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Binding of Organophosphorous Compounds in Metal-Organic Frameworks as Explored by Density Functional Theory and Infrared Spectroscopy

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Motivation

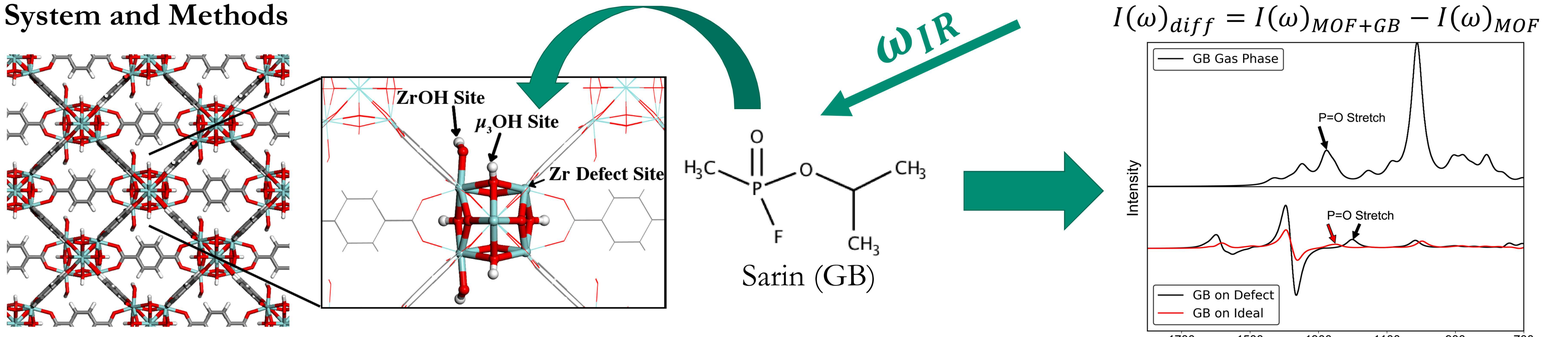
Organophorous compounds (OPCs) represent a highly toxic class of compounds. Metal-organic frameworks (MOFs) have been identified as a potential catalyst for the degradation of OPCs.[1] The degradation process in these materials likely occurs at under coordinated Lewis acid metal sites, however there are several favorable binding sites within the MOF for OPCs. Unambiguously determining these sites using a combined experimental/modeling approach will go a long way to better understanding the adsorption of highly toxic OPCs in MOFs

[1]Sava Gallis, D.F. et al. *J. Mater. Chem. A*, **2018**, 6, 3038

Research Questions

- What MOF sites play a role in the adsorption of OPCs?
- How does the binding energy of an OPC in MOF manifest itself in the P=O bond stretch frequency?
- Can we deconvolute the IR signal of bound GB into orientational effects at a given binding site?

System and Methods



Calculated Infrared Spectrum:

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

Cartesian polarizations

Born effective charge of s^{th} atom

Vibrational eigenvector

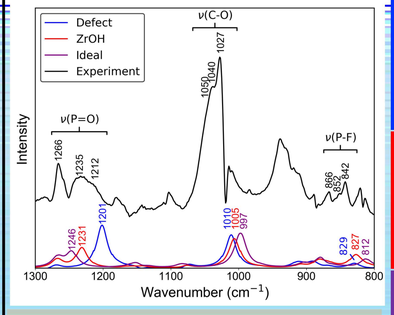
Computational:

- Projector augmented wave approach, implemented in VASP
- PBESol exchange correlation functional
- DFT-D3 with Becke Jonson damping

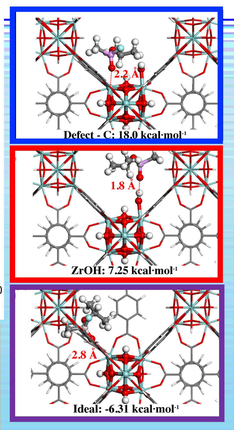
Experimental:

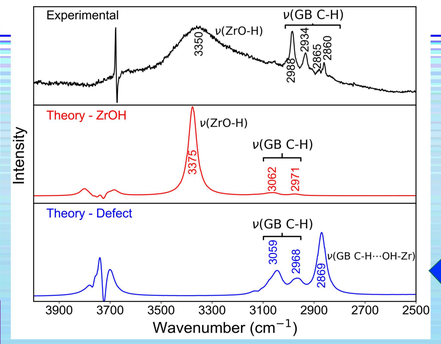
- Transmission infrared spectroscopy performed in a vacuum change under base 3x10^{-9} Torr pressure
- IR spectra taken after GB exposure with an average of 256 scans with 2 cm^{-1} resolution

Results



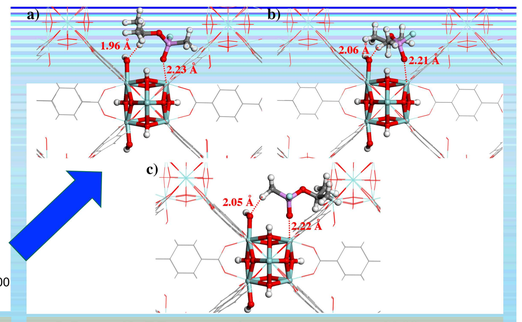
P=O stretch red shifted from the gas phase frequency according to the binding energy





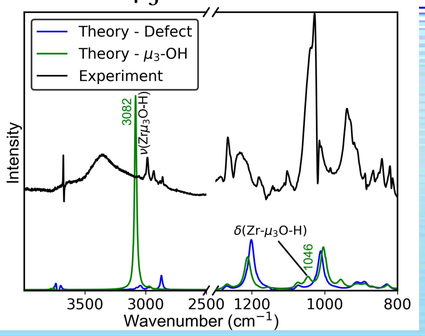
Appearance of ZrO-H stretch confirms missing-linker created ZrOH site plays a role in the adsorption process

Orientational Effect



New C-H stretches suggest different orientations of GB bound at a defect site are observed

Role of μ_3-OH site



μ_3OH is a favorable binding site with a strong peak at 3082; possibly masked by other modes

Conclusions + Future Work

- IR spectroscopy is a useful tool for probing binding sites for GB in MOFs
- Multiple sites have been observed and unambiguously assigned
- ZrOH plays a role in multiple ways; direct binding + interactions when bound at a defect site
- μ_3OH potentially plays a role
- Future work will focus on the kinetics and mechanism of degradation

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