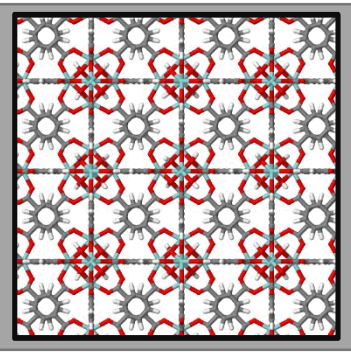
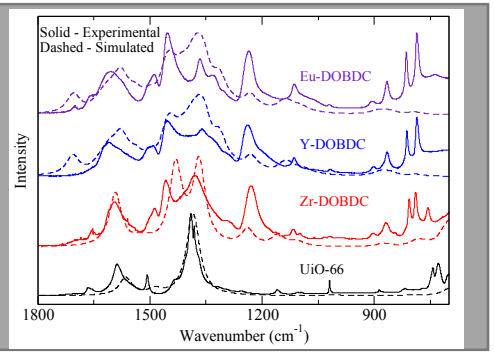
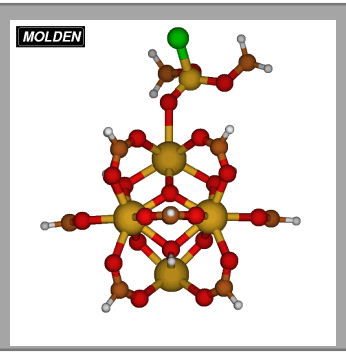
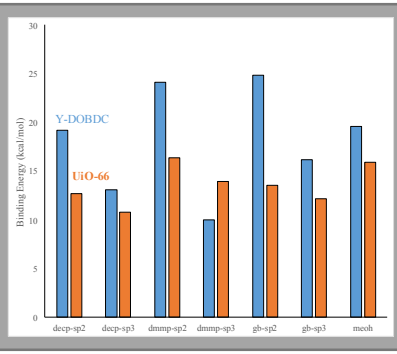
Exceptional service in the national interest

SAND2017-11621C









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

Jeffery A. Greathouse, Jacob A. Harvey, Dorina F. Sava Gallis

U.S. DEPARTMENT OF ENERGY

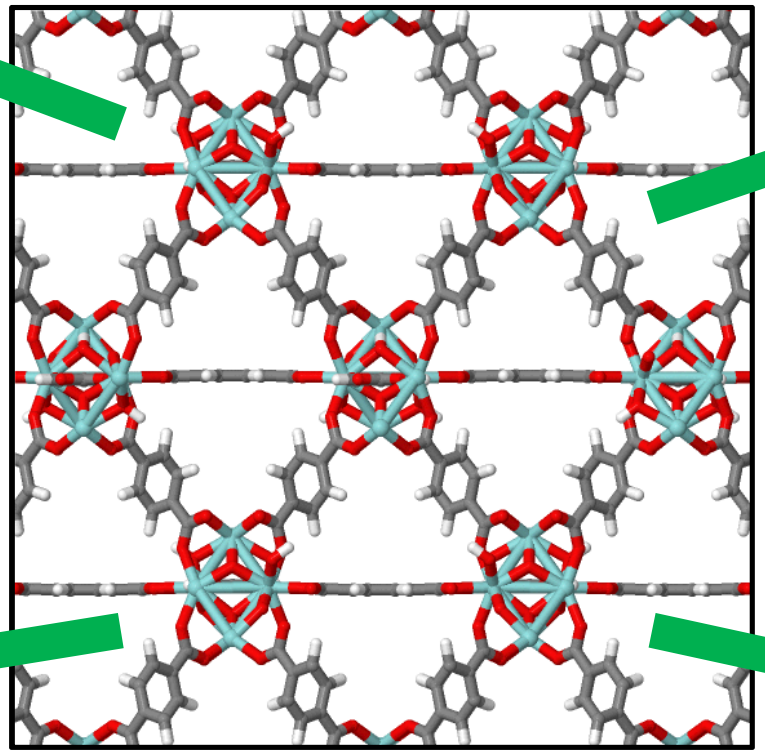
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

NNSA

Applications of Metal-Organic Frameworks

Separations

Sensing

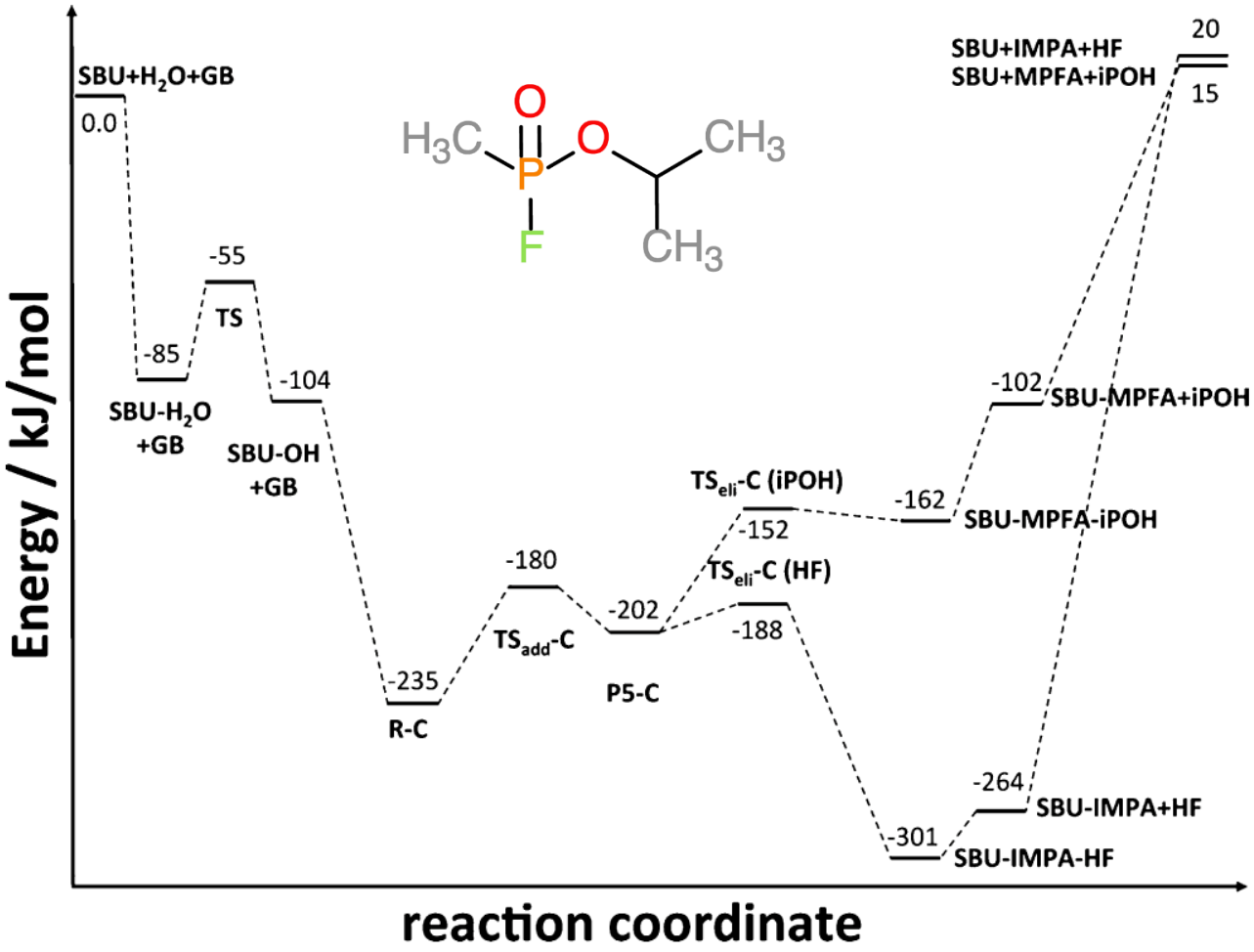


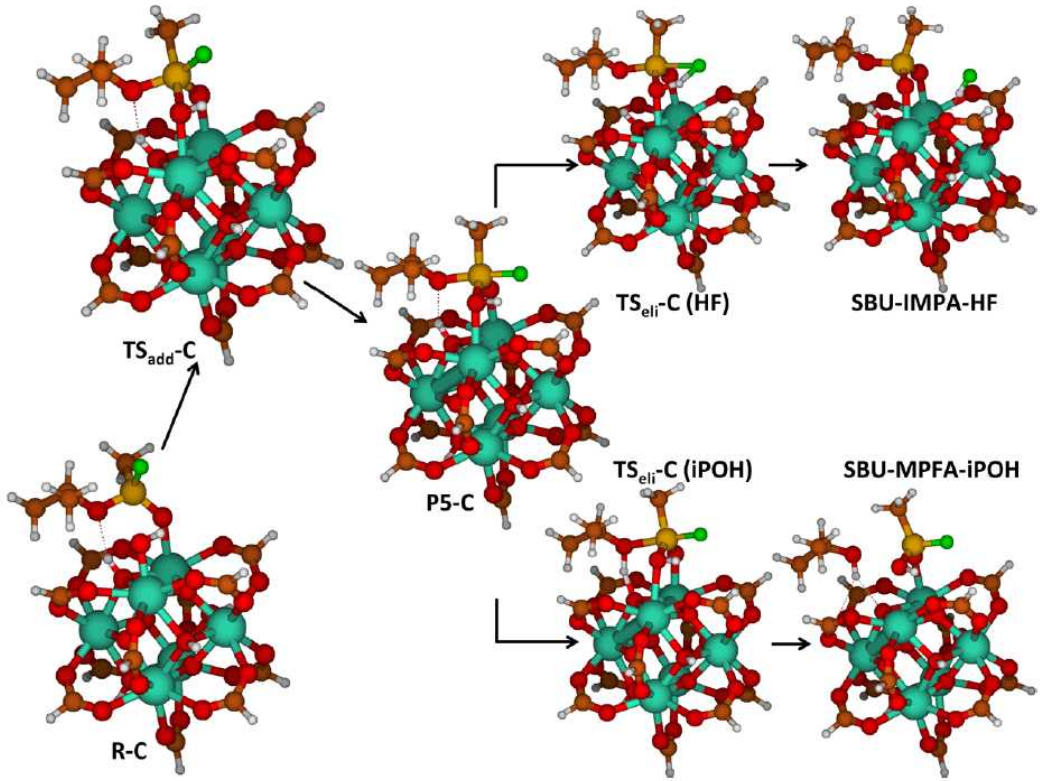
Drug Delivery

Catalysis

Degradation of chemical warfare agents (CWAs)

Computational CWA MOF Work

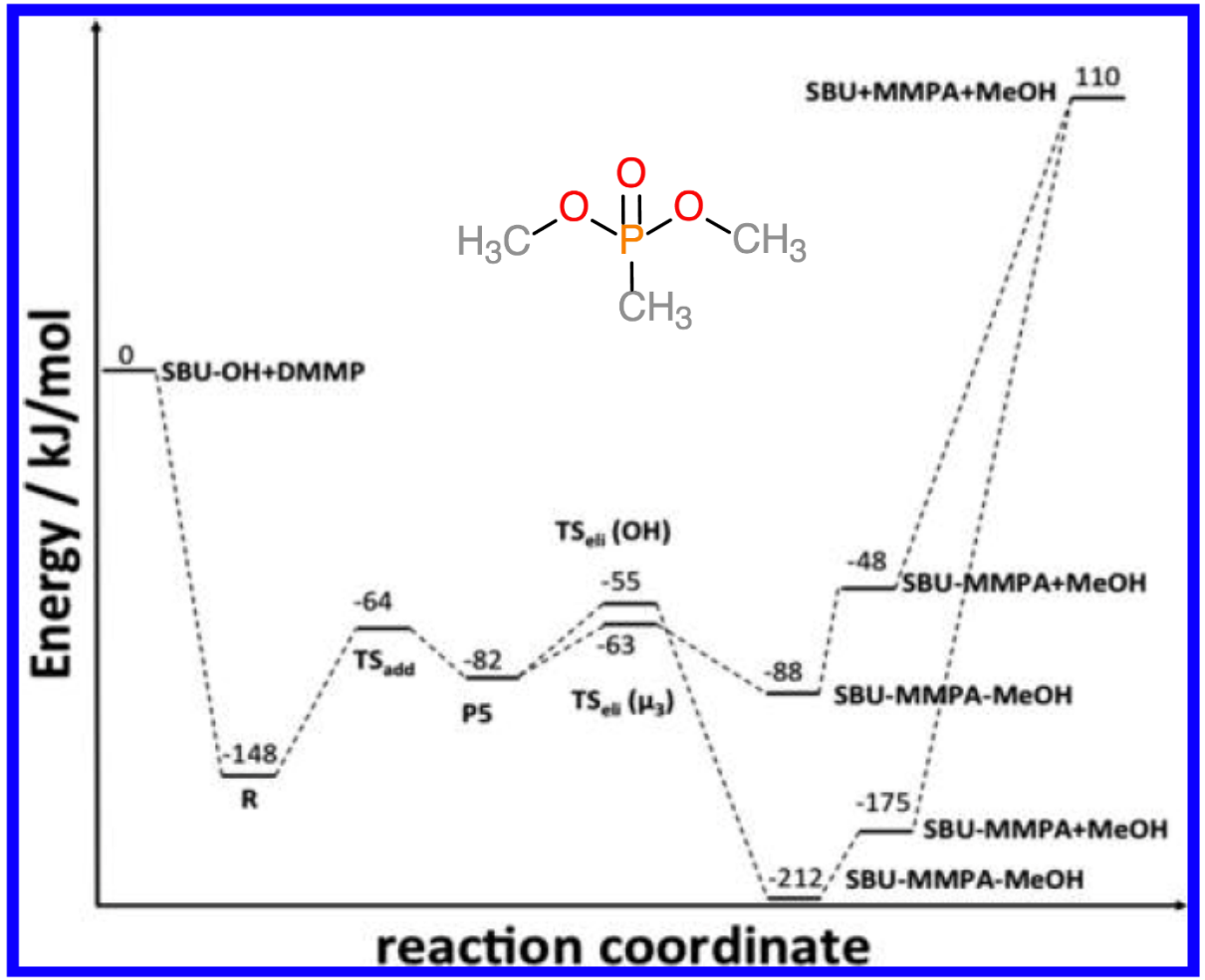


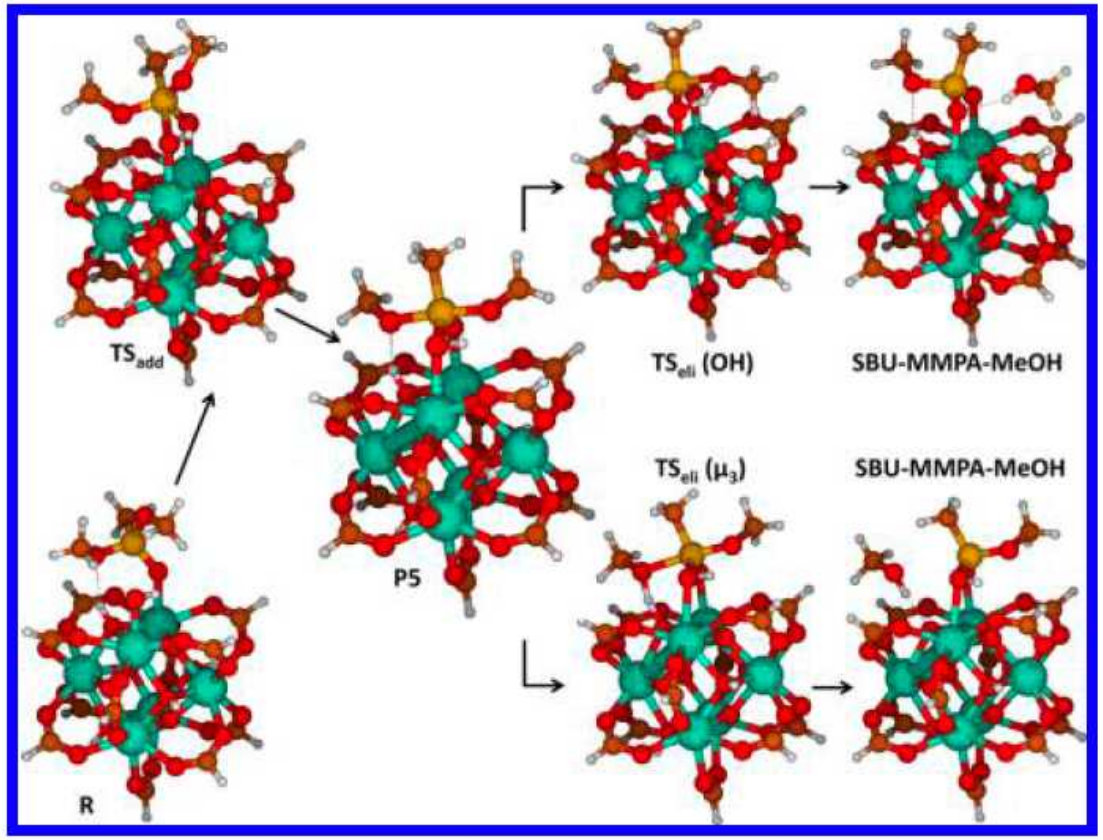


- Degradation of Sarin and DMNP on UiO-66

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

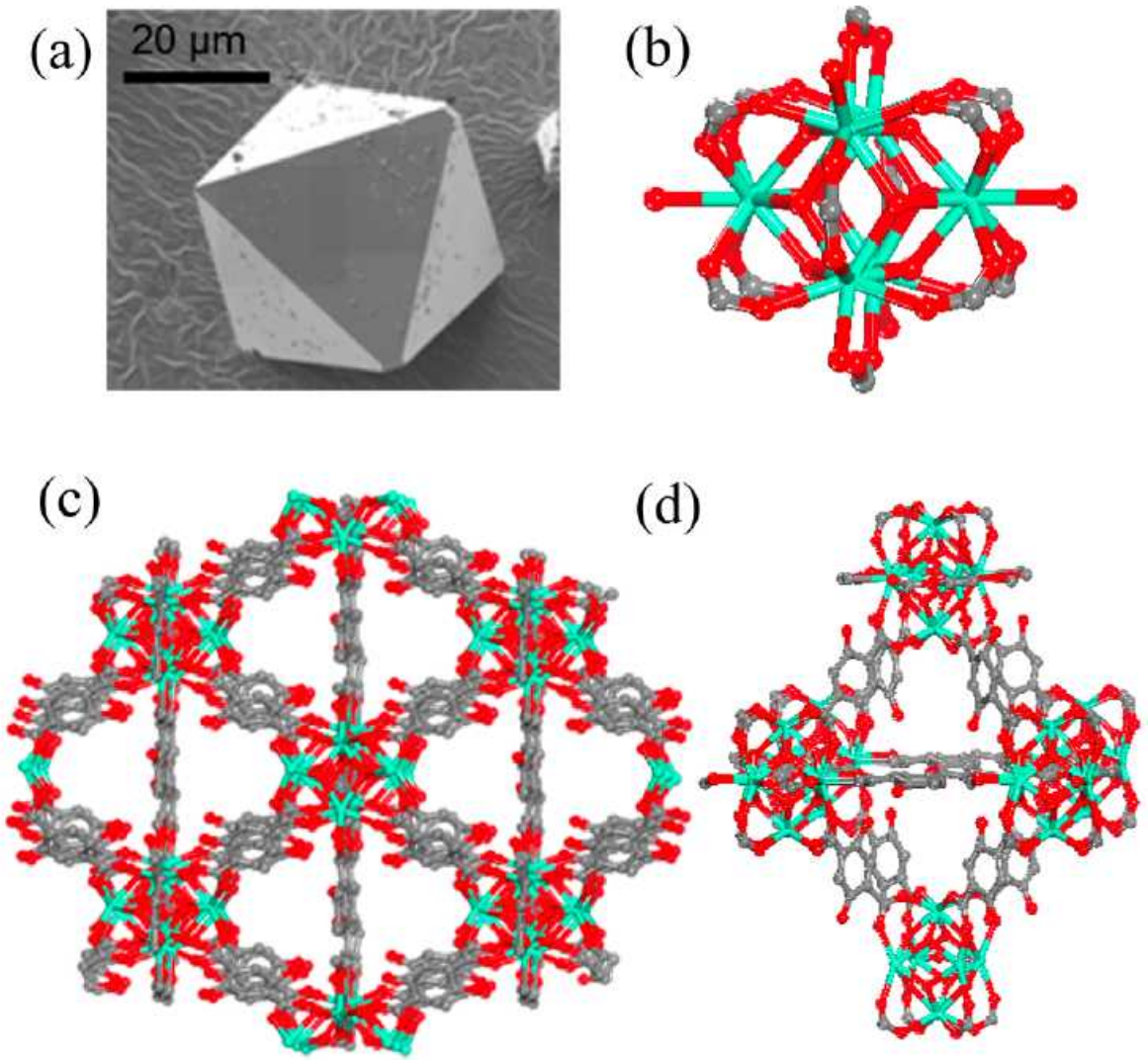
Computational CWA MOF Work

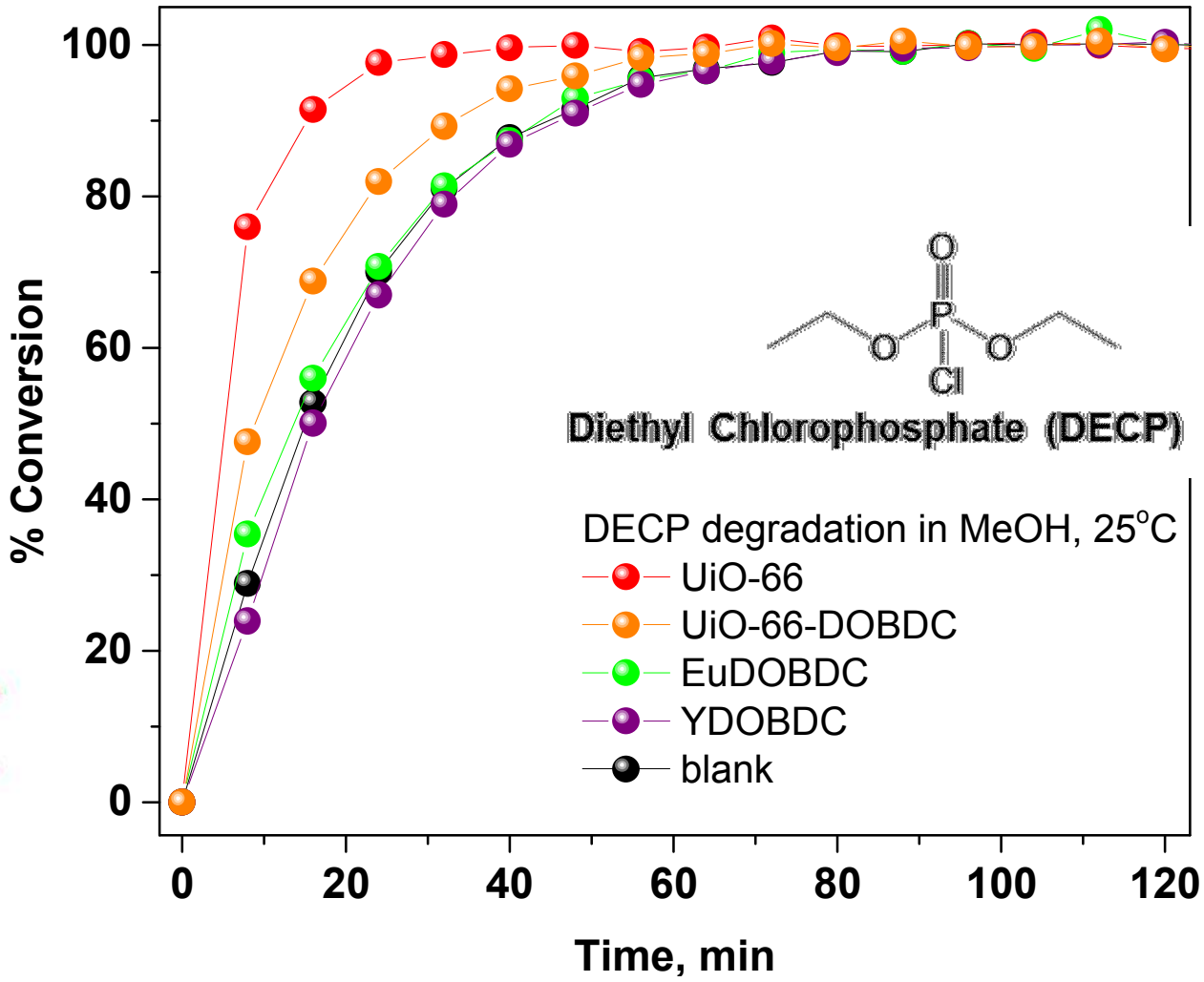




- Degradation of DMMP on UiO-66
- Computational work to date lacks systematic study of the effect of metal, ligand, and solvent

Rare-Earth Metal-Based MOFs





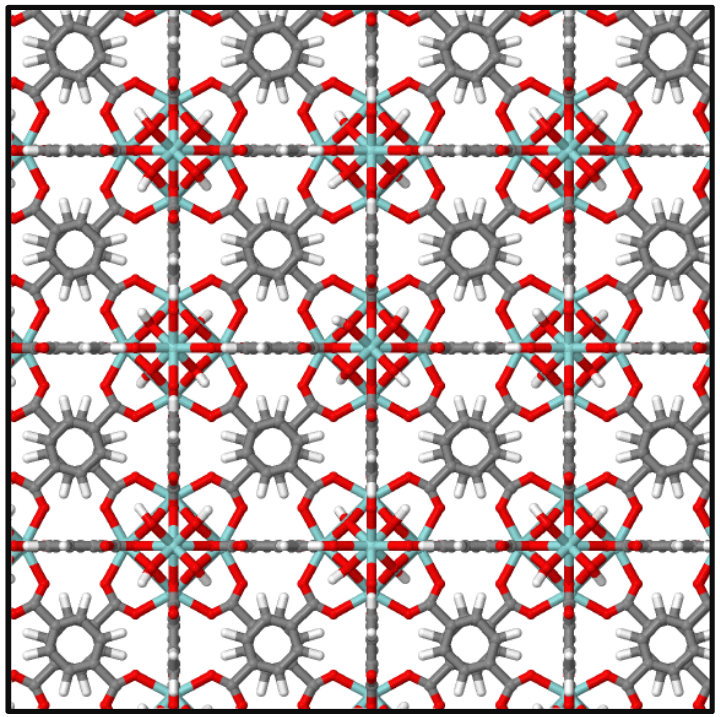
Sava Gallis et al, *ACS Appl. Mater. Interfaces* ***2017***, *9, 22268-2227*

Computational Methods

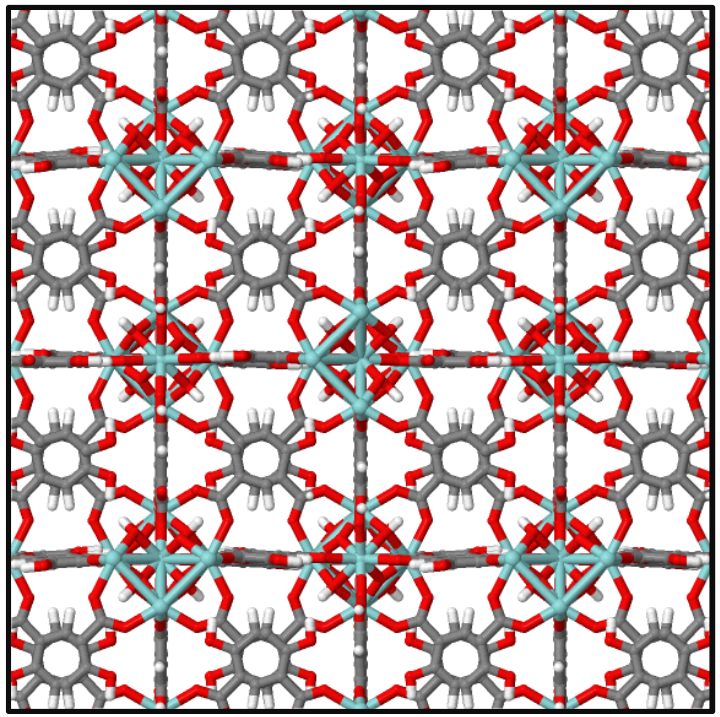
Periodic DFT:

- 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

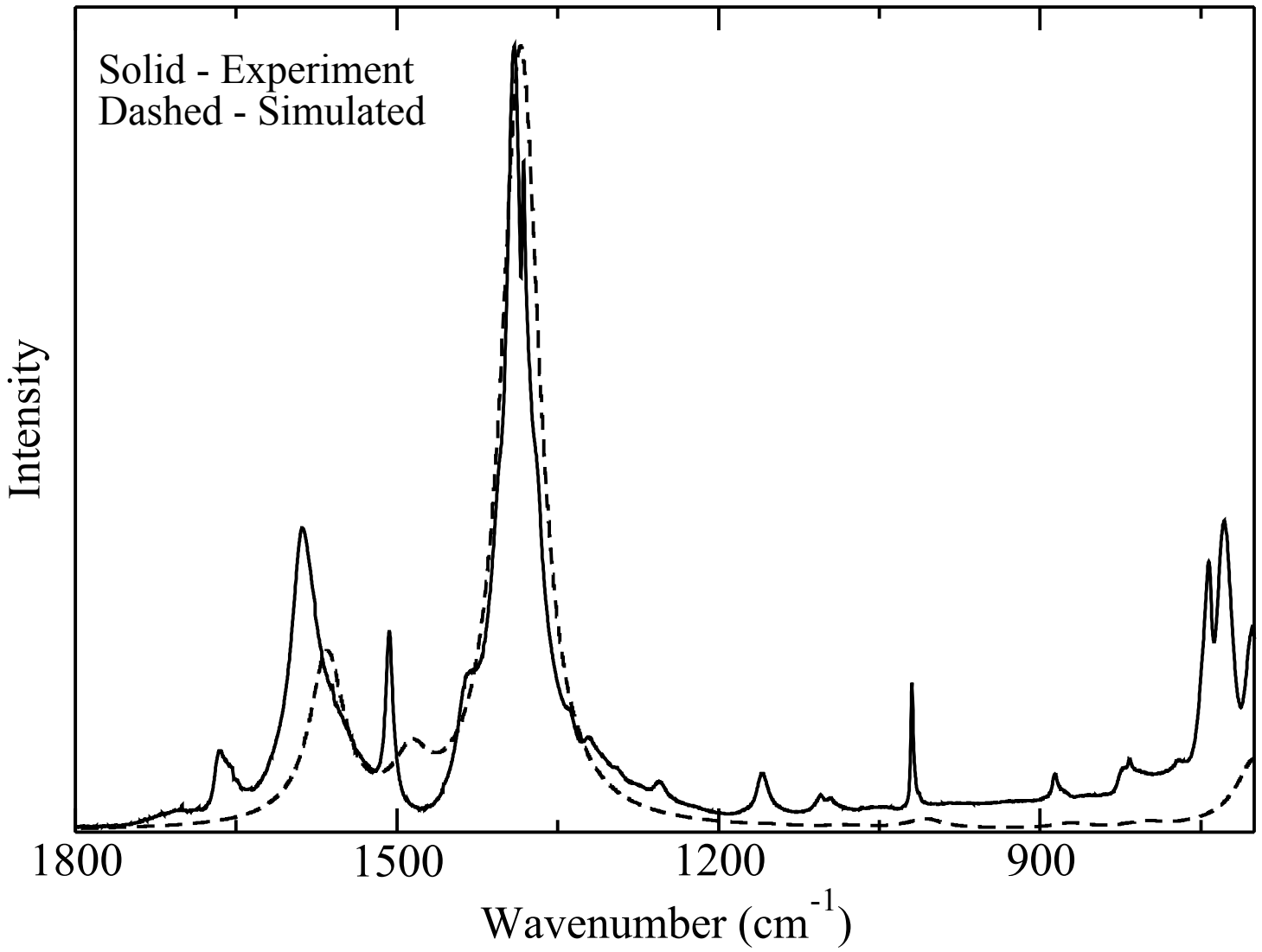
UiO-66(Zr)



M-DOBDC
(Zr, Y, Eu)



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

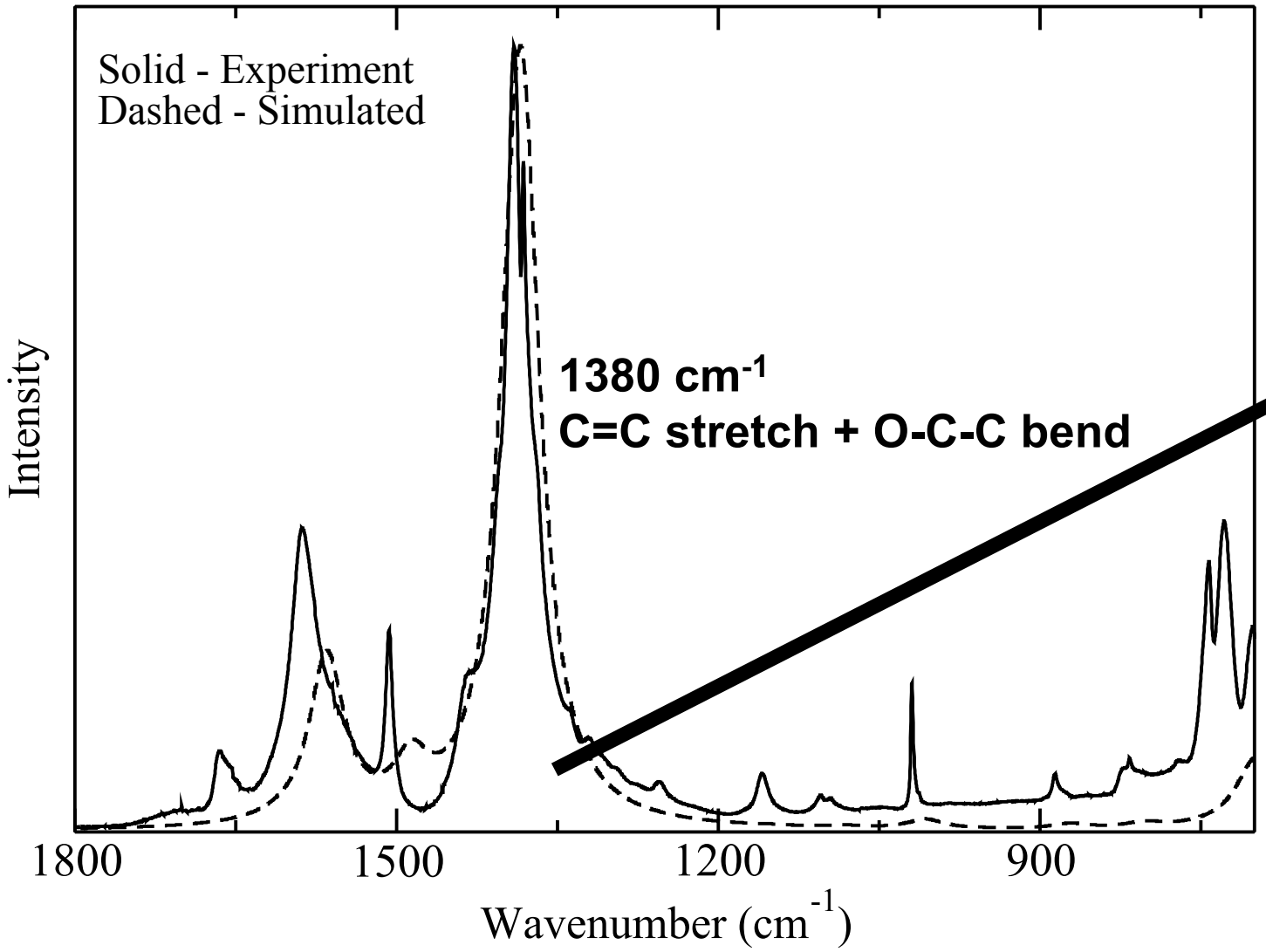
Born effective charge of s^{th} atom

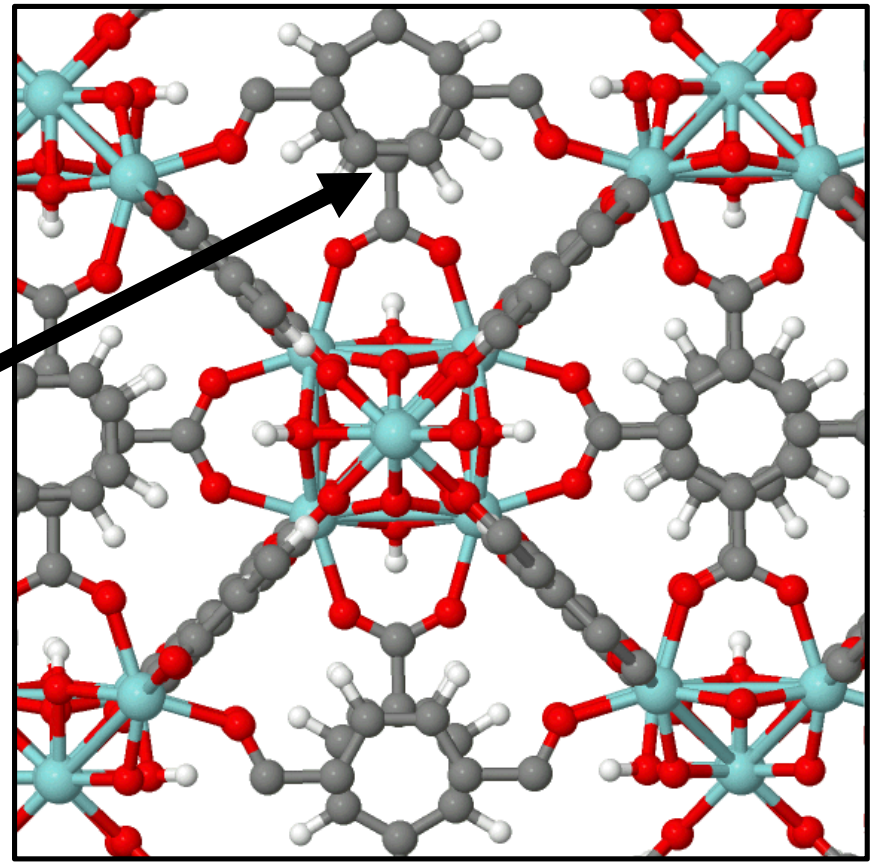
Vibrational eigenvector

- Apply Lorentzian broadening

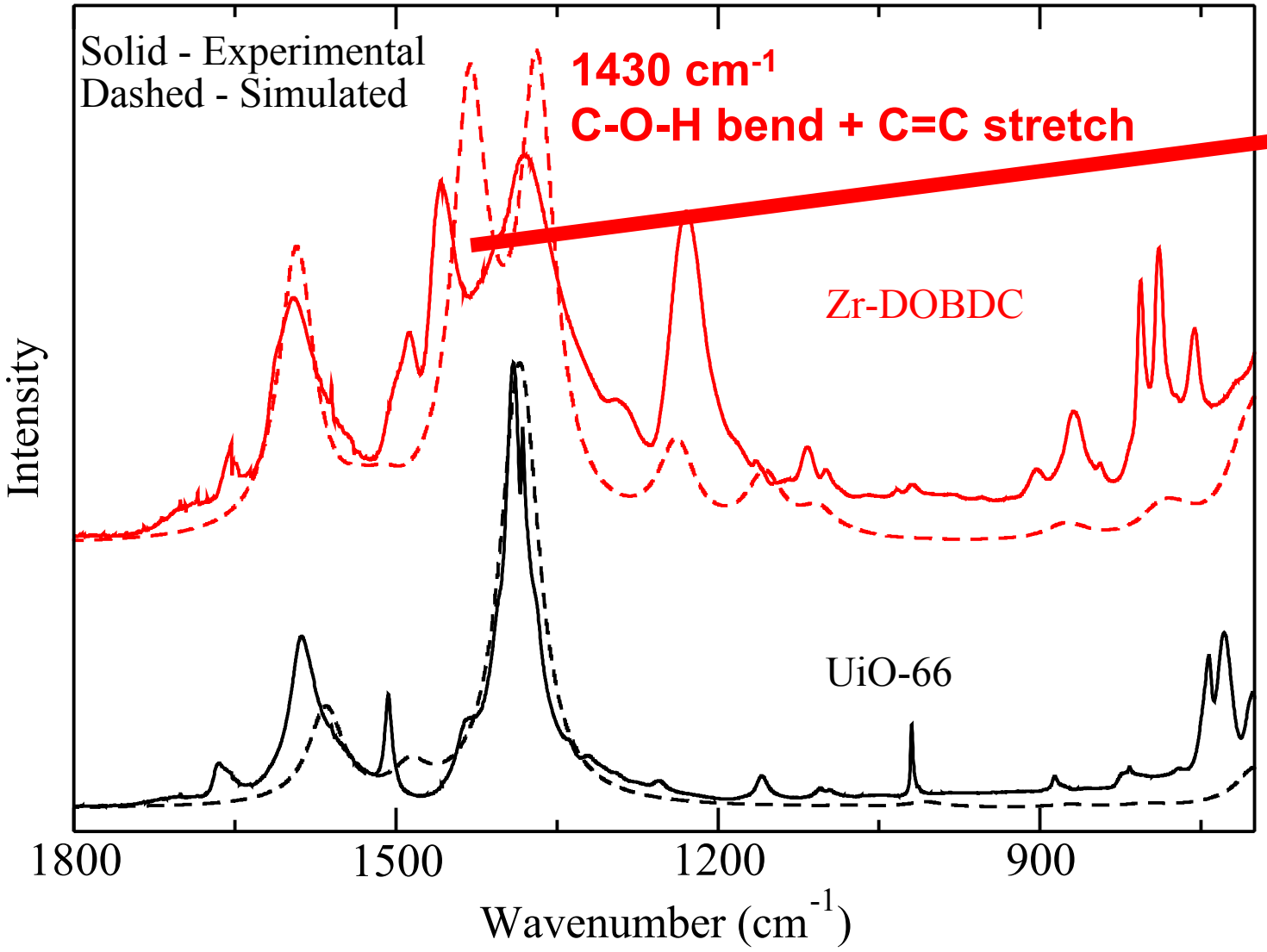
Phys. Rev. B **1991**, 43, 7231-7242
J. Chem. Phys. **1994**, 100, 8537-8539
Rev. Mod. Phys. **2001**, 73, 515-562
J. Phys. Condens. Matt. **2010**, 22, 265006

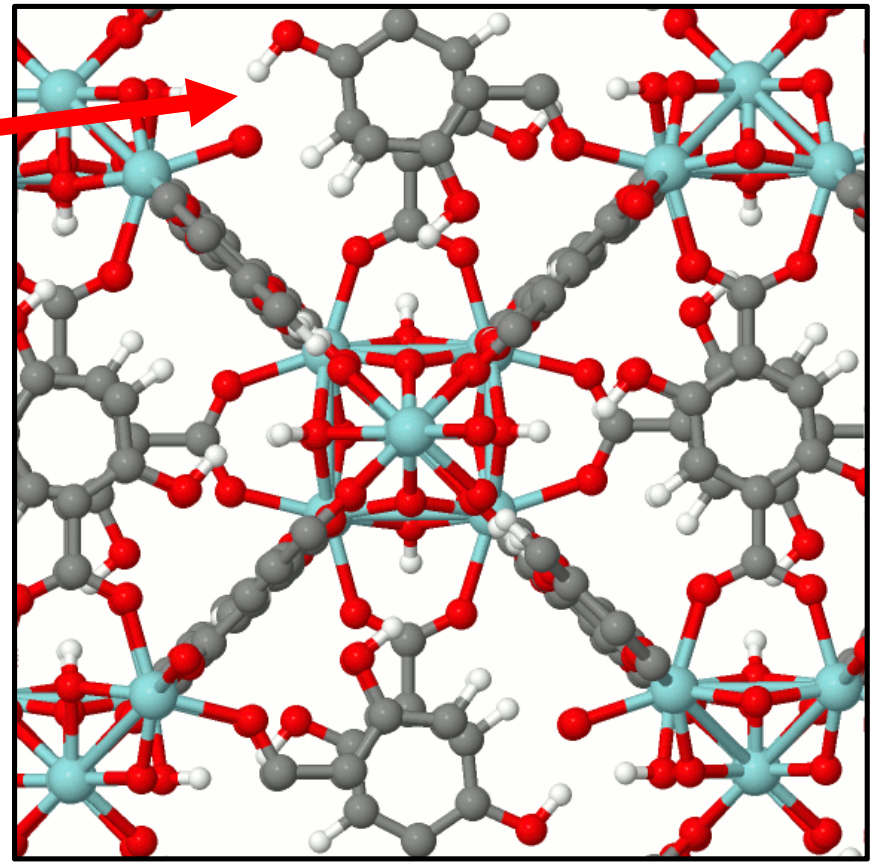
UiO-66 Infrared Spectrum



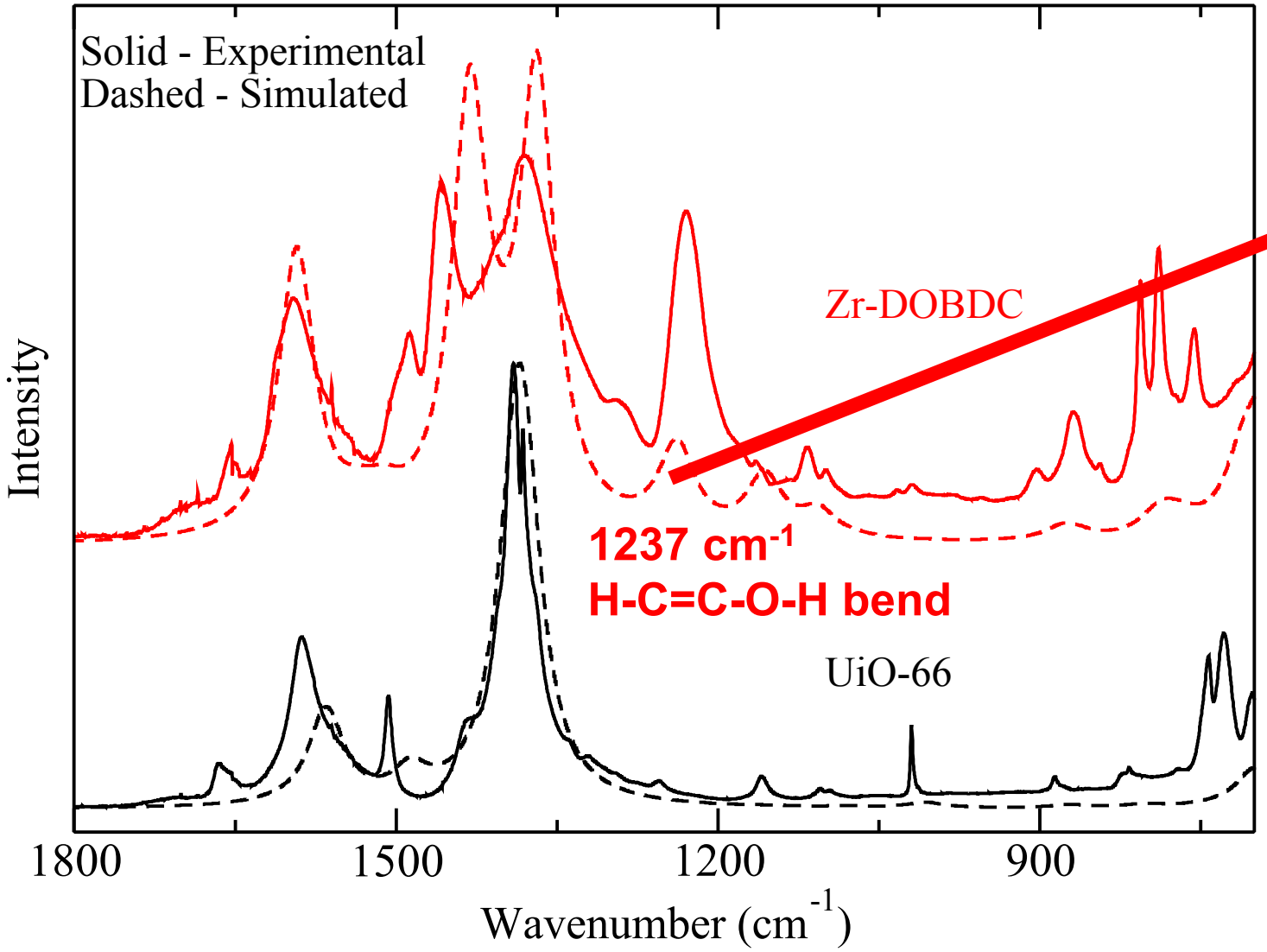


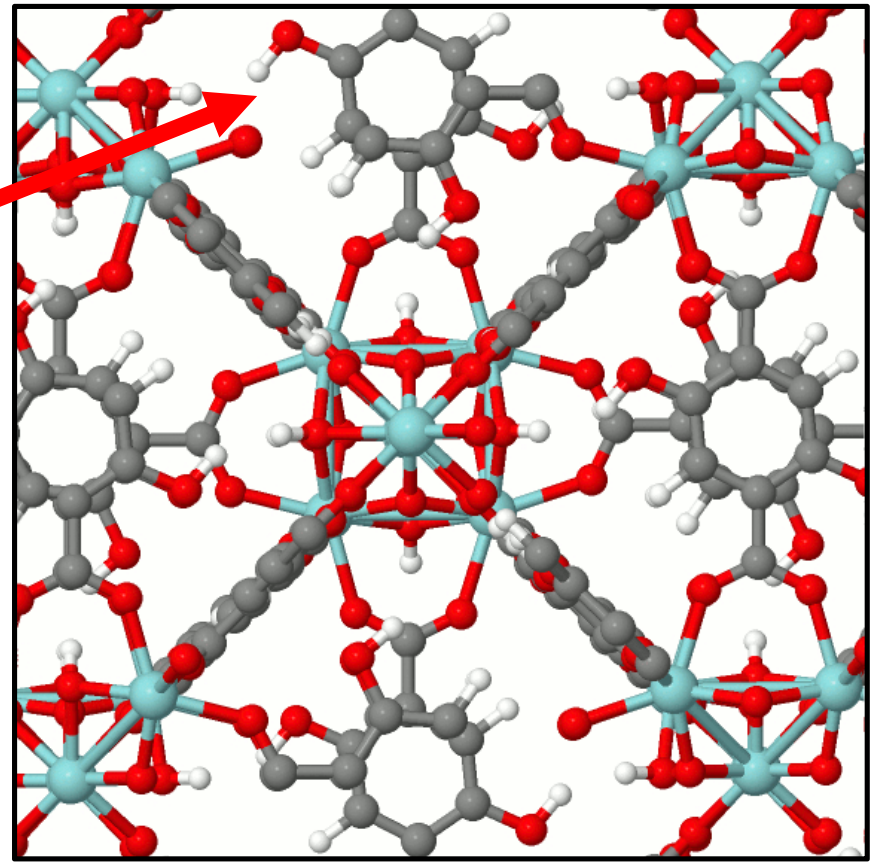
Effect of Ligand



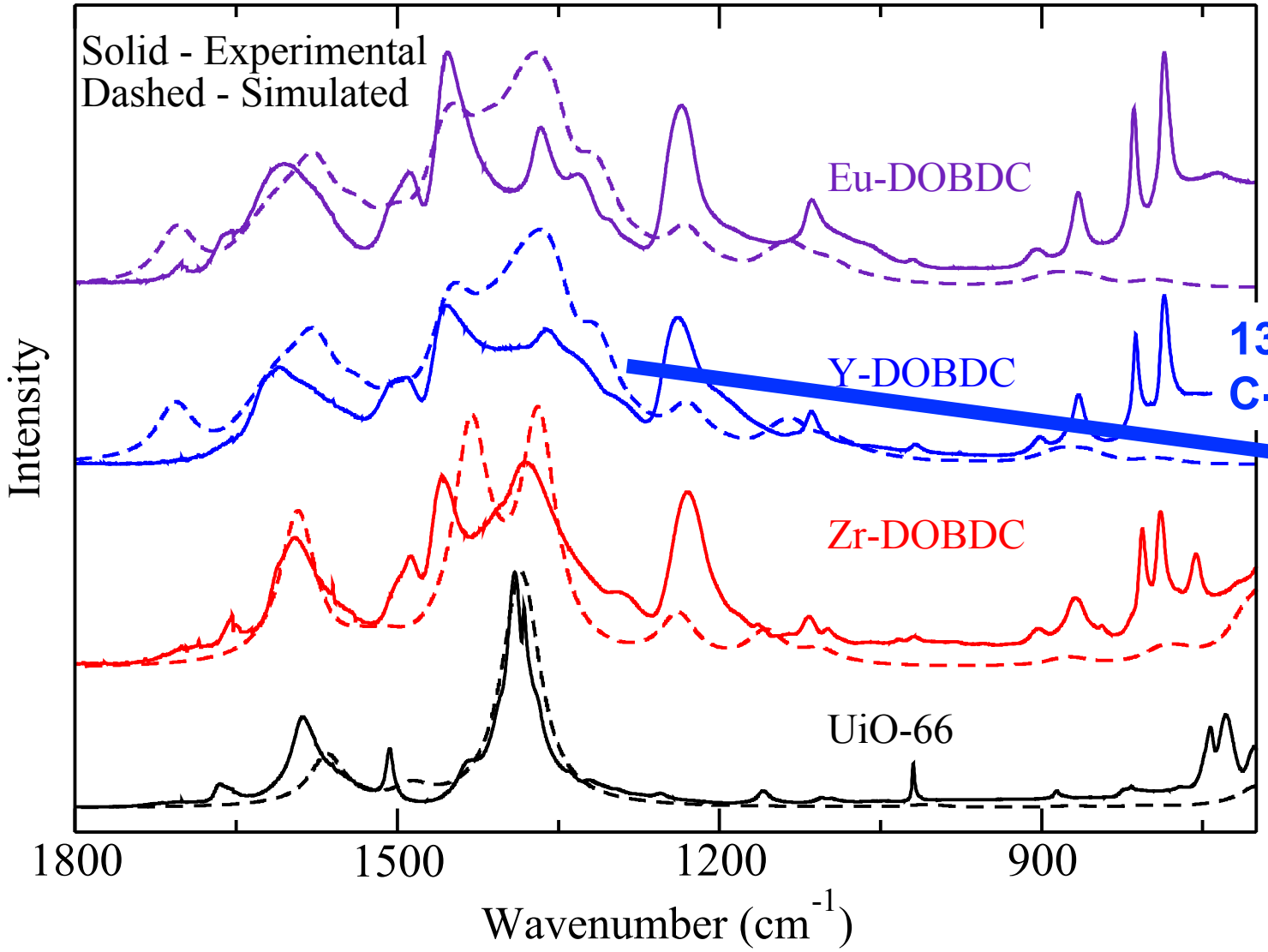


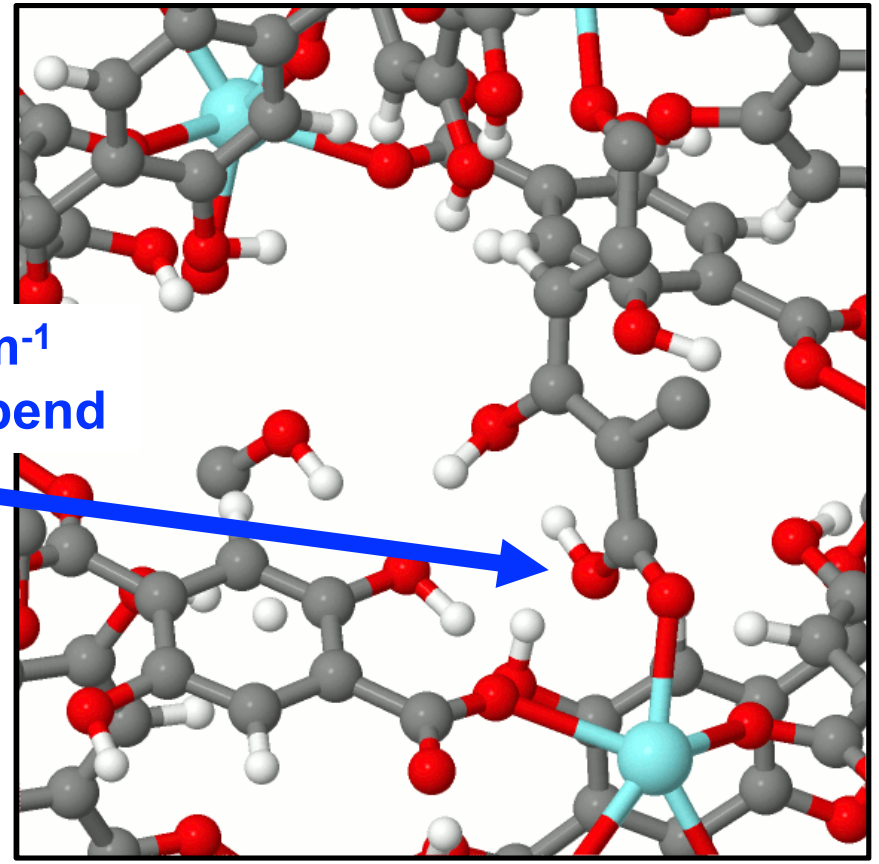
Effect of Ligand





Effect of Metal

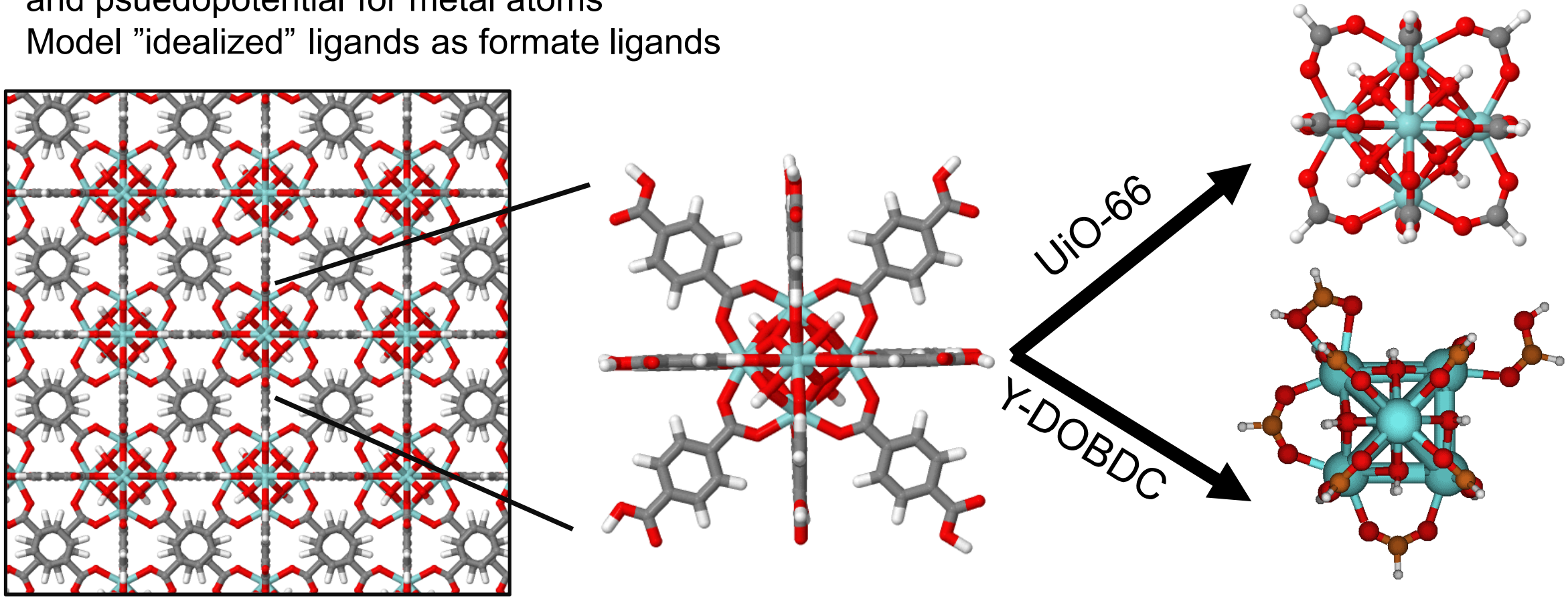




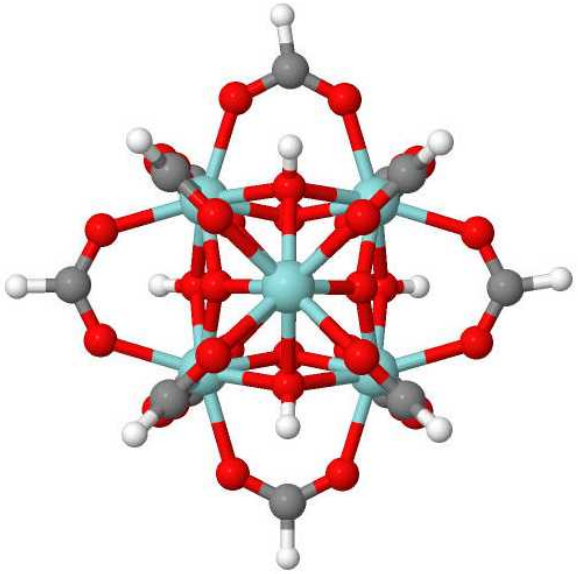
Computational Methods

Gas Phase Cluster DFT → Binding Energies

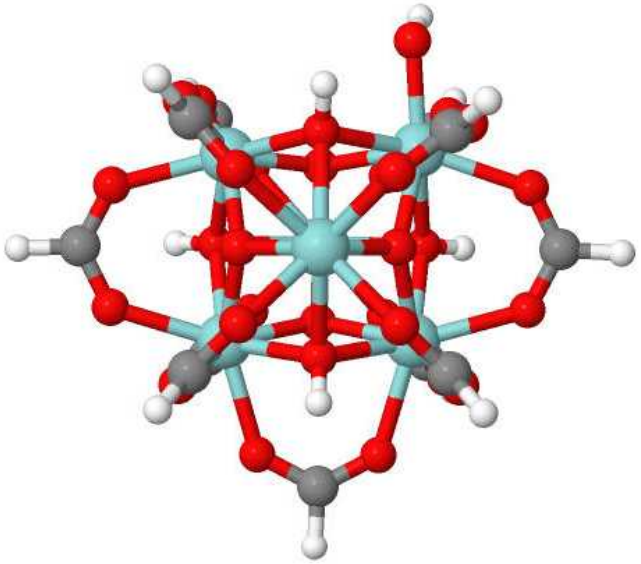
- Cut clusters from VASP optimized structure
- Optimize clusters with MO6-L functional, def2-SVP basis set for all non-metal atoms and SDD ECP and psuedopotential for metal atoms
- Model ”idealized” ligands as formate ligands



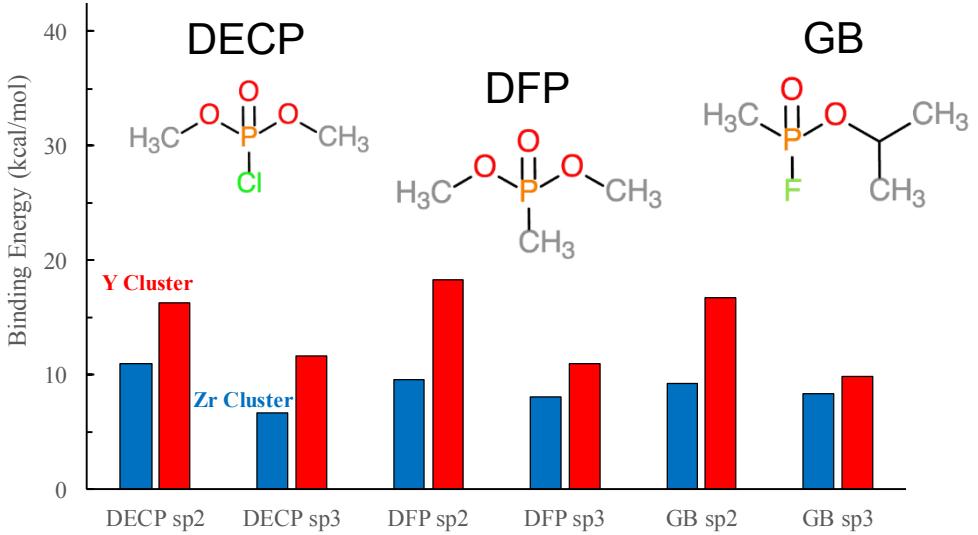
Binding Energy - Acetate Clusters

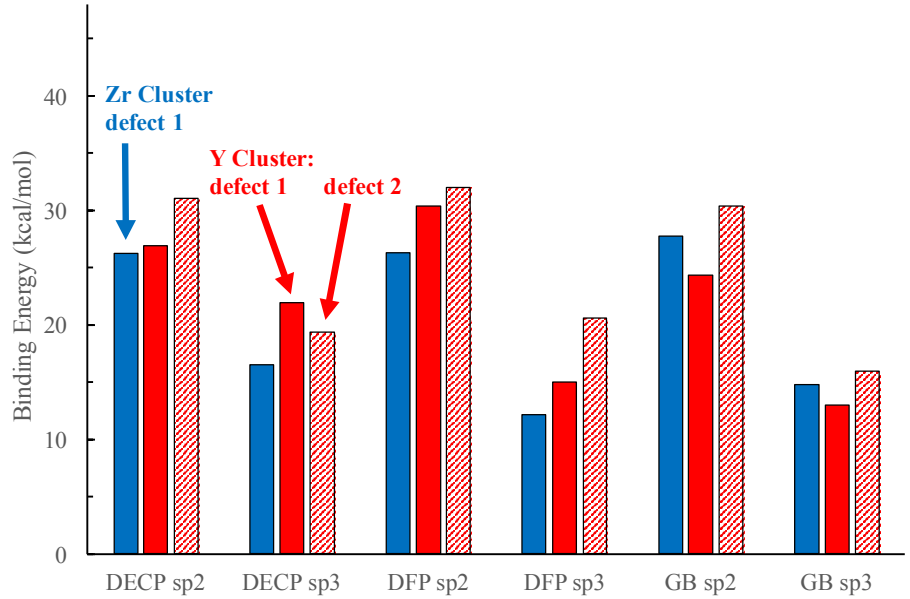


Defect-free clusters

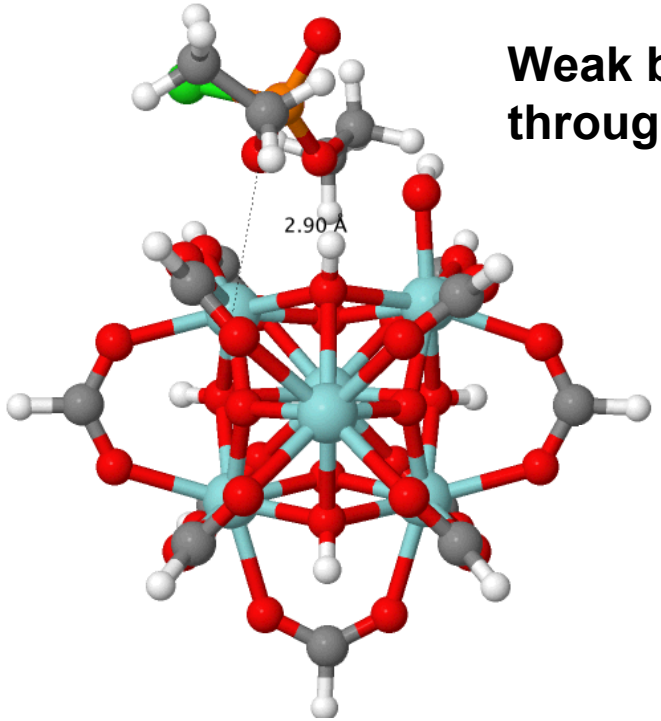


Defect sites
- CHO_2
+ H_2O
Stronger Binding

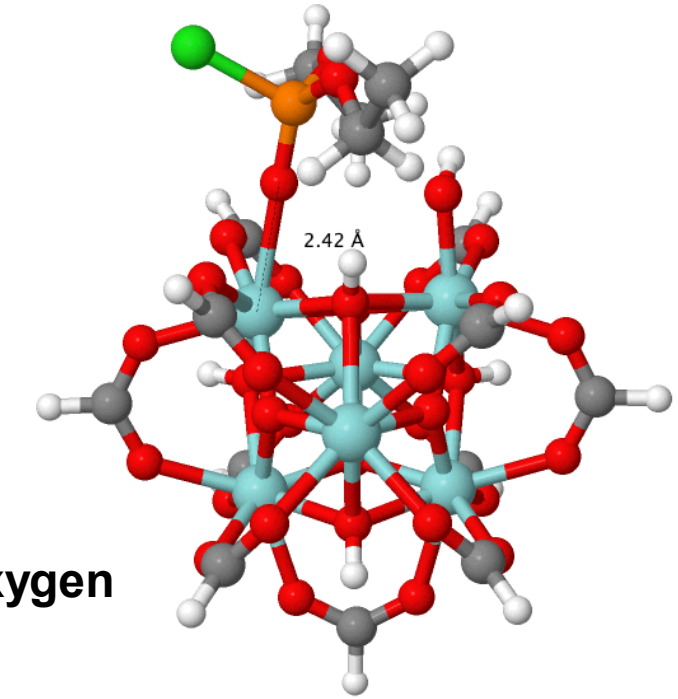




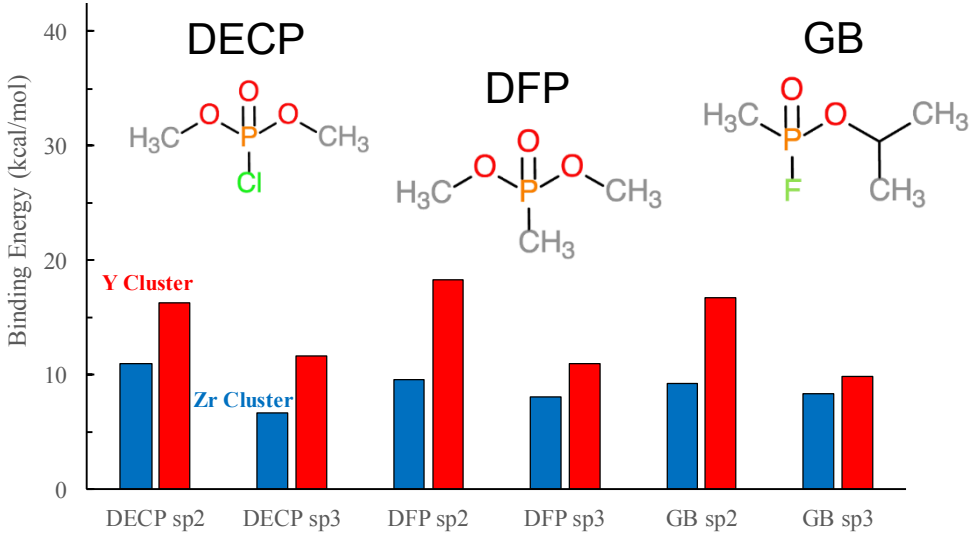
Binding Energy - Acetate Clusters

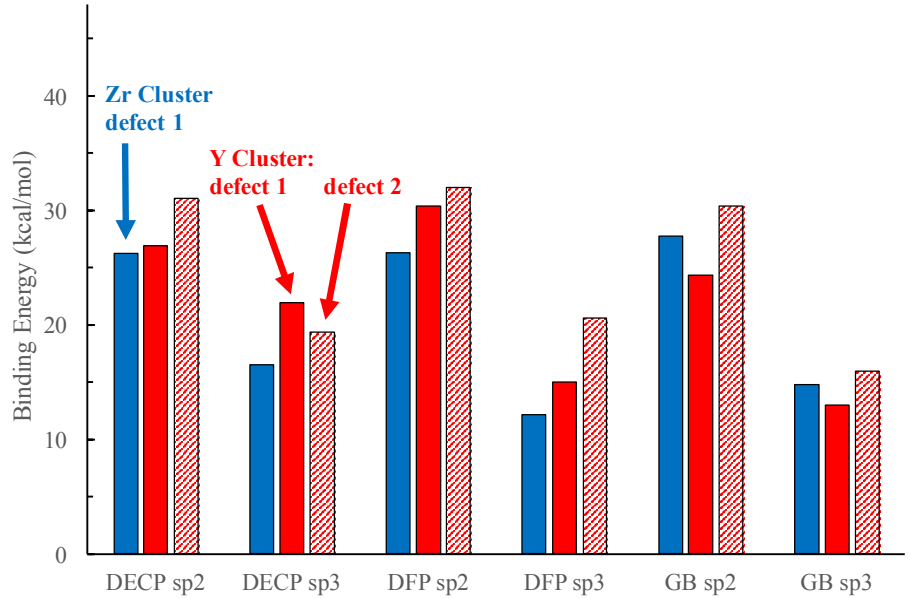


Weak binding through sp3 oxygen

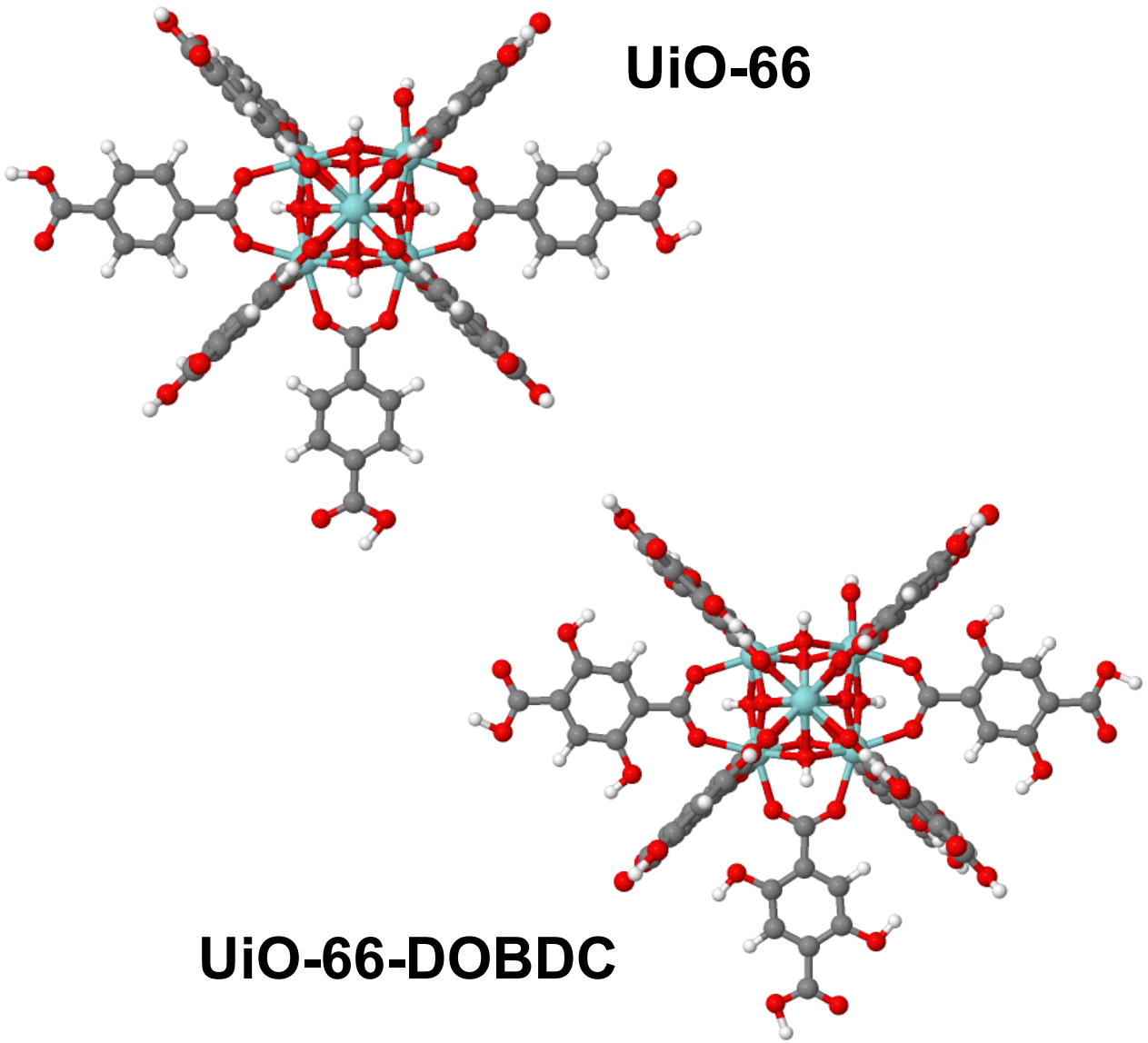


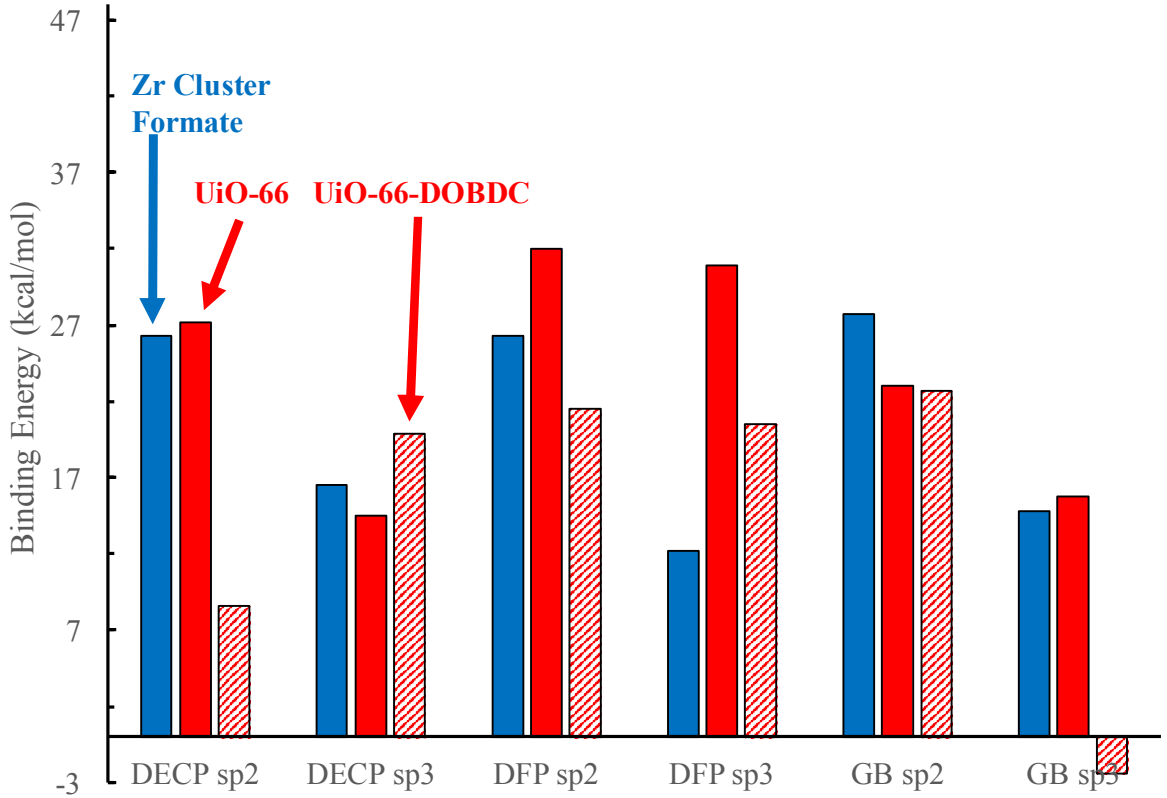
Strong binding through sp2 oxygen



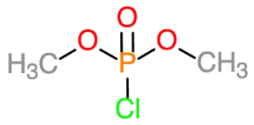


Effect of Linker

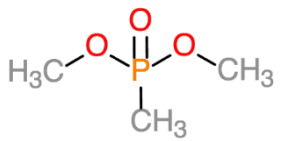




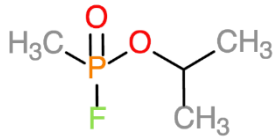
DECP



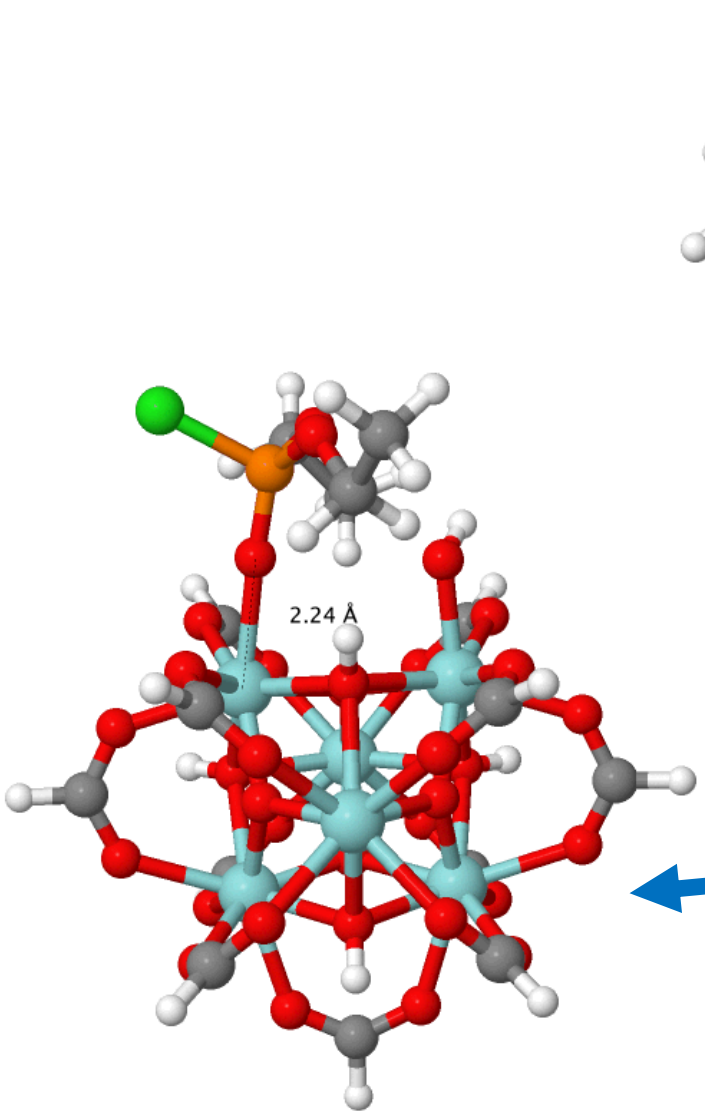
DFP

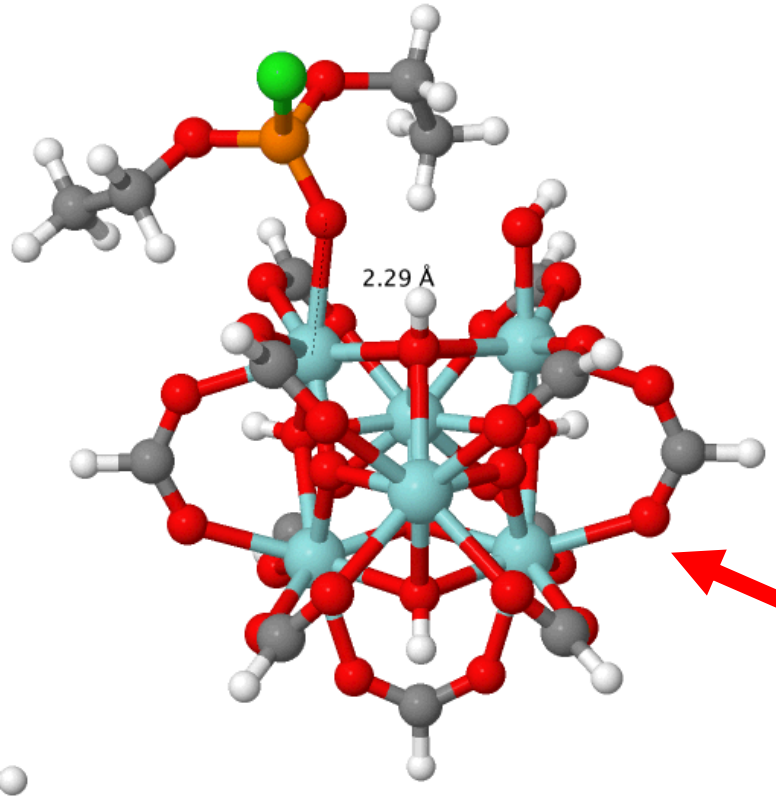


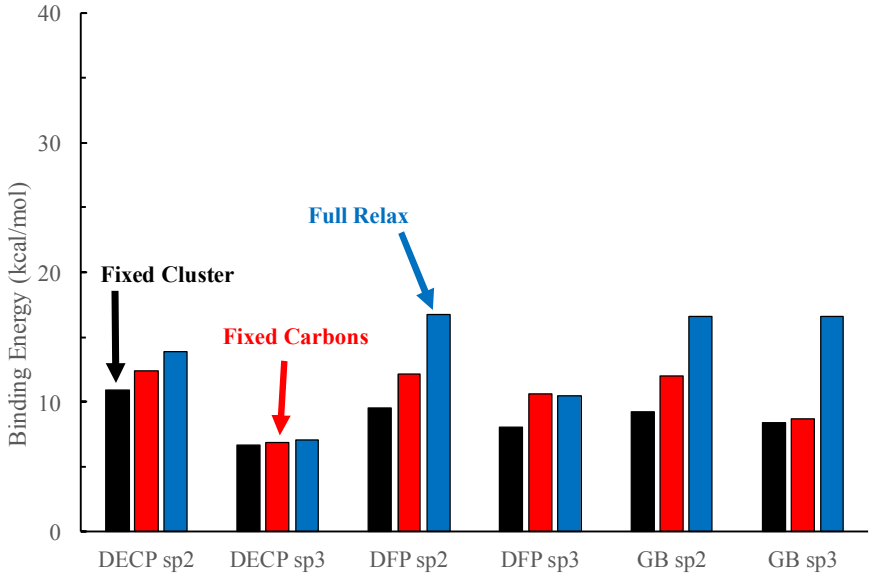
GB

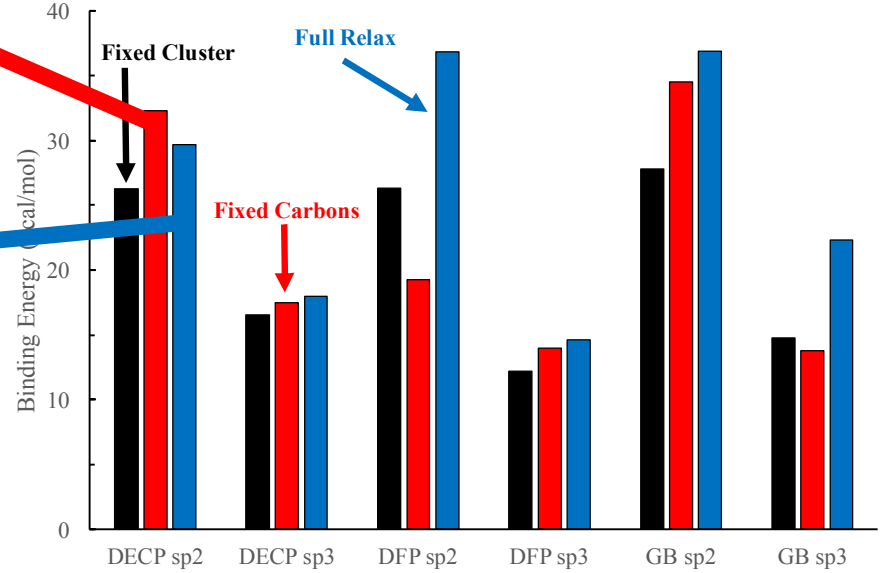


Effect of Cluster Relaxation









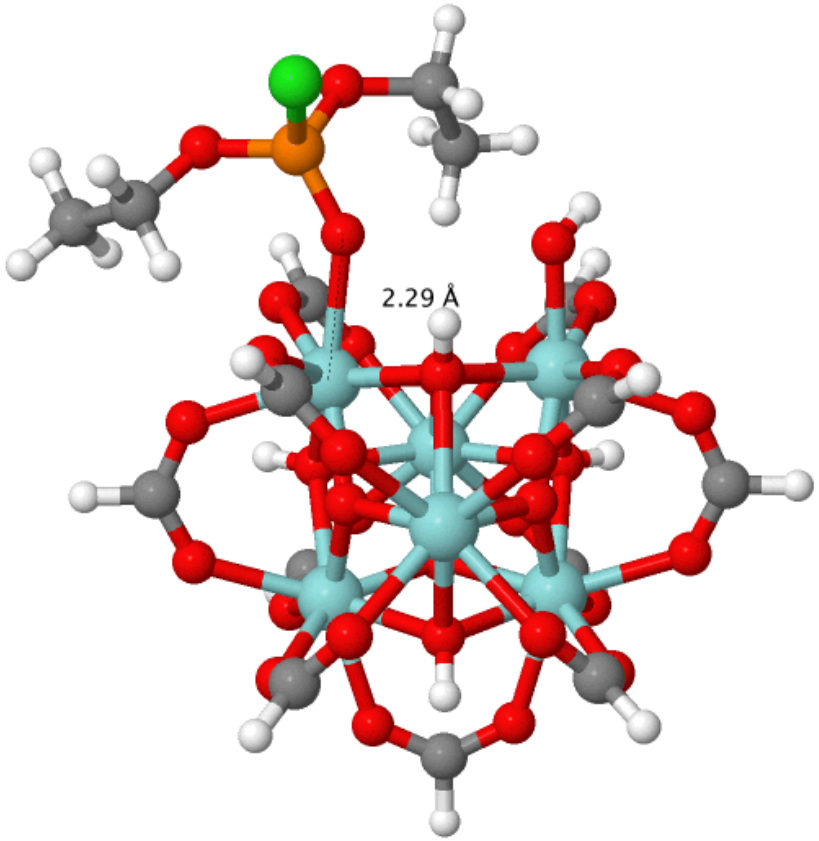
Conclusions

Periodic models

- Vibrational analysis confirms structural properties of synthesized MOFs.
- Excellent agreement with experimental spectra.
- Insight into key modes in the IR spectrum.

Cluster models

- Simulant and CWA binding by MOFs.
- Enhanced binding at defect sites and via sp2 oxygen.
- Effects due to metal type and linker functionalization are not conclusive. More calculations needed.



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.