Dynamics of Methane Adsorbed on MOFs by Disk Chopper Spectrometer

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Motivation

- Adsorbed natural gas technology
  Material-based storage
  - Low pressure
  - Light weight and portable
  - Safe
  - Cheaper than compressed natural gas technology

... ...

- DOE’s Methane Opportunities Vehicular Energy (MOVE) projects are finding innovative ways to create natural gas storage tanks.

**Porous Metal-Organic Frameworks (MOFs) for methane storage**
Each cubic unit cell contains **32 CH$_4$ molecules** on preferential sites. Given the C-H bond length (~1 Å), if the surface area are fully occupied by CH$_4$ molecules, 1 cm$^3$ MOF-5 have surface area ~2.3×10$^3$ m$^2$ which can accommodate **1/6 mol CH$_4$** molecules.
MOF-5 System

Adsorbed methane molecule
a hindered rotor

Ground Rotational Energy Splitting

- Neutron spectroscopy: various vibrational and rotational motions of adsorbed CH$_4$ molecules, e.g.,
  - CH$_4$ center-of-mass motion (phonons), ~1-20 meV, DCS
  - CH$_4$ quantum rotational tunneling (at low T), ~1 - 600 ueV, DCS
  - CH$_4$ jump diffusion (at high T), DCS
Disk Chopper Spectrometer (DCS)

- Inelastic neutron scattering

- Choppers: Select initial energy of neutrons incident on sample
  - Neutrons scattered by sample gain or lose energy
  - Time-of-flight
- Inelastic peaks → Transition energies between tunneling levels
Phonons on CH$_4$ MOFs

- Deuterated organic framework allows us to see the collective CH$_4$ framework motions.

Intensity $\approx$ Weighted phonon density of states (integrated over all Q)
Due to Van der Waals interaction between CH\textsubscript{4} and MOF, the CH\textsubscript{4} experiences a potential which hinders rotation. There are 12 positions of the CH\textsubscript{4} which are degenerate in the gas phase. In potential caused by the MOF, the ground state splits into 4 energy levels, with a total of 5 possible transitions.

Smalley & Huller 1981
Tunneling of CH$_4$ in MOF-5

- Inelastic peaks give the allowed transitions between energy levels.
- Data taken at 6K, scattering from other processes minimal.

The transition energies can be used to calculate the potential barrier in the over which the methane rotates.

- Barriers are $\sim$23 meV for 3 fold rotation, $\sim$17 meV for 3’ fold rotation.
  - Predicted barriers from DFT-D are 47 meV and 25 meV
Comparison of Tunneling of CH$_4$ in MOF-5 and UiO-66

- Data taken at 6K; all CH$_4$ absorbed
- Charged sample container
- Concentrations: 1 CH$_4$ per 1 Zn for MOF-5; 0.5 CH$_4$ per Zr UiO-66; 1 CH$_4$ per Zr UiO-66

CH$_4$ in D-MOF-5, 9 Å  

CH$_4$ in UiO-66, 9 Å
Applications of DCS

➢ Diverse Phenomena
  • Low energy vibrational and magnetic excitations
  • Translational and rotational diffusion processes
  … …

➢ Various Materials
  • Magnetic and ferroelectric materials
  • Organic molecules
  • Molecular crystals
  … …
Conclusions

- DCS is used to investigate the rotational dynamics in CH\textsubscript{4}-MOF systems, and to understand the CH\textsubscript{4}-MOF interactions.

- By analyzing the inelastic neutron scattering spectra, the transitions and rotational barriers of MOF-5 were determined.

- UiO-66 exhibits broadened inelastic peaks with respect to MOF-5 due to its structural defects.

- The experimental results are a useful comparison to DFT calculations.
Future Directions

- Analyze higher quality samples of UiO-66
- Improve DFT methods
- Rational design towards improved hydrocarbon storage
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Q&A