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

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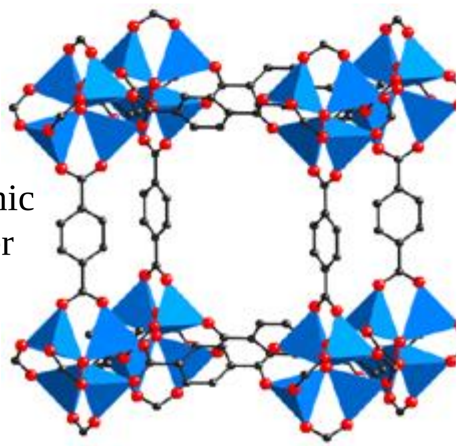
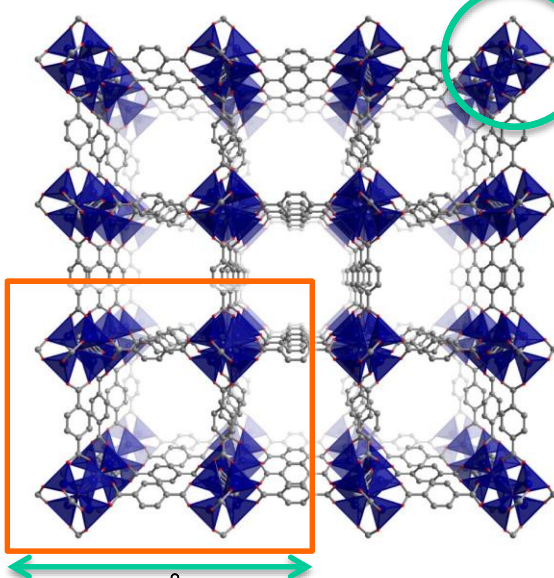
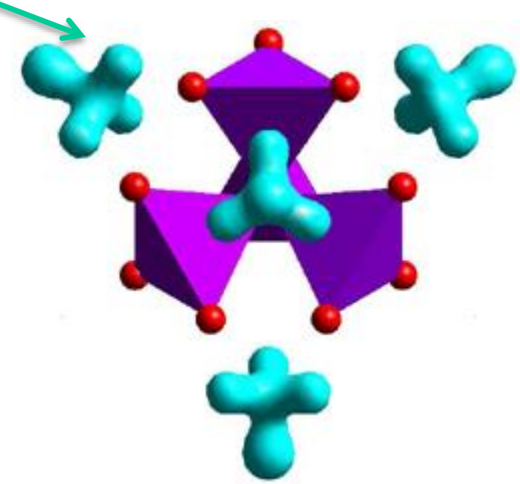
MOF-5 System



Metal-Organic Framework

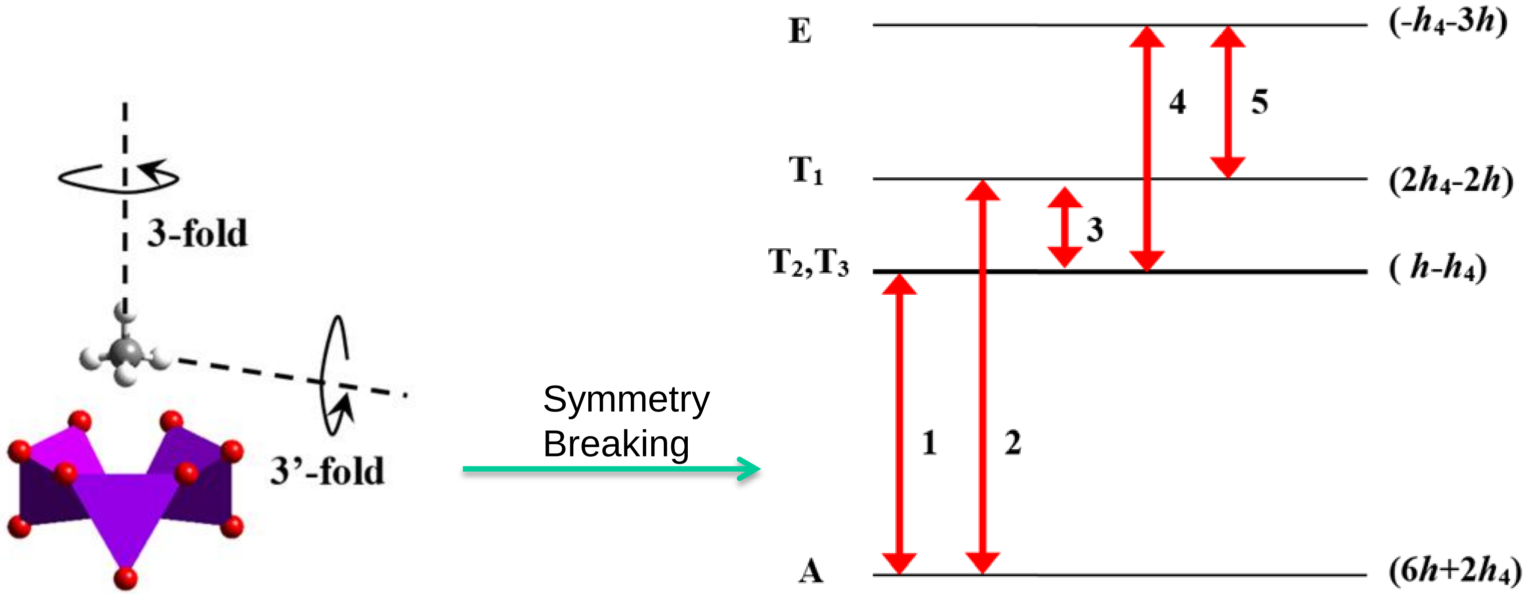


Cubic Cell



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

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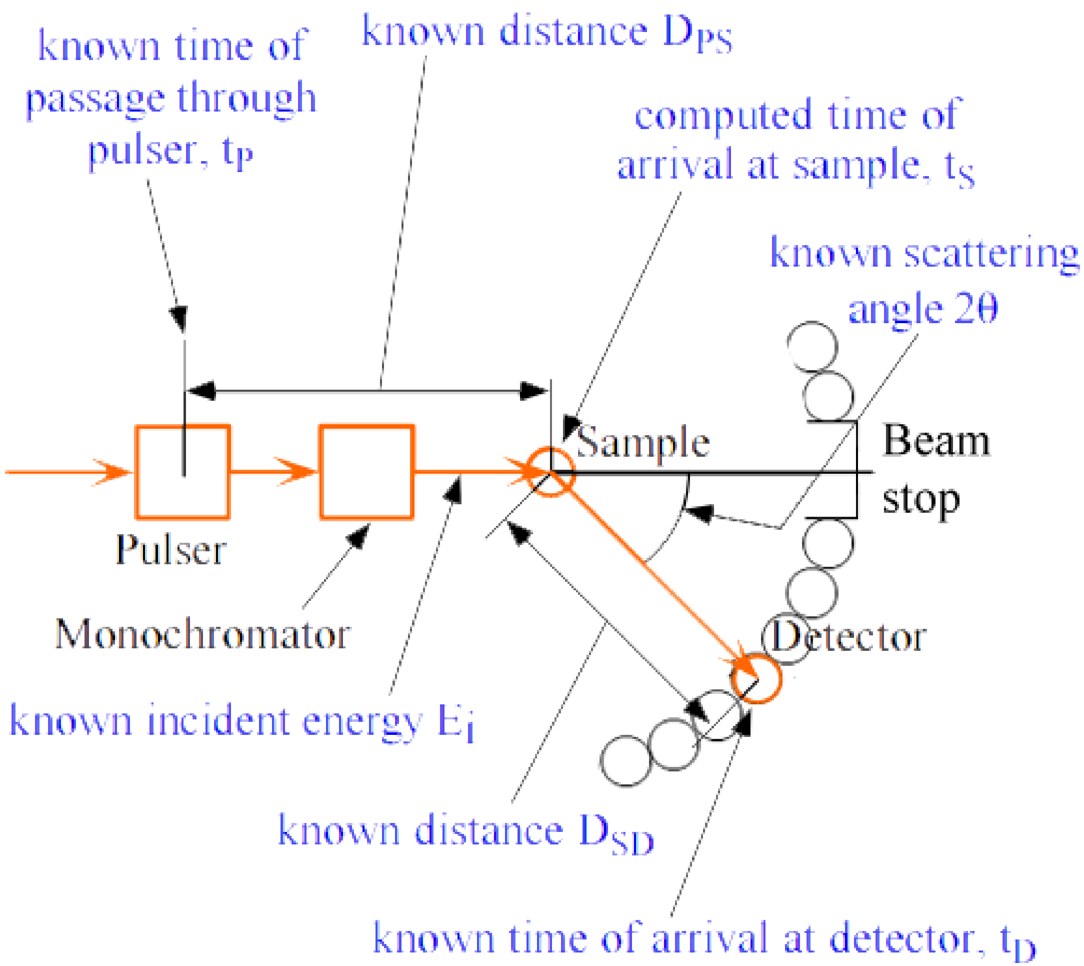
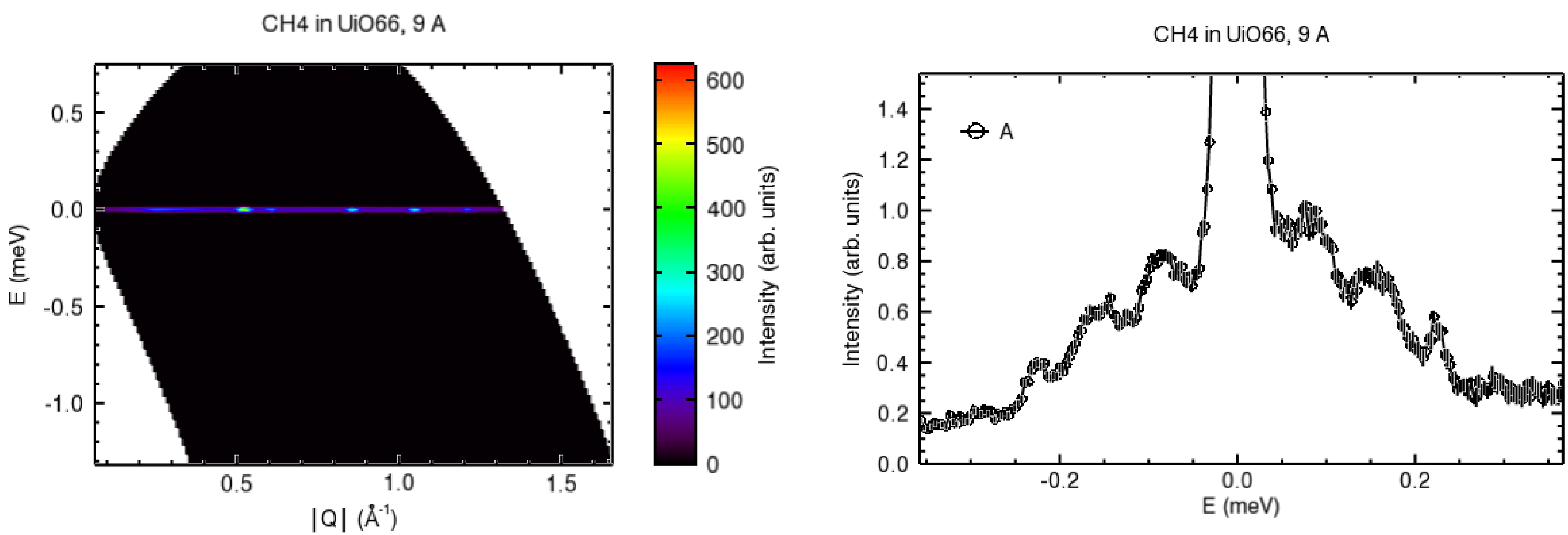
Disk Chopper Spectrometer (DCS)



- Inelastic neutron scattering
- Choppers: Select initial energy of neutrons incident on sample
- Neutrons scattered by sample gain or lose energy
  - Time-of-flight

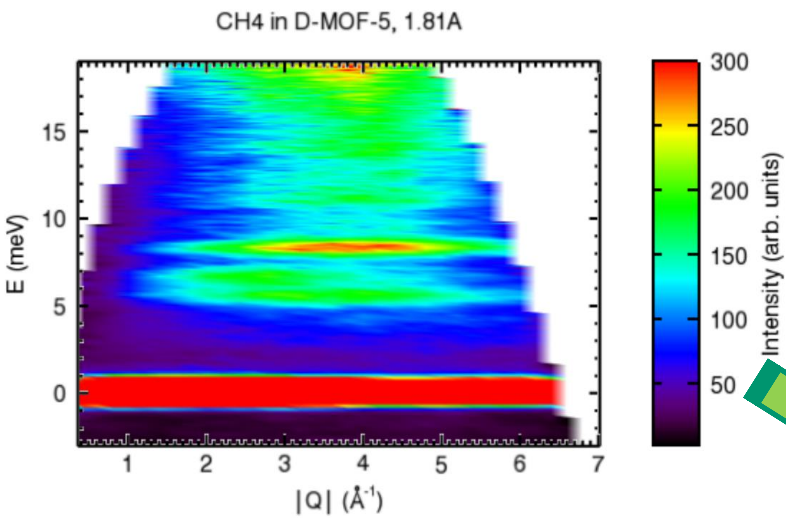
Measured Intensity

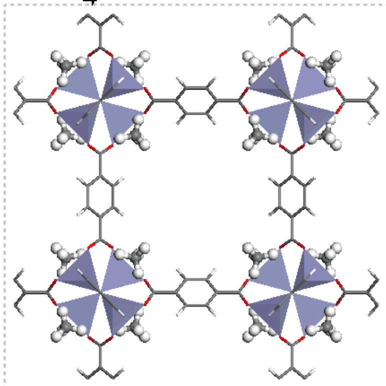


- ➢ Inelastic peaks ⟶ Transition energies between tunneling levels

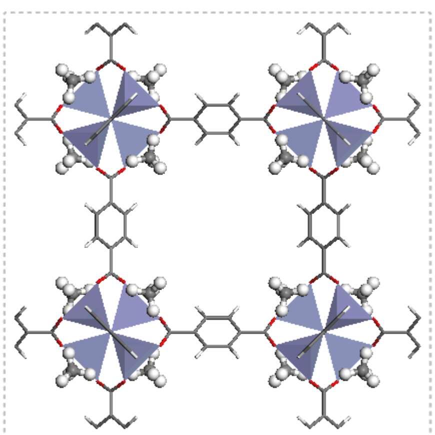
Phonons on CH_4 MOFs

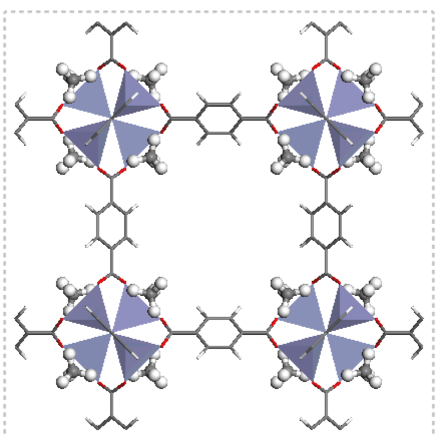
- Deuterated organic framework allows us to see the collective CH_4 framework motions.

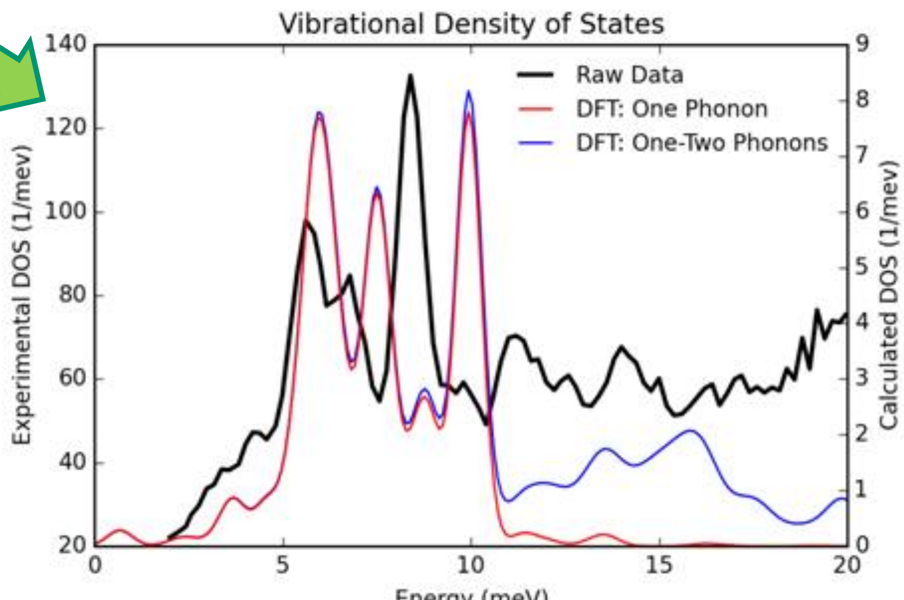




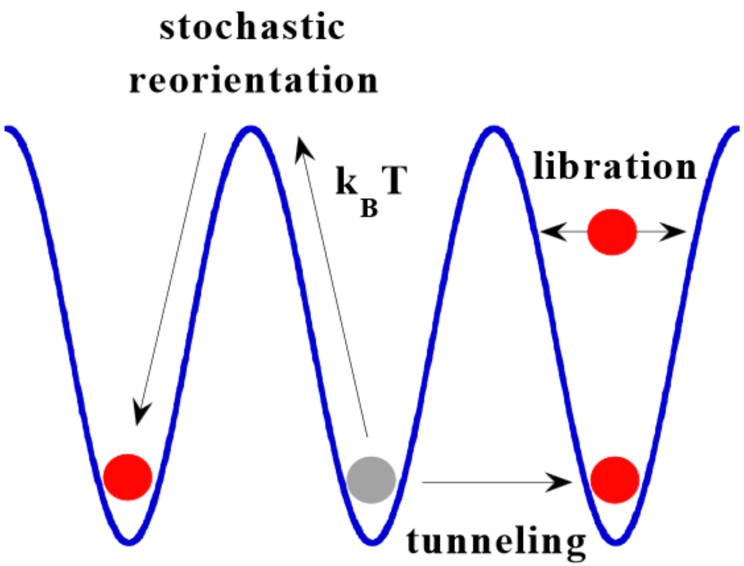
Intensity ≈ Weighted phonon density of states (integrated over all Q)



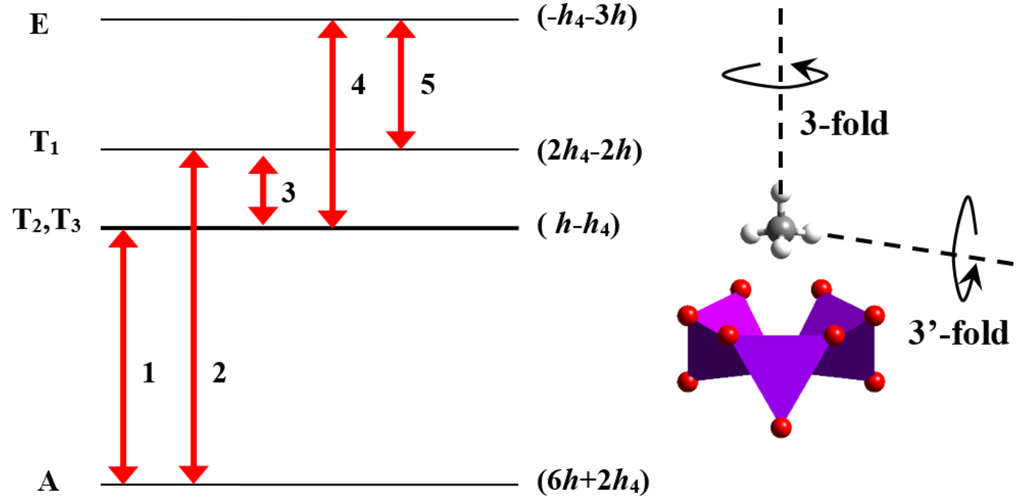




Tunneling of CH_4 in MOF



(Image credit: Rob Dimeo)



Due to Van der Waals interaction between CH_4 and MOF, the CH_4 experiences a potential which hinders rotation.

There are **12 positions** of the CH_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

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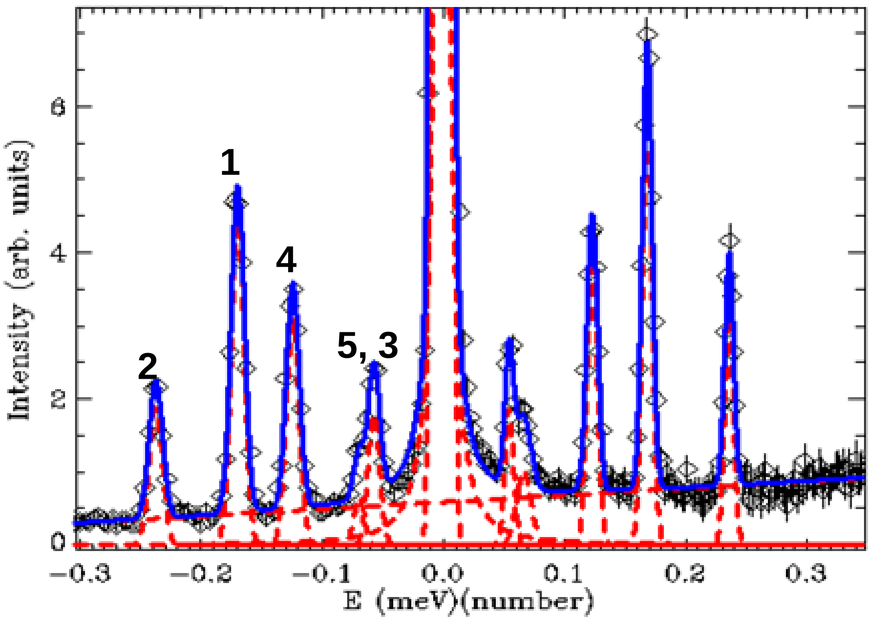
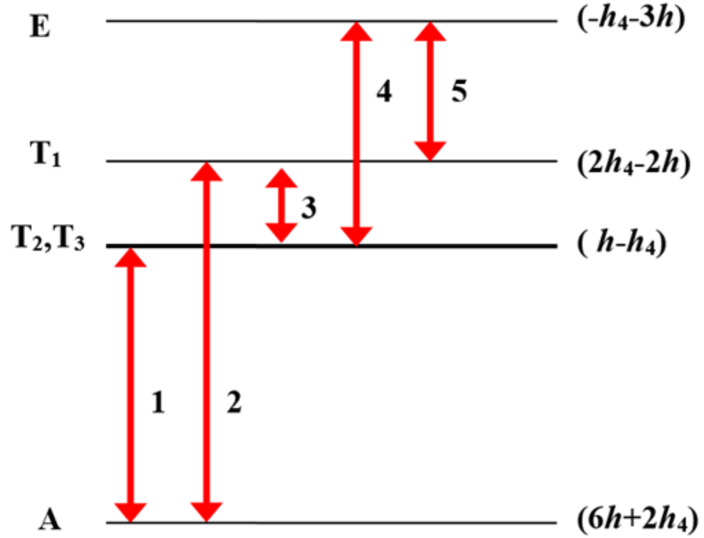
Tunneling of CH_4 in MOF-5

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

CH_4 in D-MOF-5, 9 Å



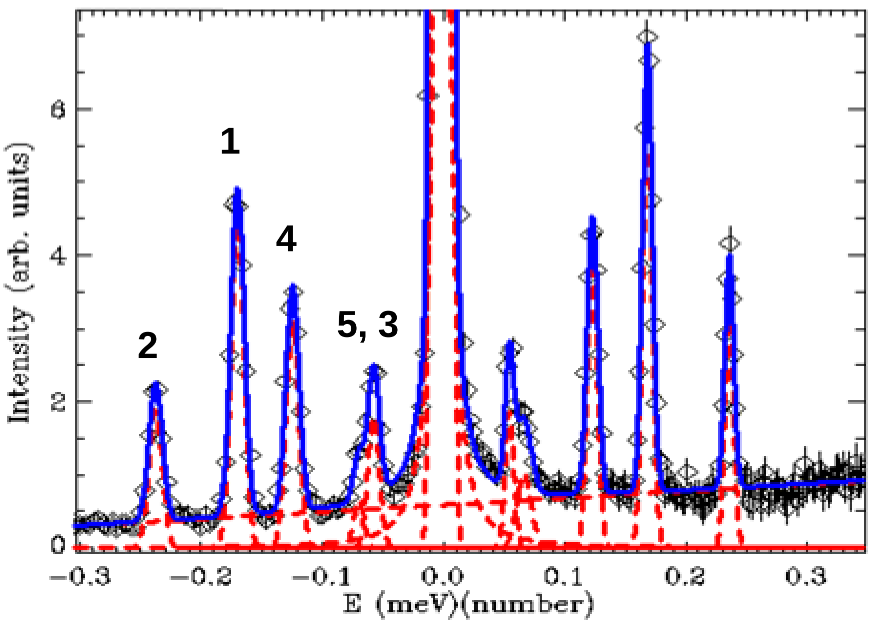


- The transition energies can be used to calculate the potential barrier in the over which the methane rotates.
- Barriers are **~23 meV** for 3 fold rotation, **~17 meV** for 3’ fold rotation.
  - Predicted barriers from DFT-D are 47 meV and 25 meV

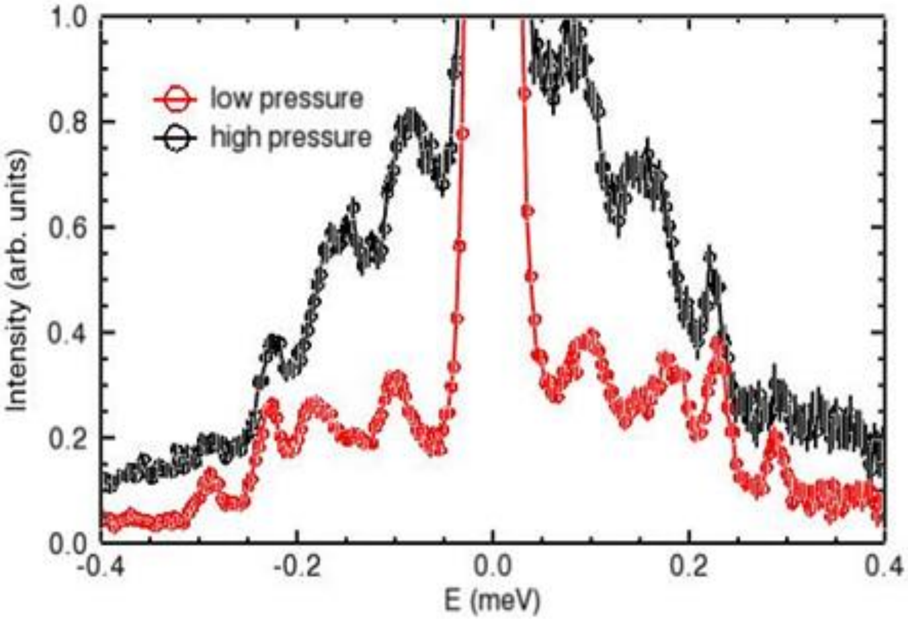
Comparison of Tunneling of CH_4 in MOF-5 and UiO-66

- 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



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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

… …

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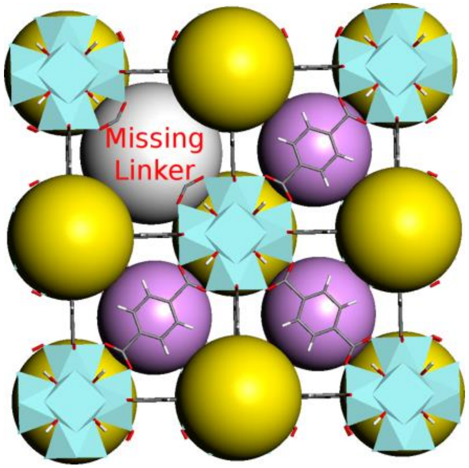
Conclusions

- DCS is used to investigate the rotational dynamics in CH_4-MOF systems, and to understand the CH_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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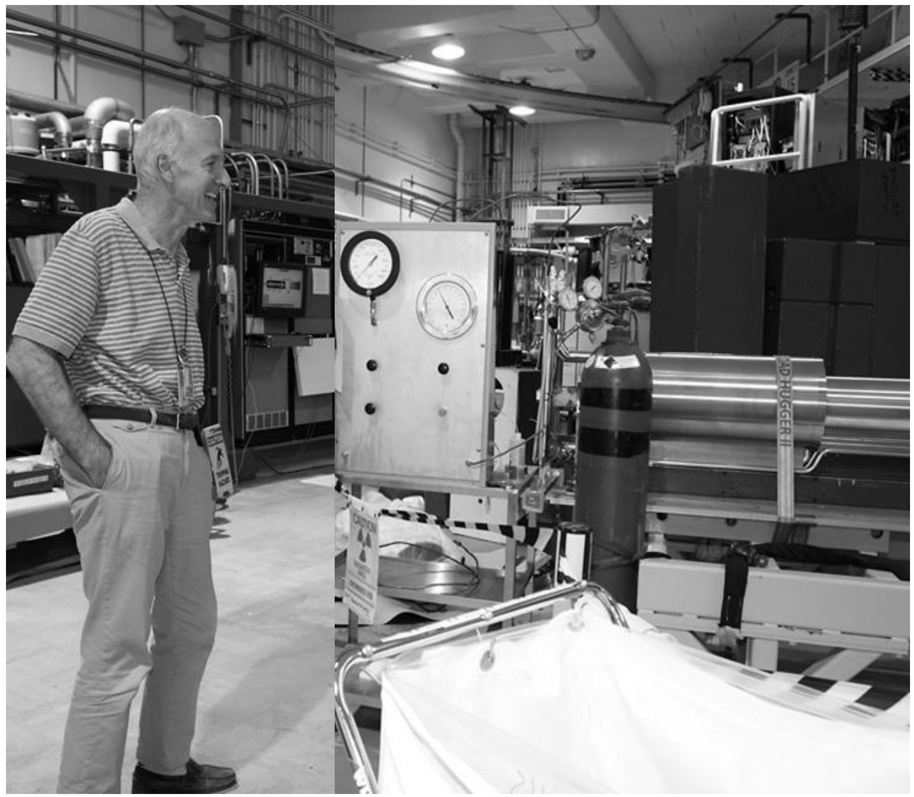

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Q&A

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