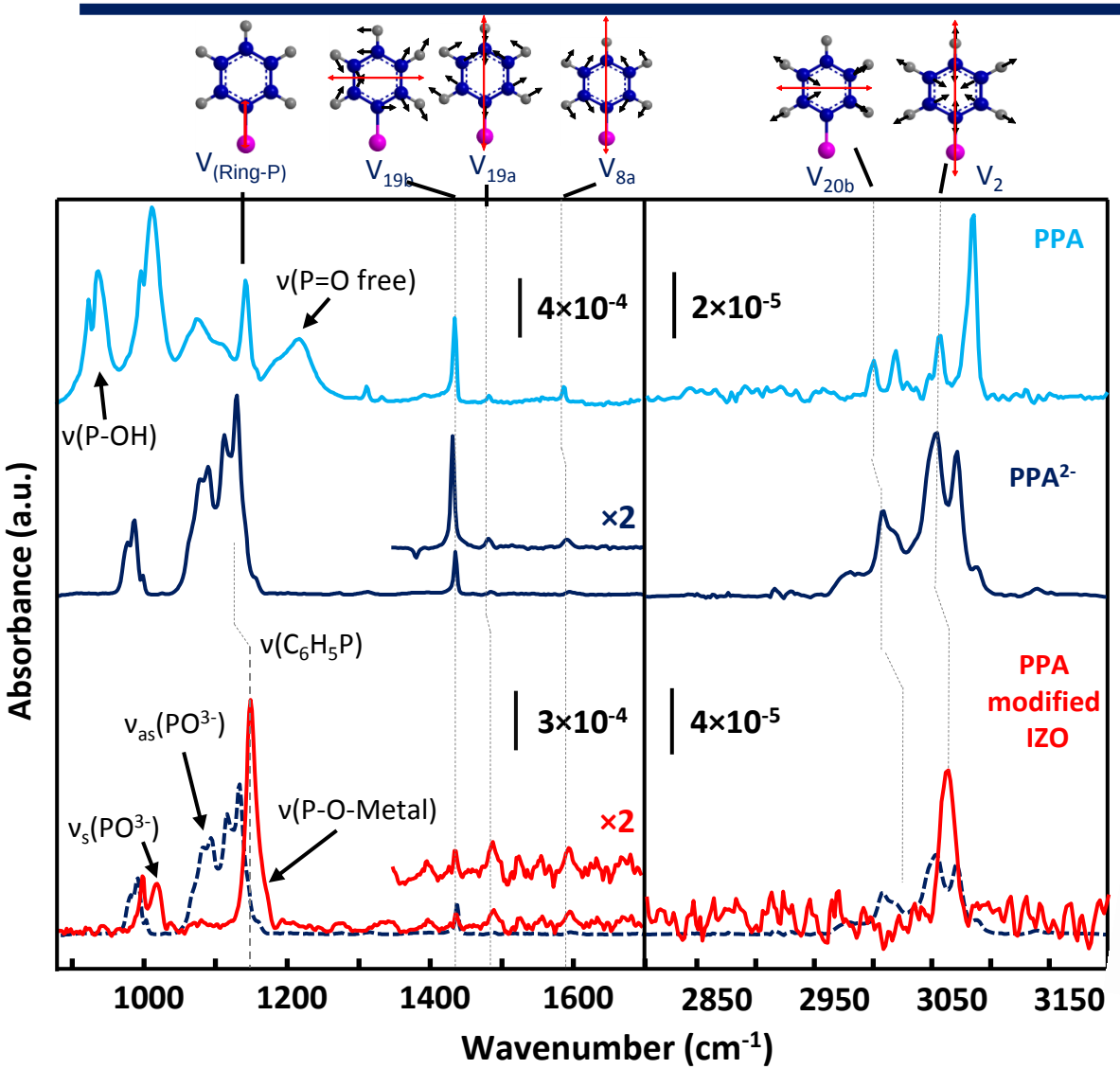


Phenyl ring orientation:

Significant decrease of V_{19b} (1436cm^{-1}) and V_{20b} (3031cm^{-1}) modes suggest V_{19b} and V_{20b} are in parallel to the substrate.

Increased intensity of $V(C_{ring}\text{-}P)$ (1148cm^{-1}), V_{19a} (1491cm^{-1}), V_{8a} (1595cm^{-1}) and V_2 (3061cm^{-1}) modes indicate their perpendicular position relative to the substrate.

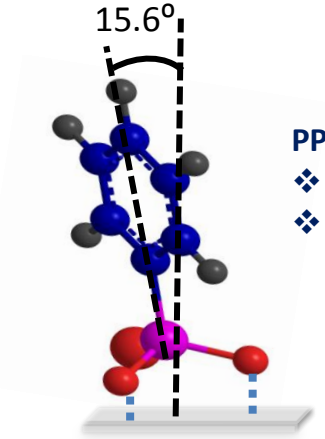
Binding and Molecular Orientation of PPA by PM-IRRAS



Quantitative orientation results:

Molecular tilt angle is calculated using modes that align with molecular long axis ($\nu(C_{ring}\text{-}P)$ at 1148 cm^{-1}, ν_{19a} at 1491 cm^{-1}, ν_{8a} at 1595 cm^{-1} and ν_2 at 3061 cm^{-1})

The results suggest PPA tilt at 15.6º ± 0.8º from surface normal

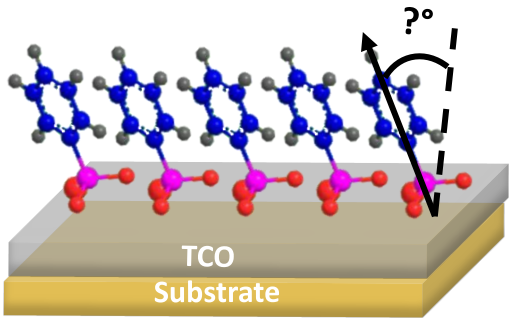


PPA:

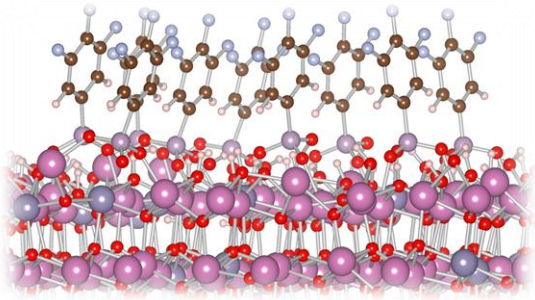
- Tridentate binding
- Tilt ca. 16º from surface normal

Collaborative Research on Molecular Orientation of PPA

Model System: PPA on IZO and ITO



Density Functional Theory (DFT) Calculations

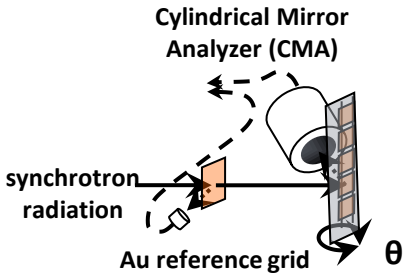


Optimized structure for PPA on ITO
(Image courtesy of the Brédas group.)

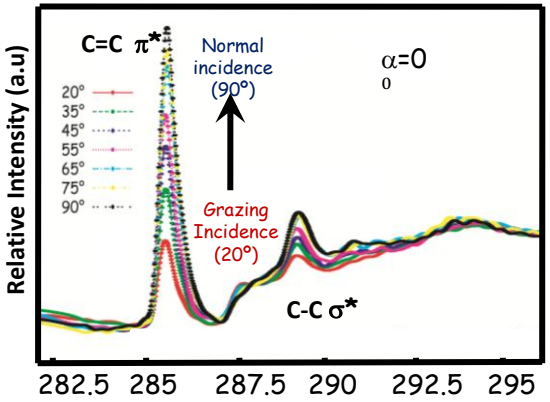
DFT calculation:
PPA tridentate bonded on ITO; ring plane mostly upright (~10° tilt)

Georgia Institute of Technology

NEXAFS at SLAC

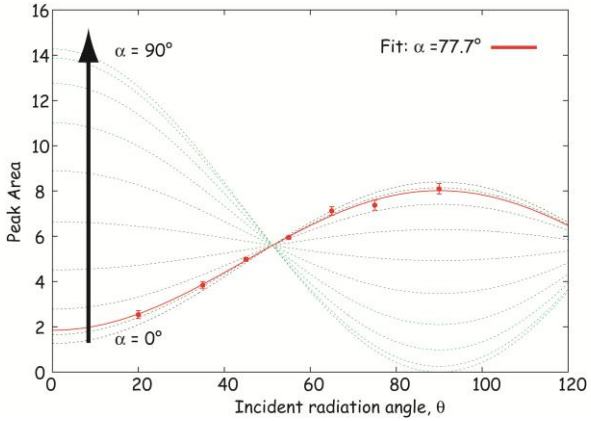


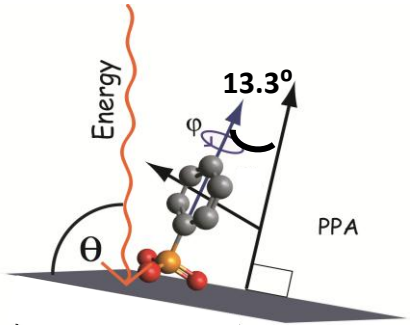
UNIVERSITY OF WASHINGTON SLAC



Incidence Radiation Energy (eV)

NEXAFS spectra for PPA on an IZO surface with increasing incident angle of x-radiation

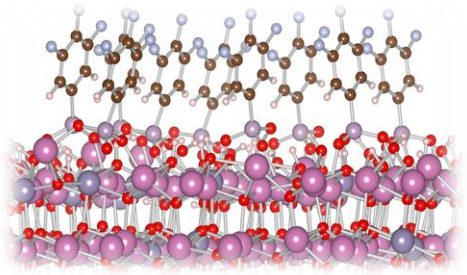




NEXAFS Results

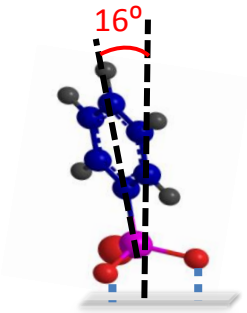
Molecular Orientation via Three Independent Techniques

DFT Calculations

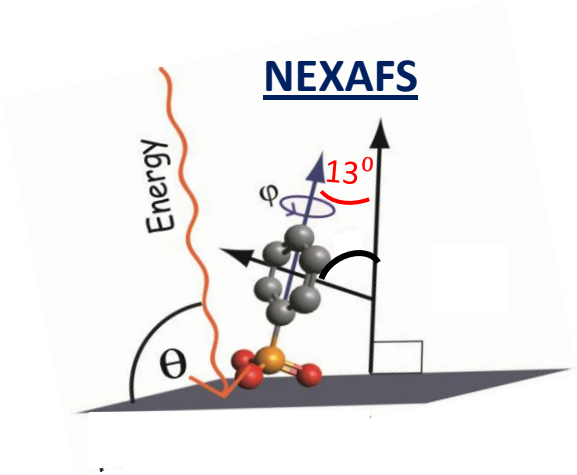


Optimized structure for PPA on ITO

PM-IRRAS



NEXAFS



Conclusion:

- PPA is largely tridentate bound to IZO surfaces as indicated by the vibrational signatures of the phosphonic acid modes and DFT calculations
- DFT calculations, PM-IRRAS, and NEXAFS results all agree that PPA is well-ordered and largely upright on IZO substrates with small tilt angle of molecular axis from surface normal

Acknowledgements

Pemberton Research Group:

Dr. Jeanne Pemberton
Dr. Anoma Mudalige
Dr. Matthew Schalnat
Dr. Hui Wang
All the group members

Collaborators

Dr. David Ginger (UW)
Kristina Knesting (UW)
Matthew Gliboff (UW)
Dr. Joseph Berry (NREL)
Ajay Sigdel (NREL)
Dr. Jean-Luc Bredas (GT)
Dr. Hong Li (GT)
Dr. Seth Marder (GT)
Anthony Giordano (GT)

Family and friends

Research supported as part of the Center for Interface Science: Solar-Electric Materials (CIS:SEM), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0001084. Instrumentation supported by the National Science Foundation through Award Number CHE-0848624.