Infrared Characterization of Metal Organic Framework Compounds

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Funded by Defense Threat Reduction Agency
Goals

• Metal Organic Framework compounds (MOFs) have been shown to be useful catalysts in the decontamination of Chemical Warfare Agents (CWAs)
• Goal is to use Fourier Transform Infrared Spectroscopy to characterize MOFs, such as UiO-66
• Examine MOFs with different defect densities and particle sizes
• Perform in operando measurements by pumping CWA gas simulants into the particle to see how the structure of the MOFs changes during catalysis of the simulant
**Project Overview**

**Virginia Tech**
- MOF samples are synthesized in the form of powder
- XRD measurements to determine type of defect
- TGA measurements to quantify linker defects

**UNC**
- NMR to see molecular dynamics and diffusion of guest molecules
- Raman and FTIR to characterize and compare vibrational modes of pristine and defective samples

**University of Oklahoma + University of Pittsburgh**
- DFT (Density Functional Theory) Calculations – finds vibrational modes computationally

**US Army Edgewood Chemical Biological Center (ECBC)**
- MOFs are tested with CWAs
Taking IR Measurements

• Powder samples must be made into pellets using a hydraulic press in order to facilitate transmission IR spectroscopy
• Sample is ground together with KBr and pressed into pellet
• Pellet is mounted vertically in spectrometer
• IR light is shone through the sample and a spectrum is produced showing the wavenumbers at which the light is absorbed
• Absorbance peaks correspond to specific vibrational motions of the atoms
• Spectrum acts as a chemical fingerprint for each compound
Molecular Vibrations and Infrared Spectroscopy

- Infrared absorption causes specific atoms in a compound to vibrate
- Vibrational motion of atoms in the simplest cases can be explained by simple harmonic motion and Hooke’s law
- Vibrational frequencies are modeled by:
  \[ \nu = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{\mu}} \]
  where \( \kappa \) is the force constant and \( \mu \) is the effective mass between the bonded molecules
- Larger molecules, like MOFs have many degrees of freedom and require more complicated calculations to understand normal modes
- DFT calculations are used to compute these modes
Wavenumbers

- Wavenumber = \( \frac{2\pi}{\lambda} \)
- Frequency = \( \nu \)
- \( \nu = \frac{c}{\lambda} \)

Heavier atoms vibrate at a lower frequency, just like a heavy mass on a spring moves slower than a lighter one, therefore heavier atoms will show vibrational modes in the lower wavenumber region and lighter atoms will exhibit vibrations in the higher wavenumber region.
Metal Organic Framework Compounds (MOFs)

• Highly porous 3D structures that are made up of a metal center and organic linkers
• Large pores make them optimal for the uptake of CWAs
• Tunable design
  • Fine tuned using modulators, which are used in synthesis to compete with linkers in bonding to open metal sites

Image taken from Influences of Structural Design on Molecular Accessibility, Kinetics, Adsorption, and Reactivity: Degradation of CWAs by MOFs
UiO-66

• UiO-66 has a zirconium center and benzene 1,4 dicarboxylate (BDC) linkers
• Some UiO-66 compounds are synthesized with defects in the form of missing linkers or missing clusters
• UiO-66 with no measurable defects is referred to as “Pristine”
Types of Samples Analyzed

• Particle size series
  • UiO-66 samples with varying particle size but roughly the same defect density

• Defect series
  • UiO-66 samples with varying defect densities but roughly the same particle size

SEM Image from Dr. Morris’ Lab at VT

Image made by Brandon Yost

Missing Linker
Confirms what we would expect: There should be no changes in vibrational modes since the structure does not change, only the size.
Defect Density Series

FTIR Spectra of UiO-66 by Defect Density (Normalized)

- complex motion of Benzene ring
- Pristine
- AA300: 13% 695nm
- FA100: 20% 159nm
- FA200: 22% 436nm
- FA300: 25% 615nm
- single crystal: 33% 16 microns
Vibrations in this region are likely to involve zirconium because it is a heavy atom.

Clear difference between Pristine and the rest of the defective samples.

Modeling peaks with Lorentzian functions in Python shows that changes in peak centers or widths do not correlate with increasing defect density.
Peaks in the Lower Wavenumber Range

Peak around 570 cm\(^{-1}\) is responsible for O-Zr-O stretching
Peaks in the Lower Wavenumber Range

• Peak around 670 cm\(^{-1}\) corresponds to Zr-O stretching
Peaks in the Lower Wavenumber Range

- Peak around 750 cm\(^{-1}\) corresponds to a wagging motion of the O-H and C-H bonds.
Interpreting the rest of the Spectra

• The peaks represented come from DFT calculations on the pristine sample
• Still unclear what is exactly is causing the change in the spectrum between pristine UiO-66 and the defective samples
• Comparisons with Raman interpretations as well as more DFT calculations will help us better understand the difference in the spectra
In Operando Measurements

• Plan to create a cell in which gas CWA simulants can be pumped into the sample as an infrared spectrum is being measured

• Spread sample in between two windows of a substance that has a low absorbance in the MOFs’ fingerprint regions as well as low reactivity with the simulant

• Challenges come from:
  • Mounting the sample vertically
  • Finding an appropriate window material
  • Making sure the cell can operate safely without leaking gas
    • KBr can be prone to cracking if not pressed perfectly and is not inert
Contributors

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