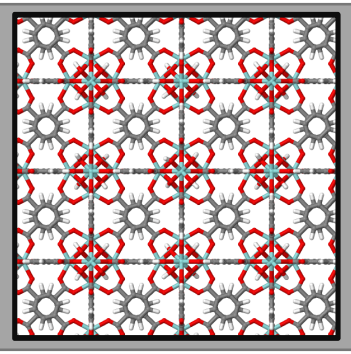
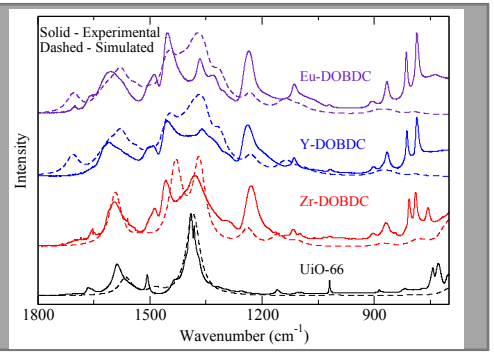
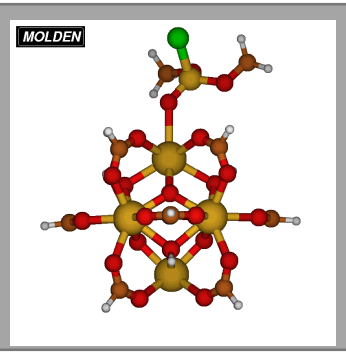
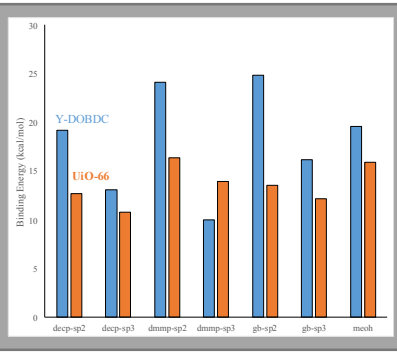
Exceptional service in the national interest

SAND2017-8894C









Molecular Modeling Insights into the Adsorption and Degradation of Chemical Warfare Agents by Metal Organic Frameworks

Jacob Harvey, Dorina Sava Gallis, Jeffery Greathouse

U.S. DEPARTMENT OF ENERGY

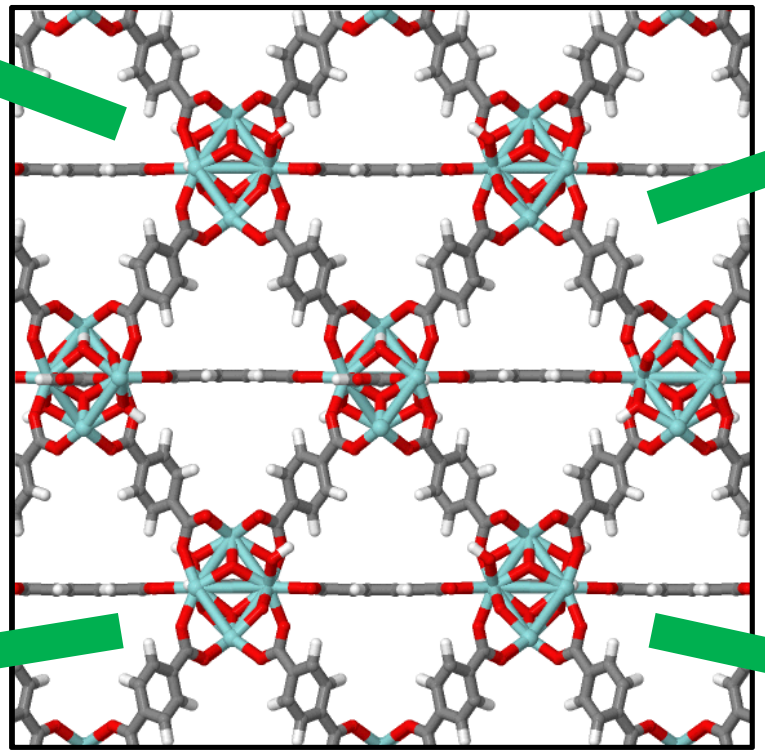
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

NNSA

Applications of Metal-Organic Frameworks

Separations

Sensing

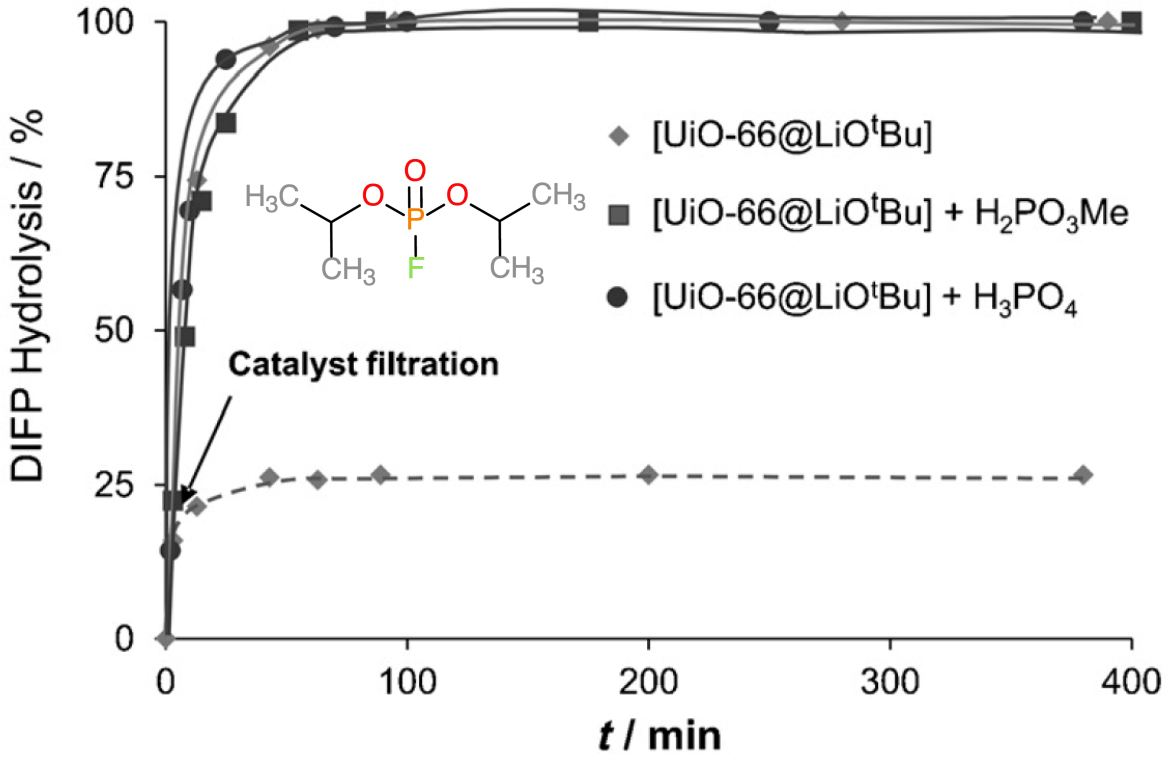


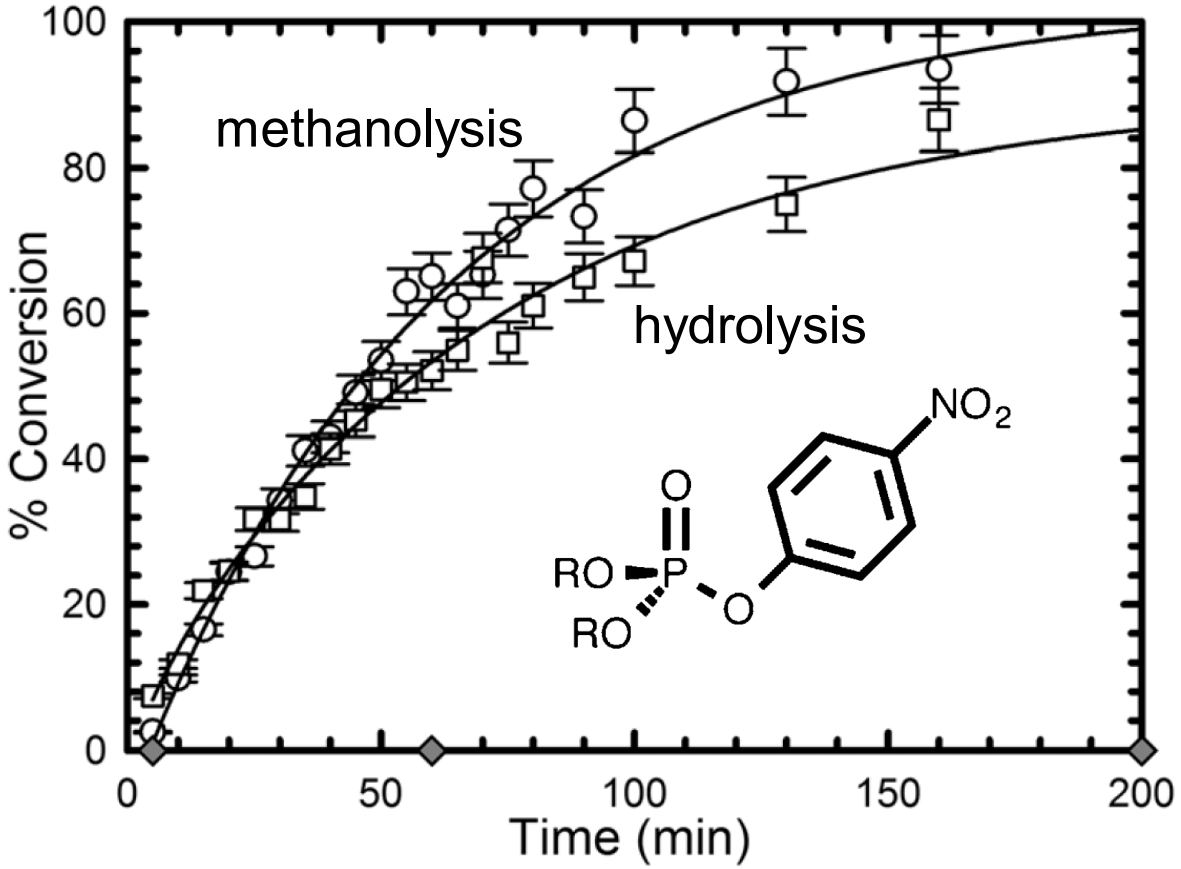
Drug Delivery

Catalysis

Degradation of chemical warfare agents

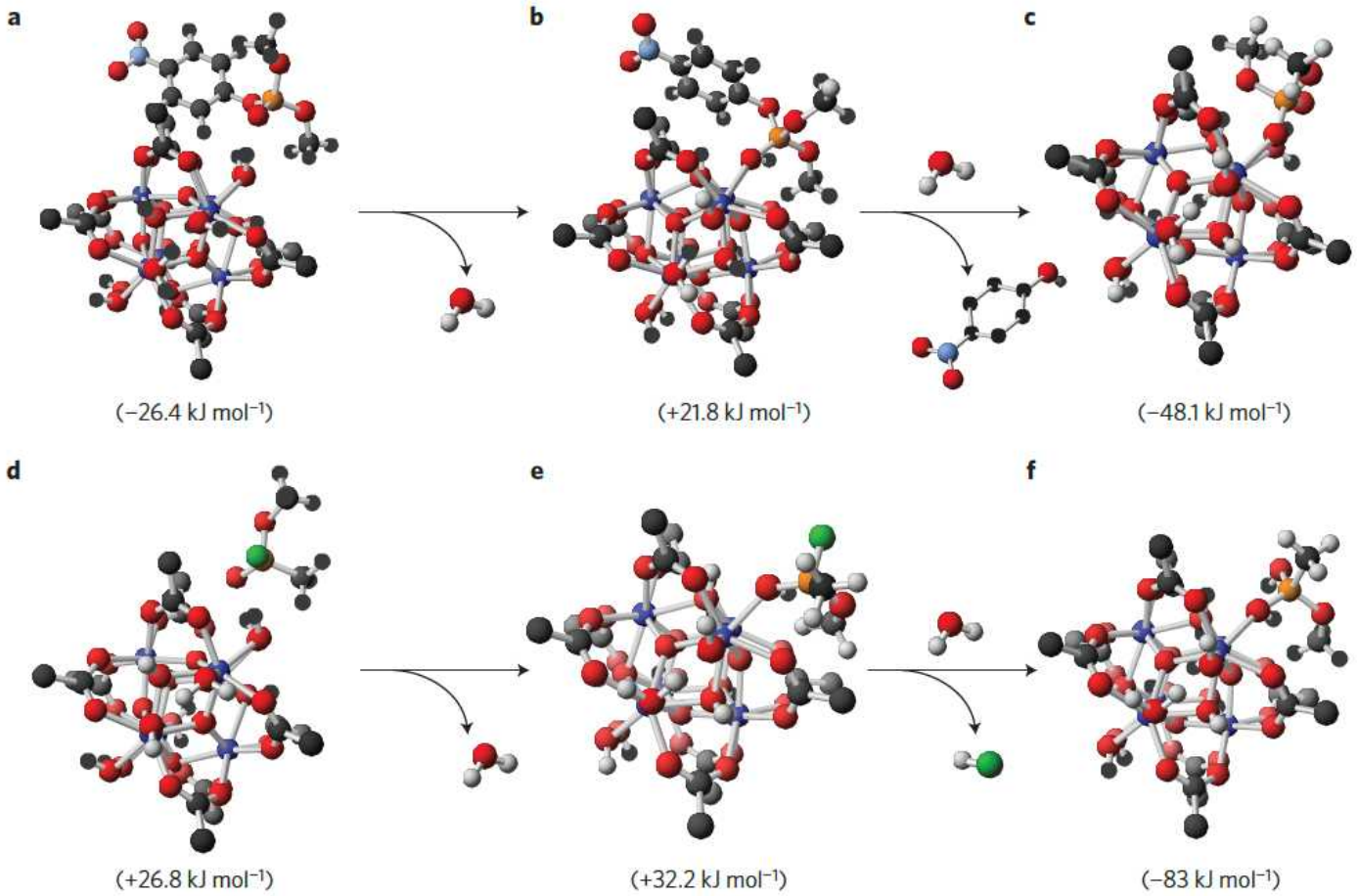
MOFs used in decontamination

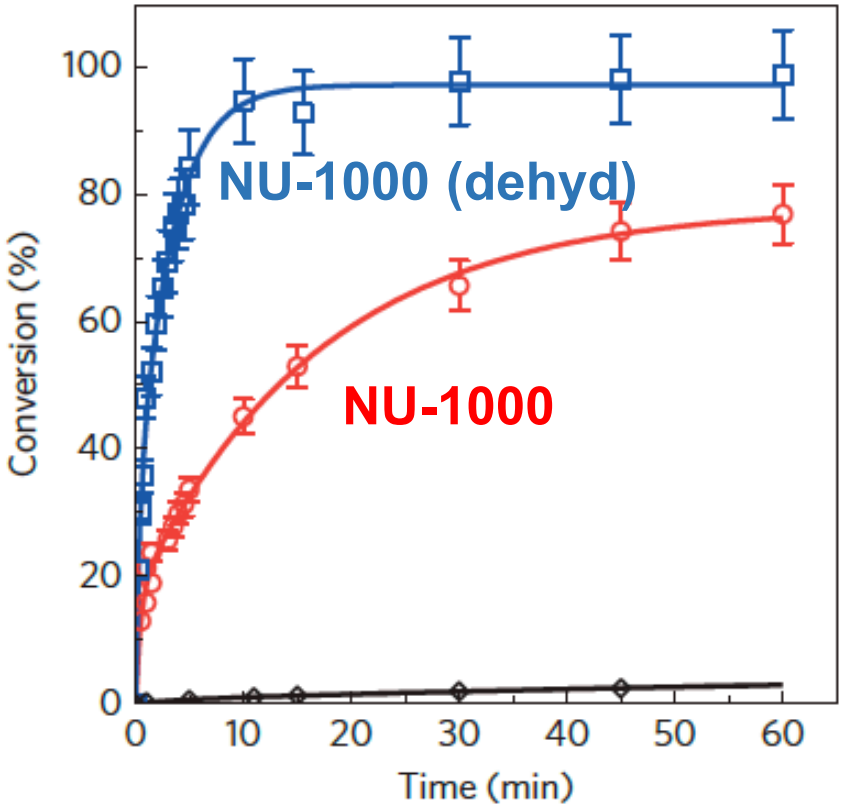




- Majority of work focuses on hydrolysis of CWAs
- Need to develop non-aqueous degradation
- Difficult to develop mechanistic and structural data experimentally

Computational CWA MOF Work

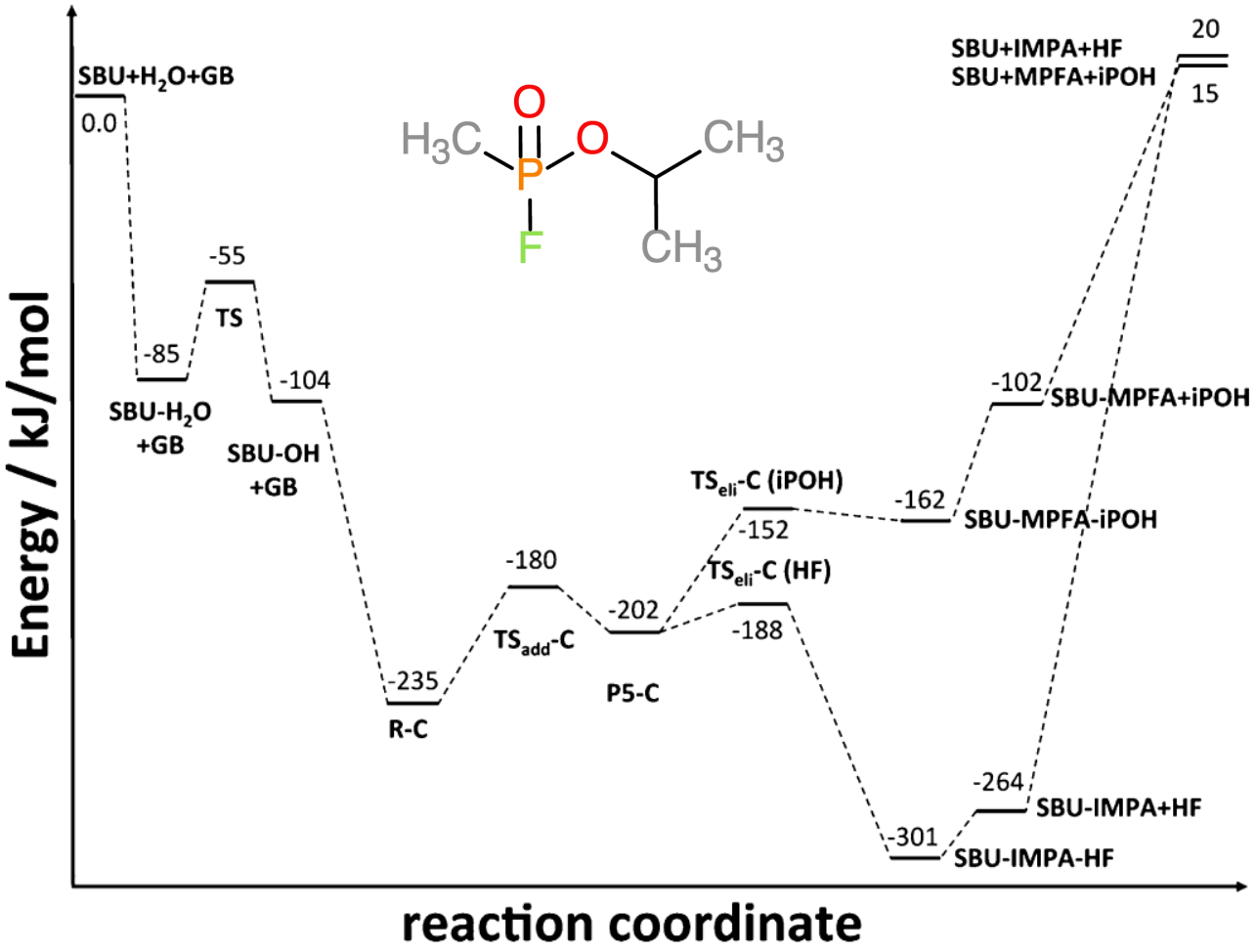


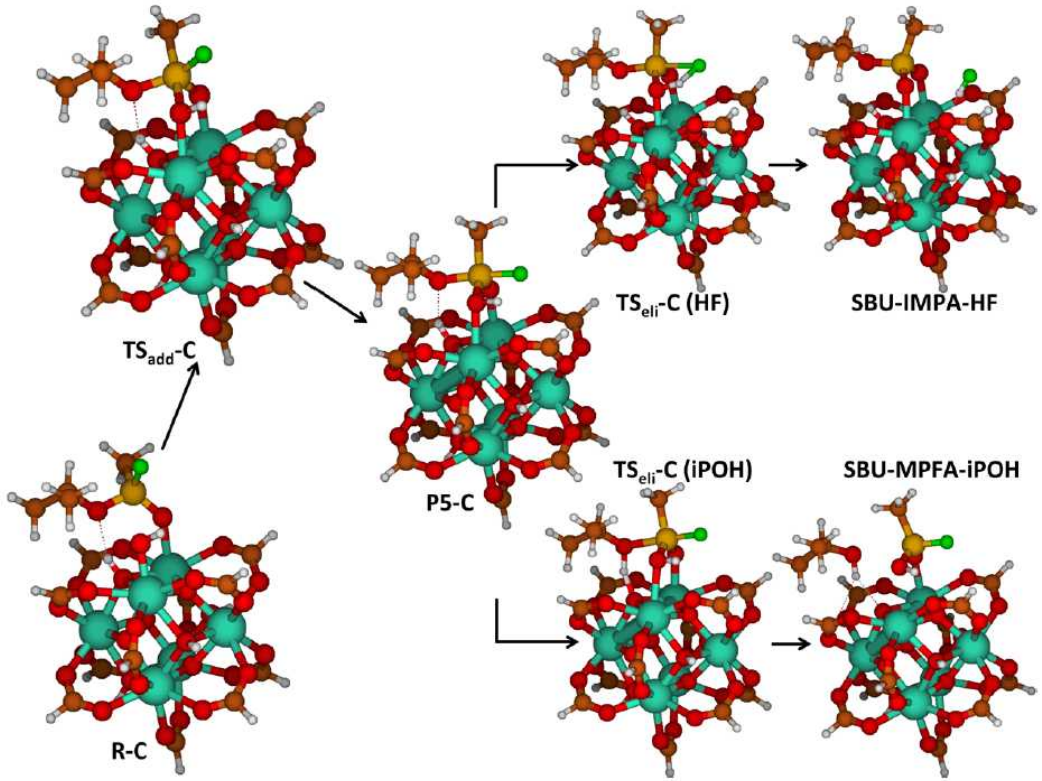


- Degradation of Sarin and DMNP on NU-1000

Nat. Mater. **2015**, 14, 512-516

Computational CWA MOF Work

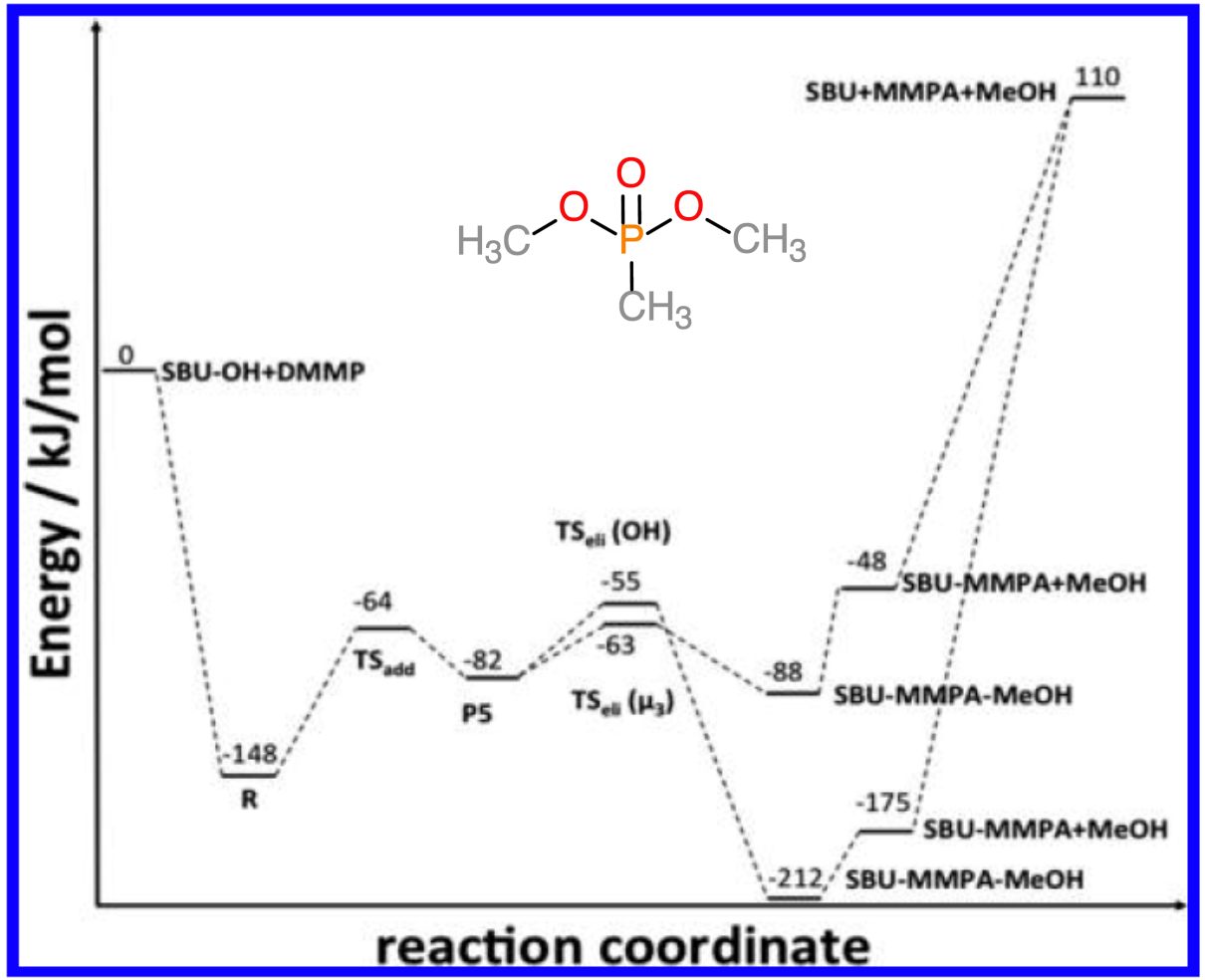


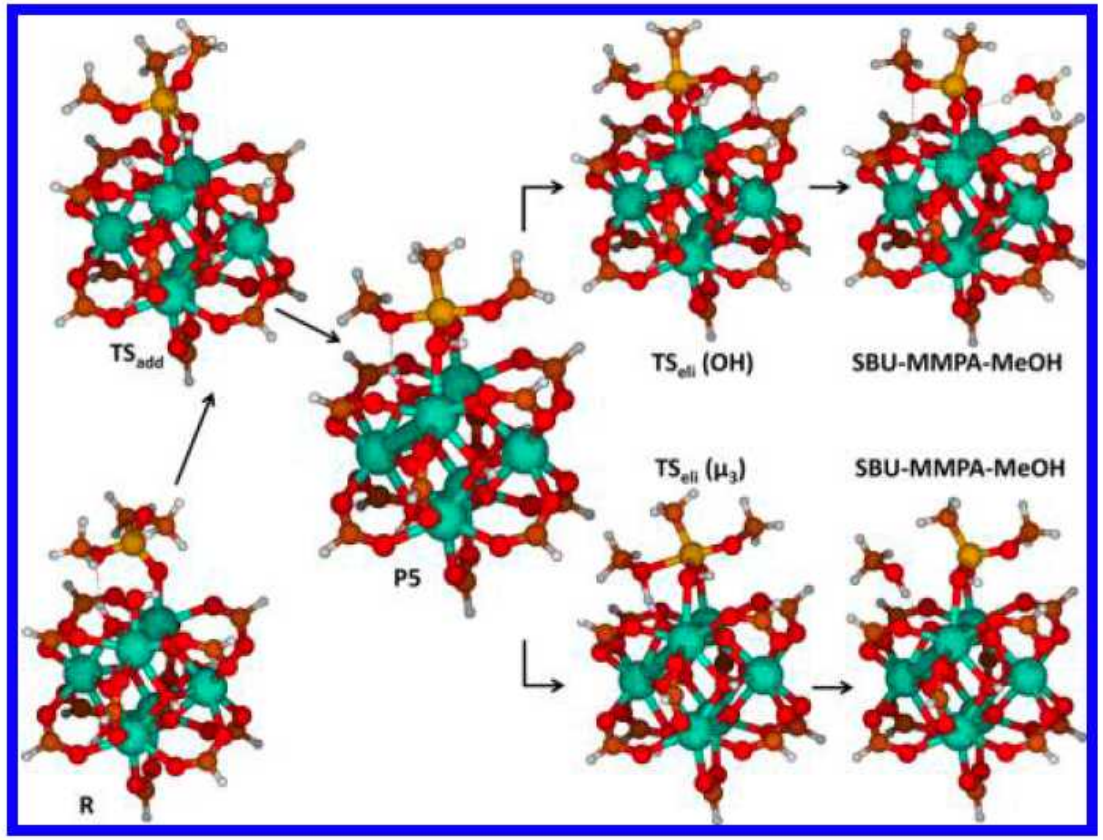


- Degradation of Sarin and DMNP on UiO-66

J. Phys. Chem. C **2016**, 120, 29312-29323

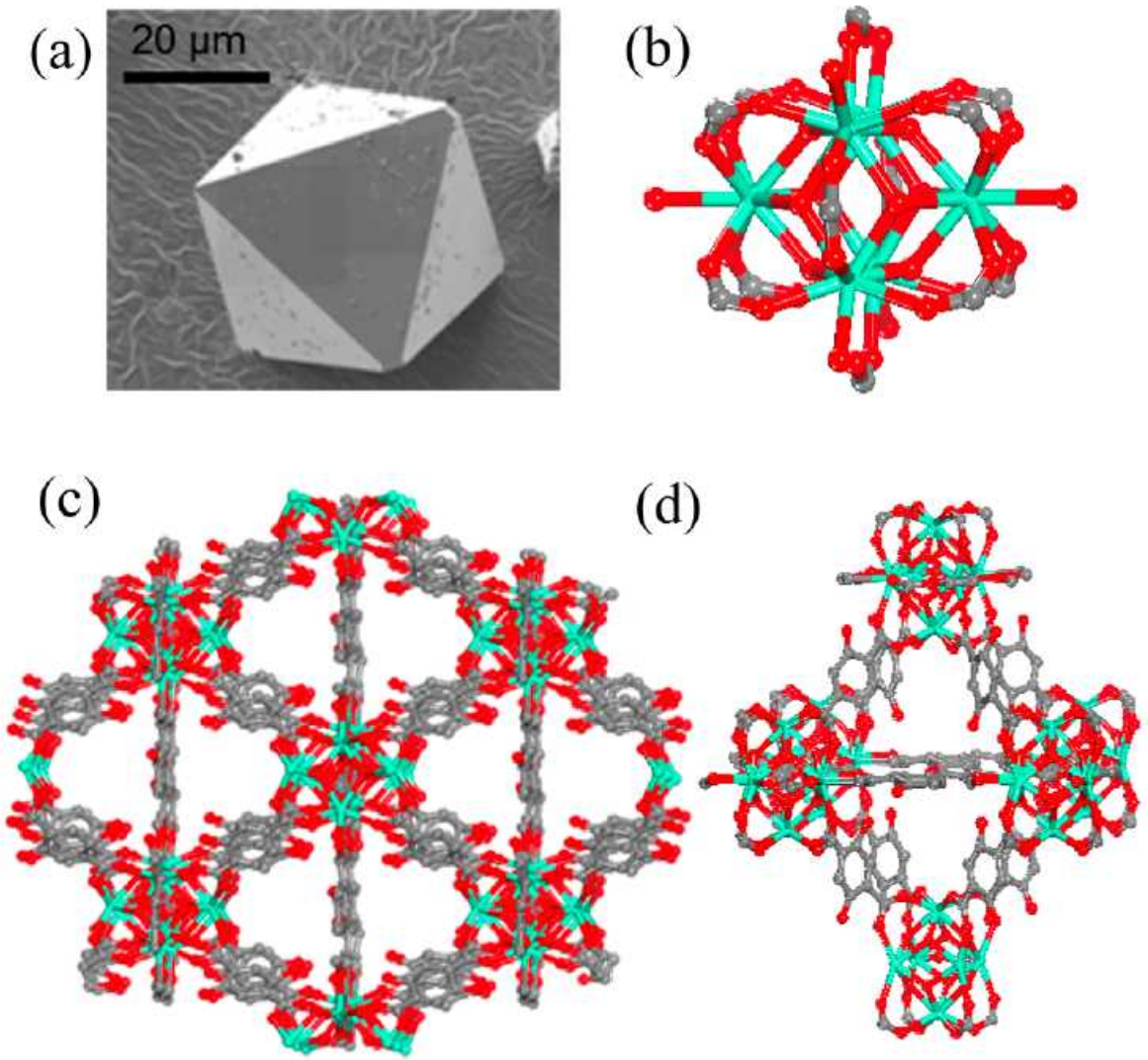
Computational CWA MOF Work

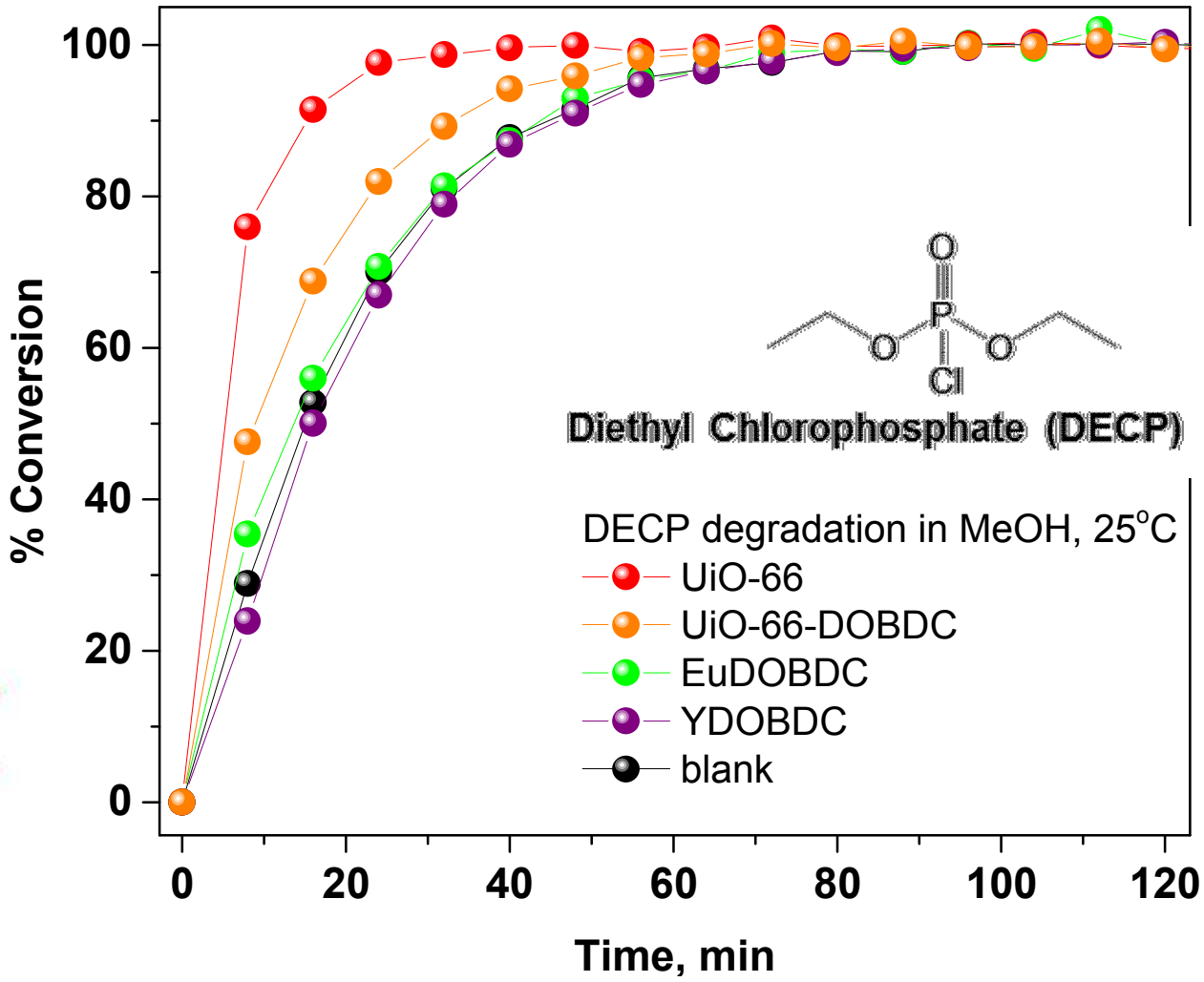




- Degradation of DMMP on UiO-66
- Computational work to date lacks systematic study of the effect of metal, ligand, and solvent

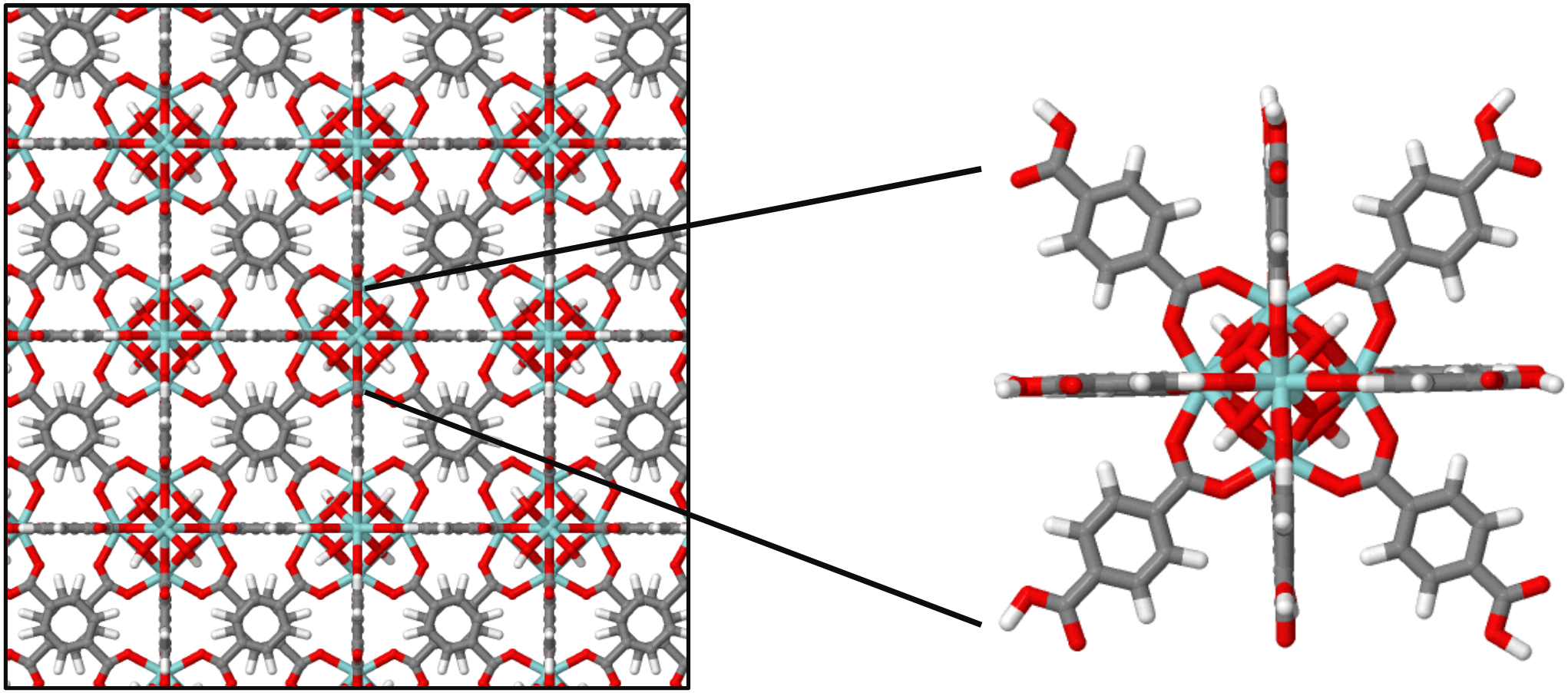
Rare-Earth Metal-Based MOFs





ACS Appl. Mater. Interfaces ***2017***, *9, 22268-2227*

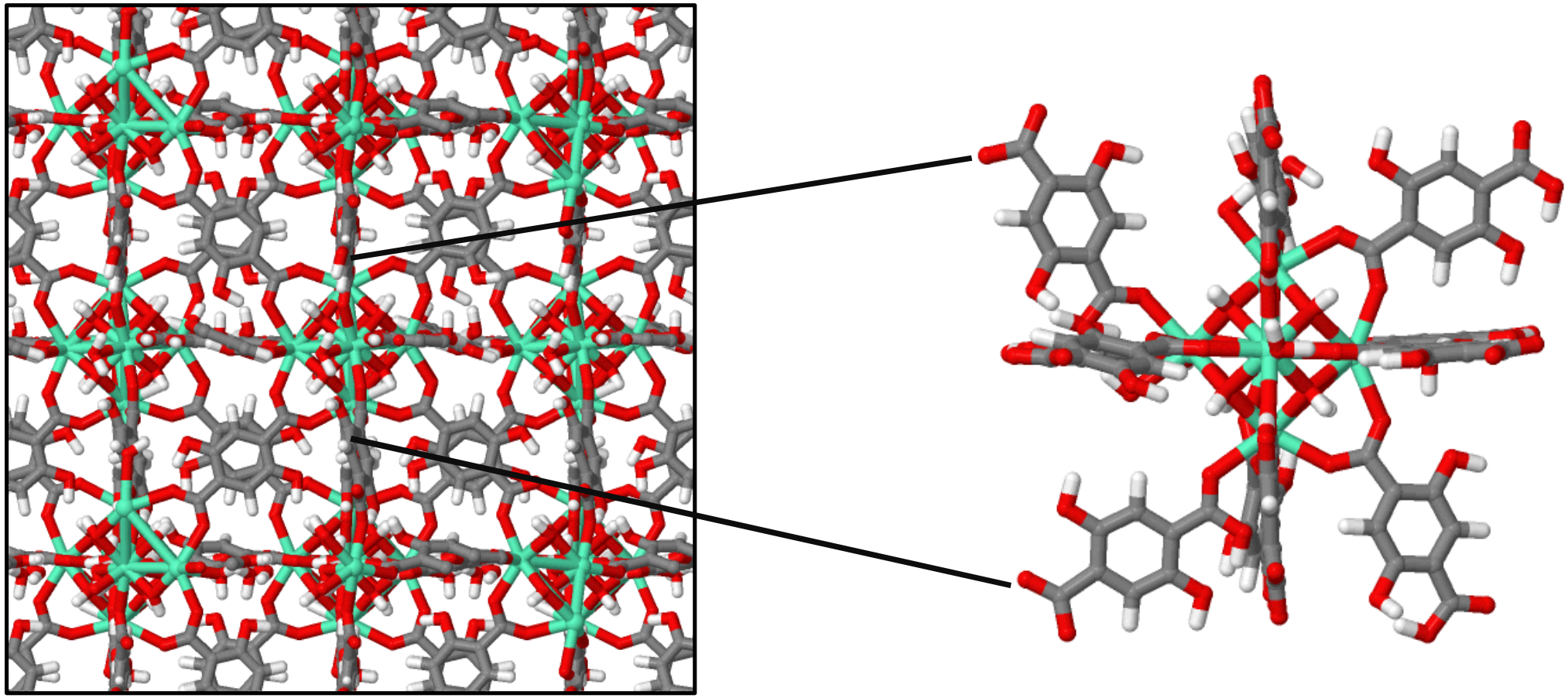
UiO-66 3D Structure



- $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ + 6 benzenedicarboxylate ($C_8H_4O_6$) ligands pre unit cell
- Each ligand is bidentate → Requires defects

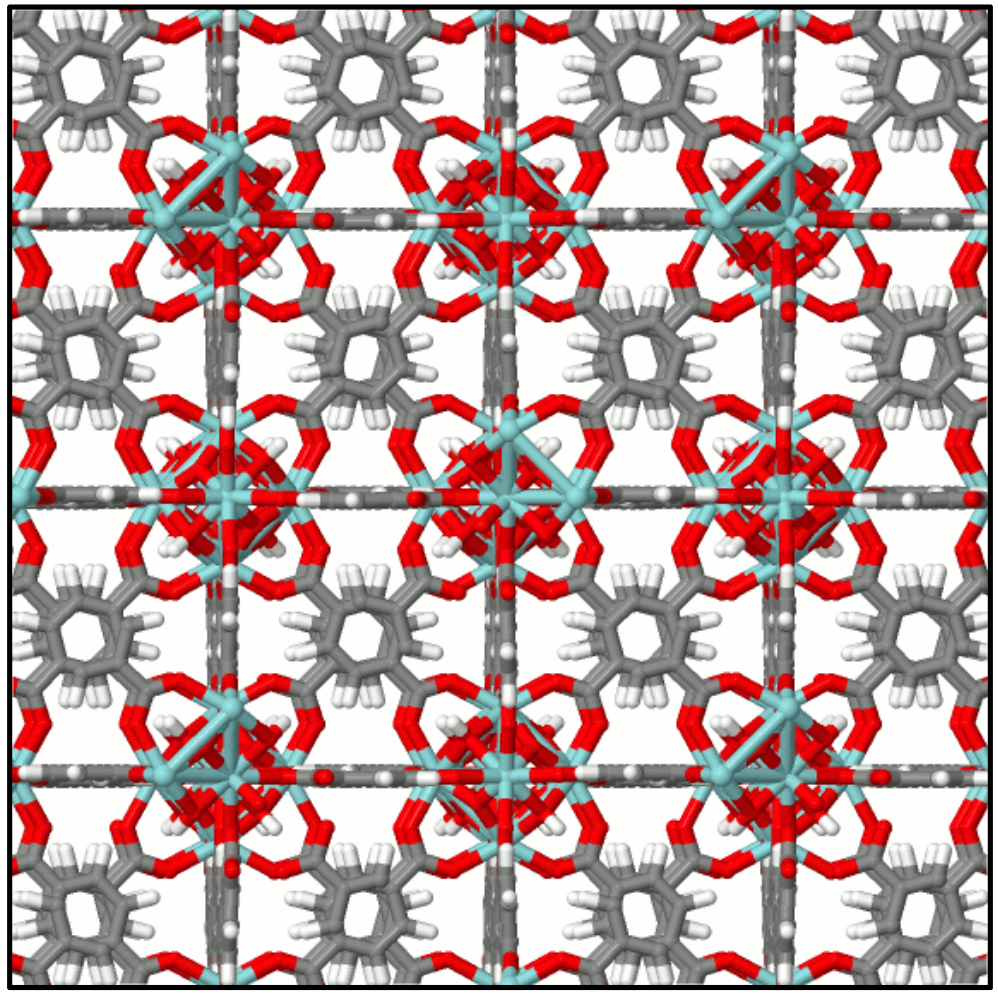
JACS **2008**, 130, 13850-13851

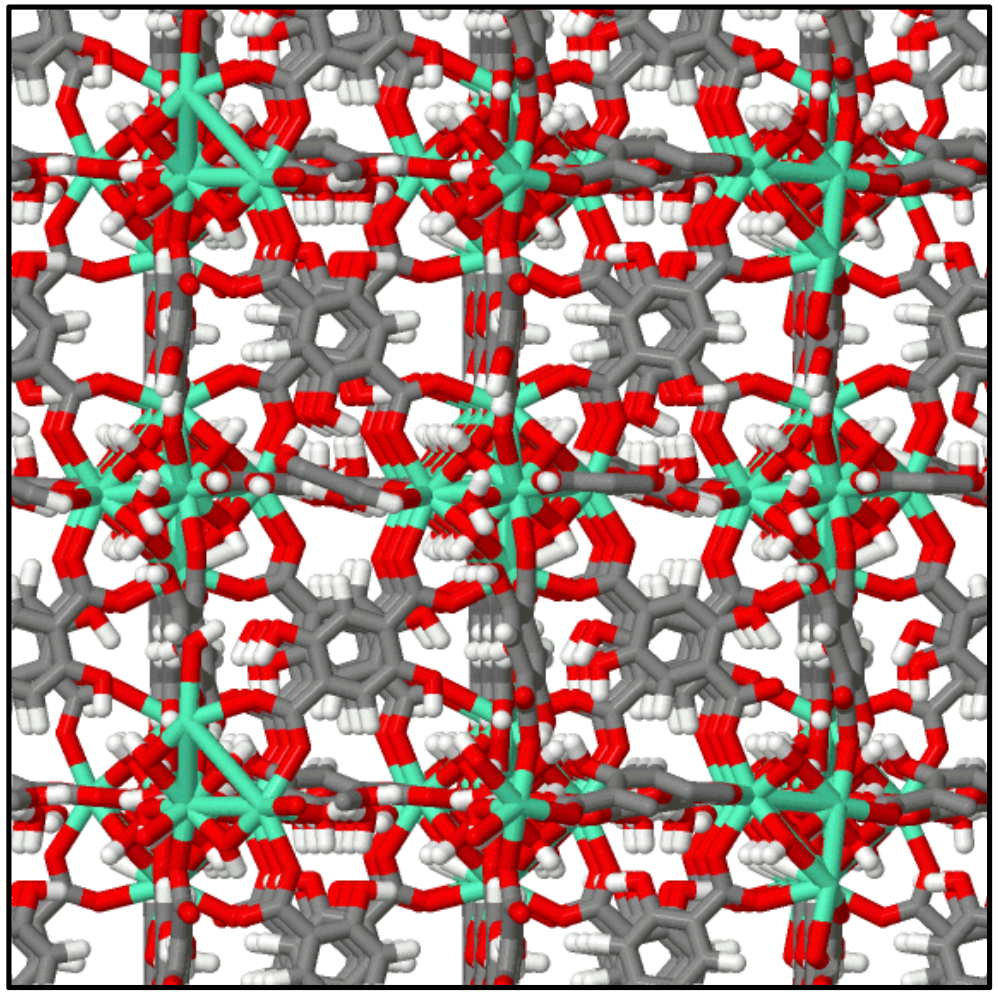
Eu-DOBDC 3D Structure



- $Eu_6(\mu_3\text{-}OH)_6$ + 6 dioxido-benzenedicarboxylate ($C_8H_4O_6$) ligands per unit cell
- Coordination chemistry forces twist in ligands and 2 (1 per unit cell) are monodentate

3D Structure



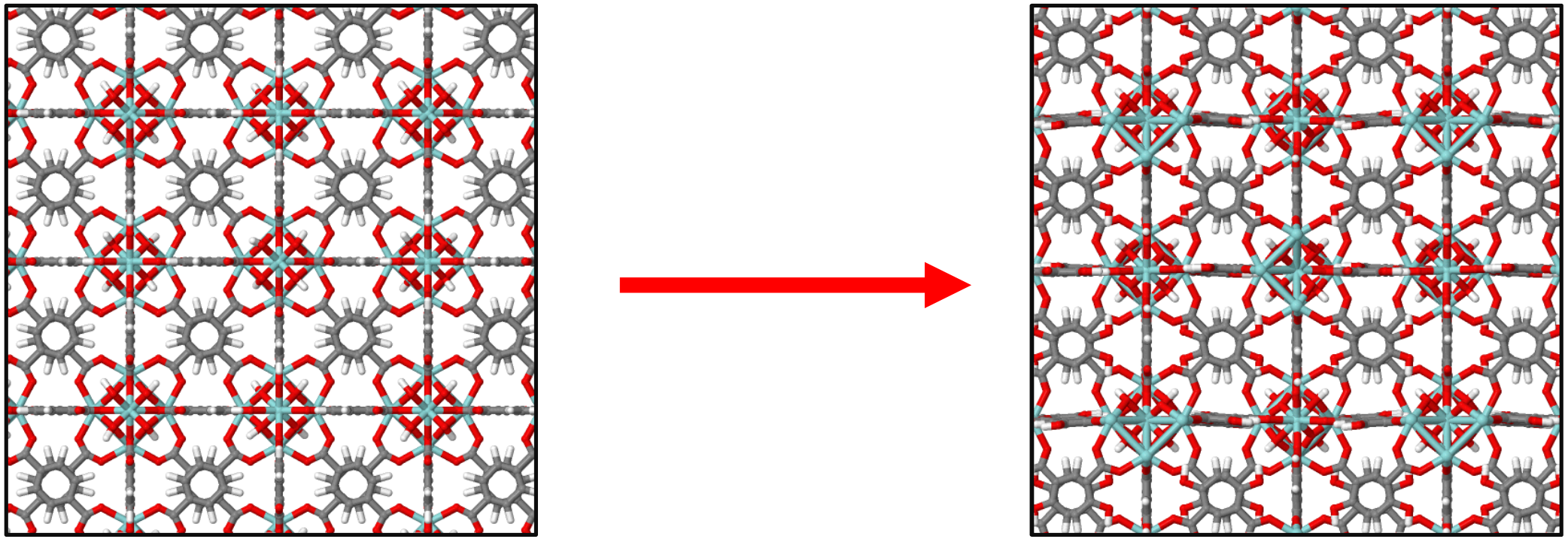


- Can we confirm the known experimental structures computationally through IR?
- Open metal sites should allow better access to lewis acid sites → Faster catalysis?

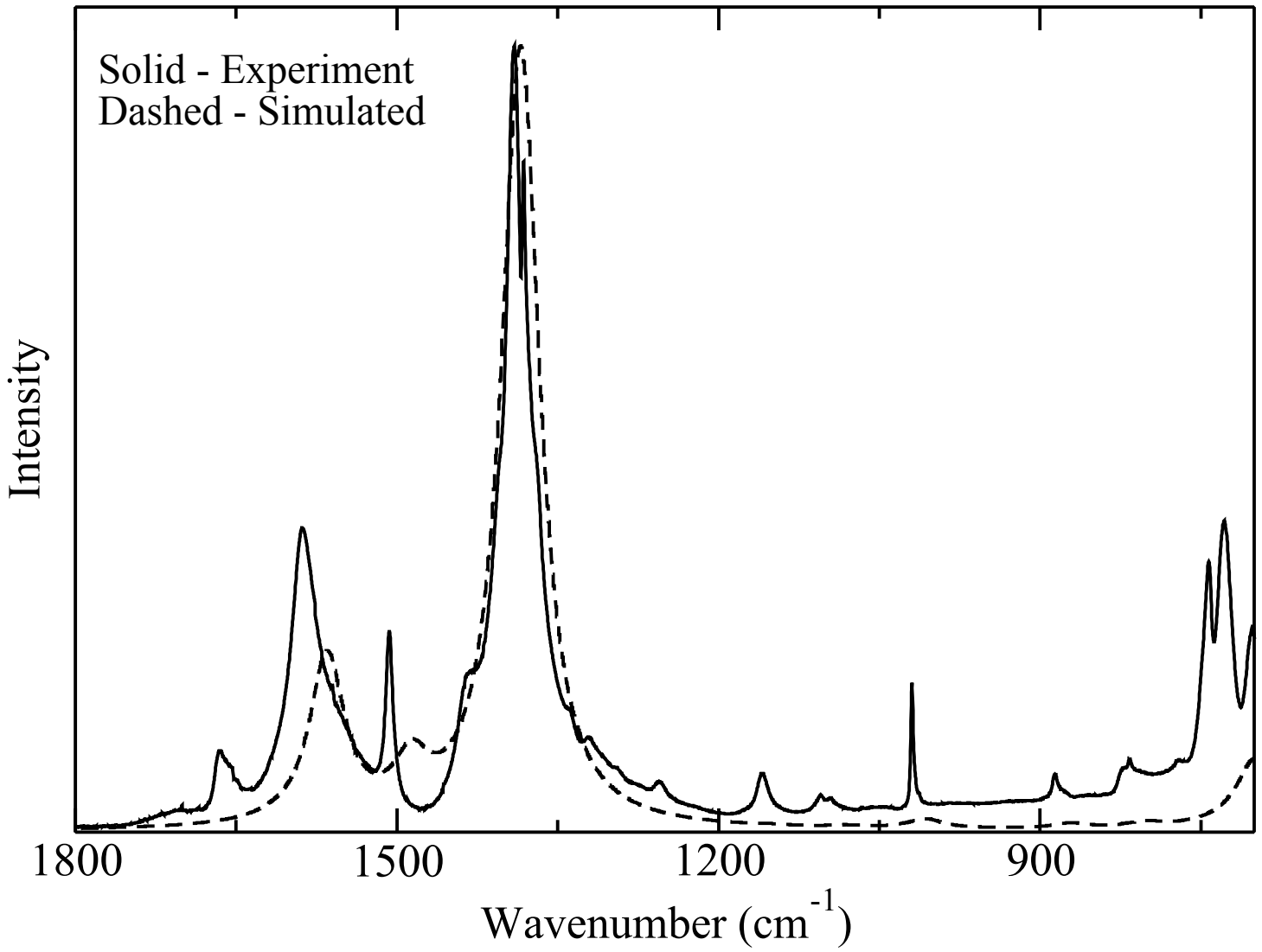
Computational Methods

Periodic DFT:

- Y structure created by changing the identity of the metal in the Eu-DOBDC structure
- UiO-66-DOBDC created by adding OH groups to UiO66 crystal structure
- Optimize crystal structure with VASP
- PAW approach with PBESol functional
- VDW interactions via DFT-D3 method



UiO66 Infrared Spectrum



- Vibrational spectrum calculated on periodic structures using DFPT

$$I(\omega) = \sum_{\alpha=1}^{3} \left| \sum_{s=1}^{M} \sum_{\beta=1}^{3} Z^{*}_{\alpha\beta}(s) e_{\beta}(s) \right|^2$$

Cartesian polarizations

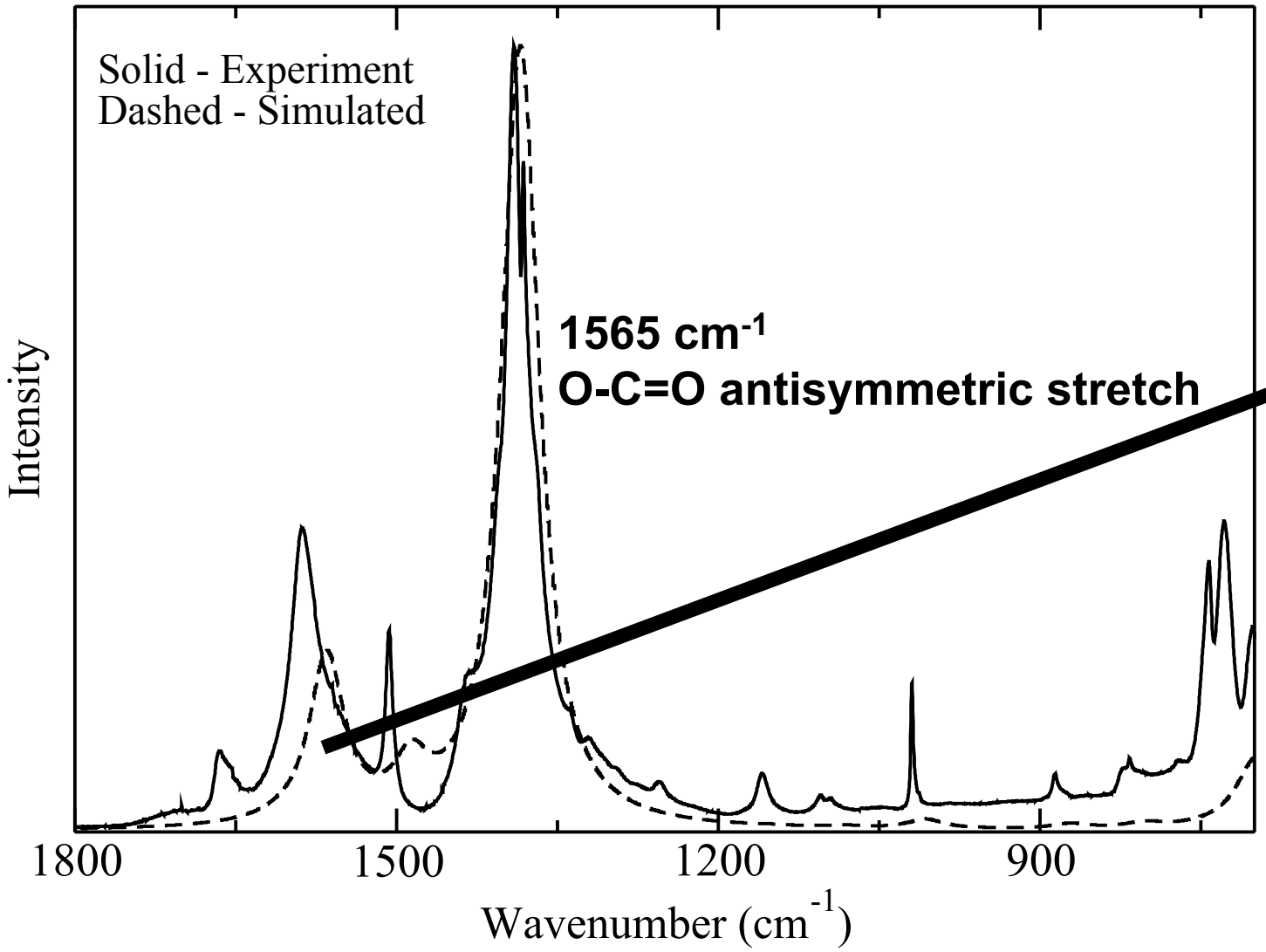
Born effective charge of s^{th} atom

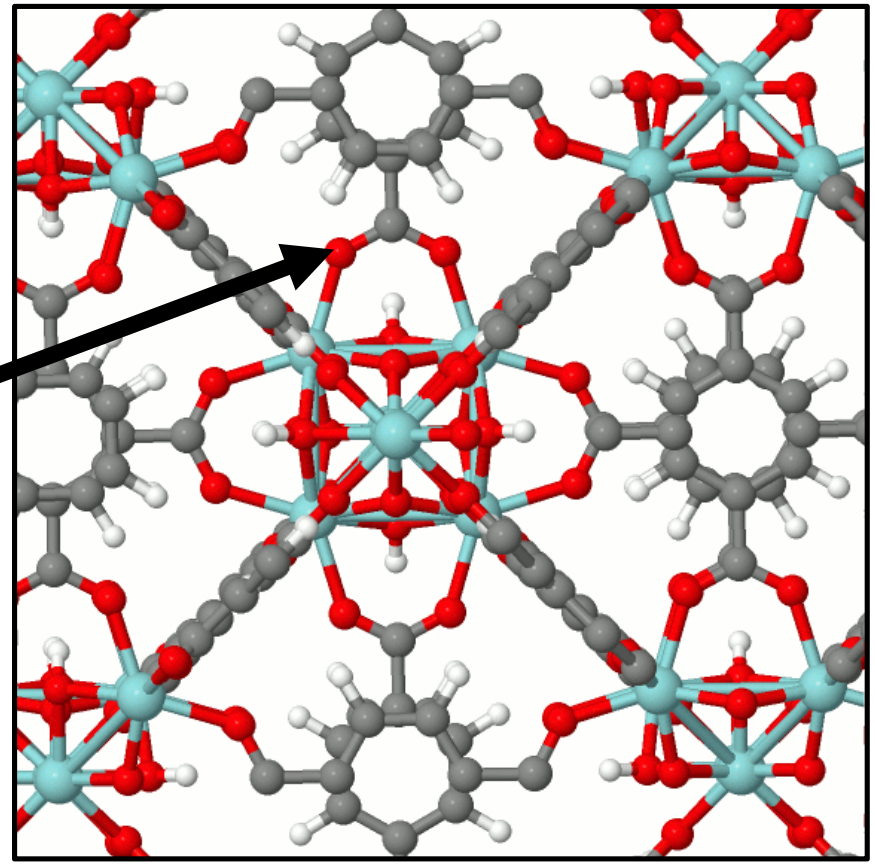
Vibrational eigenvector

- Apply Lorentzian broadening

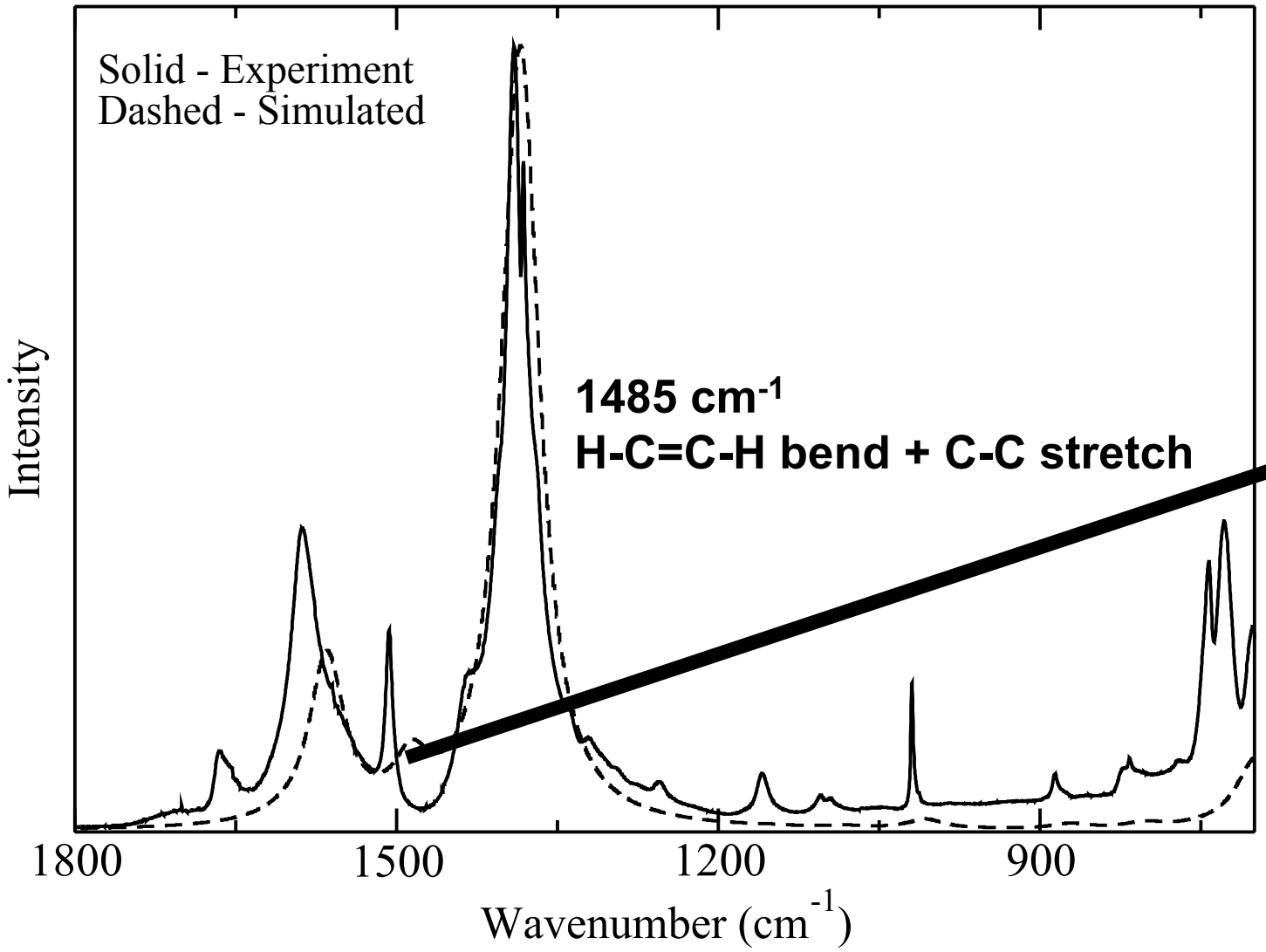
Phys. Rev. B **1991**, 43, 7231-7242
J. Chem. Phys. **1994**, 100, 8537-8539
Rev. Mod. Phys. **2001**, 73, 515-562
J. Phys. Condens. Matt. **2010**, 22, 265006

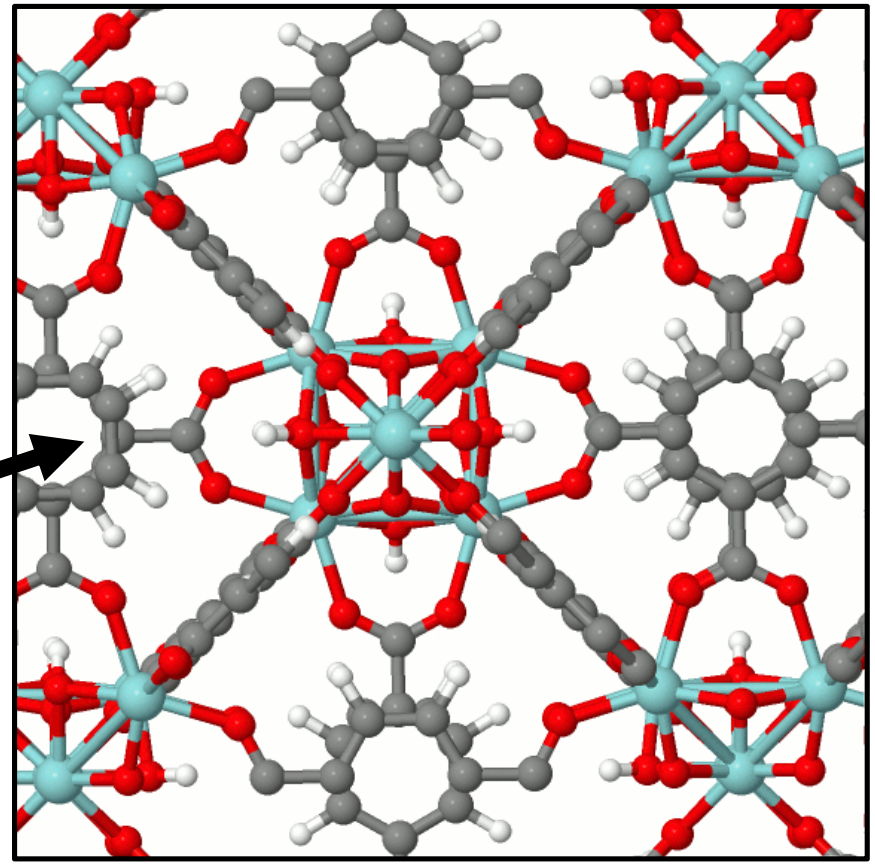
UiO-66 Infrared Spectrum



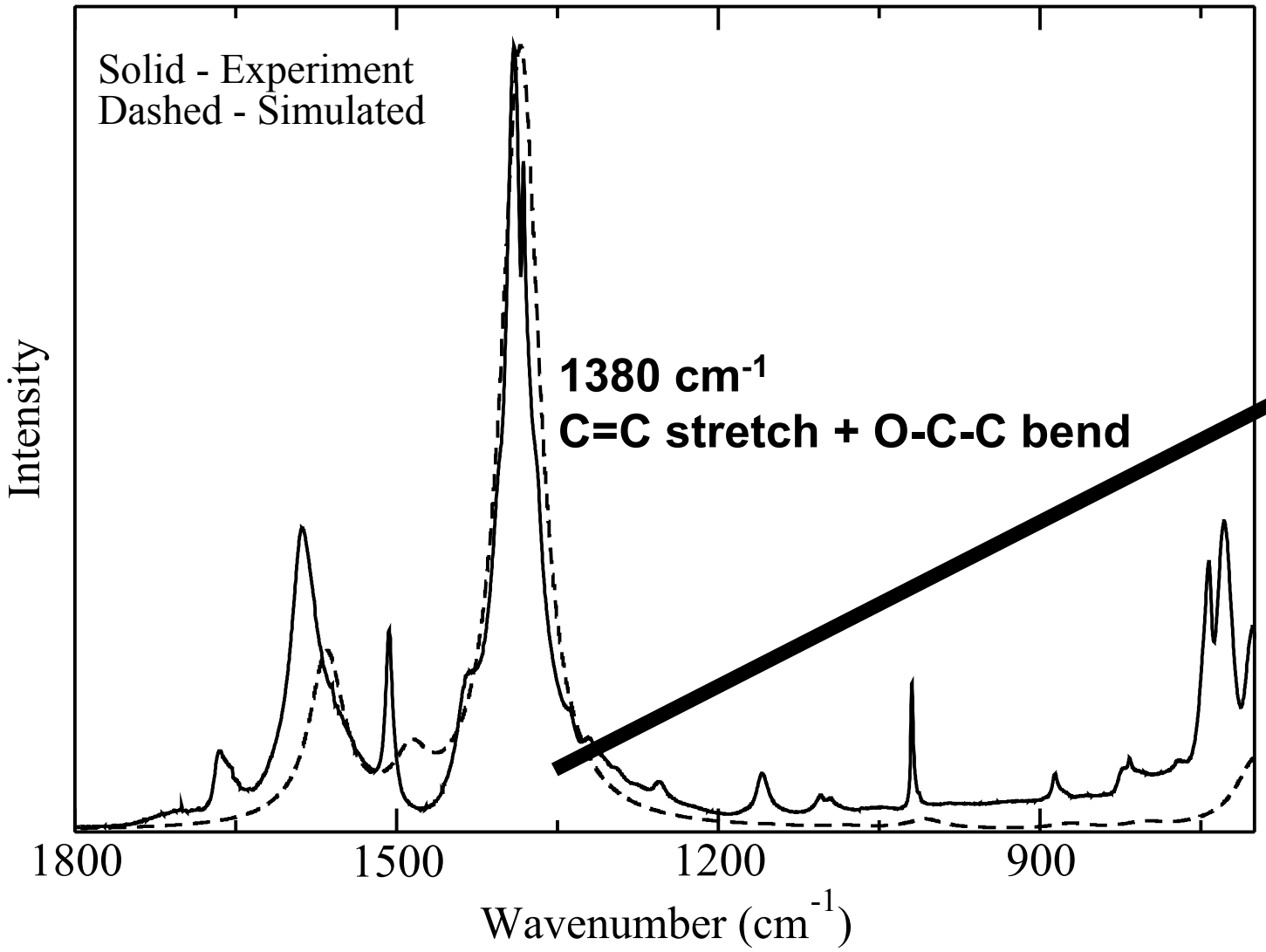


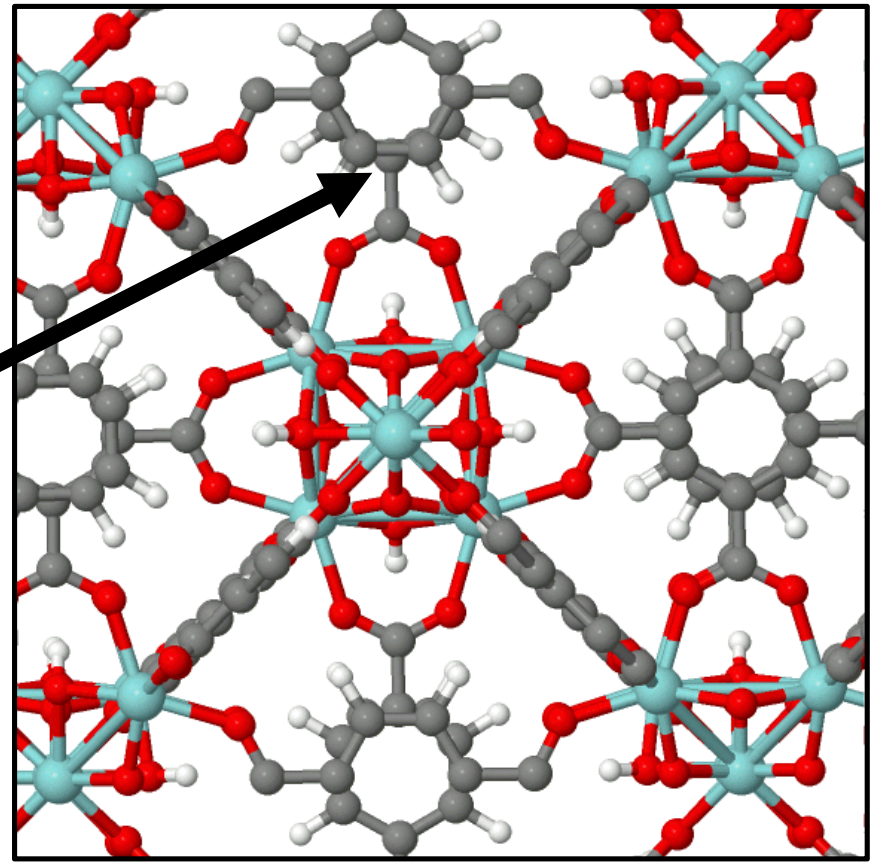
UiO-66 Infrared Spectrum



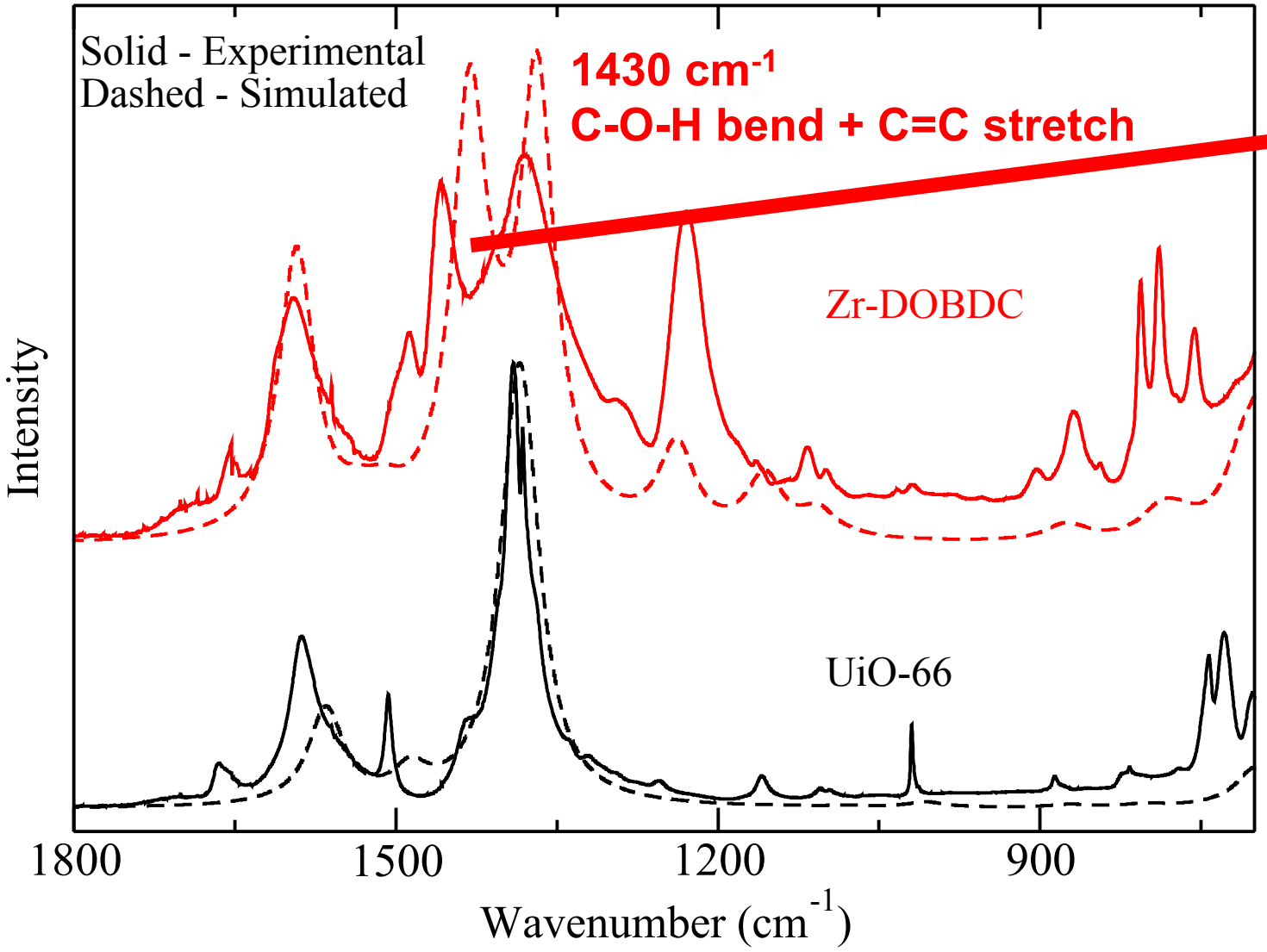


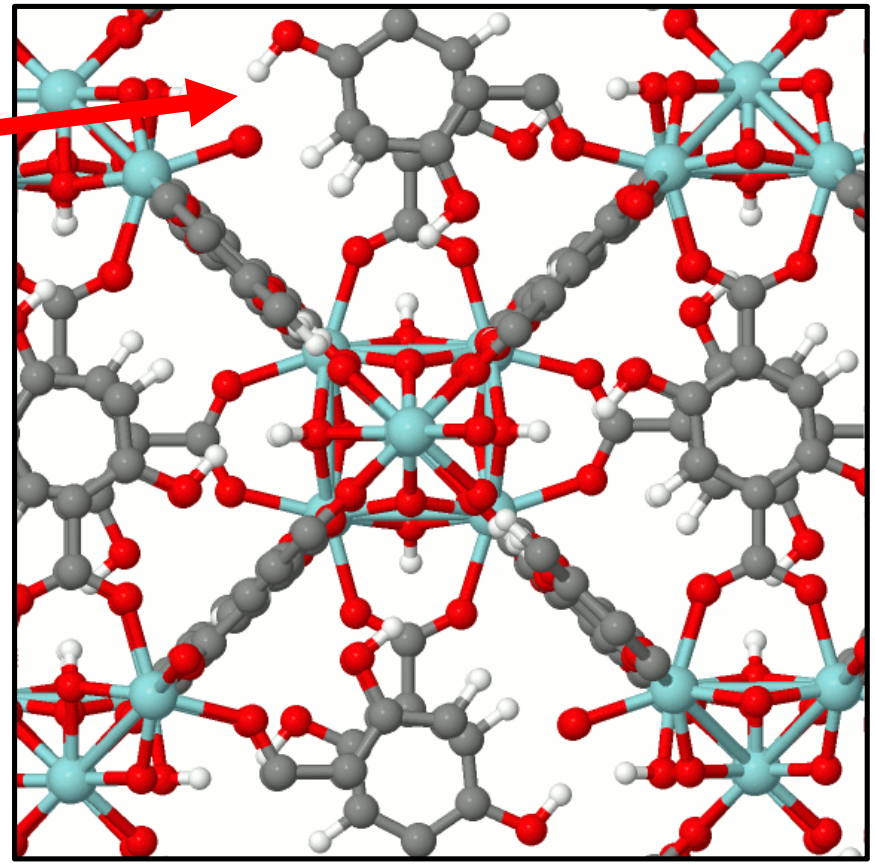
UiO-66 Infrared Spectrum



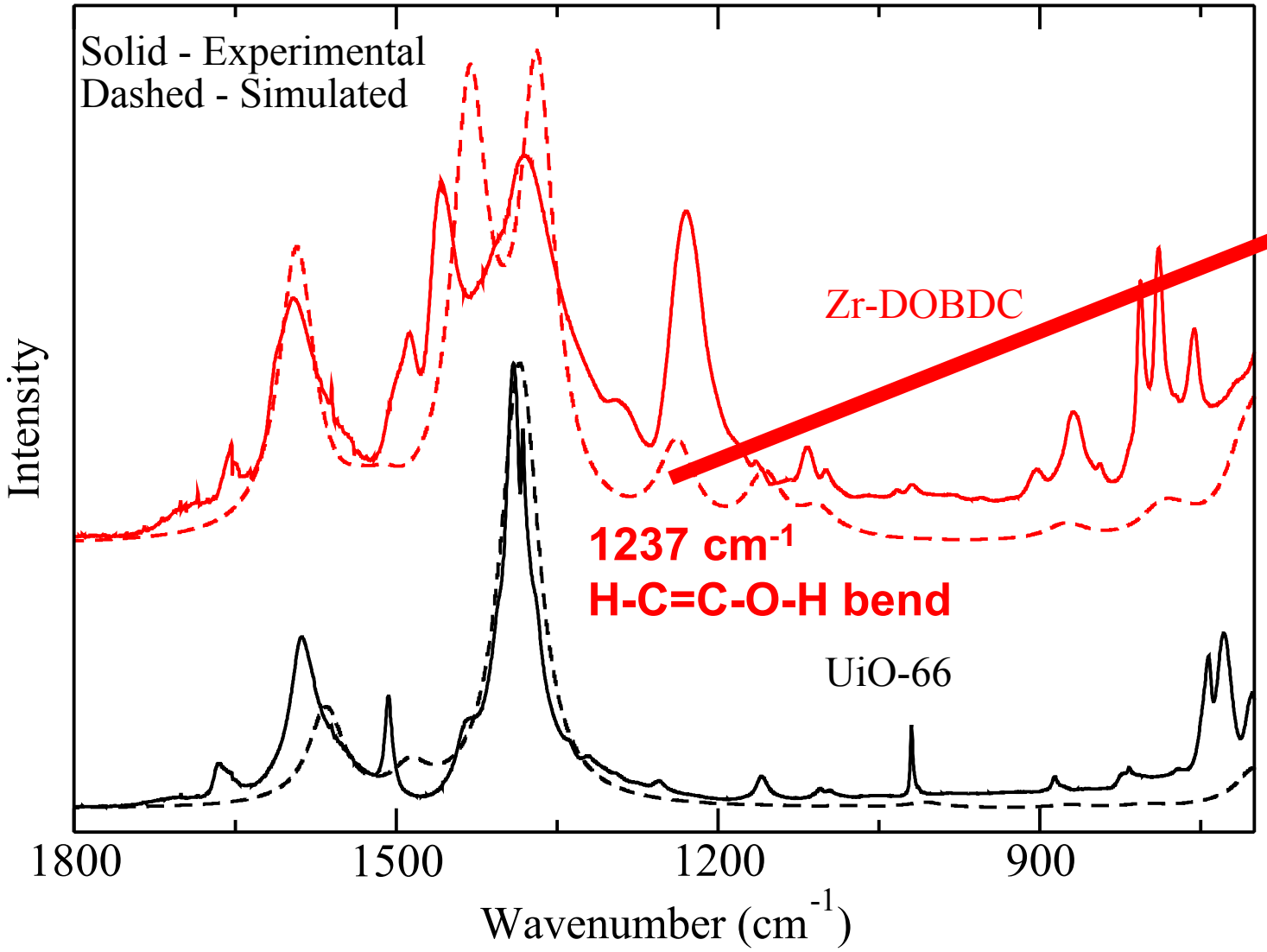


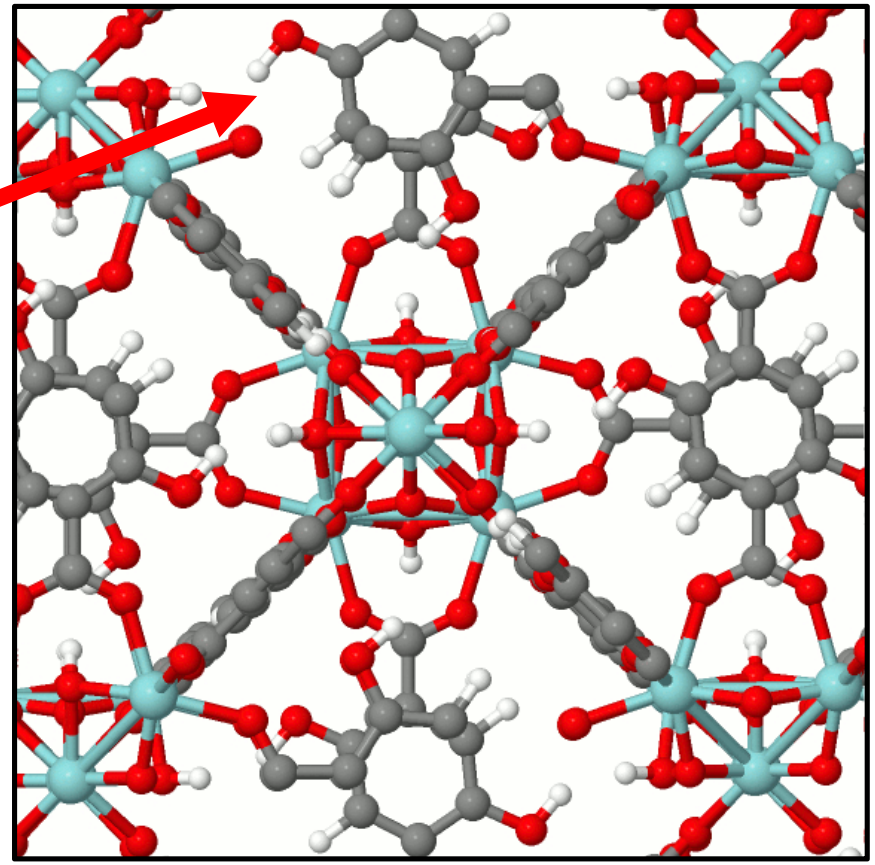
Effect of Ligand



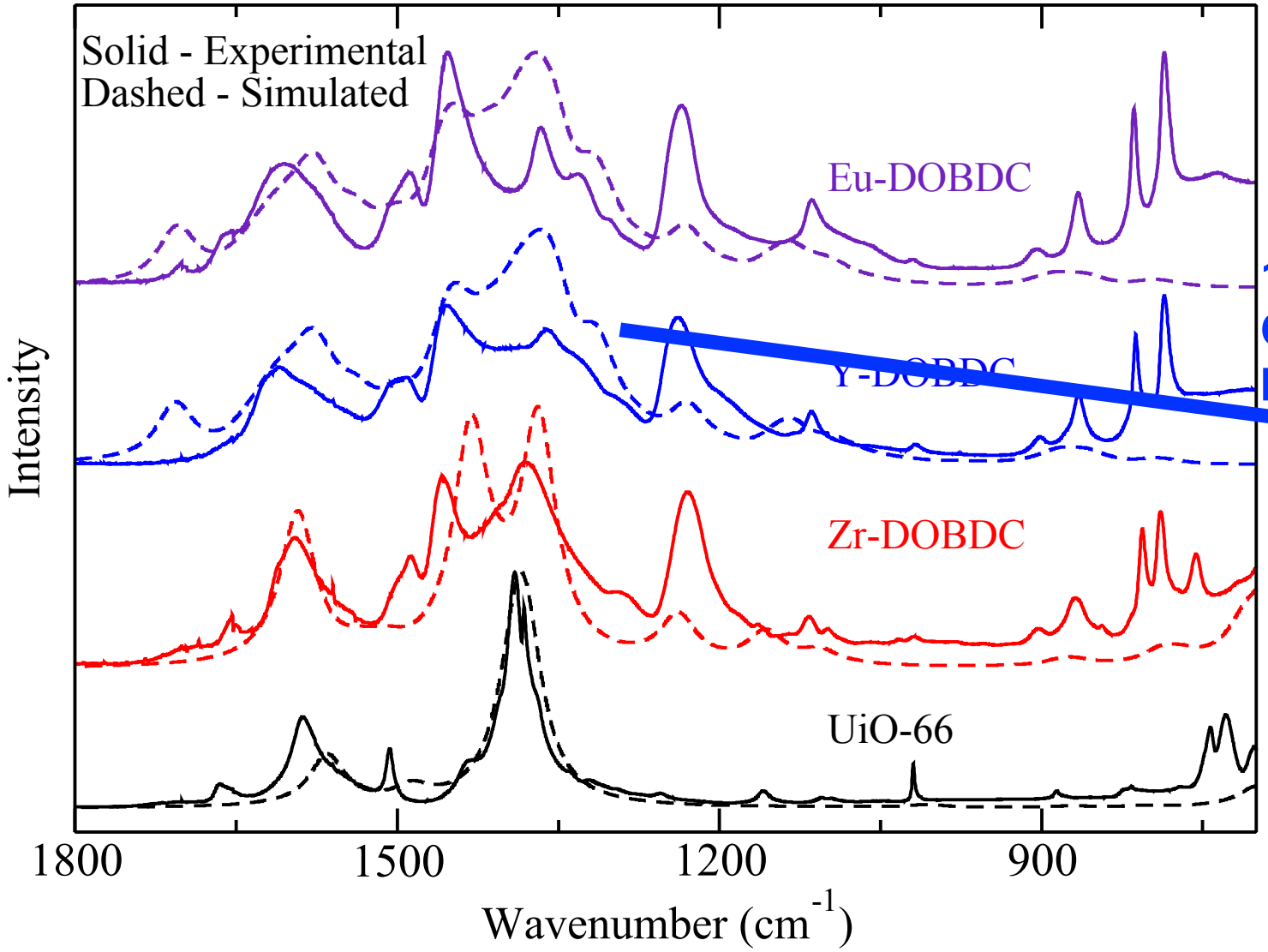


Effect of Ligand

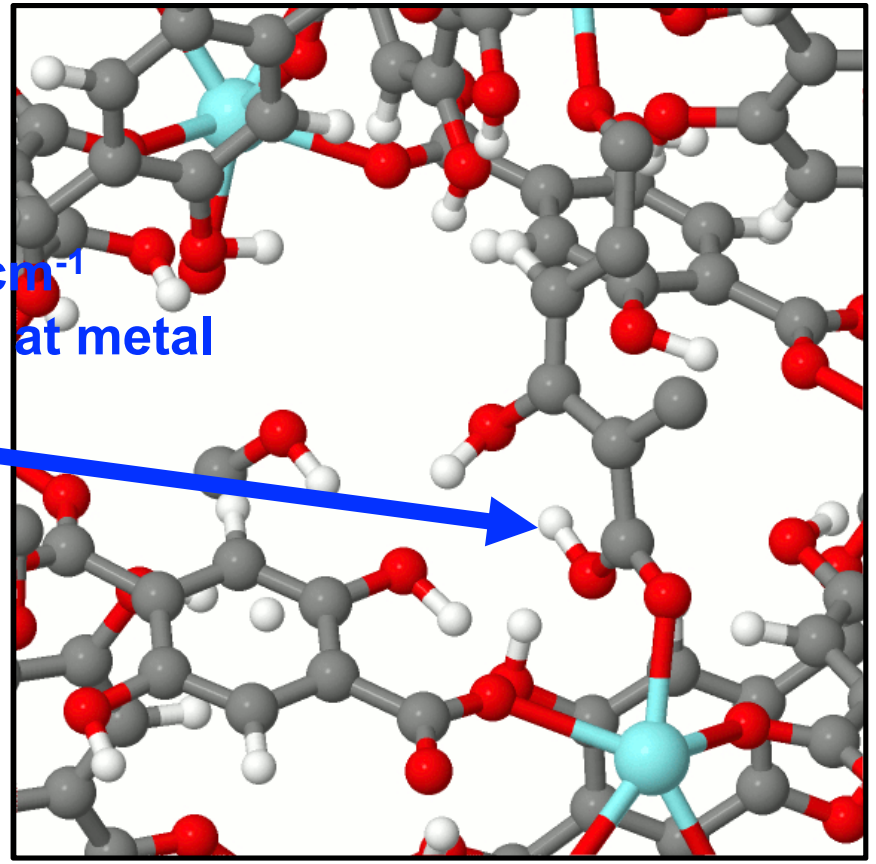




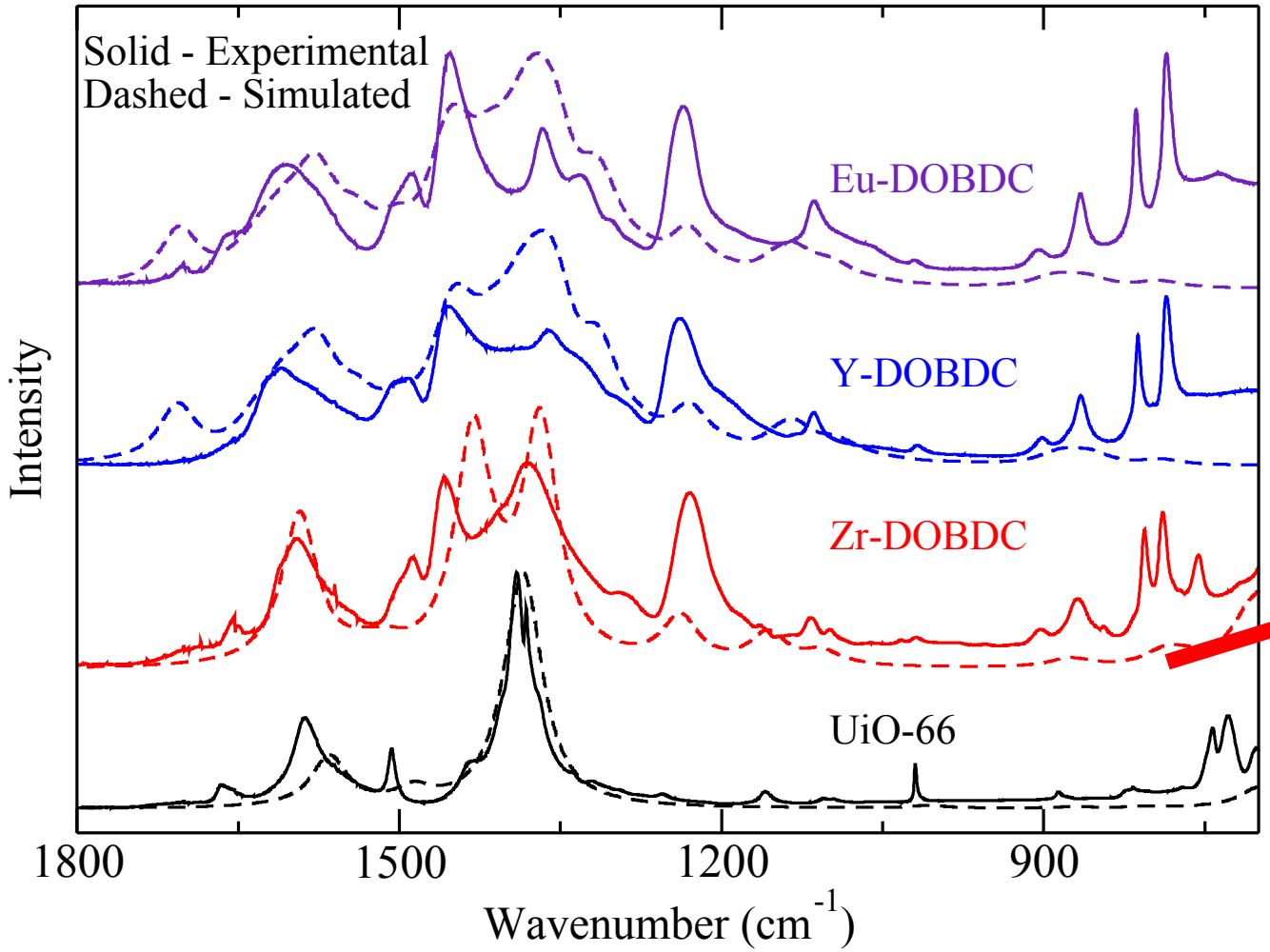
Effect of Metal

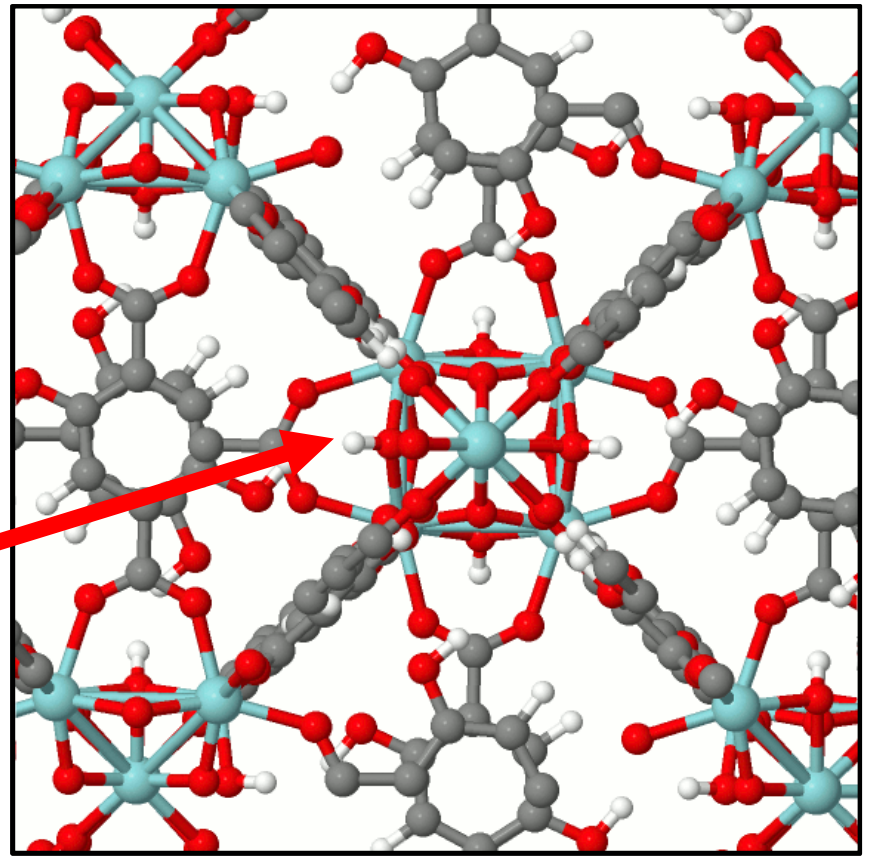


1315 cm^{-1}
C-O-H at metal bend



Effect of Metal





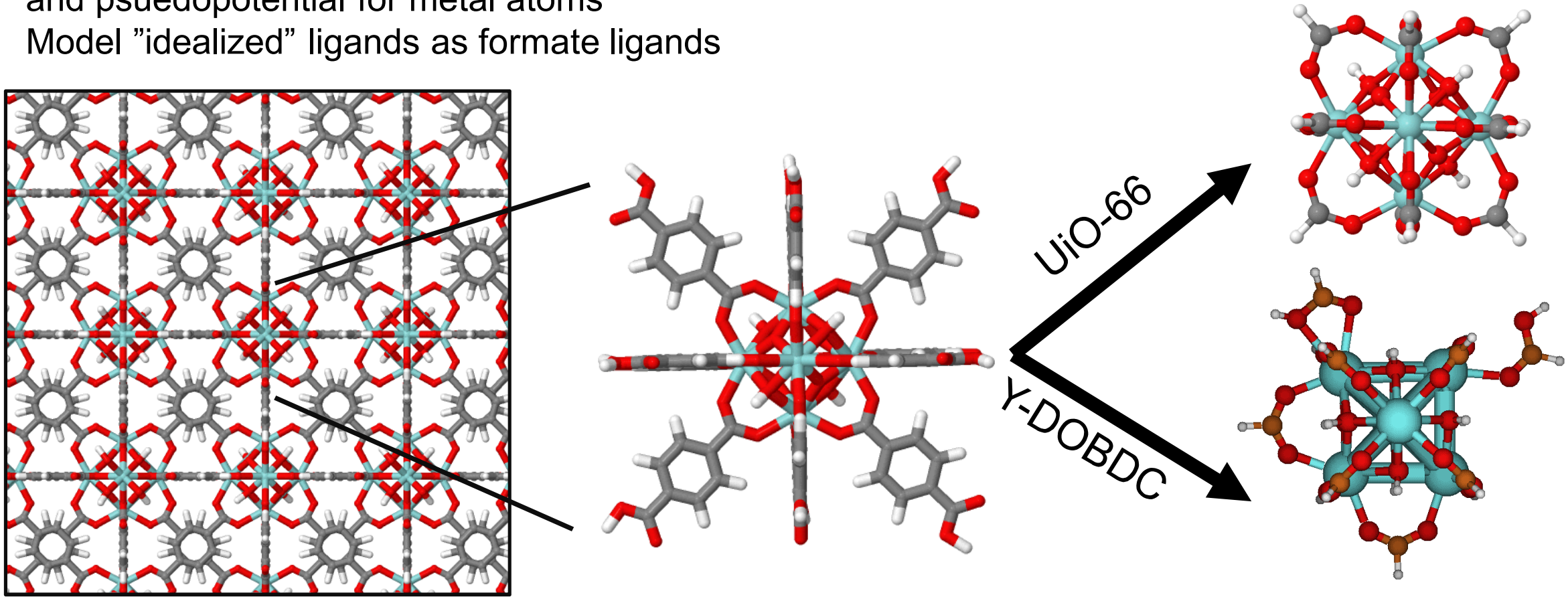
M-O-H bends

- Simulated infrared spectra suggest the optimized periodic structures well represent the experimental structures

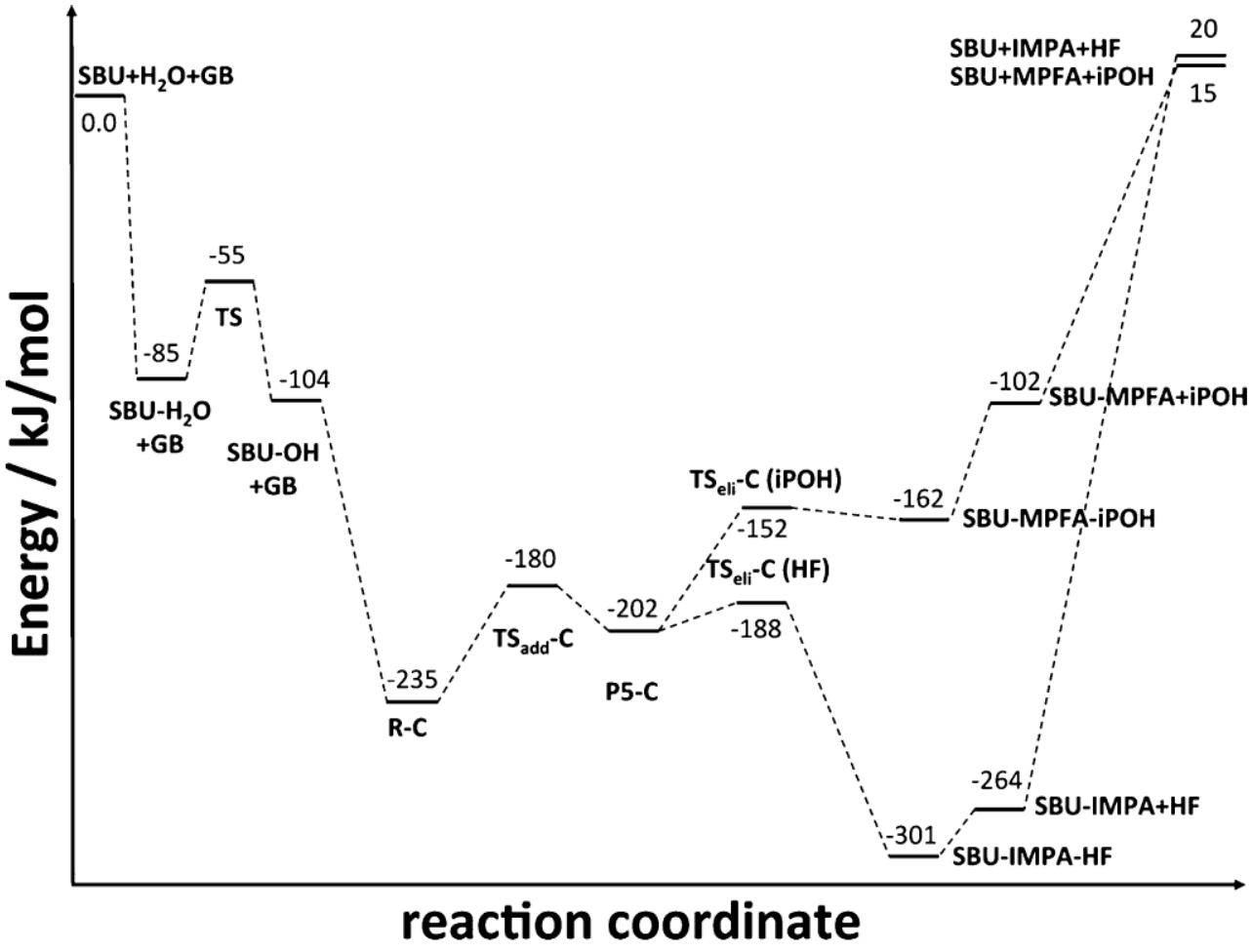
Computational Methods

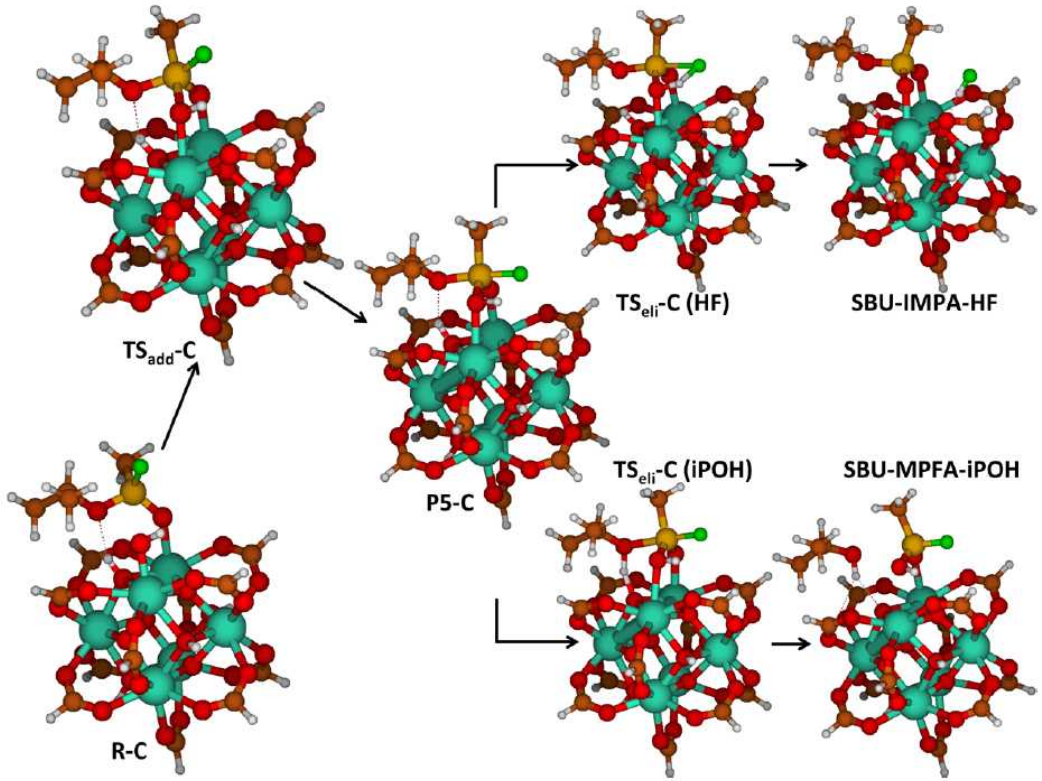
Gas Phase Cluster DFT:

- Cut clusters from VASP optimized structure
- Optimize clusters with MO6-L functional, def2-SVP basis set for all non-metal atoms and SDD ECP and psuedopotential for metal atoms
- Model ”idealized” ligands as formate ligands



Computational Methods

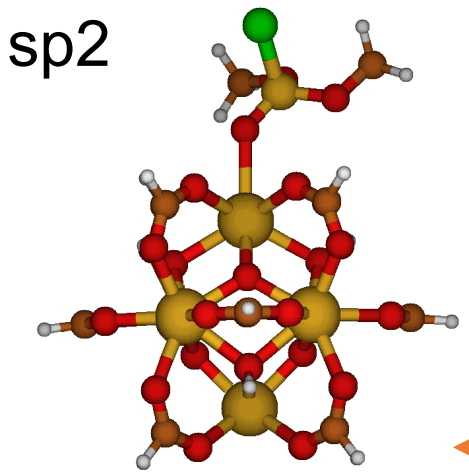


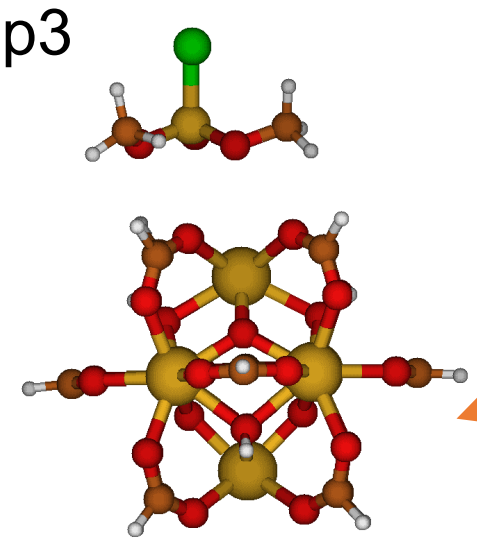


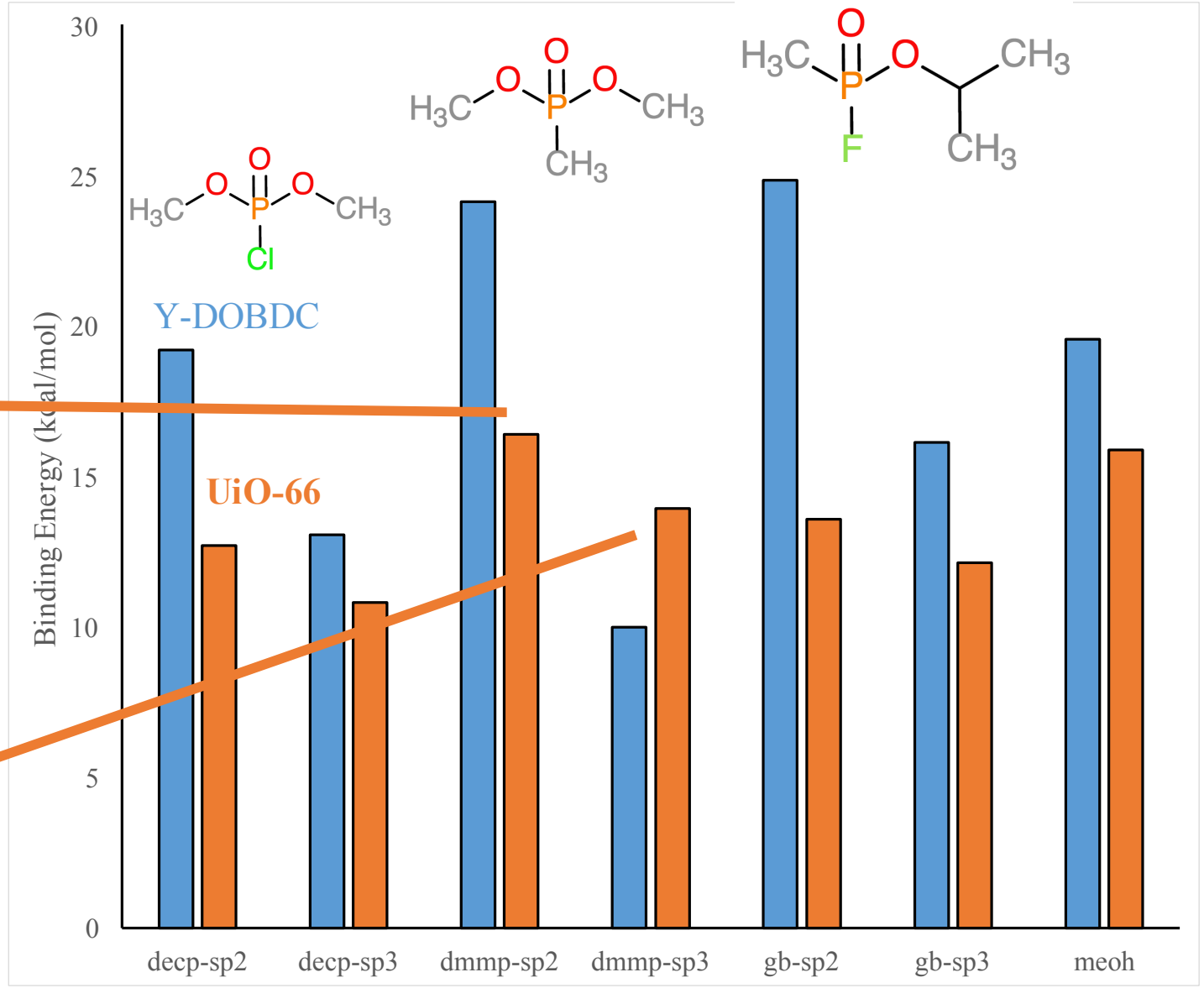
- Average 2 KJ/mol deviation in stationary states energy in formate vs full benzoate ligands

J. Phys. Chem. C **2016**, 120, 29312-29323

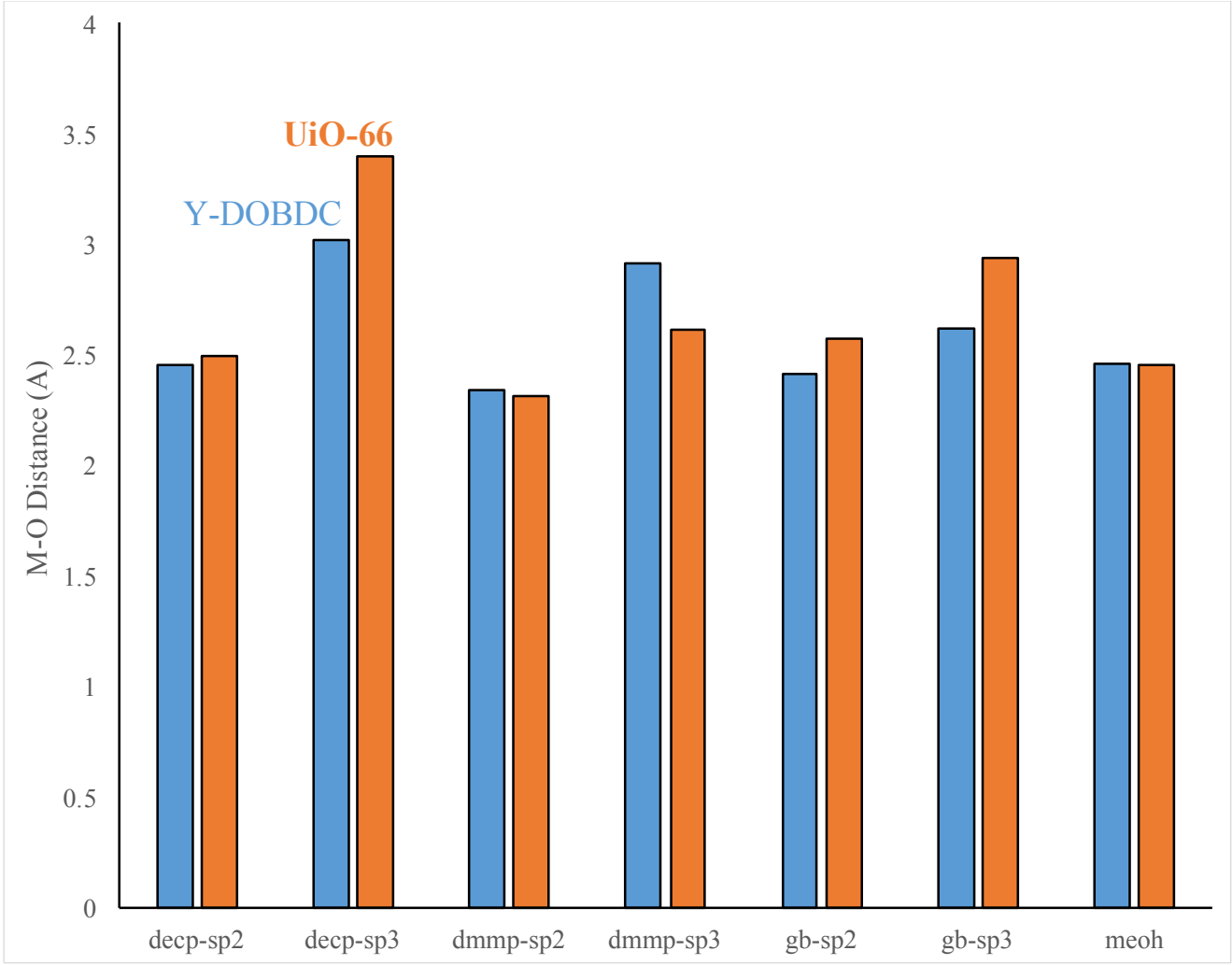
Binding Energy





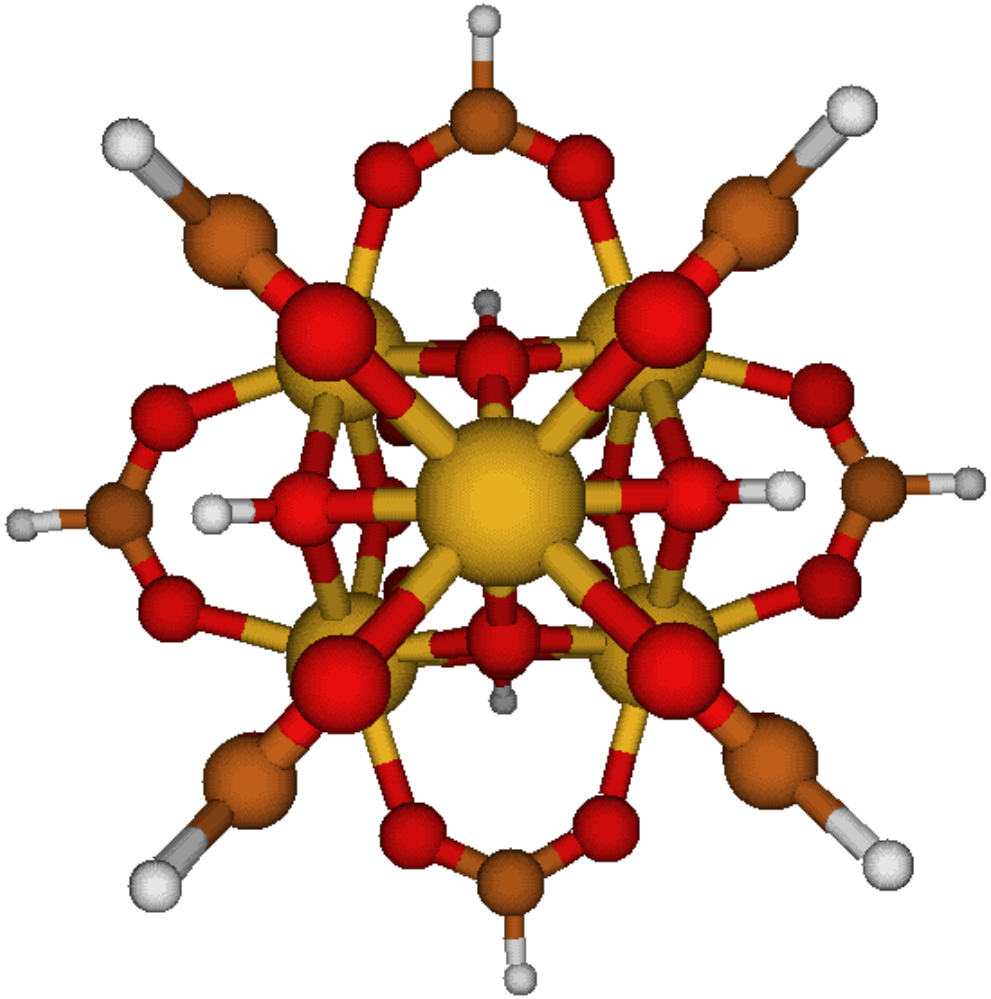


Binding Energy



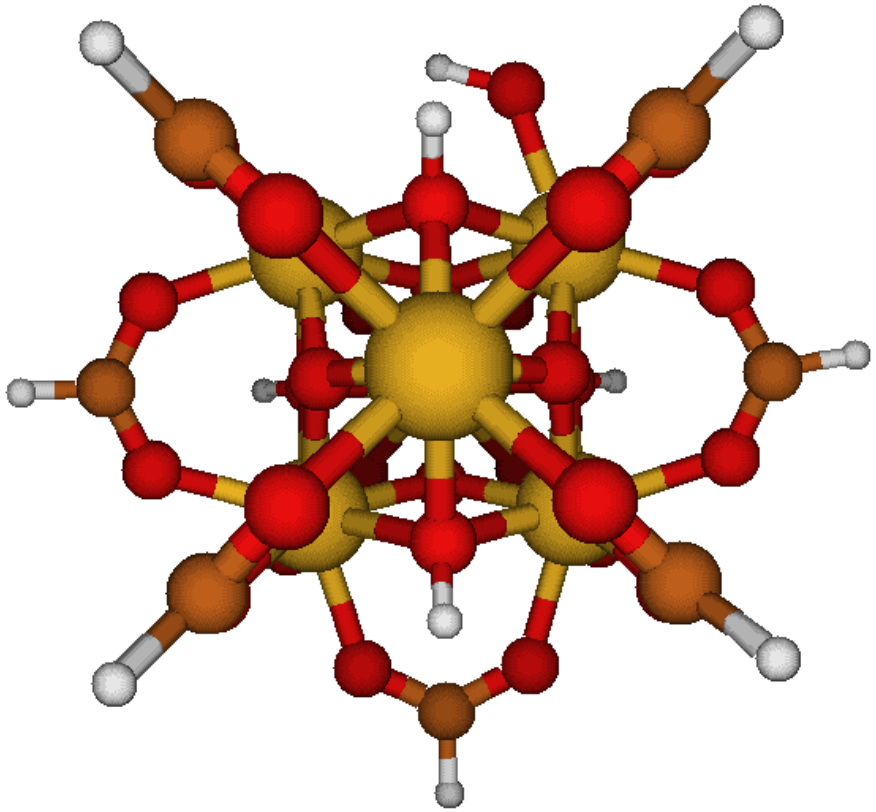
- M-O binding distance is unchanged by the identity of the metal

Defect Zr SBU



$- CHO_2$

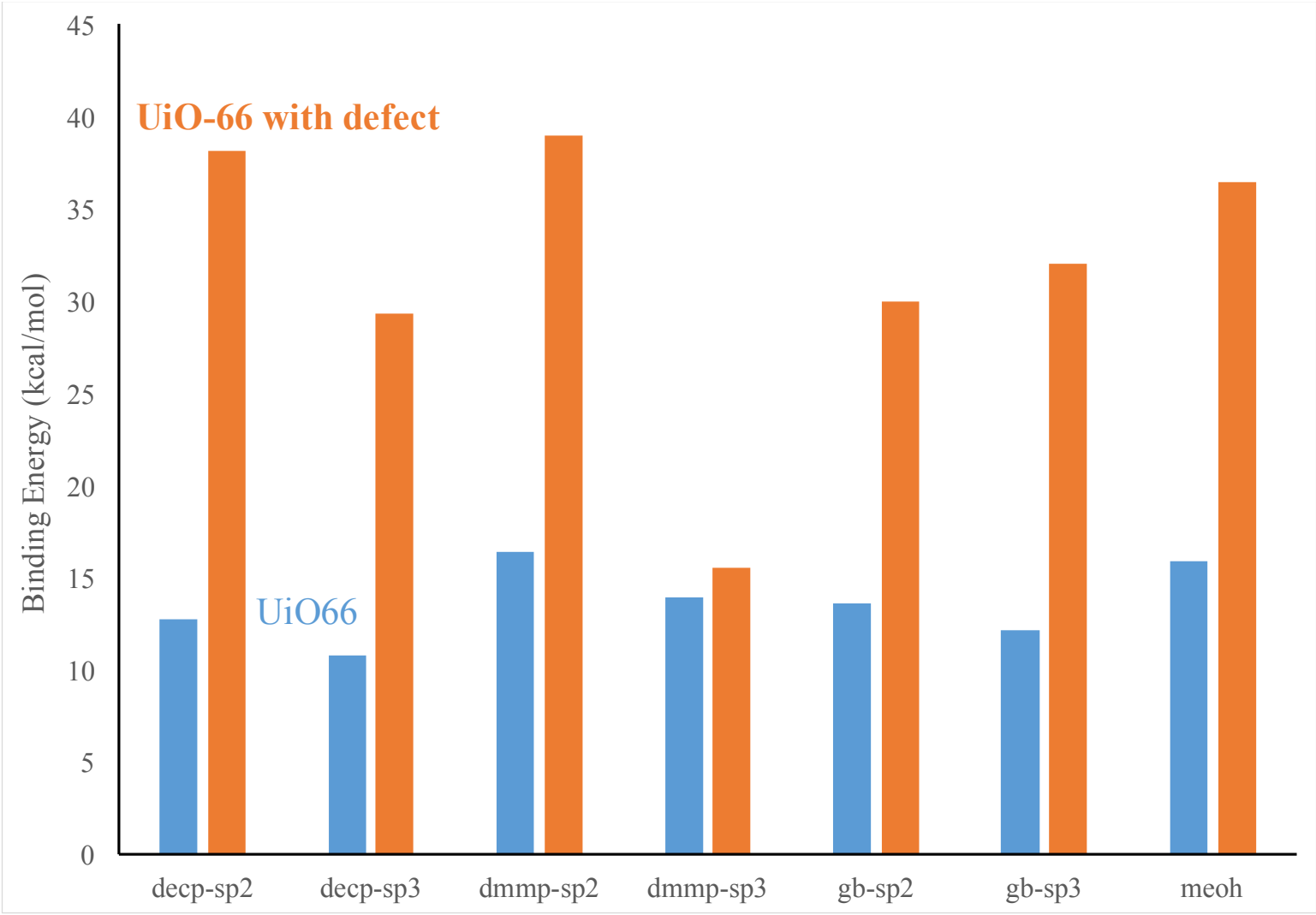
$+ H_2O$



- Remove a ligand and add water → 8 coordinated Zr and 7 coordinated Zr

Angew. Chem. Int. Ed. **2015**, 54, 11162-11167
Chem. Sci. **2016**, 7, 4706-4712

Defect Zr SBU



- Defect drastically increases binding energy

Acknowledgements

- Charles Pearce
- Mark Kinnan

This work was supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.