Unleashing the Potential of Metal-Organic Frameworks: Understanding and Engineering Phonon Properties for Controlling Mechanical and Thermal Characteristics

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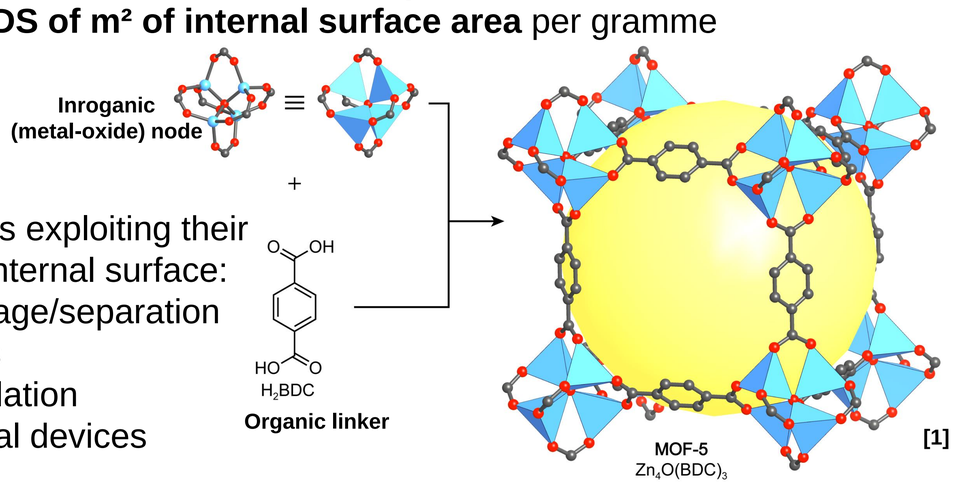
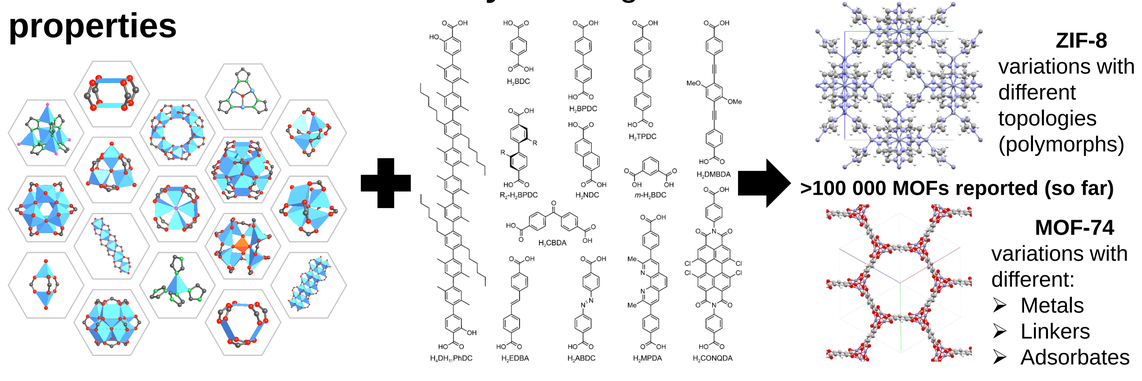
Metal-Organic Frameworks (MOFs)

- **MOFs** are novel hybrid materials incorporating **metal ions** and **organic moieties**
- Framework-like atomic structures ➔ **pores at nanoscale** often with **THOUSANDS of m² of internal surface area** per gramme



- Applicaitions exploiting their enormous internal surface:
  - Gas storage/separation
  - Catalysis
  - Encapsulation
  - Functional devices
- Incredible **structural versatility** to design materials with **tailor-made properties**



Project Motivation

- Many **relevant properties** of MOFs can be described via lattice vibrations („**phonons**“)

HARMONIC Properties
- **Vibrational spectra** → Phase identification
- Vibrational **free energy/entropy** → Stability
- **Band dispersion** → Wave propagation
- **Elastic constants** → Heteroepitaxy

ANHARMONIC Properties
- **Thermal expansion** → Temperature effects
- **Thermal conductivity** → Heat dissipation

➔ **Understanding phonons and related quantities in MOFs enables and facilitates materials design**

Work Packages and Goals

HARM

HARMONIC PROPERTIES

- How and why do **lattice vibrations (phonons)** change upon varying the building blocks?
- How do these changes affect **physical observables** (such as **elastic constants**)?

ANHARM

ANHARMONIC PROPERTIES

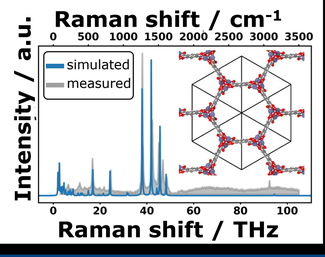
- How „**anharmonic**“ are the lattice vibrations in MOFs?
- How do these anharmonicities impact e.g. the **thermal expansion**?
- Can one **identify trends** in the **anharmonic lattice vibrations**?

Methods

- **Quantum-Mechanical Modelling**
  - **Density Functional Theory**
  - **Ab-Initio Thermodynamics**
- **Experimental Investigation**
  - **Vibrational Spectroscopy**
  - **X-Ray Diffraction**
  - **Atomic Force Microscopy + Nanoindentation**

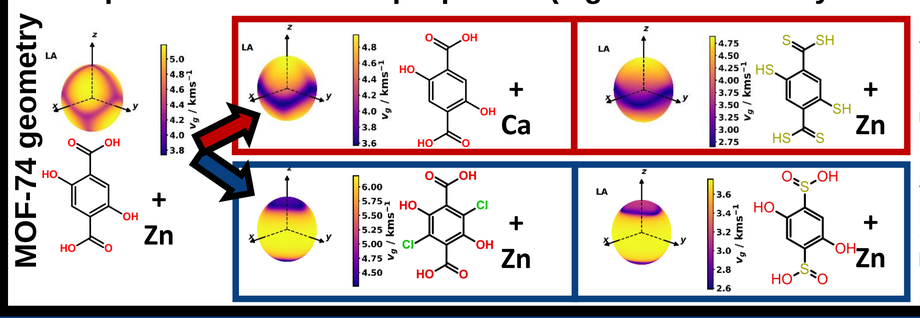
VASP b-initio ienna imulation ackage [2]

PHONOPY [3]
https://atztogo.github.io/phonopy/



Harmonic Phonon Properties

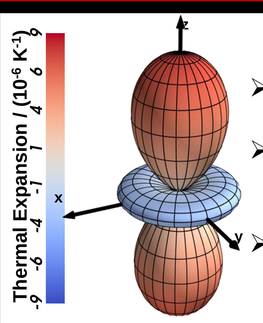
Understanding of how phonons change as a function of the composition [4] → manipulation of material properties (e.g. sound velocity distributions)



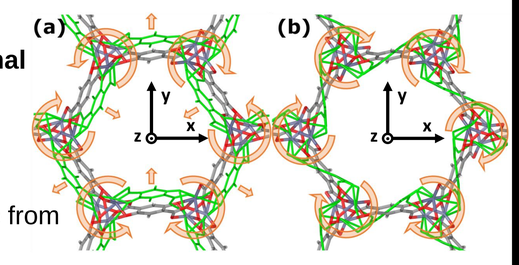
Acoustic waves faster in *z*-direction
→ Heat transport tends to be more efficient in *z*-direction

Acoustic waves slower in *z*-direction
→ Heat transport tends to be less efficient in *z*-direction

Anharmonic Properties – MOF-74

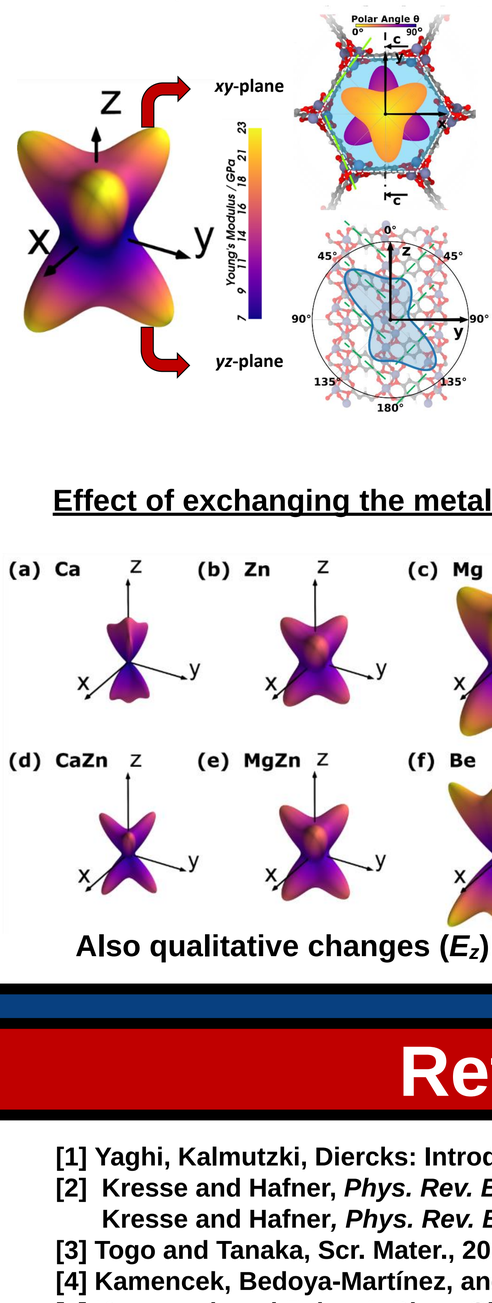


- MOF-74 shows **anisotropic thermal expansion** behaviour [6]
- Similar as for other MOFs, certain **optical modes** (see right) have large contributions
- Much larger contributions originate from **acoustic phonons**



Elastic Properties – MOF-74

Simulation of Anisotropic Young‘s Modulus [5]
(=mechanical resistance in a given direction)



- The elastic properties follow **general trends** determined by the **porosity** and the **internal bonding forces** in the MOF
- **Deviations from those trends** can be understood by analysing the **internal deformations** of the MOF under applied stress
- This allows to identify **deformation mechanisms** for various external mechanical stimuli

Effect of exchanging the metal ions

Also qualitative changes (E_z)!

Spring networks → flexibility of the linkers

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[5] Kamencek and Zojer, *J. Phys. Chem. C.* 2021, in press
[6] Kamencek, Resel, Falcaro, and Zojer, 2021, in preparation