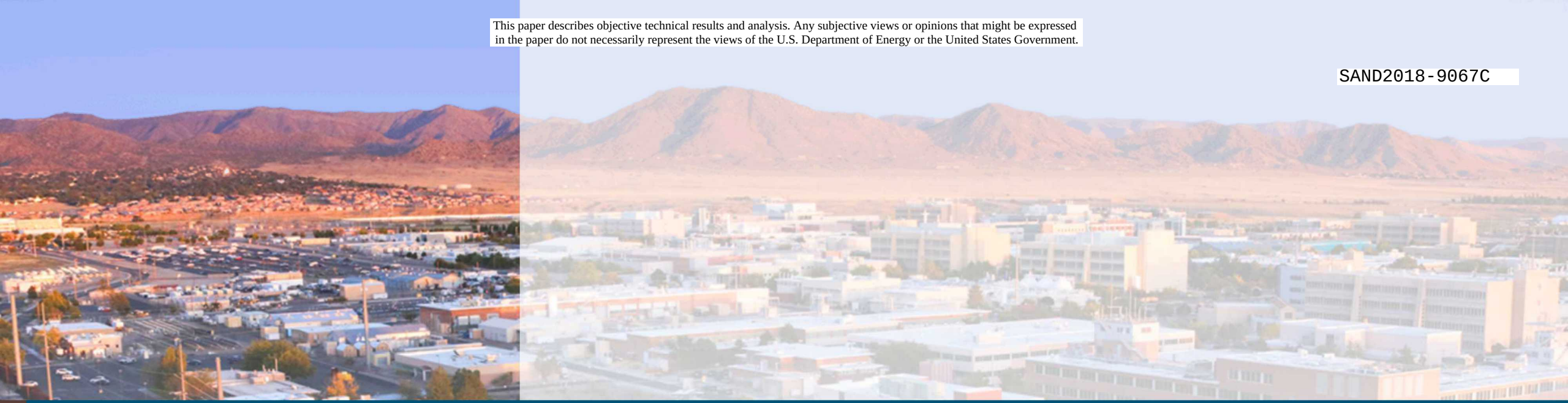
SAND2018-9067C



Insights into the binding and degradation of organophosphates on MOFs from a complementary experimental-modeling study

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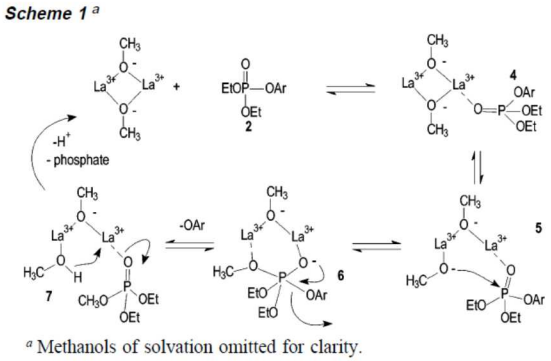
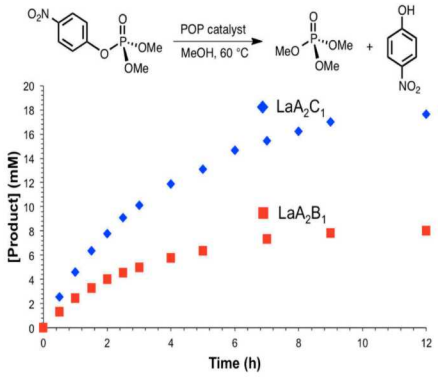
[§] Laboratories, Albuquerque, NM 87185, USA

Goal: Investigate chemistries to degrade organophosphorous compounds in water free environments; identify suitable simulants

Billion-fold Acceleration of the Methanolysis of Paraoxon Promoted by La^{3+} complexes



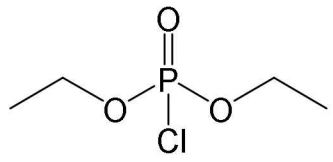
La $^{3+}$ catechol-functionalized POPs show accelerated activity towards methanolysis



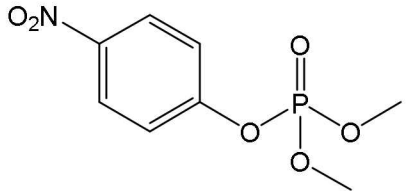
Methanolysis of organophosphates is accelerated by La-based catalysts

- The molecular structure/reactivity of simulants vs. Chemical Warfare Agents (CWAs) is different
- Tests performed on CWAs are not trivial and conducted only at authorized facilities
- Simulants allow screening of materials

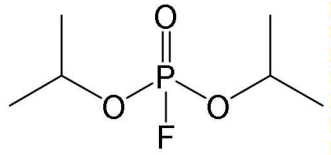
Increase in Correlation to Live Agent?



Diethyl Chlorophosphate (DECP)



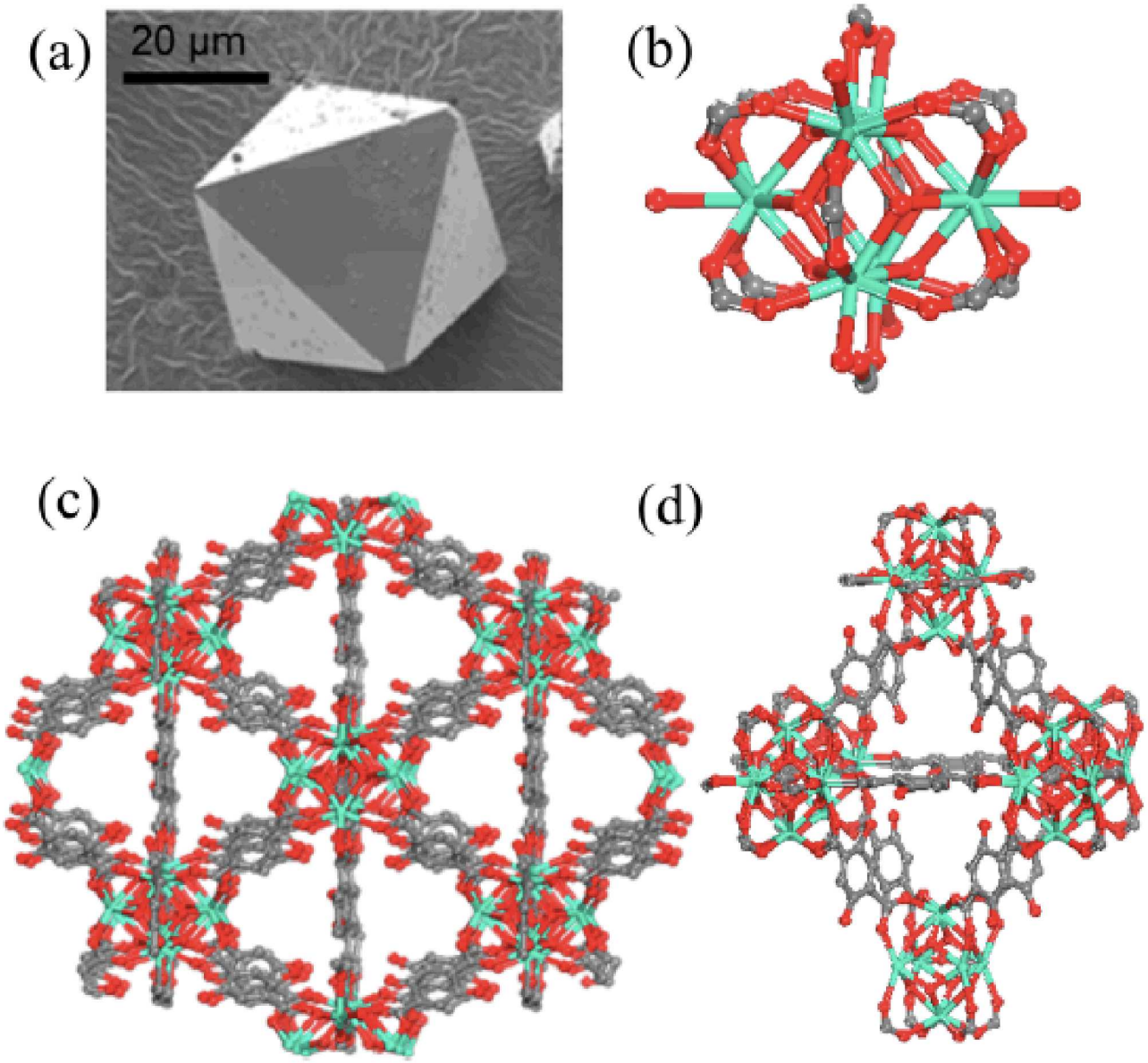
Dimethyl Nitrophenylphosphate (DMNP)

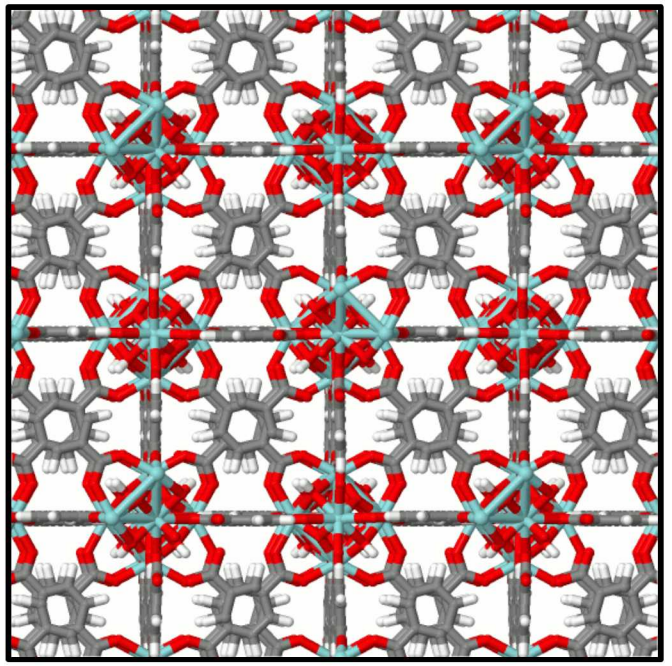


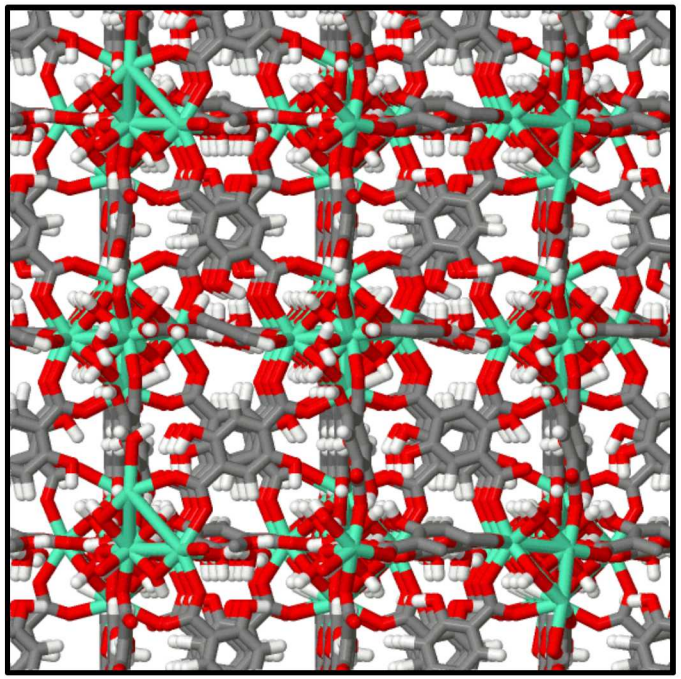
Diisopropyl Fluorophosphate (DFP)

J. Am. Chem. Soc. **2003**, *125*, 7602-7607.
ACS Catal. **2013**, *3*, 1454−1459

Rare-Earthed Based MOFs: 3D Structure

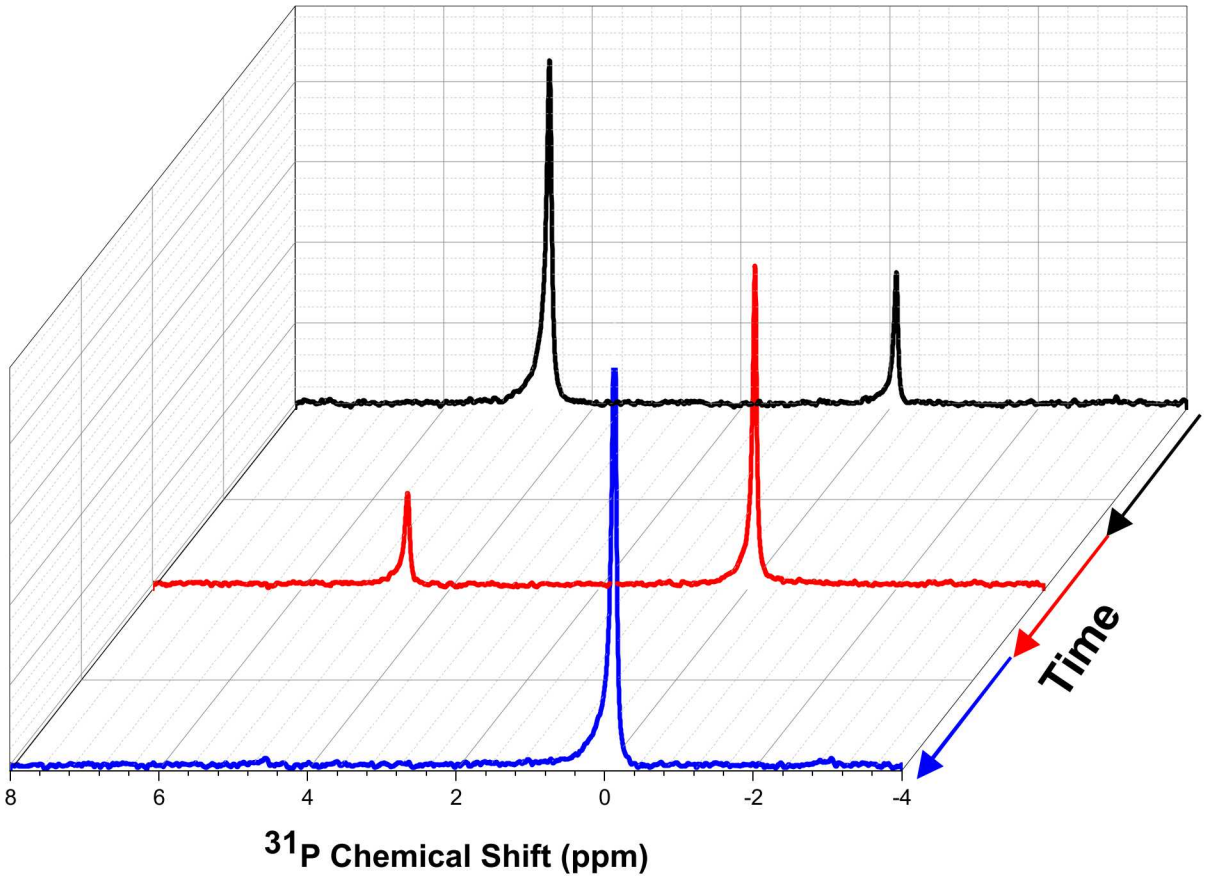


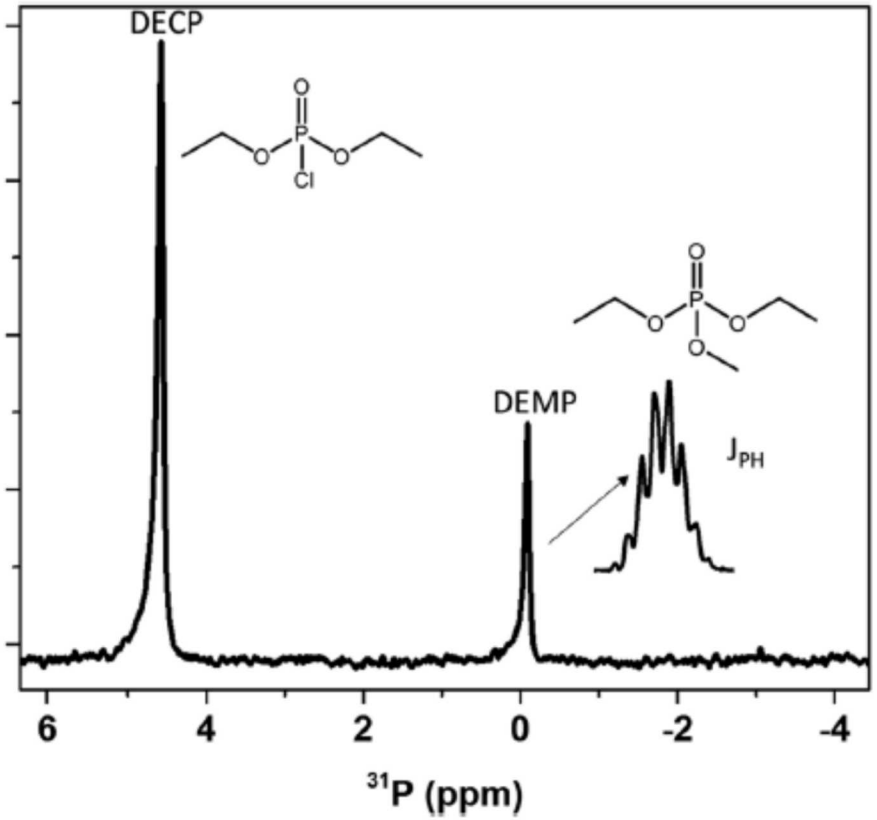




ACS Appl. Mater. Interfaces **2017**, 9, 22268-22277

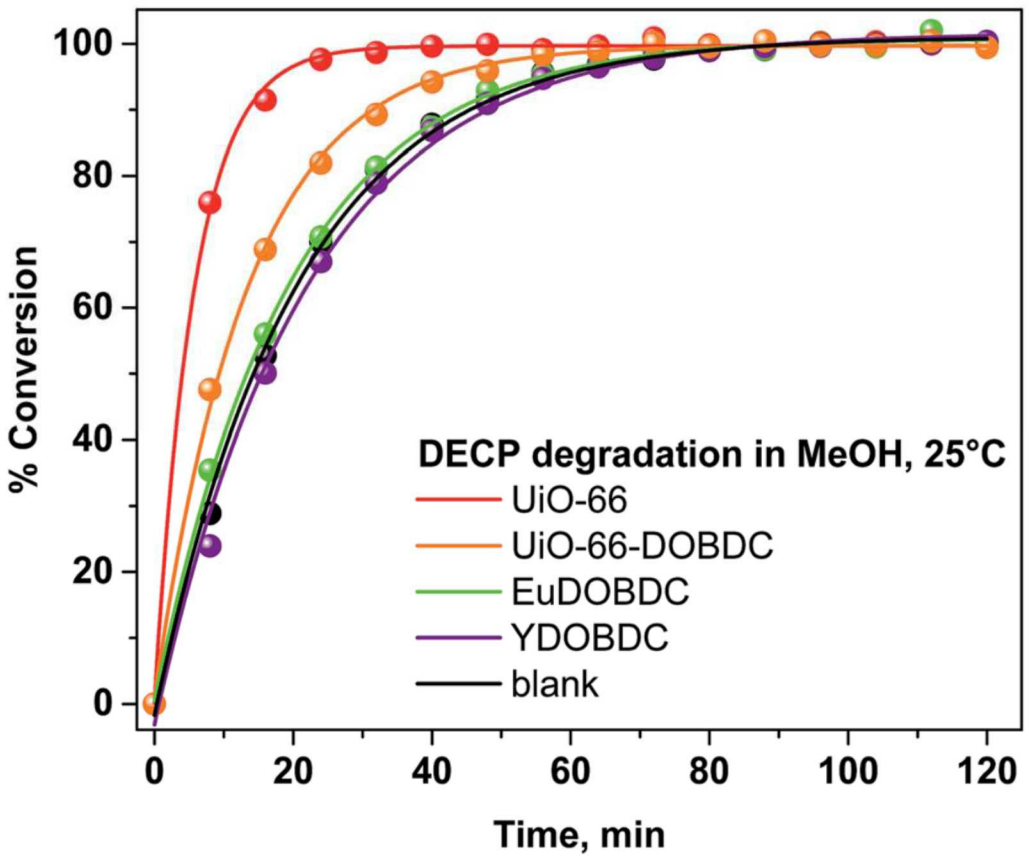
An Example NMR Spectrum for Degradation Monitoring

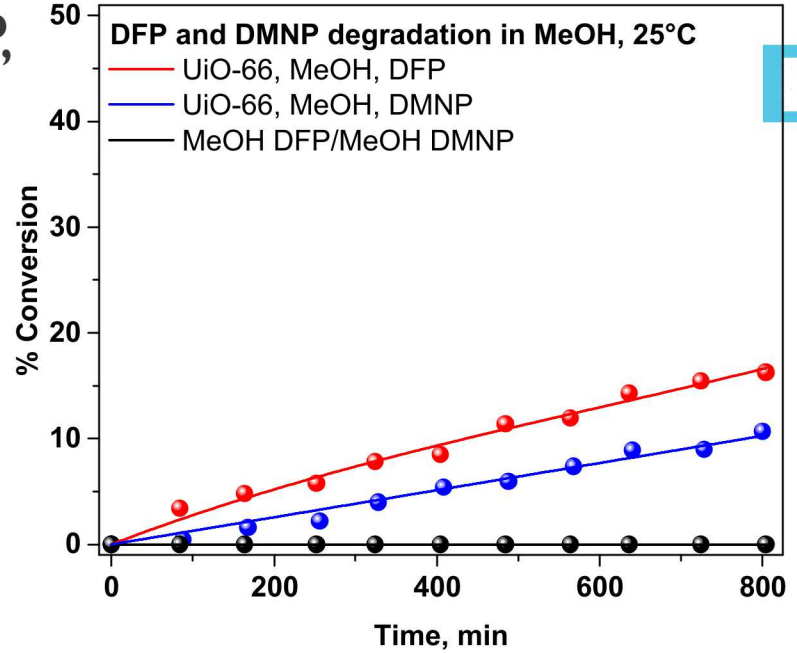


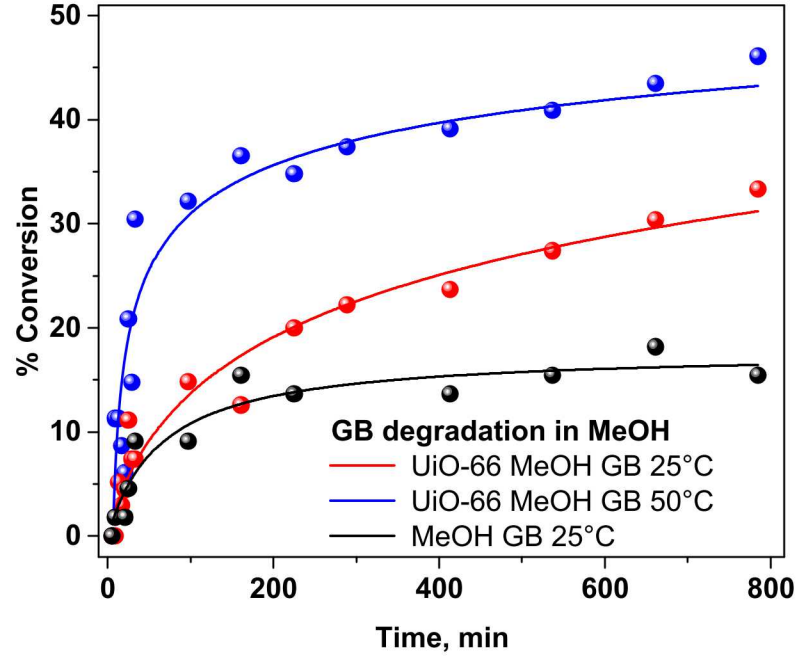


- NMR allows for quantitative and sensitive monitoring of degradation process; and unambiguous determination of the product species

Rare Earth and UiO-66 degradation of DECP, DMNP, DFP, and GB



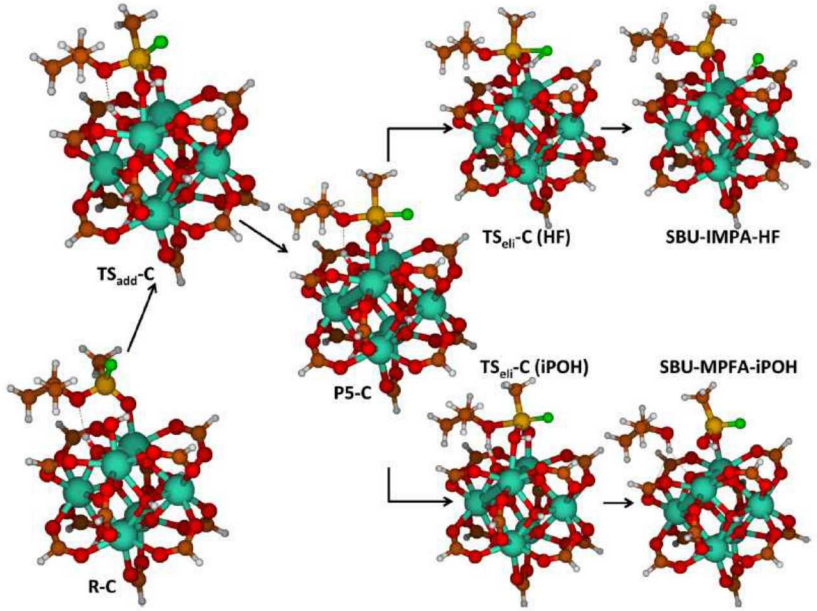


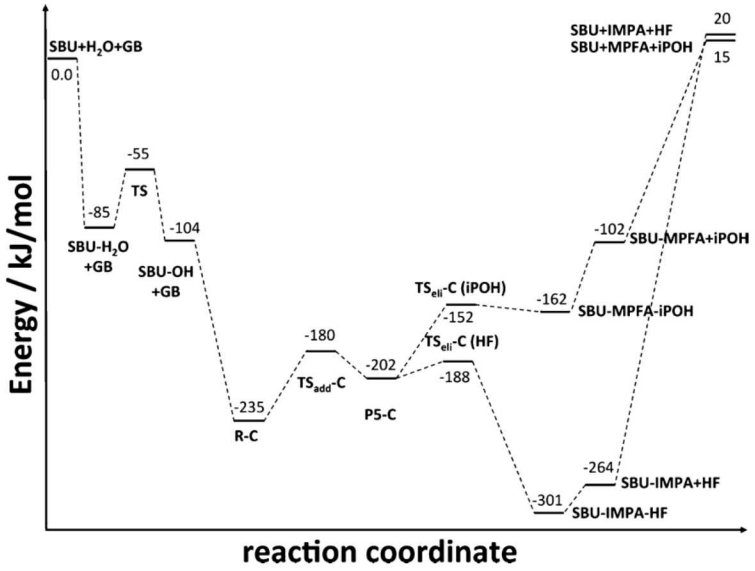


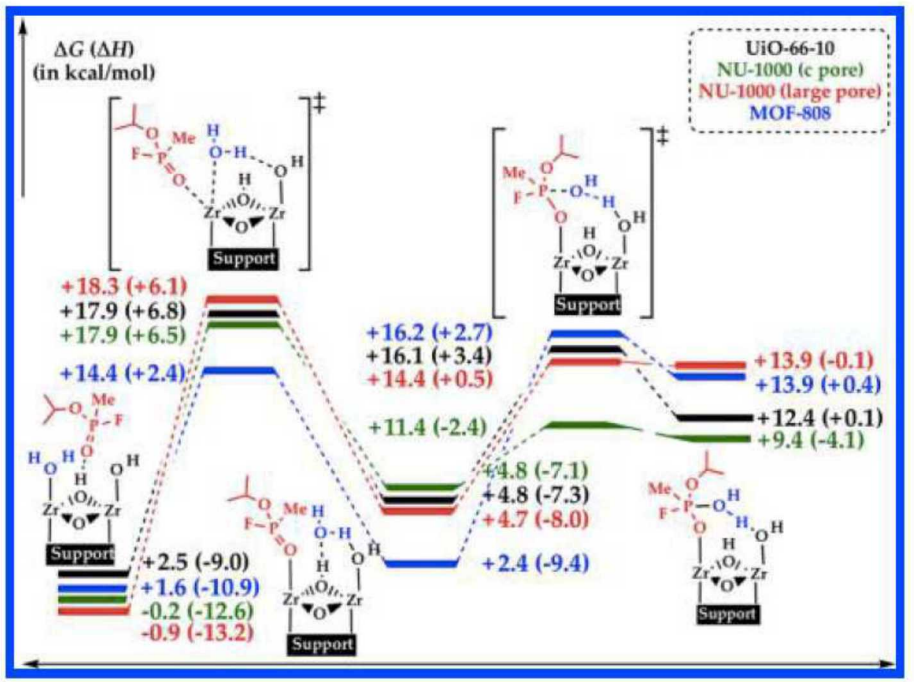
- DECP degradation significantly faster than GB; DMNP/DFP much more reliable simulants
- DMNP and DFP degradation run in parallel with GB, suggesting similar mechanisms
- What do computational results suggesting regarding the degradation mechanism?

J. Mater. Chem. A, **2018**, 6, 3038-3045

Importance of Adsorption of Organophosphorous Compounds in MOFs



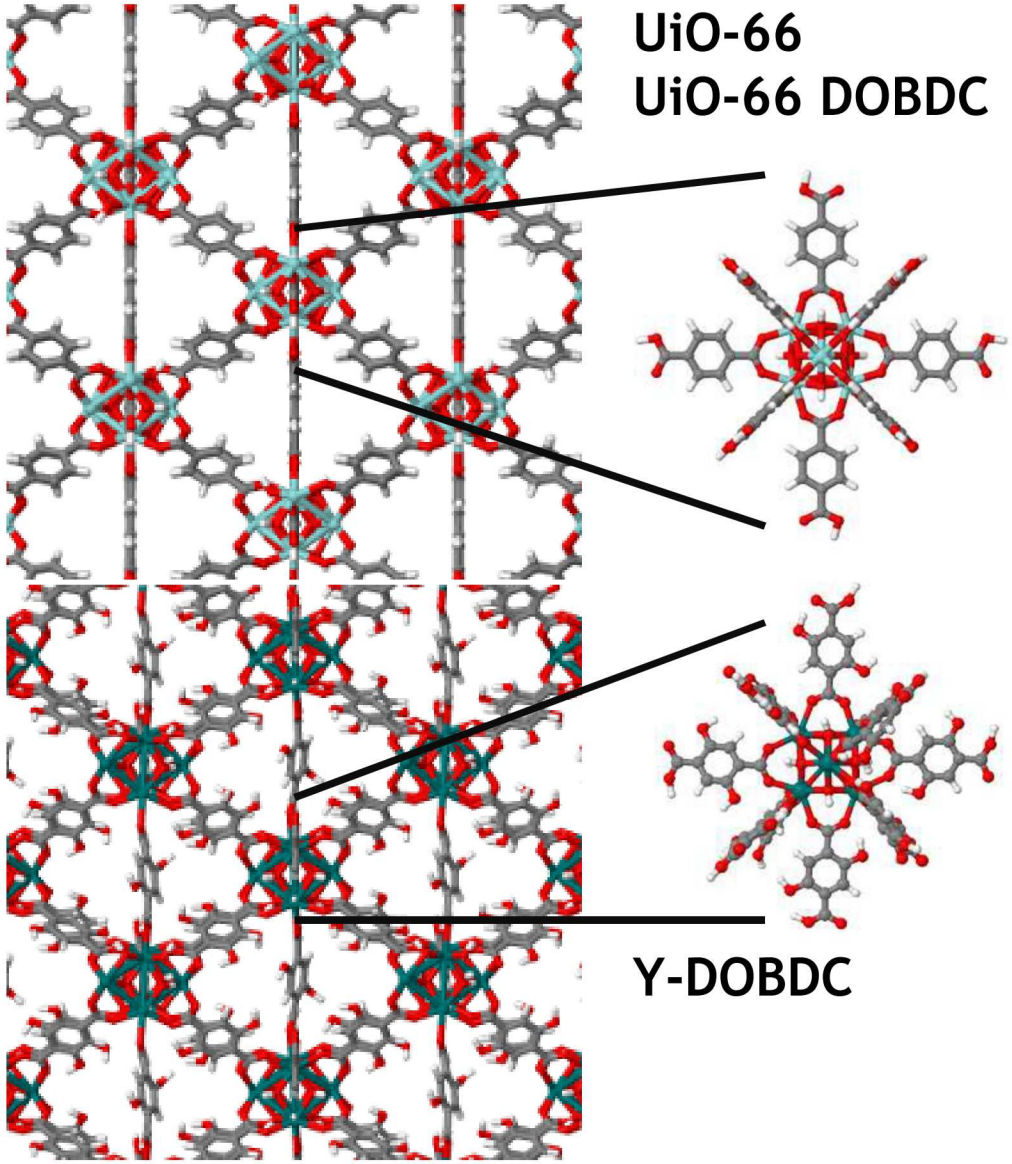




- Adsorption of GB in MOFs is a critical first step towards the degradation, however this process is poorly understood
- Assumption that degradation happens via adsorption onto a defect site has never been confirmed experimentally.

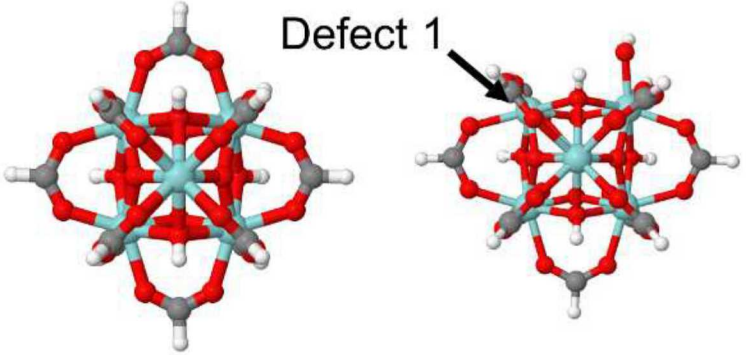
Troya, D., *J. Phys. Chem. C*, **2016**, 120, 29312-29323
Momeni, M. R.; Cramer, C. J., *ACS Appl. Mater. Interfaces*, **2018**, 10, 18435-19439

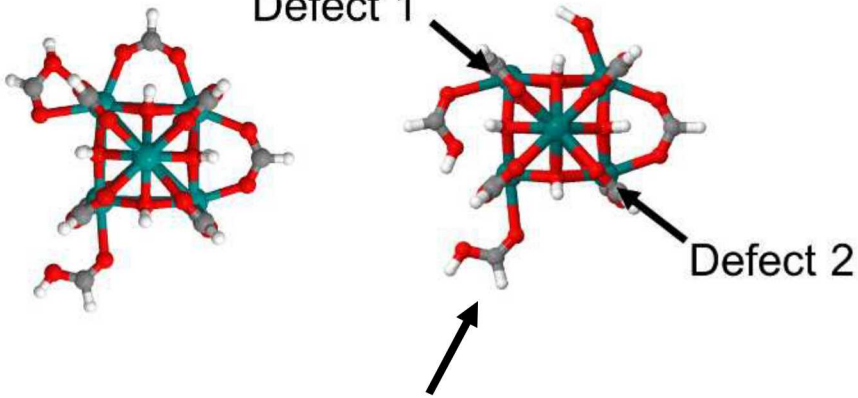
Missing Linker and Structural Defect Metal Sites



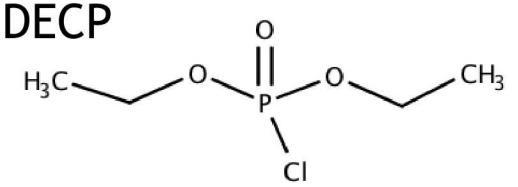
UiO-66
UiO-66 DOBDC

Y-DOBDC

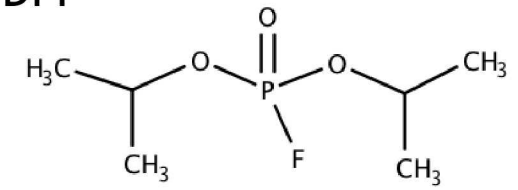




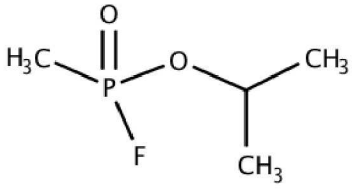
DECP



DFP



GB

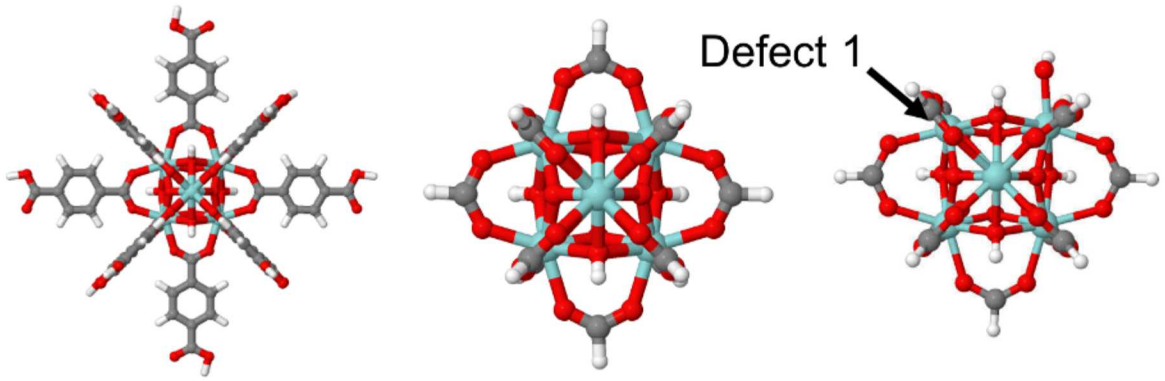


2 unique defects possible in Y-DOBDC:

- Missing linker defect identical to UiO-66 (defect 1)
- Twisted linker defect (defect 2)

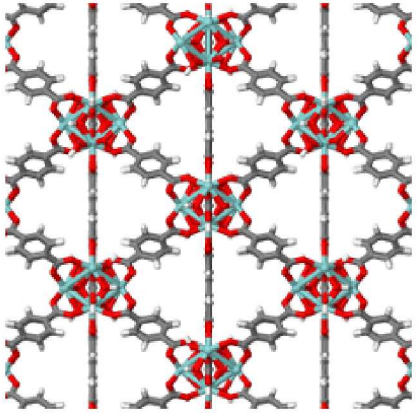
Computational Methods

Cluster Models:



- Representative clusters cut from periodic structures
- Each cluster consists of full hexanuclear metal cluster and 12 linkers
- Linkers shortened to formate groups
- M06-L density functional with def2-SVP basis set for all non-metal atoms; ECP28MWB basis and associated pseudopotentials for metal atoms

Periodic Models:

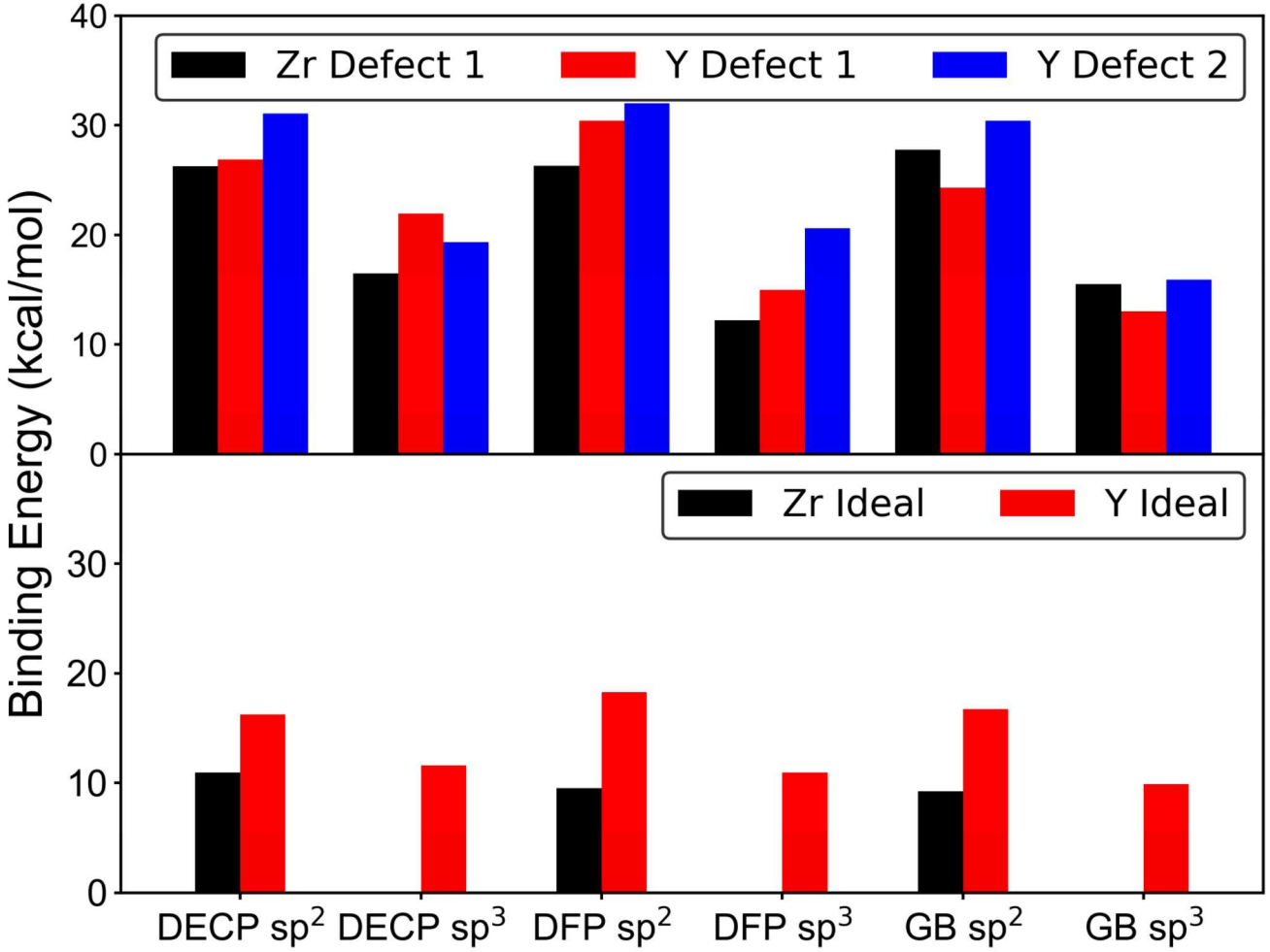


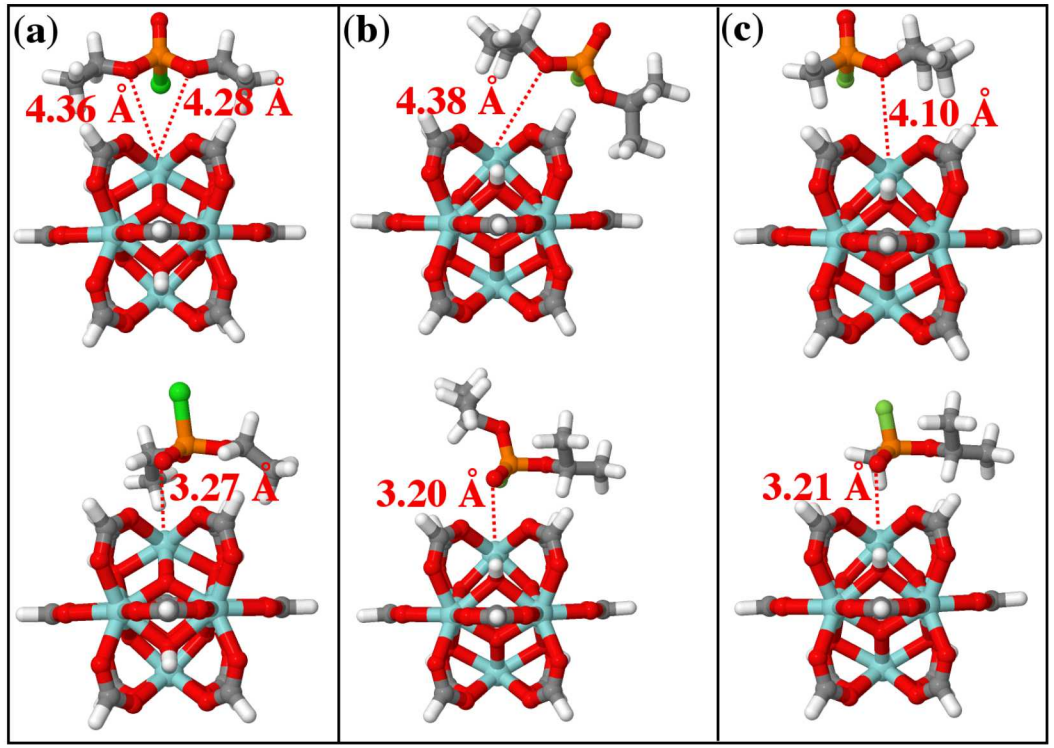
- Projector augmented wave approached implemented in VASP
- Perdew-Burke-Ernzerhof revised for solids (PBEsol) exchange correlation functional
- DFT-D3 with Becke-Jonson damping for empirical vdw interactions

$$\Delta E_{binding} = -[E_{substrate+MOF} - (E_{substrate} + E_{MOF})]$$

Positive binding energy = favorable

Binding Energy in Clusters: Effect of Metal and Structural Defects

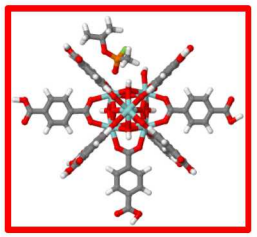


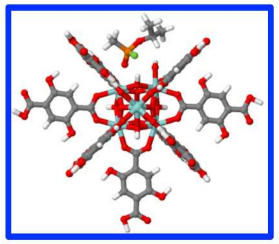


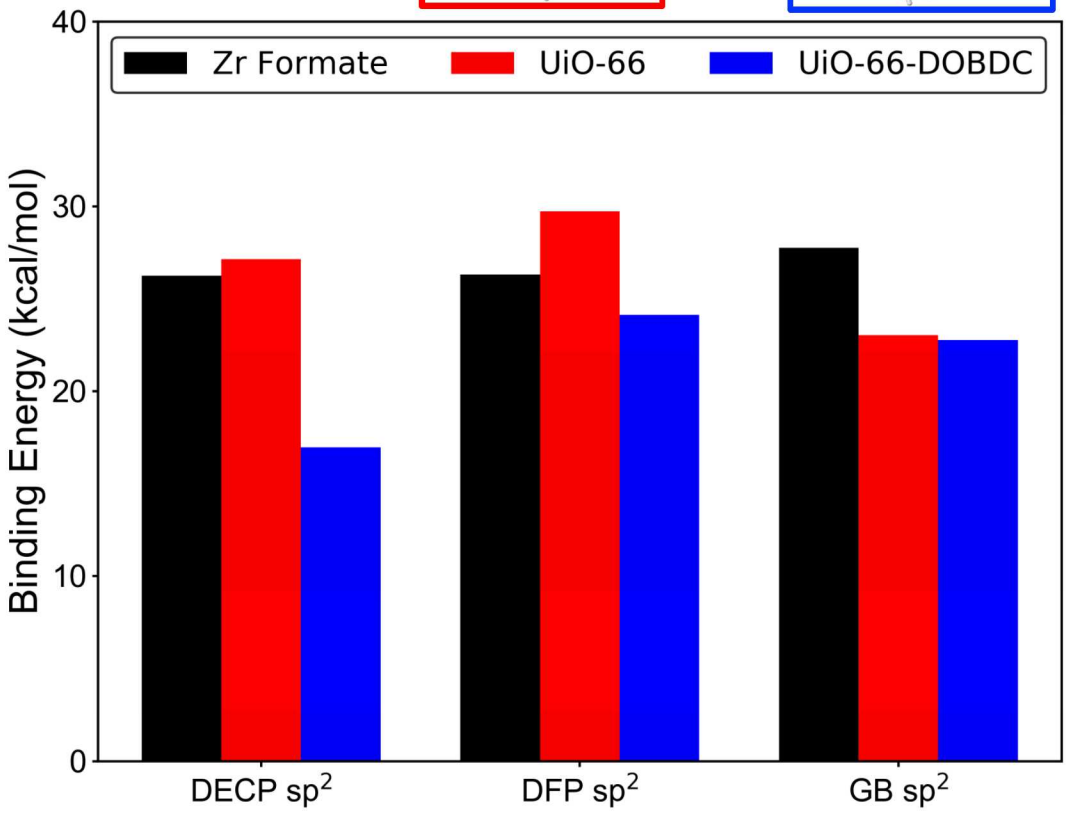
- O(sp^2) binding significantly more favorable then O(sp^3)
- Y binds fully coordinated sites more favorably than Zr, but with defects the metals are similar
- Twisted linker defects are competitive with missing linker defects → Synthetic advantage

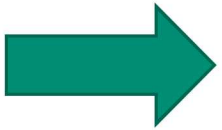
J. Phys. Chem. C, *submitted*

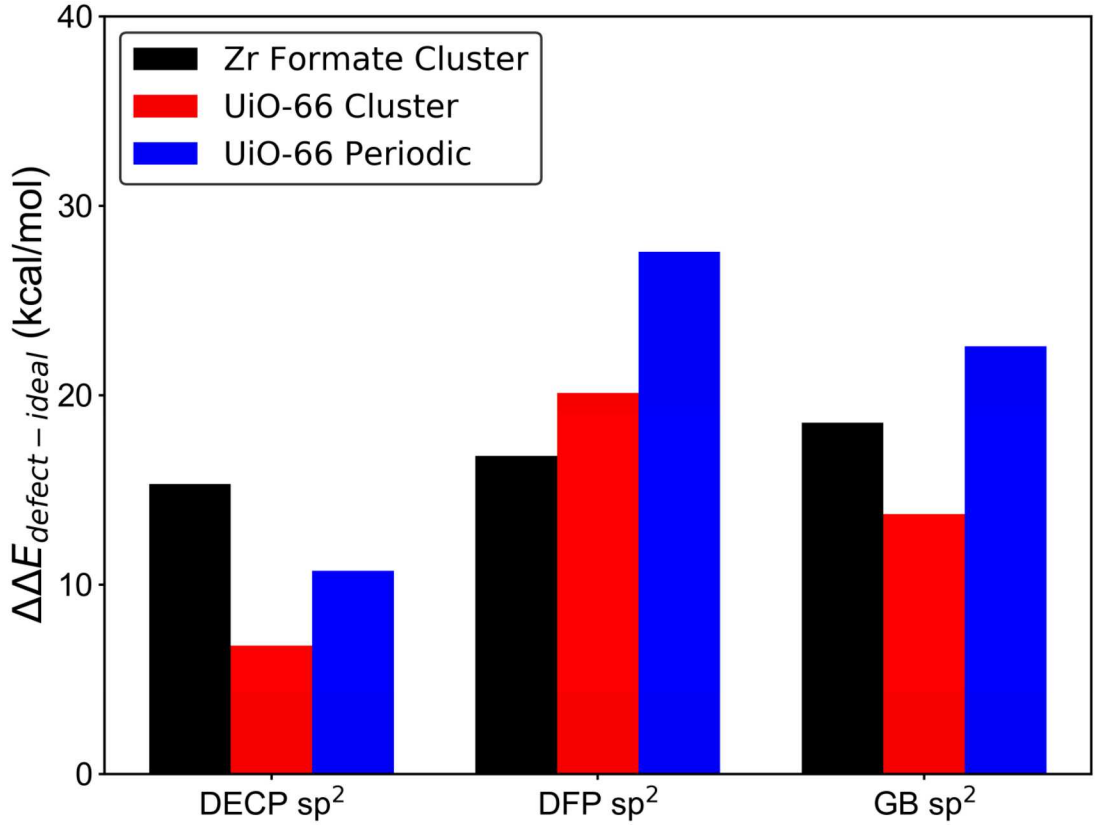
Effect of Linker and Cluster Model on Binding Energies







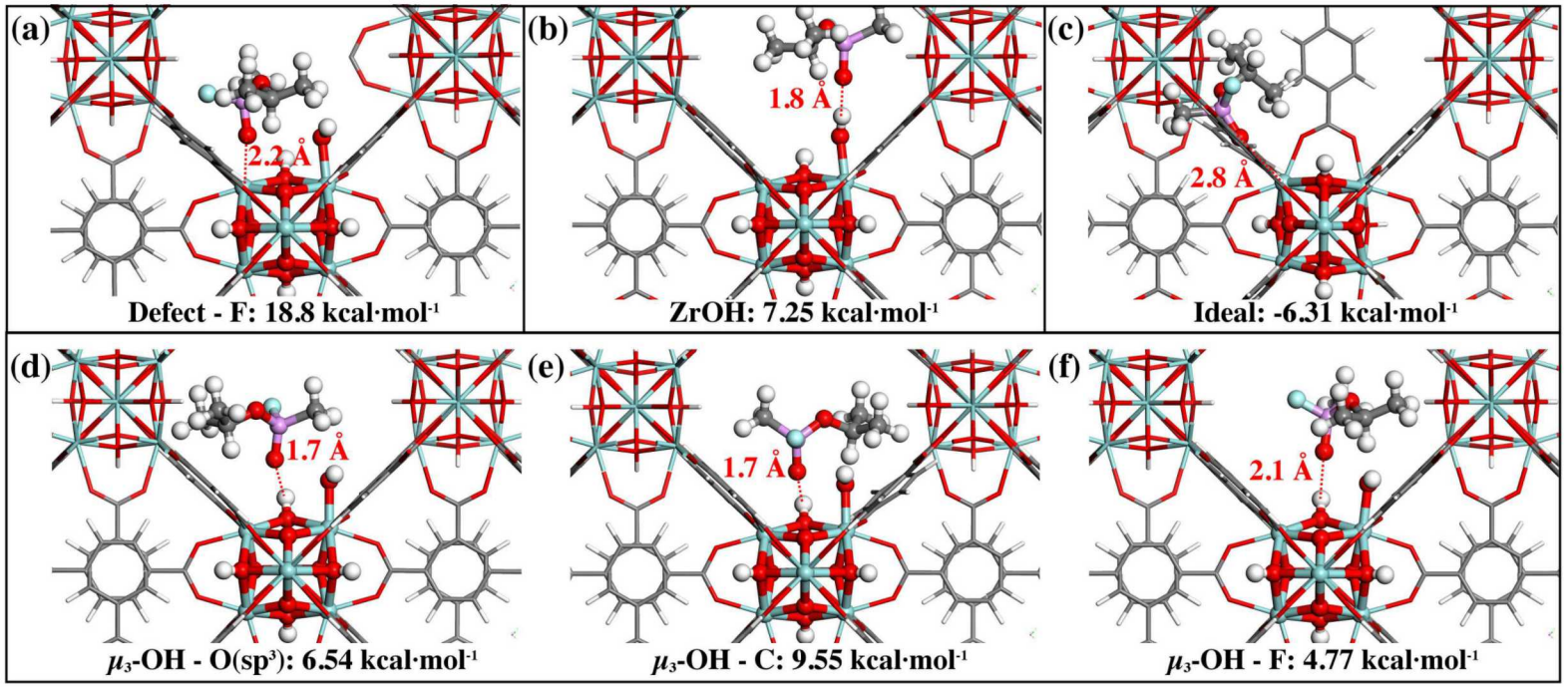




- Linkers play a distinct role in the binding process, however the trend is not general
- OH groups largely decrease the binding energy → Mirrors reactivity results
- Formate clusters tend to over estimate binding at ideal sites and erase steric effects

J. Phys. Chem. C, *submitted*

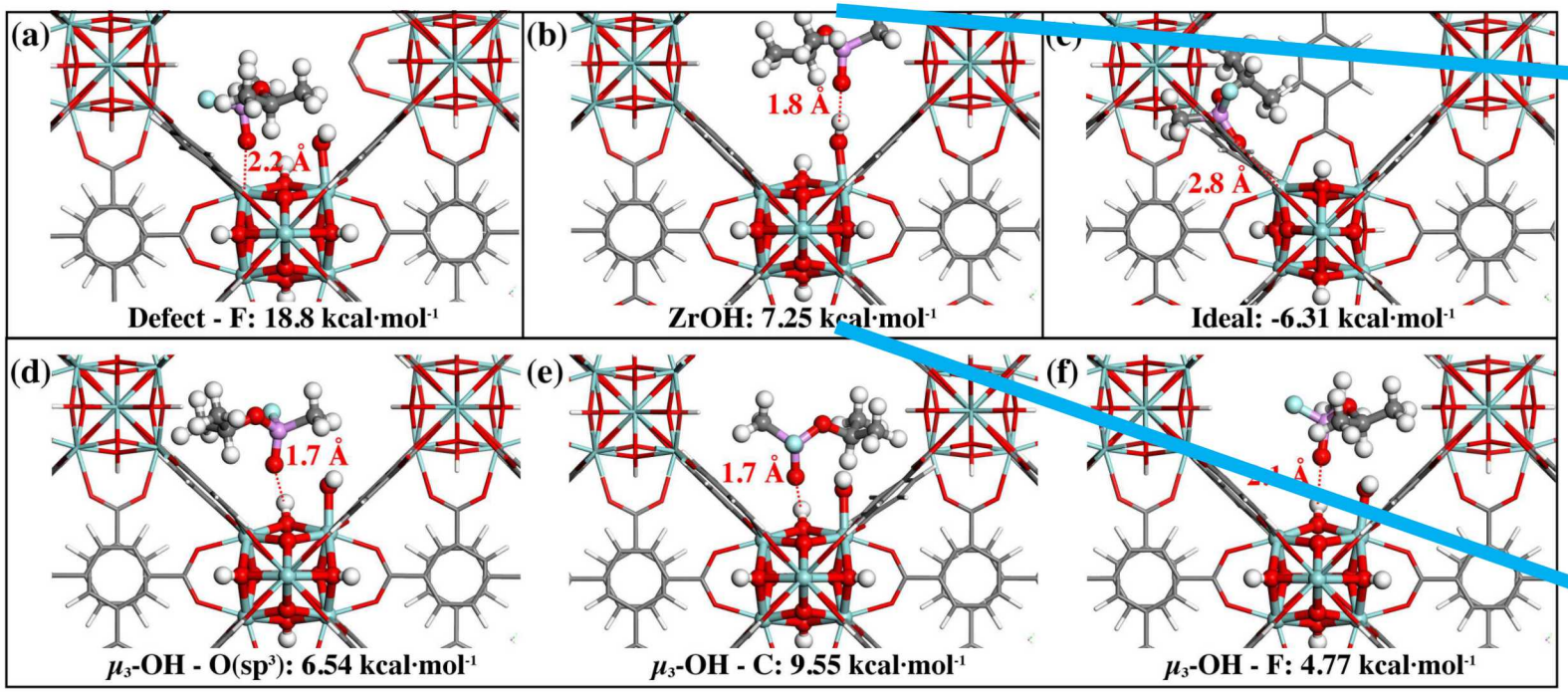
Additional Binding Sites in UiO-66

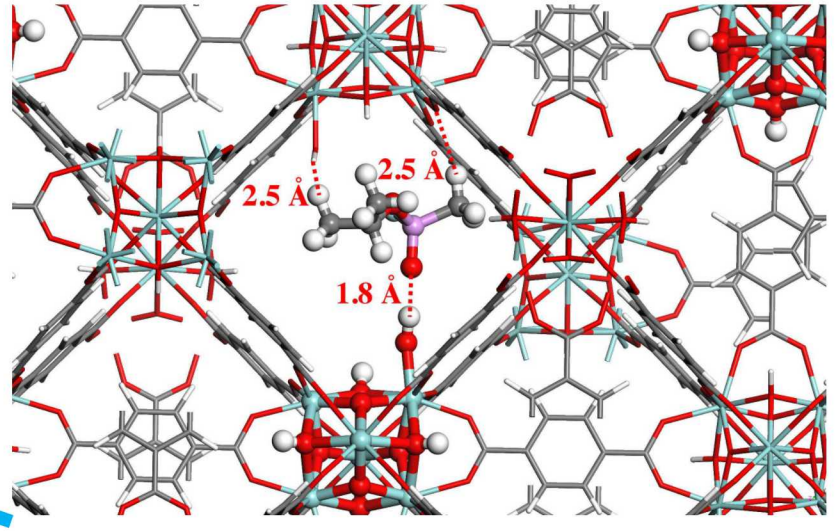


- Additional favorable binding sites for GB within UiO-66 exist; Missing linker ZrOH group, μ^3-OH group
- Strong orientational effects are observed

J. Phys. Chem. C, *submitted*

Additional Binding Sites in UiO-66

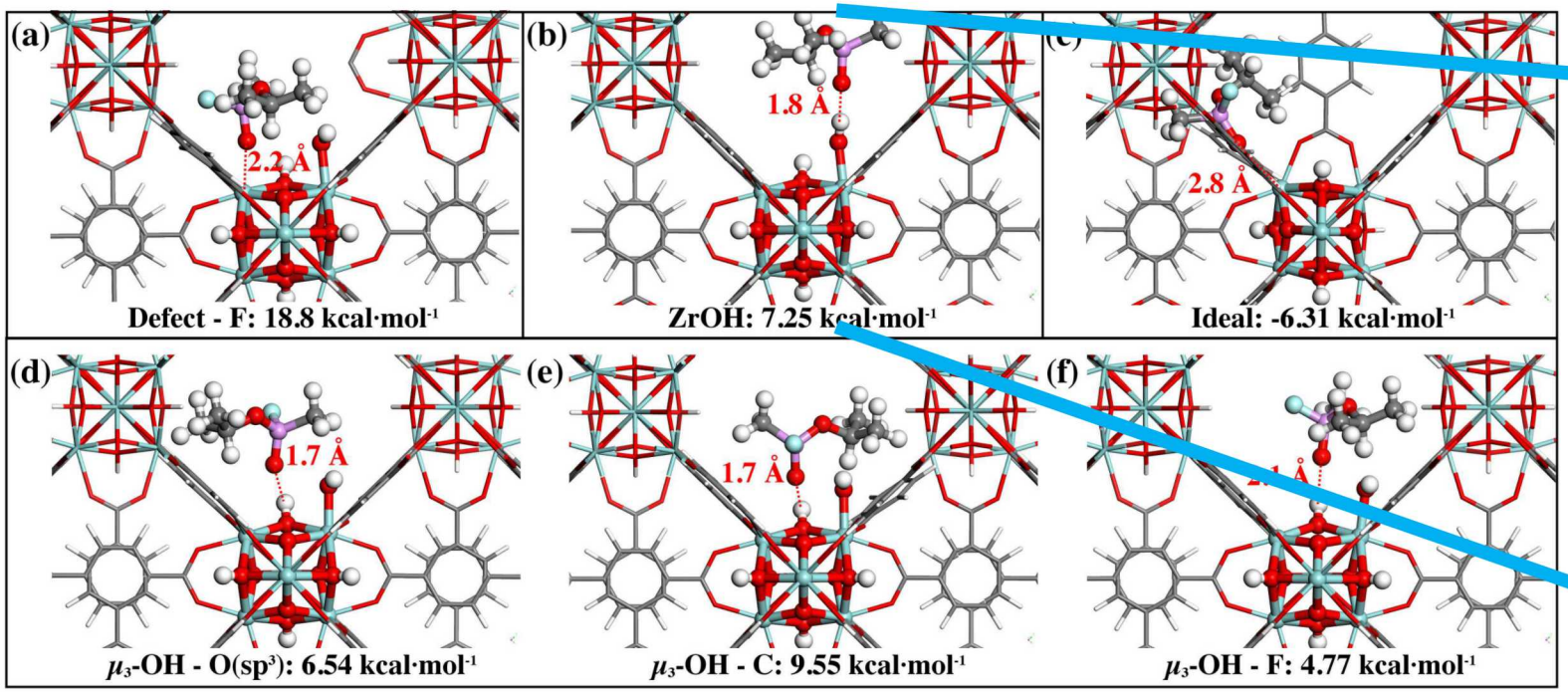


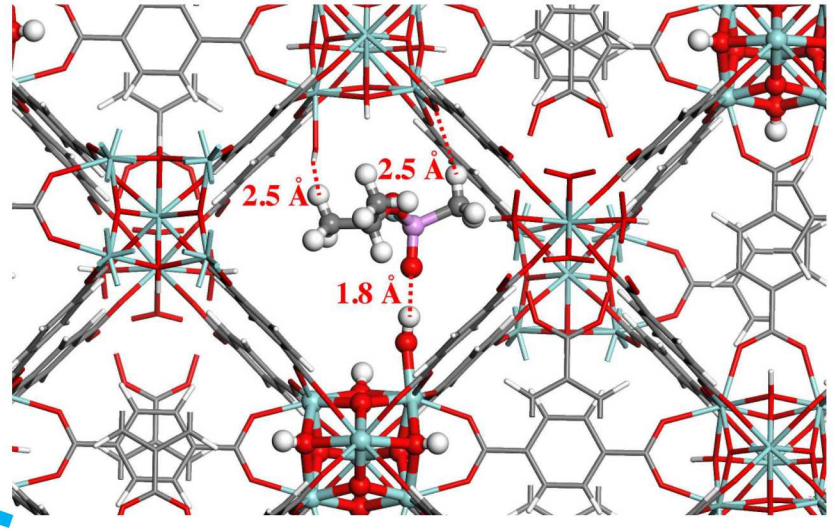


- Additional favorable binding sites for GB within UiO-66 exist; Missing linker ZrOH group, μ_3-OH group
- Strong orientational effects are observed
- ZrOH binding creates interactions with entire pore → Perioidic systems are necessary to capture this interaction

J. Phys. Chem. C, *submitted*

Additional Binding Sites in UiO-66



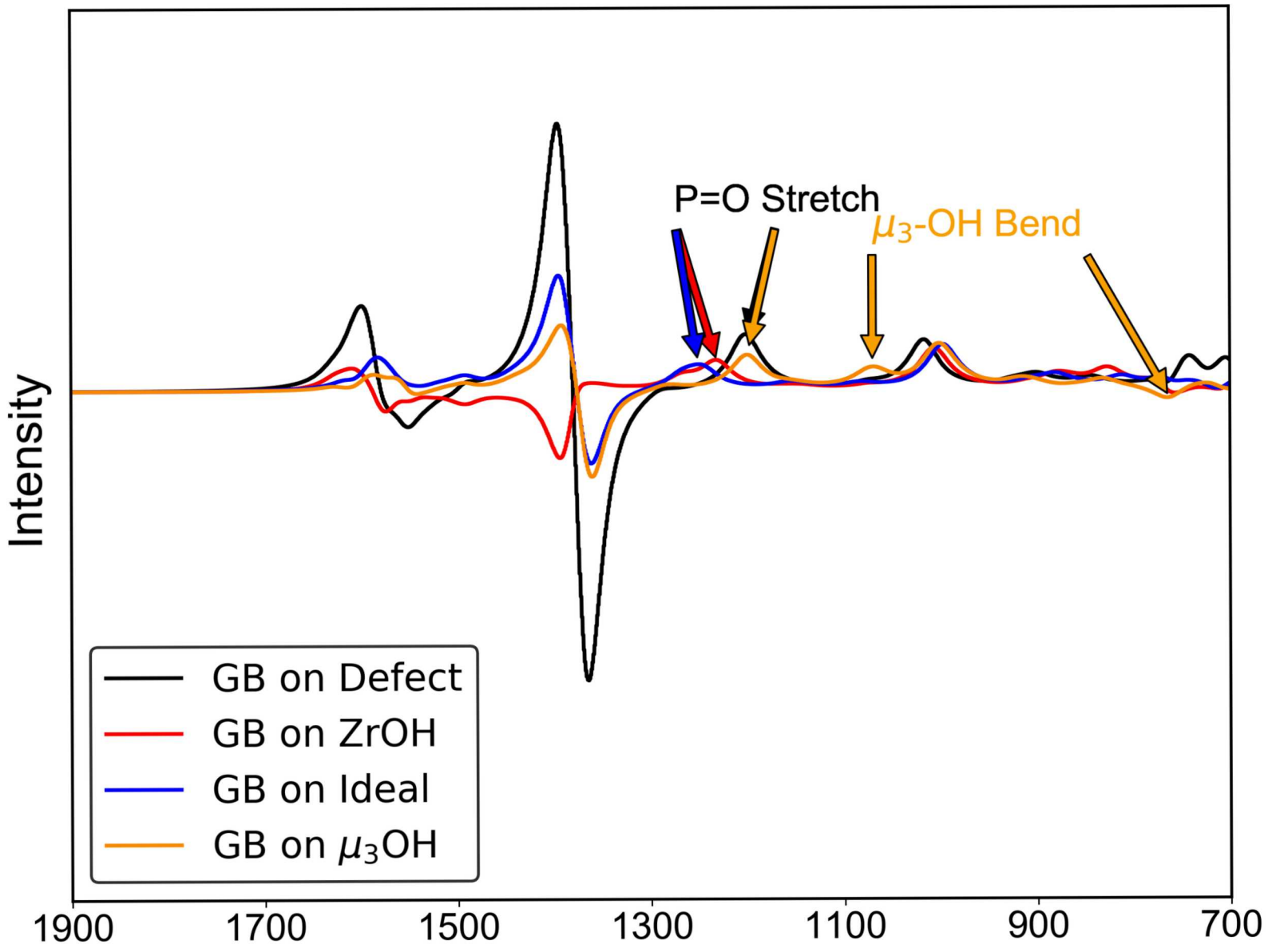


- Additional favorable binding sites for GB within UiO-66 exist; Missing linker ZrOH group, μ_3-OH group
- Strong orientational effects are observed
- ZrOH binding creates interactions with entire pore → Periodic systems are necessary to capture this interaction

- Wide variety of binding sites and binding energies within UiO-66; is this observable with IR spectroscopy?

J. Phys. Chem. C, *submitted*

Identification of Binding site via the P=O Stretch



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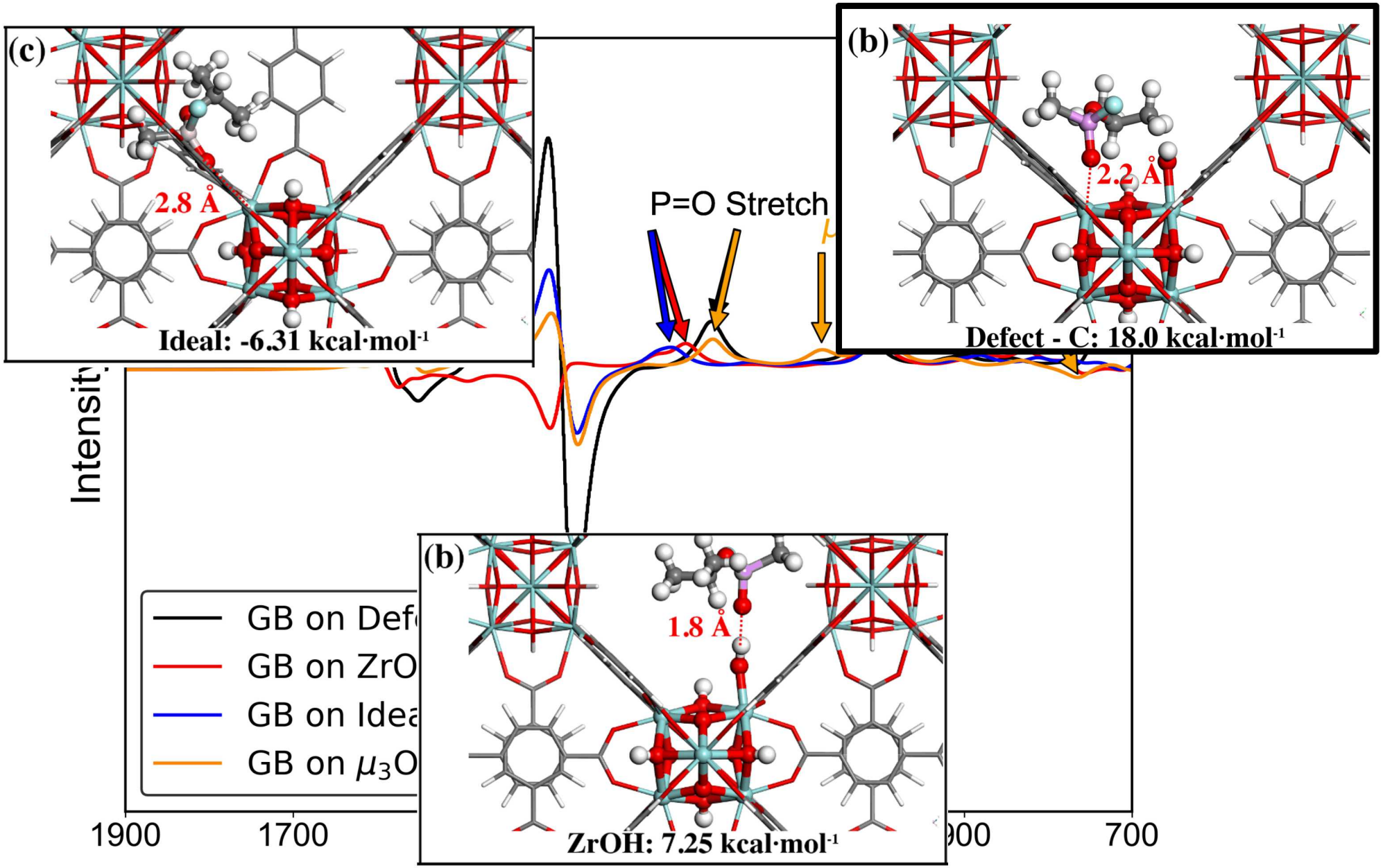
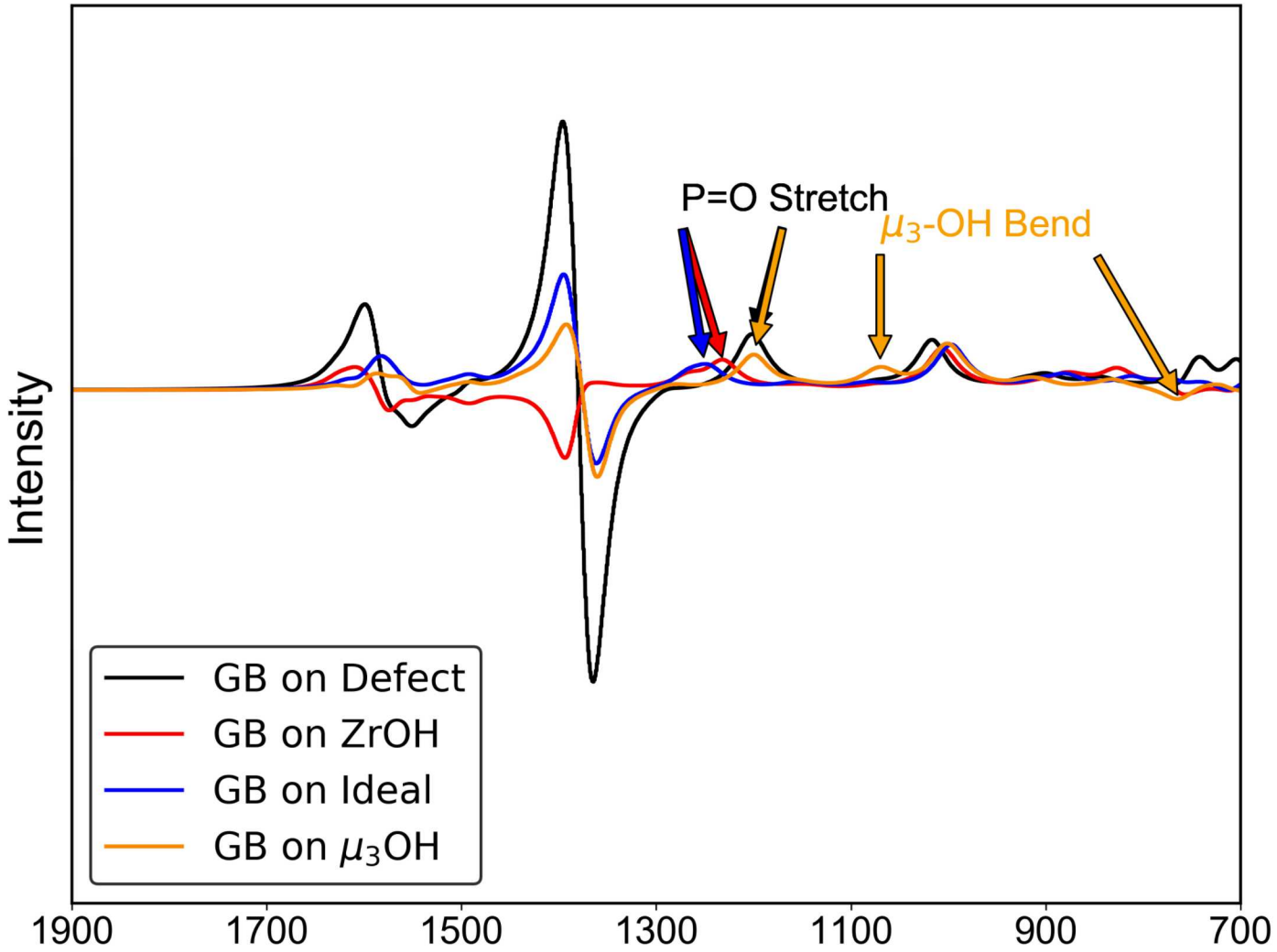


Identification of Binding site via the P=O Stretch



- Ideal vs defect site binding show a 50 cm-1 difference in the P=O stretch
- A 3rd site, possibly the defect created ZrOH, is observed in between the defect and ideal site binding

Acknowledgements

- Sandia:
  - Jeffery A. Greathouse
  - Dorina F. Sava Gallis
  - Charles J. Pearce
  - Mark K. Kinnan

- ECBC:
  - Jared B. DeCoste

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