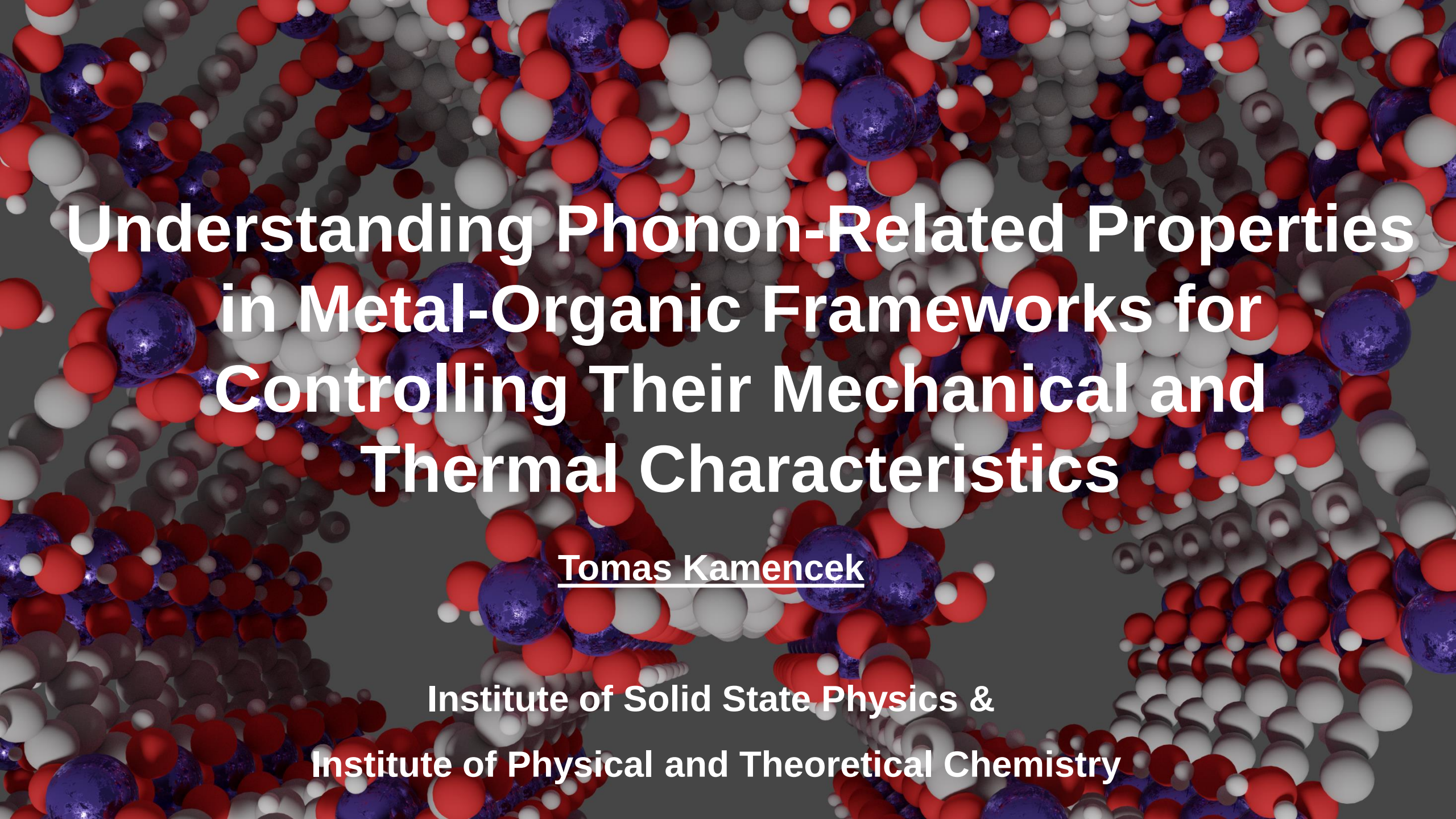


Understanding Phonon-Related Properties in Metal-Organic Frameworks for Controlling Their Mechanical and Thermal Characteristics

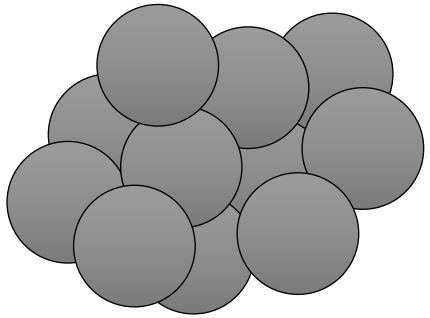
Tomas Kamencek

Institute of Solid State Physics &

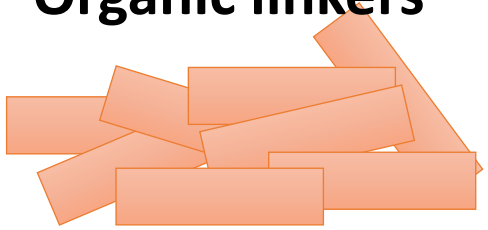
Institute of Physical and Theoretical Chemistry

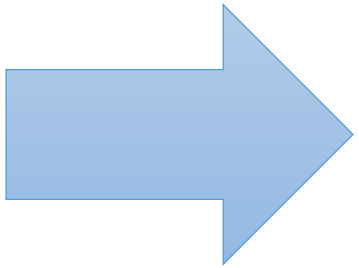
Metal-Organic Frameworks (MOFs)

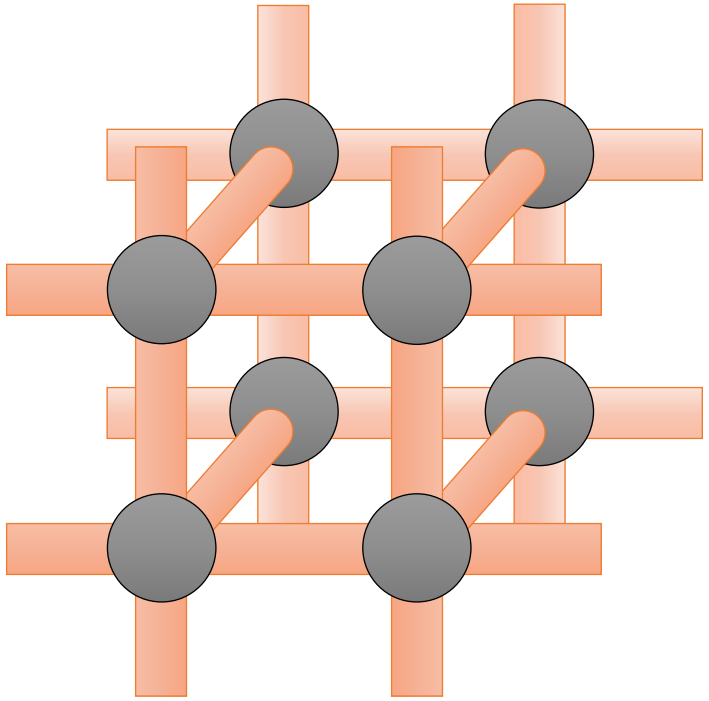
Metal (oxide) nodes



Organic linkers







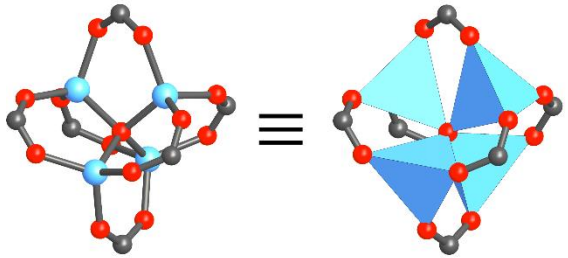
Science, **2013**, 341, 1230444
Microporous Mesoporous Mater., **2004**, 73,3

THOUSANDS of m² per gramme of the material

Gas storage	Catalysis	Gas separation	Encapsulation	Functional decives

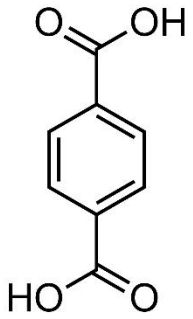
A Prototypical MOF: MOF-5

Metal (oxide) nodes



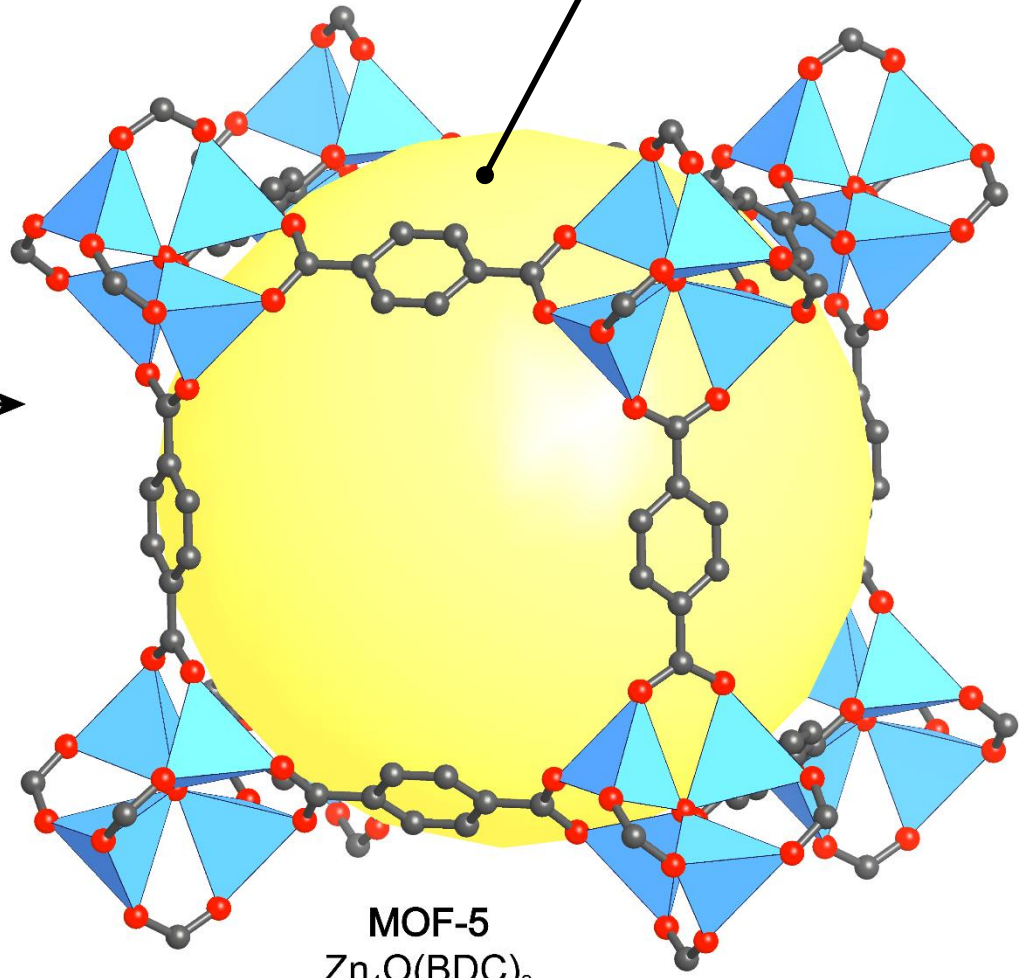
+

Organic linkers



H_2BDC

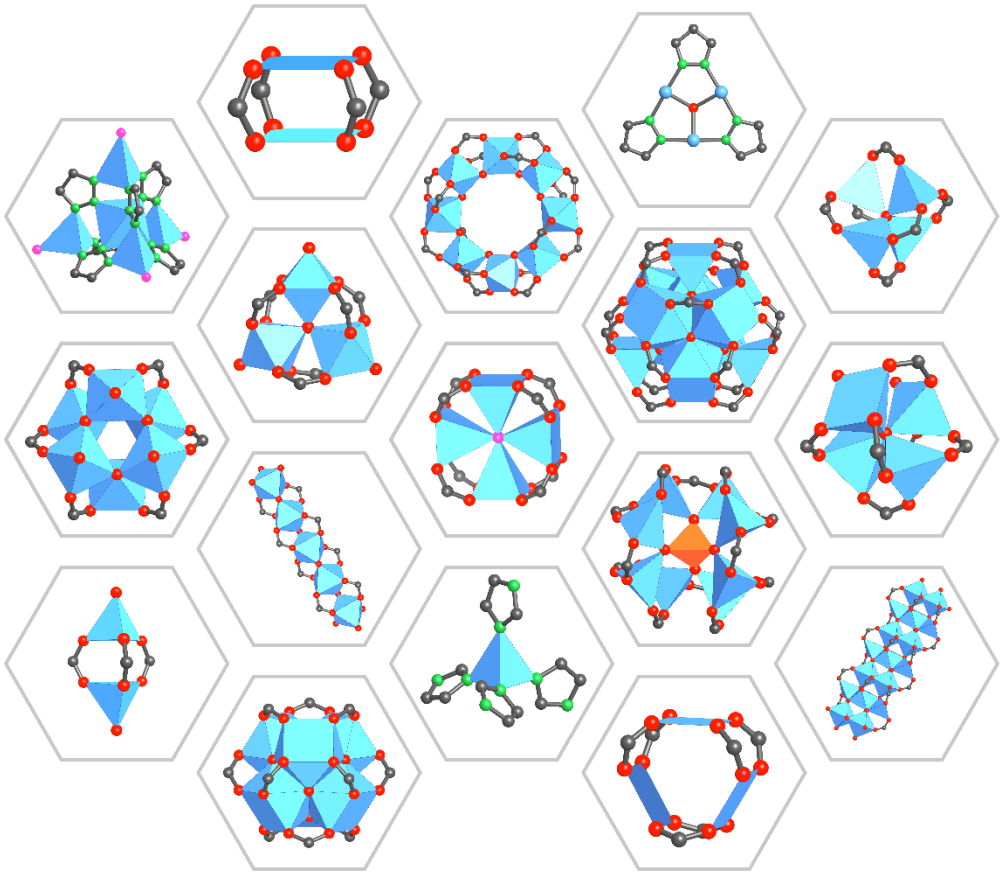
„Largest Included Sphere“

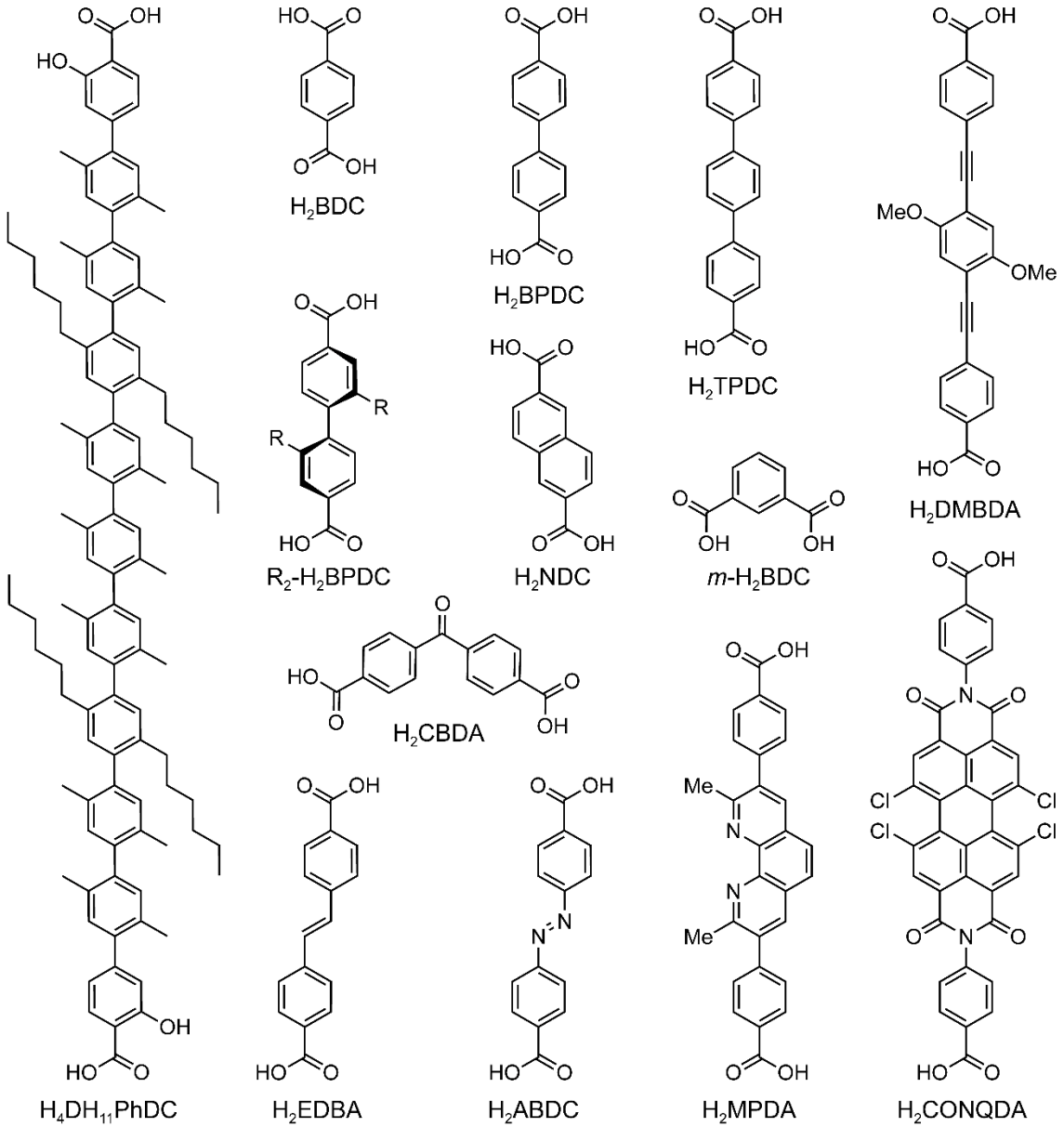


MOF-5

$Zn_4O(BDC)_3$

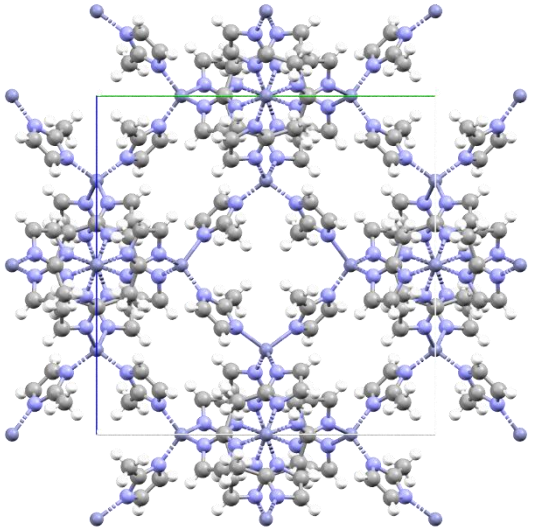
Nodes + Linkers





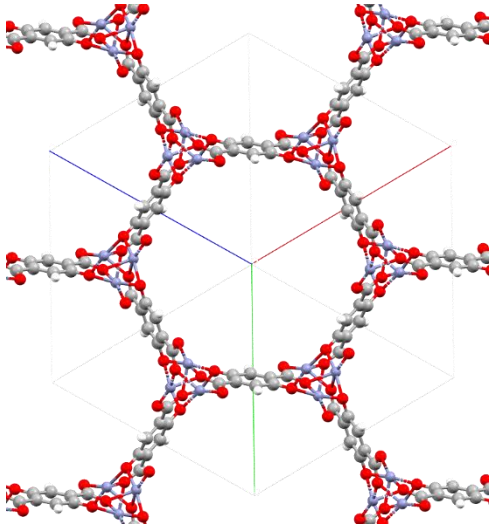
Some Famous MOFs

ZIF-8



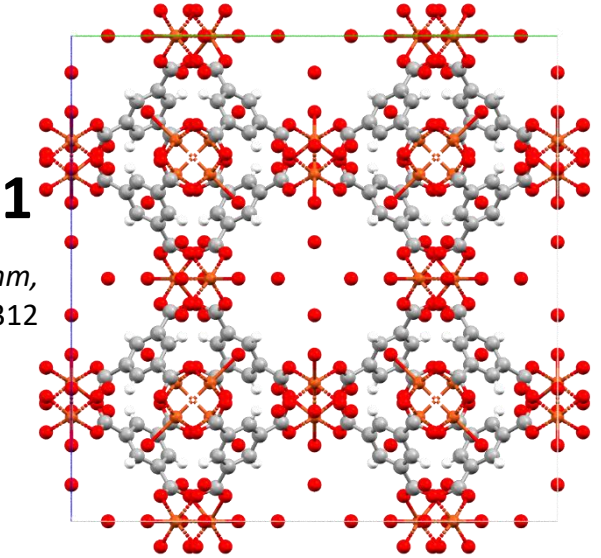
Phys. Rev. Lett., **2012**, 108, 1-6

MOF-74

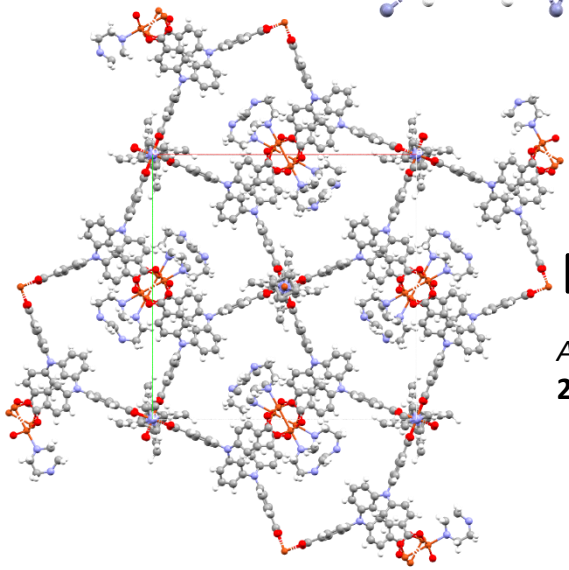


J. Mater. Chem. A, **2015**, 3, 986-995

HKUST-1

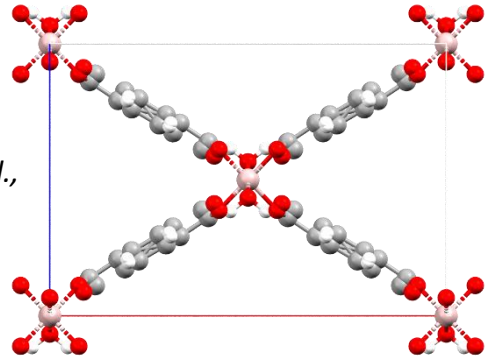


CrystEngComm, **2016**, 18, 4303-4312



DUT-90

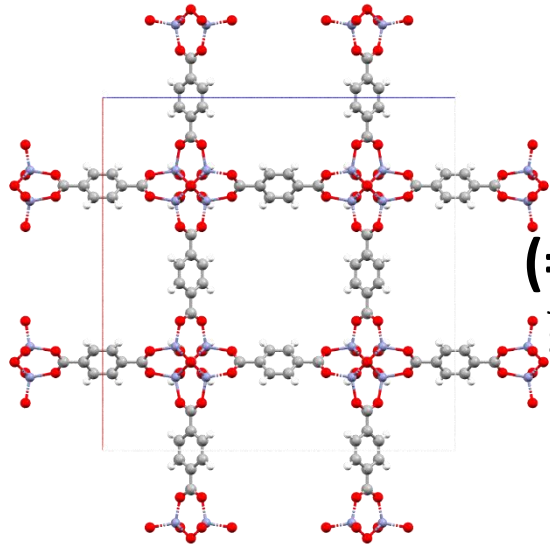
Angew. Chemie –Int. Ed., **2018**, 57, 13780-13783



MIL-53

Phys. Rev. Lett., **2012**, 109, 1-5

J. Chem. Phys., **2013**, 138, 174703

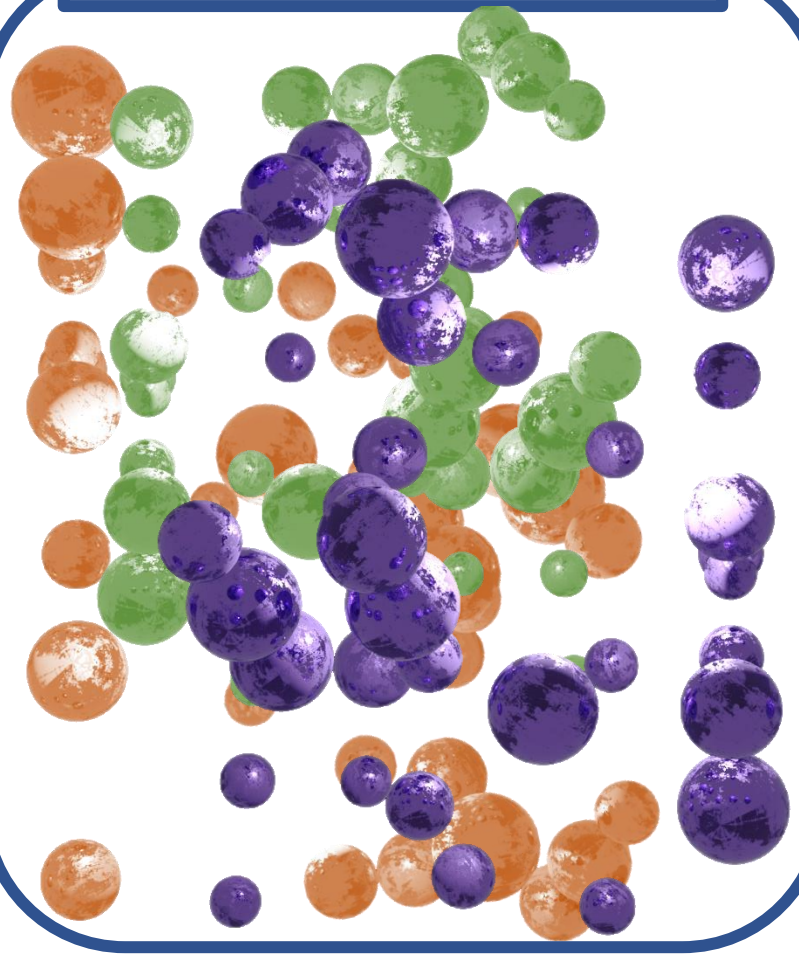


MOF-5 (=IRMOF-1)

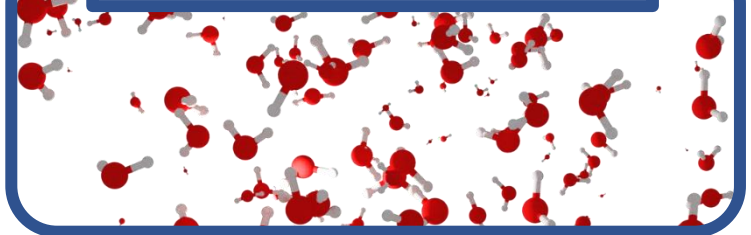
J. Chem. Phys., **2017**, 146, 184705

Properties in Metal-Organic Frameworks

Metal (Oxide) Nodes



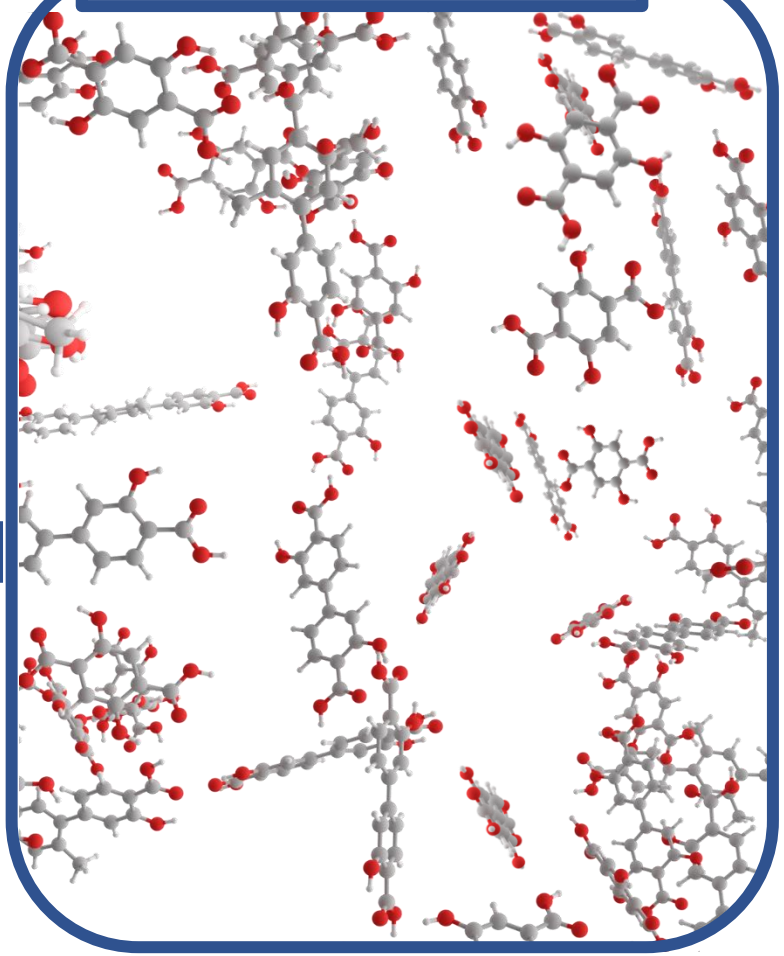
Adsorbates



?

Properties

Organic Linkers



Relevant Properties of MOFs

Phonons determine many of the relevant properties of a MOF!

Γ-Phonons

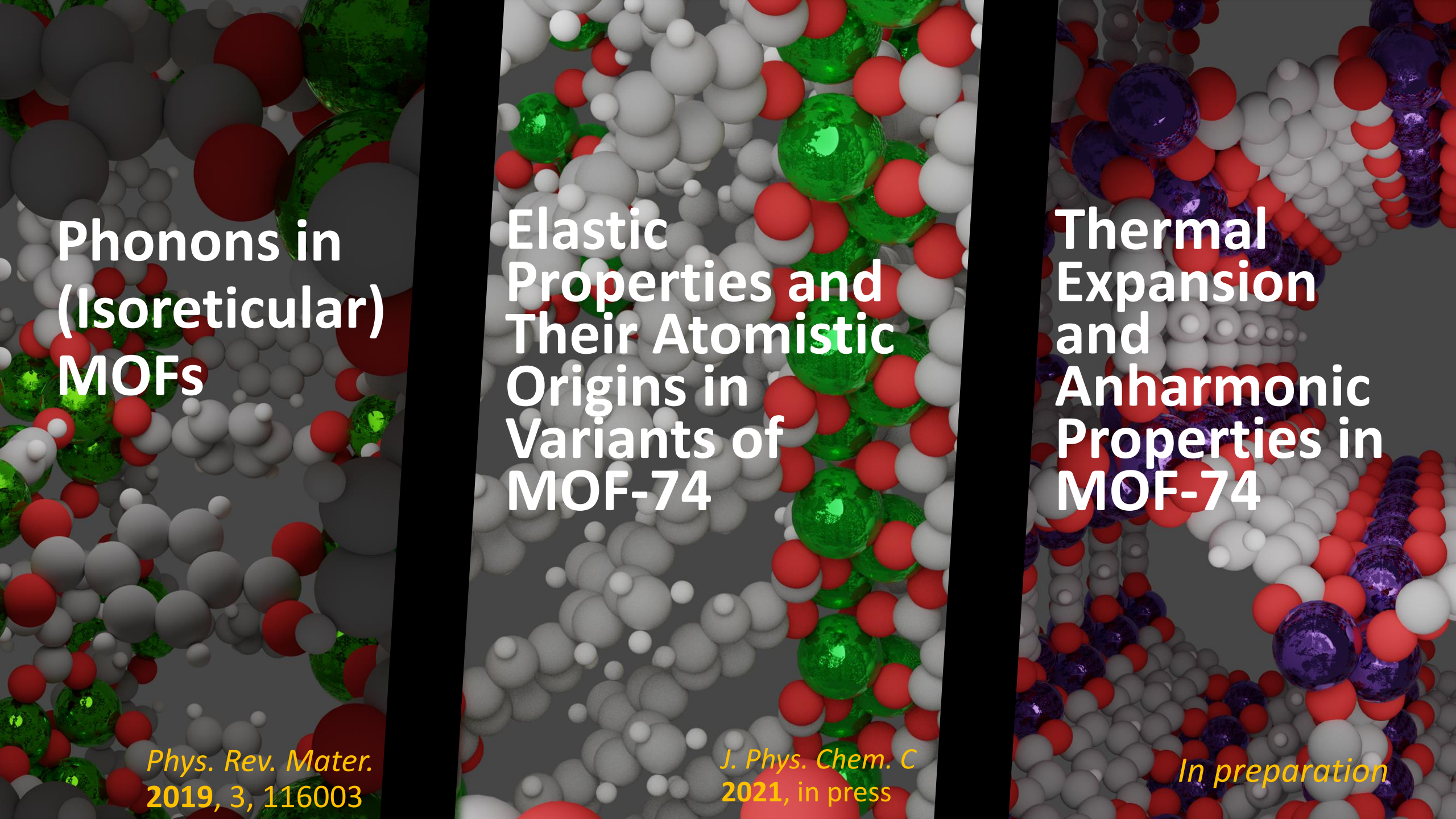
- Characterisation: Raman/IR Spectroscopy
- Phase Identification

Band Structures

- Vibrational Free Energy / Entropy
- Elastic Constants
- Band Dispersion (Group Velocities)

Anharmonicities

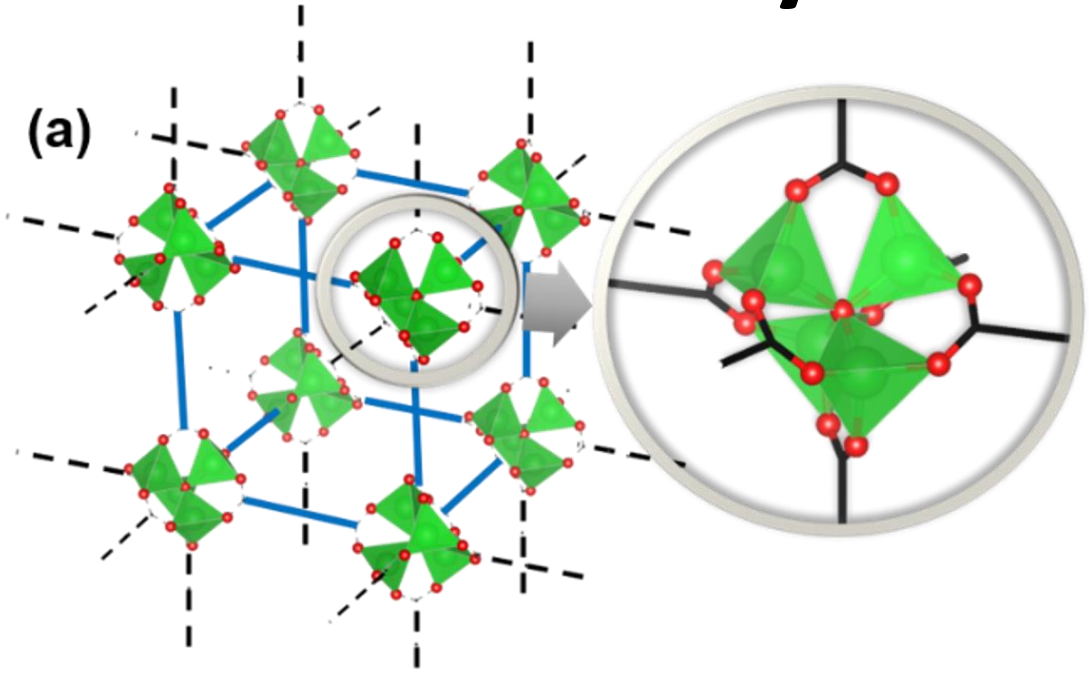
- Thermal Expansion
- Phonon Lifetimes
- Thermal Conductivity

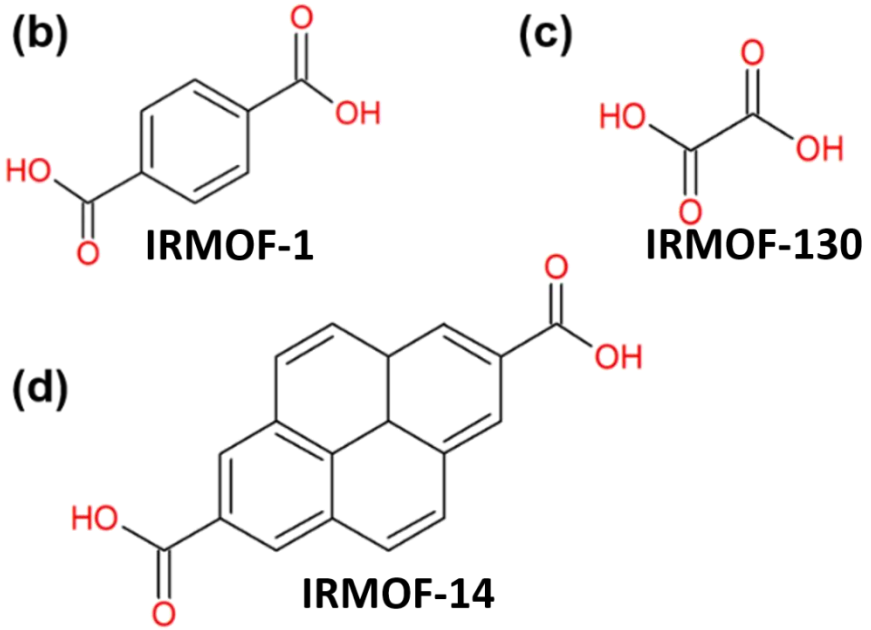

Phonons in (Isoreticular) MOFs
Phys. Rev. Mater. 2019, 3, 116003
Elastic Properties and Their Atomistic Origins in Variants of MOF-74
J. Phys. Chem. C 2021, in press
Thermal Expansion and Anharmonic Properties in MOF-74
In preparation

Phonons in (Isoreticular) MOFs

Kamencek, Bedoya-Martínez, and Zojer; *Phys. Rev. Mater.* **2019**, 3, 116003

Goals of the Study





- **Systematic analysis** of the phonon band structures as a function of
  - The metal ions (Mg^{2+}, Ca^{2+})
  - The linker (→ IRMOF-1, IRMOF-130, IRMOF-14)
- In which **frequency regimes** can one find certain phonon modes?

Methods

Kresse and Hafner, *Phys. Rev. B*, **1993,** 47 (1), 558
Kresse and Hafner, *Phys. Rev. B*, **1994,** 49 (20), 14251

Aradi et al. *J. Phys. Chem. A,* **2007**, 111 (26), 5678

Togo and Tanaka, *Scr. Mater.,* **2015,** 108, 1

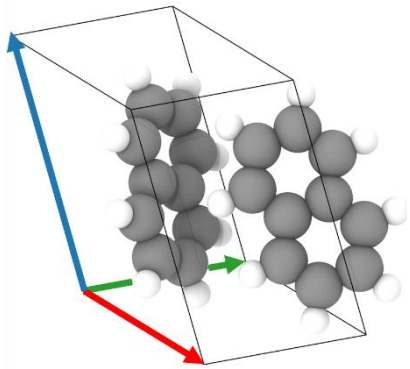
PHONOPY

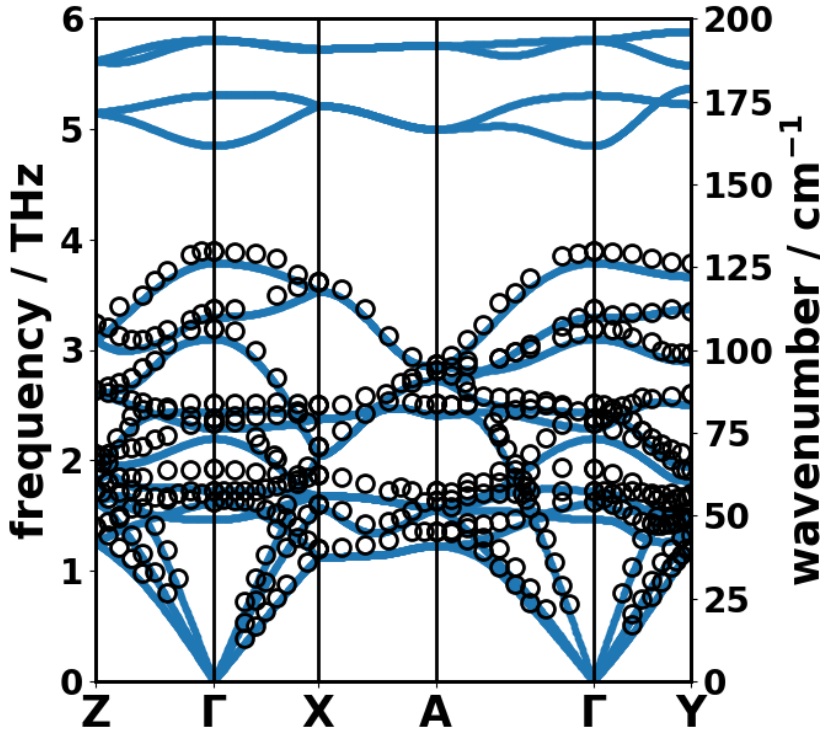
https://atztogo.github.io/phonopy/

D3-BJ correction:

Grimme et al., *J. Chem. Phys.,* **2010**, 132 (15), 154104; Grimme et al., *J. Comput. Chem.,* **2011**, 32 (7), 1456

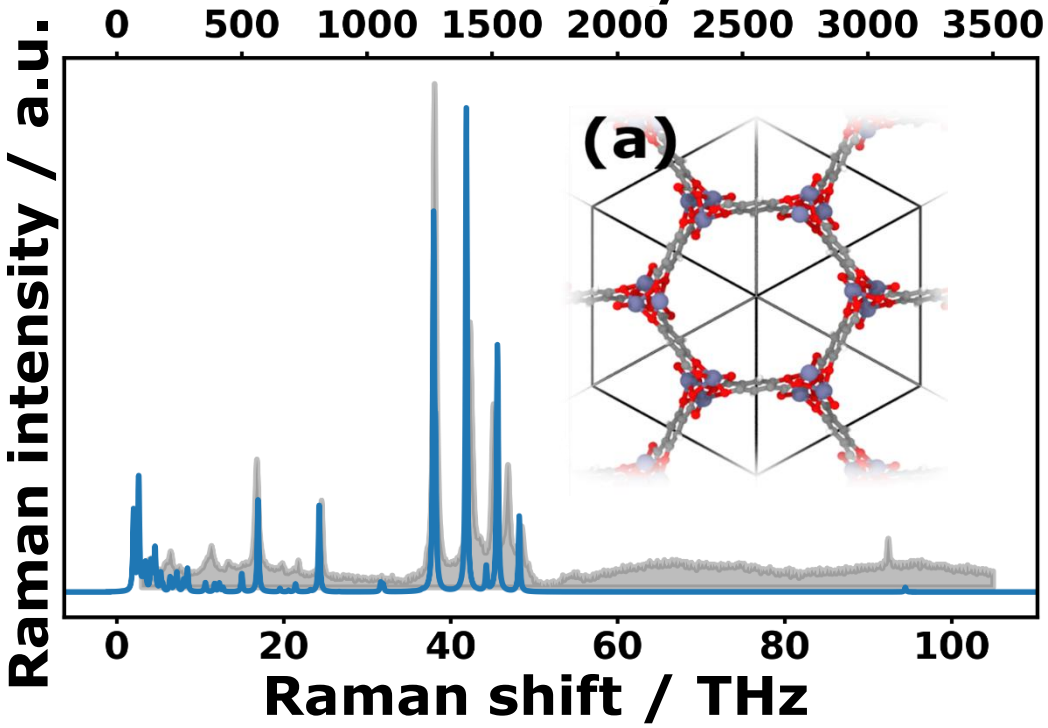
Crystalline Naphthalene



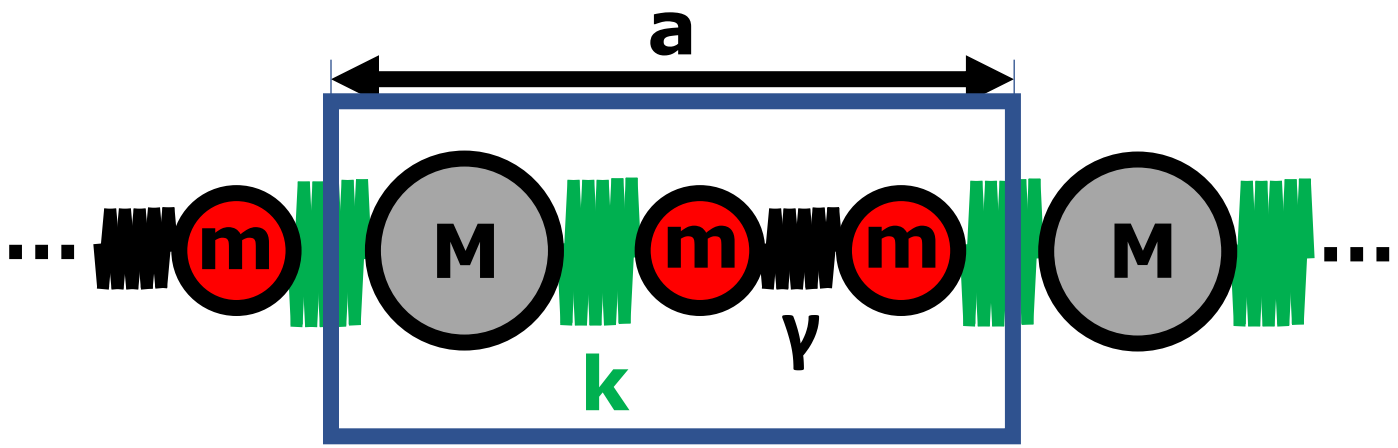


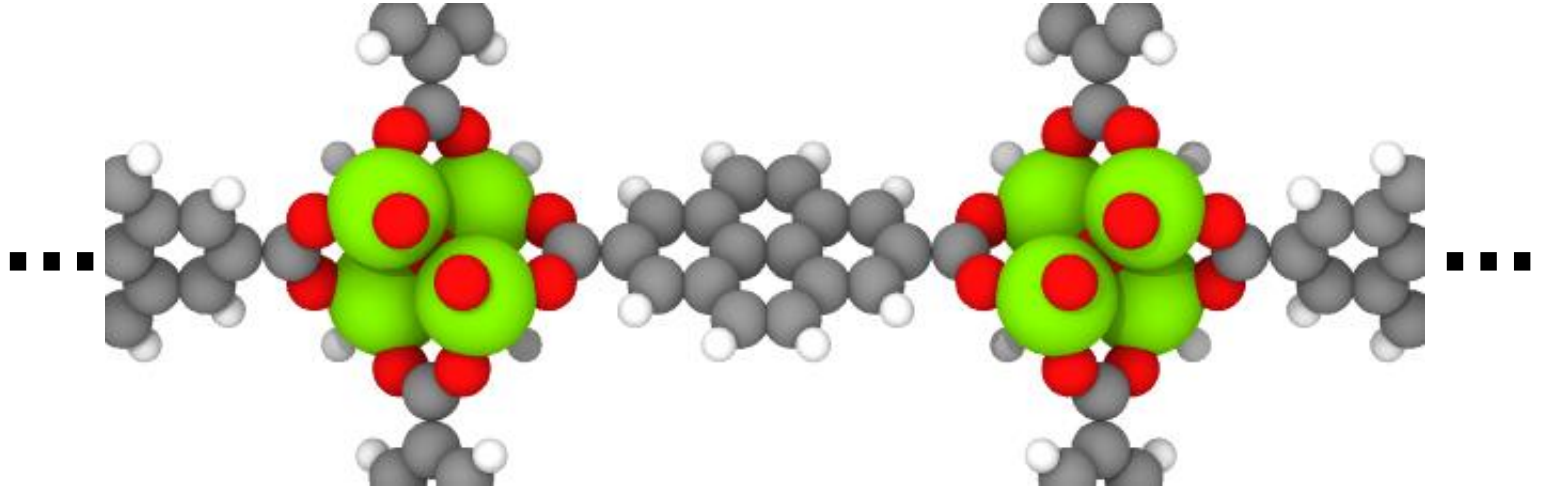
Kamencek, Wieser, Zojer et al., *J. Chem. Theory Comput.* **2020**, 16, 4, 2716–2735

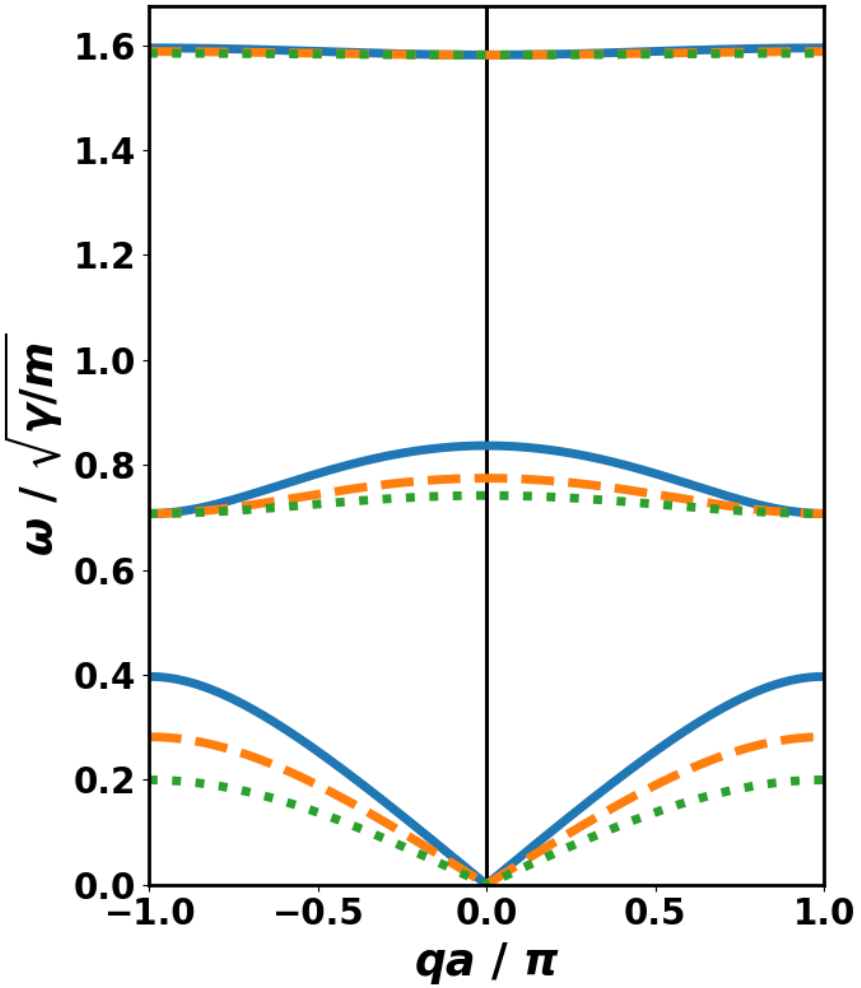
MOF-74



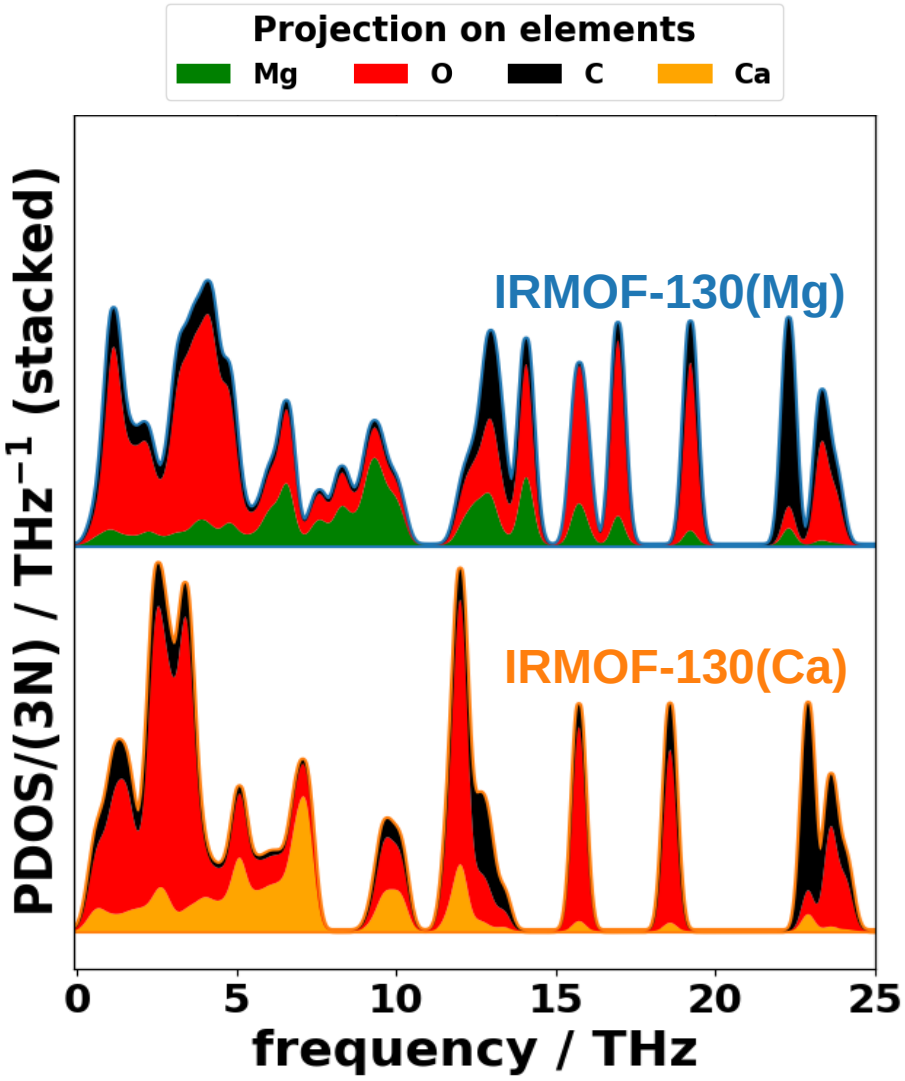
Which Phonon Bands to Expect?

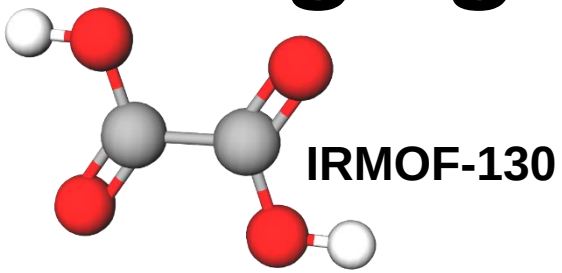






Projected Density of States: Exchanging Metals



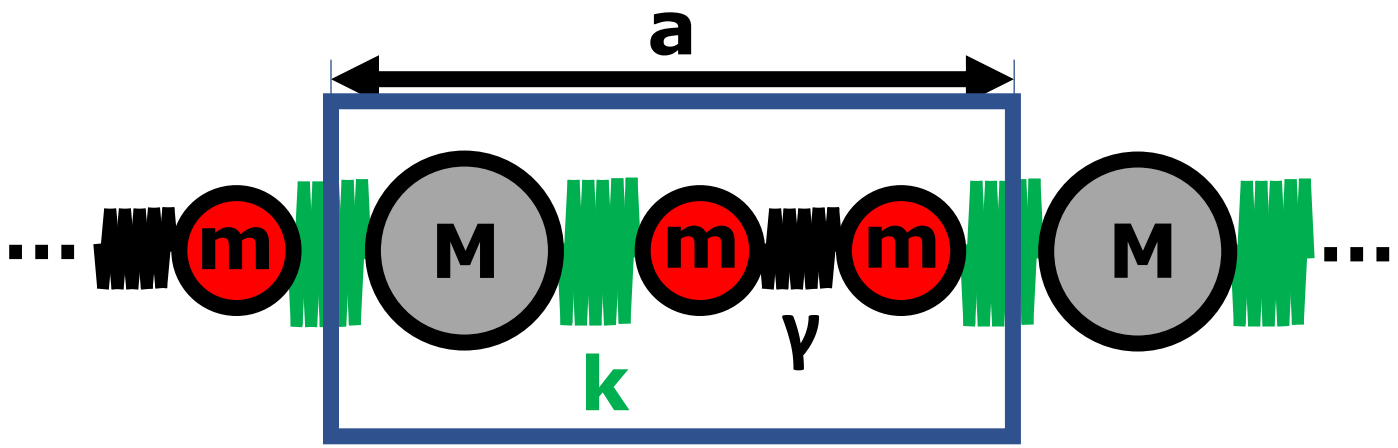


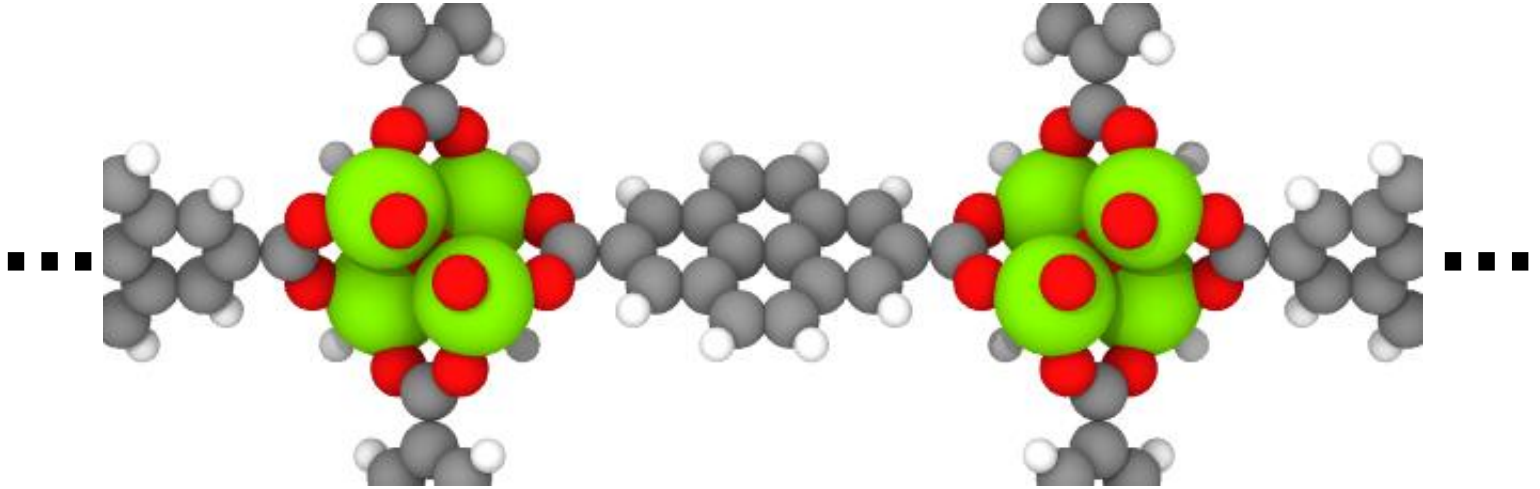
Low frequency region
- dominated by O and Mg/Ca

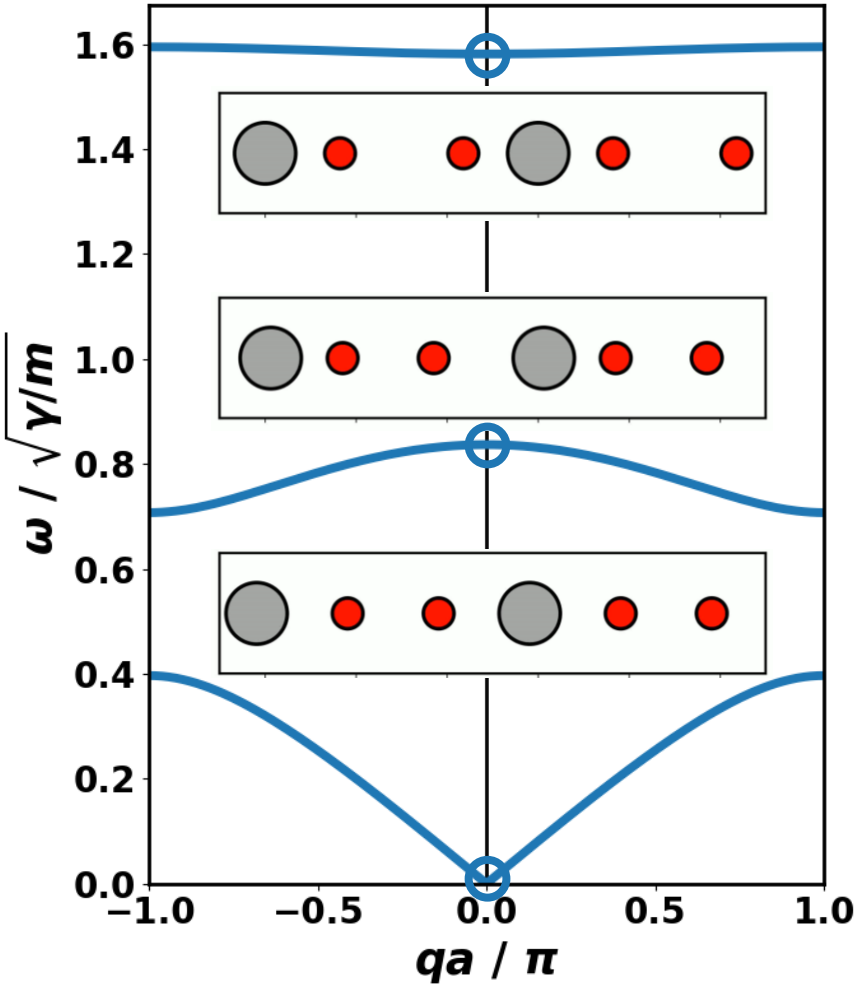
Higher frequencies
- C contributions
- Sharp peaks

Mg→Ca: Modes shifted to lower frequencies

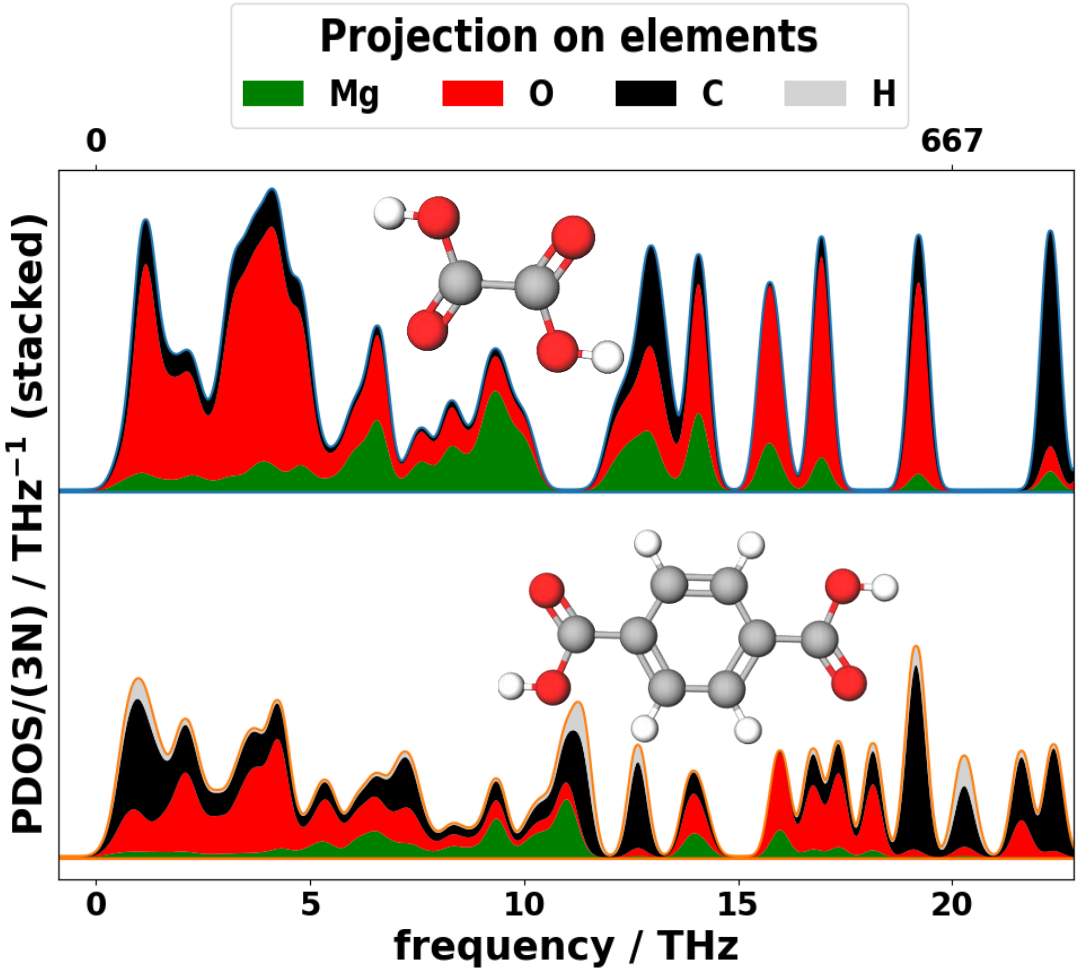
Which Phonon Bands to Expect?





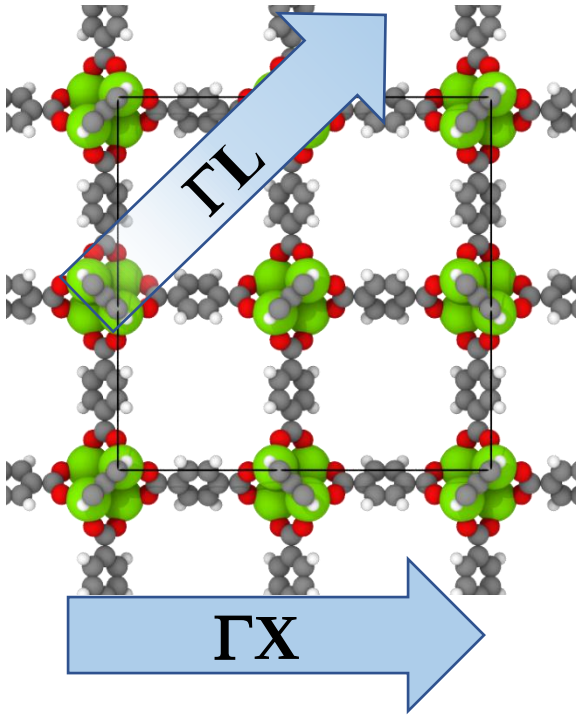


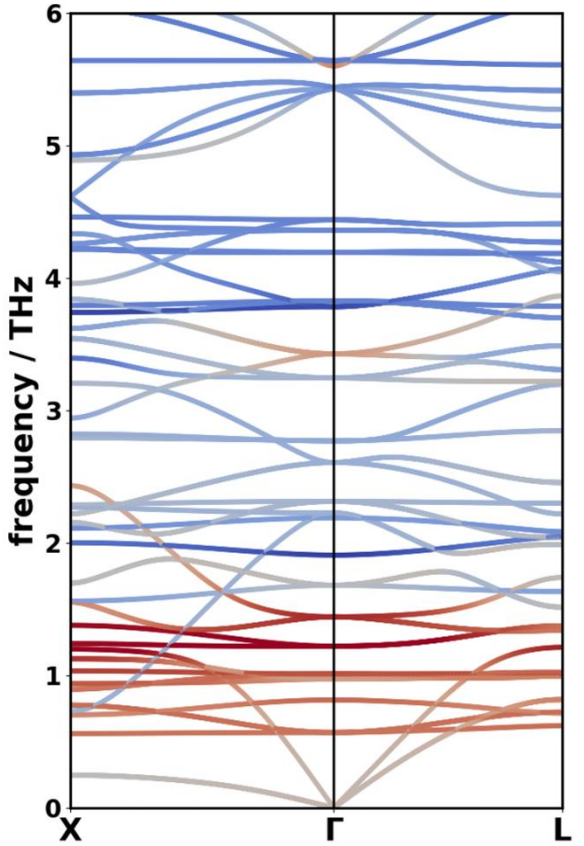
Projected Density of States: Exchanging Linkers

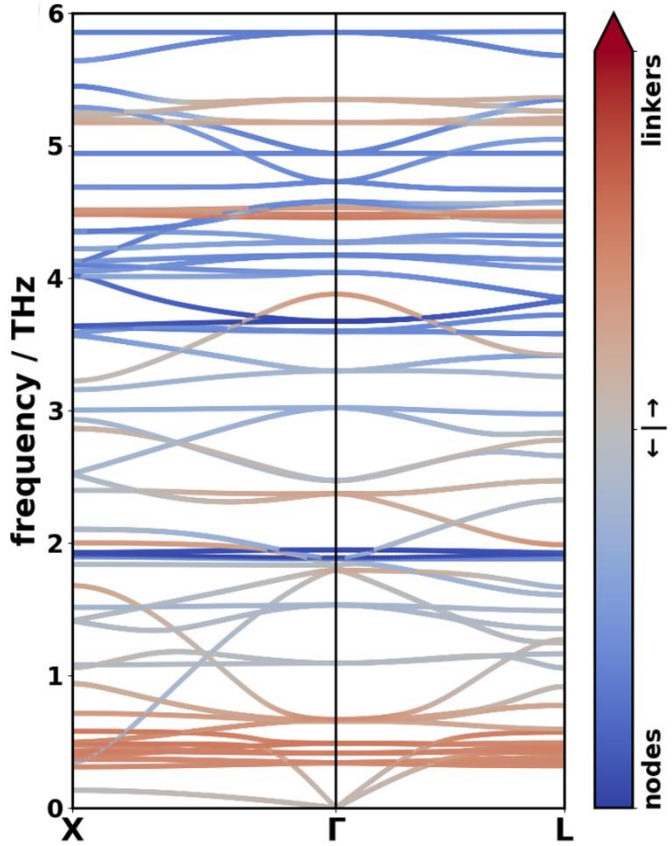


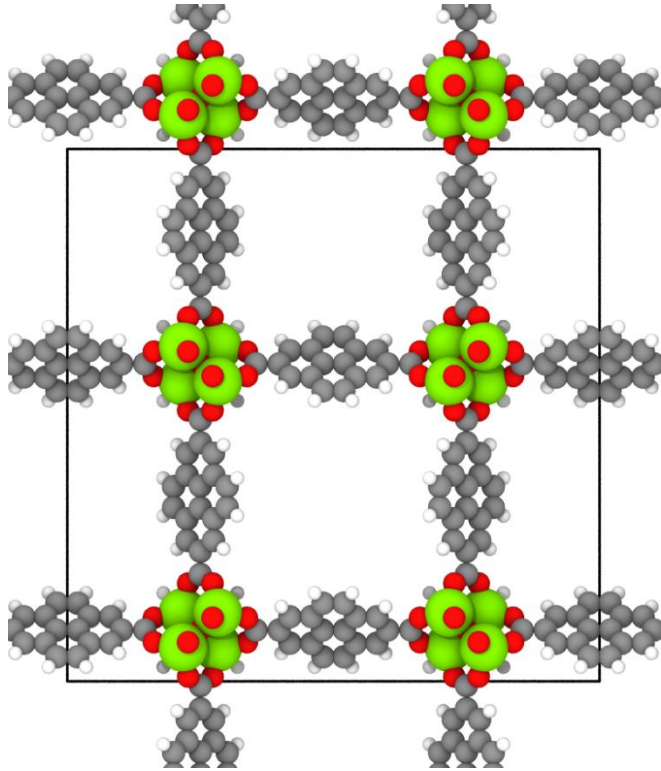
- more **C** contribution
- **low energy** motion (torsion, bending, rotation of linkers): **rigid unit modes**

Increasing Complexity of the Linker: More Low-Energy Linker Modes

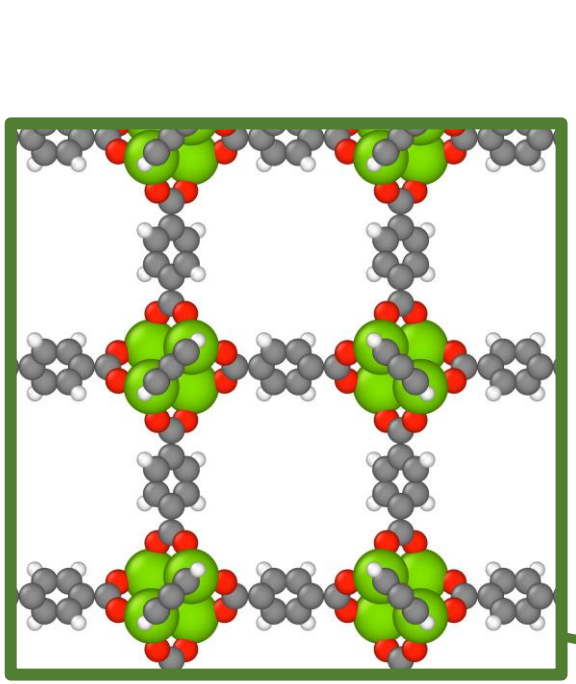


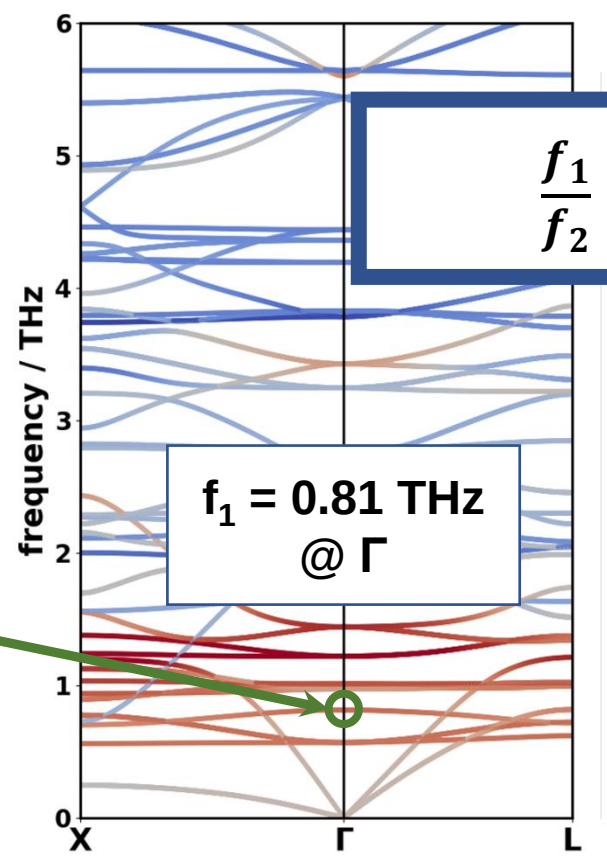






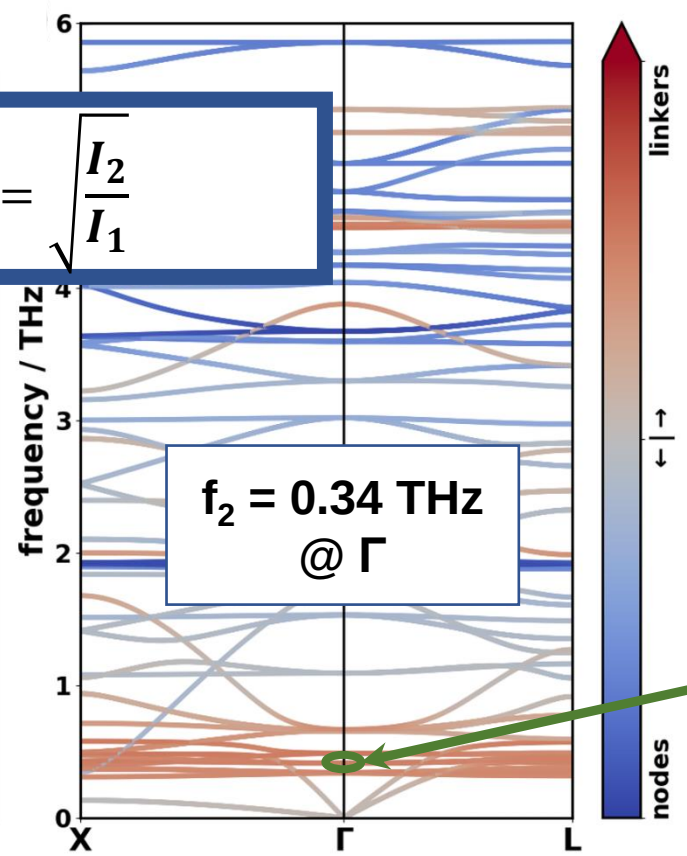
Increasing Complexity of the Linker: Quantitative Trends



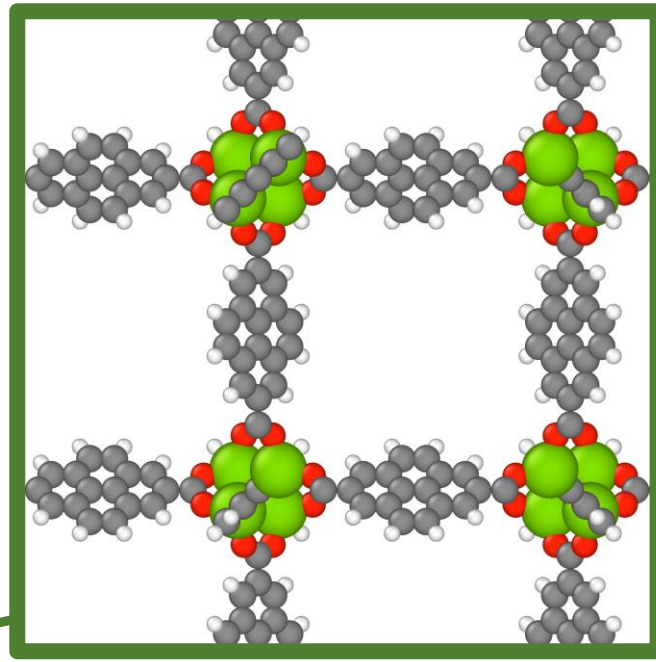


$$\frac{f_1}{f_2} = \sqrt{\frac{I_2}{I_1}}$$

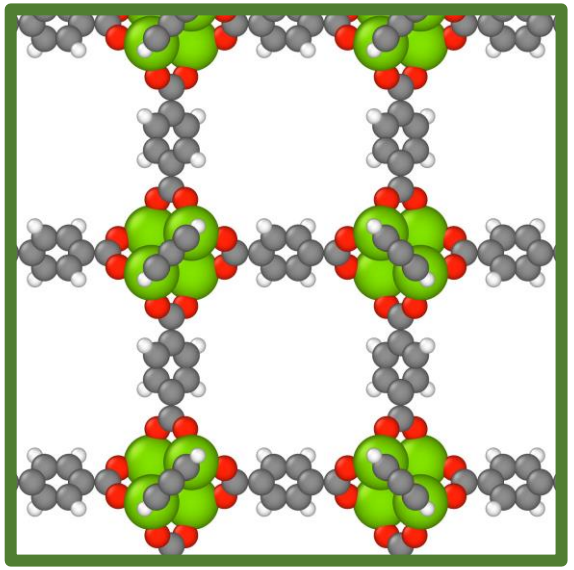
f_1 = 0.81 THz @ Γ

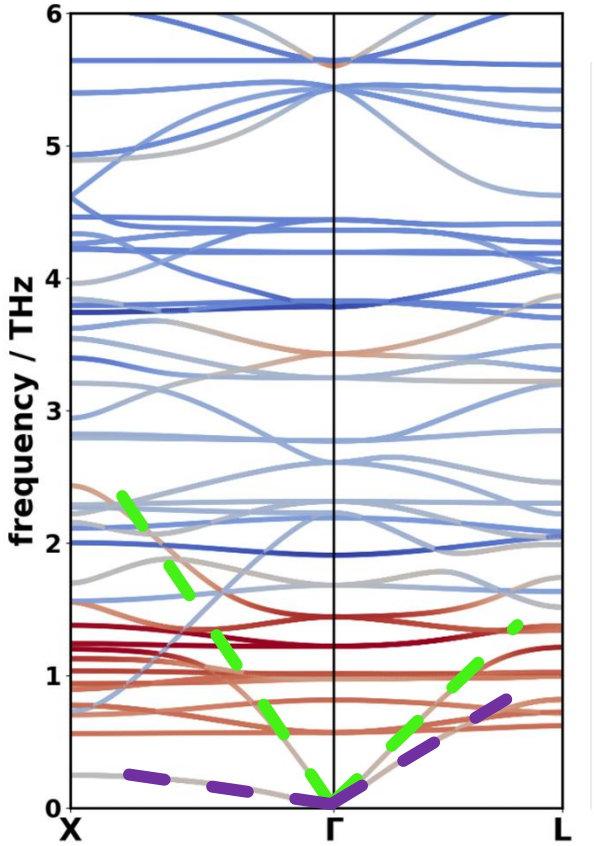


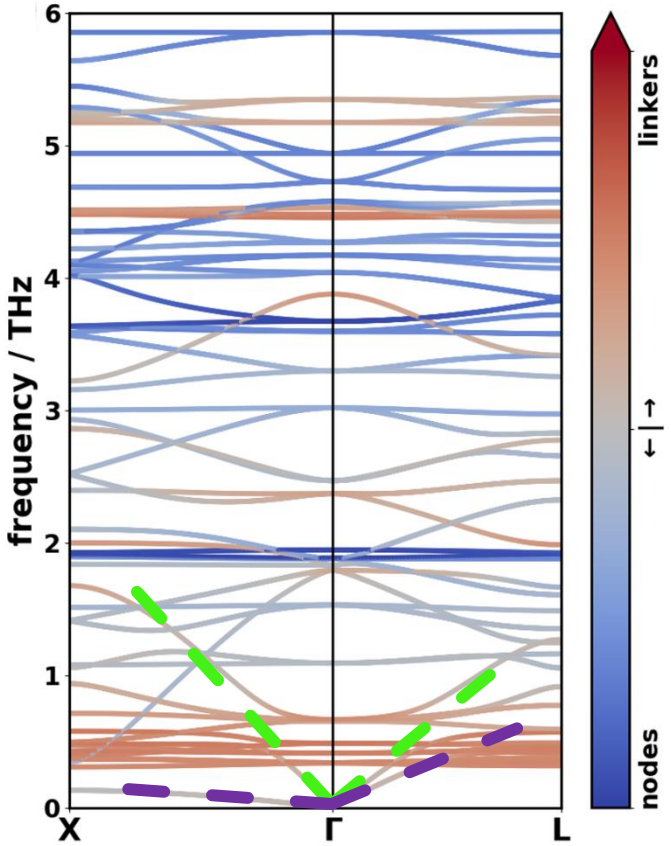
f_2 = 0.34 THz @ Γ

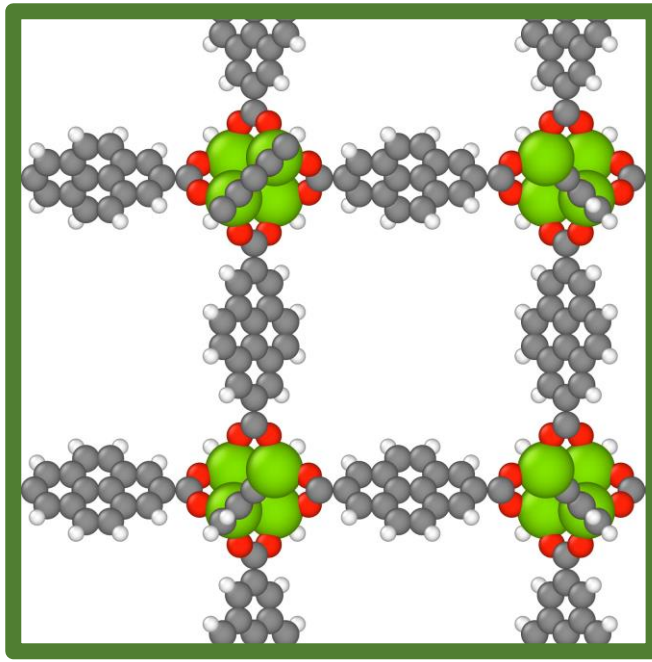


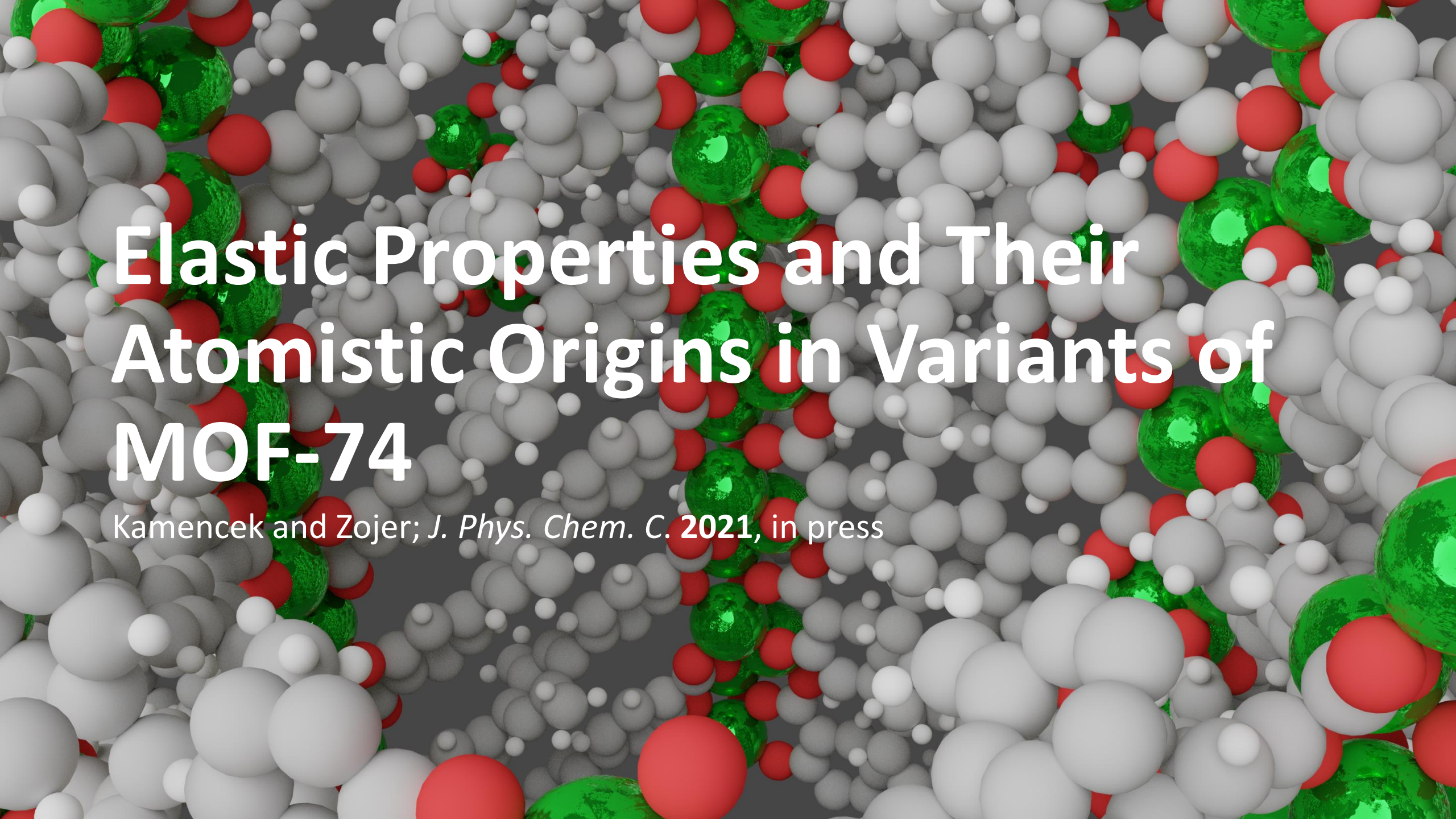
Increasing Complexity of the Linker: Quantitative Trends







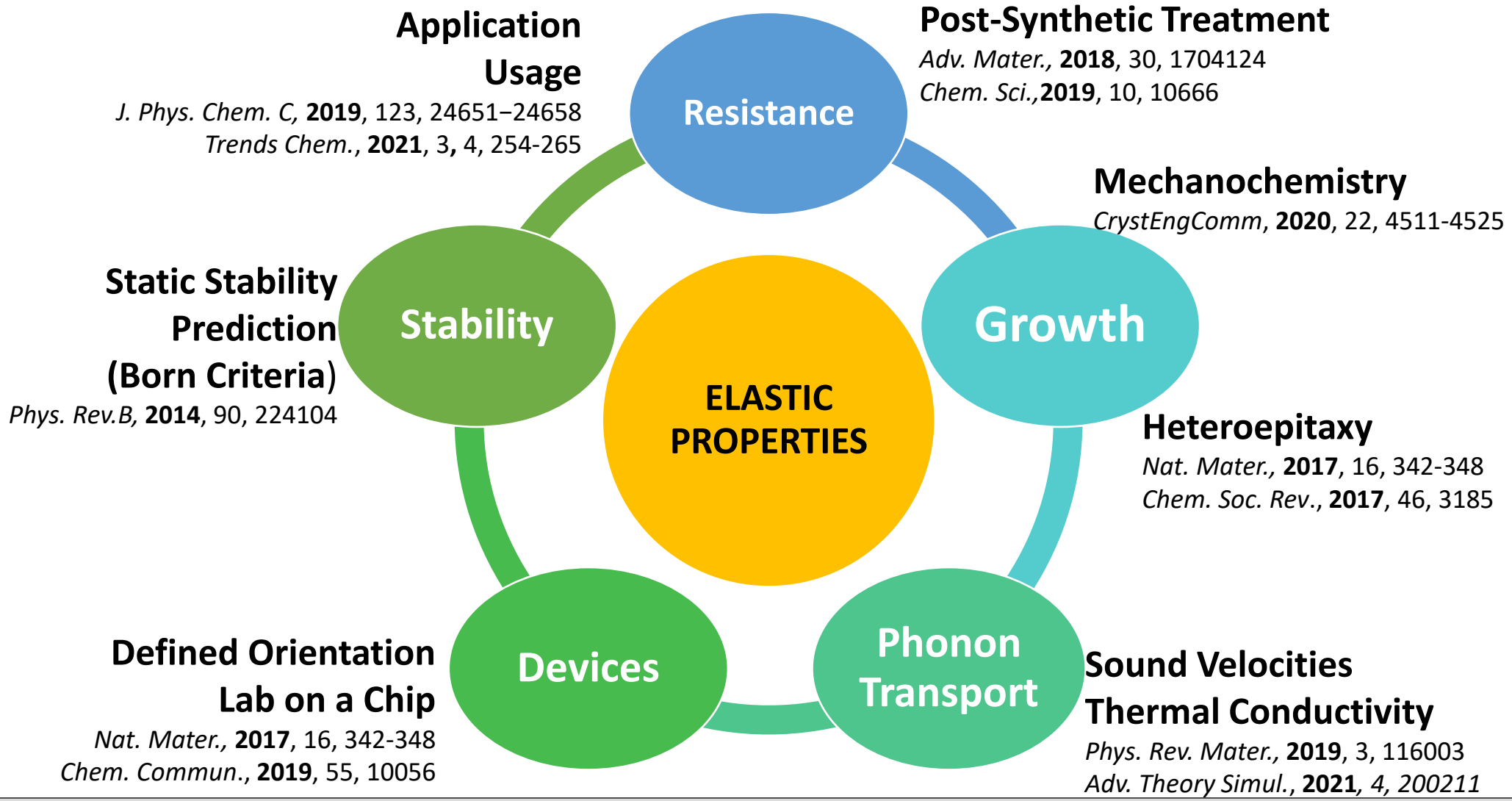




Elastic Properties and Their Atomistic Origins in Variants of MOF-74

Kamencek and Zojer; *J. Phys. Chem. C.* **2021**, in press

Why Elastic Properties?

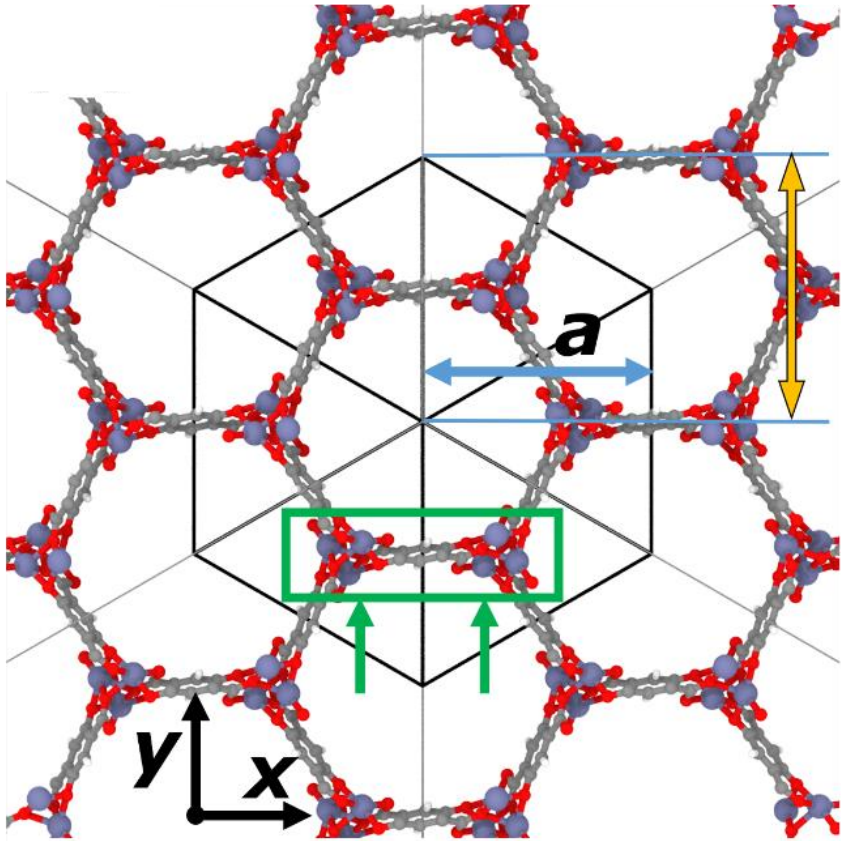


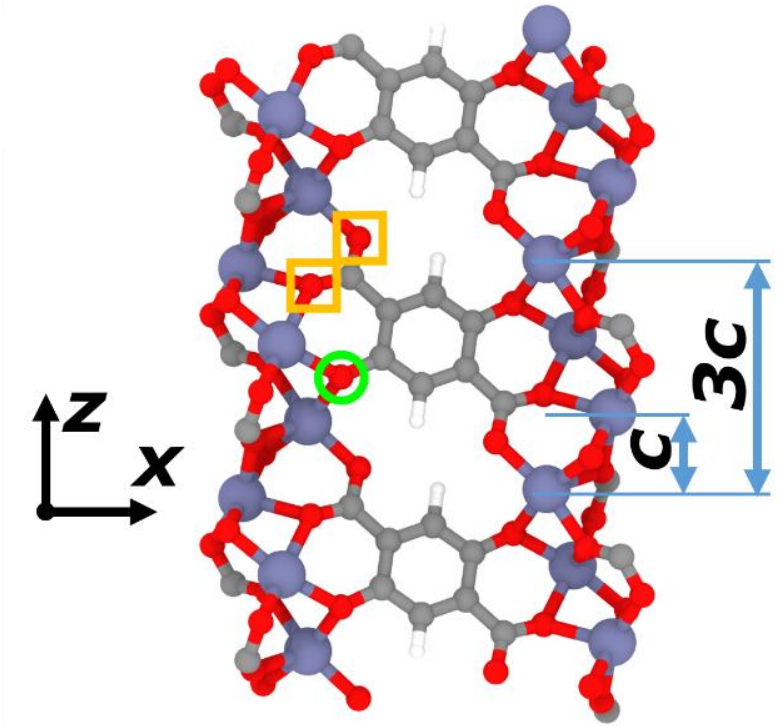
MOF-74(Zn)

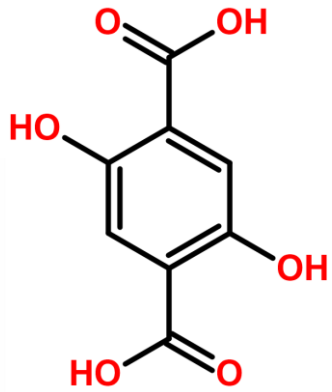
J. Am. Chem. Soc., 2005, **127**, 1504-1518
Science ,2012, **336**, 1018

Density Functional Theory: PBE/D3-BJ

→ **Full Elastic Tensor**



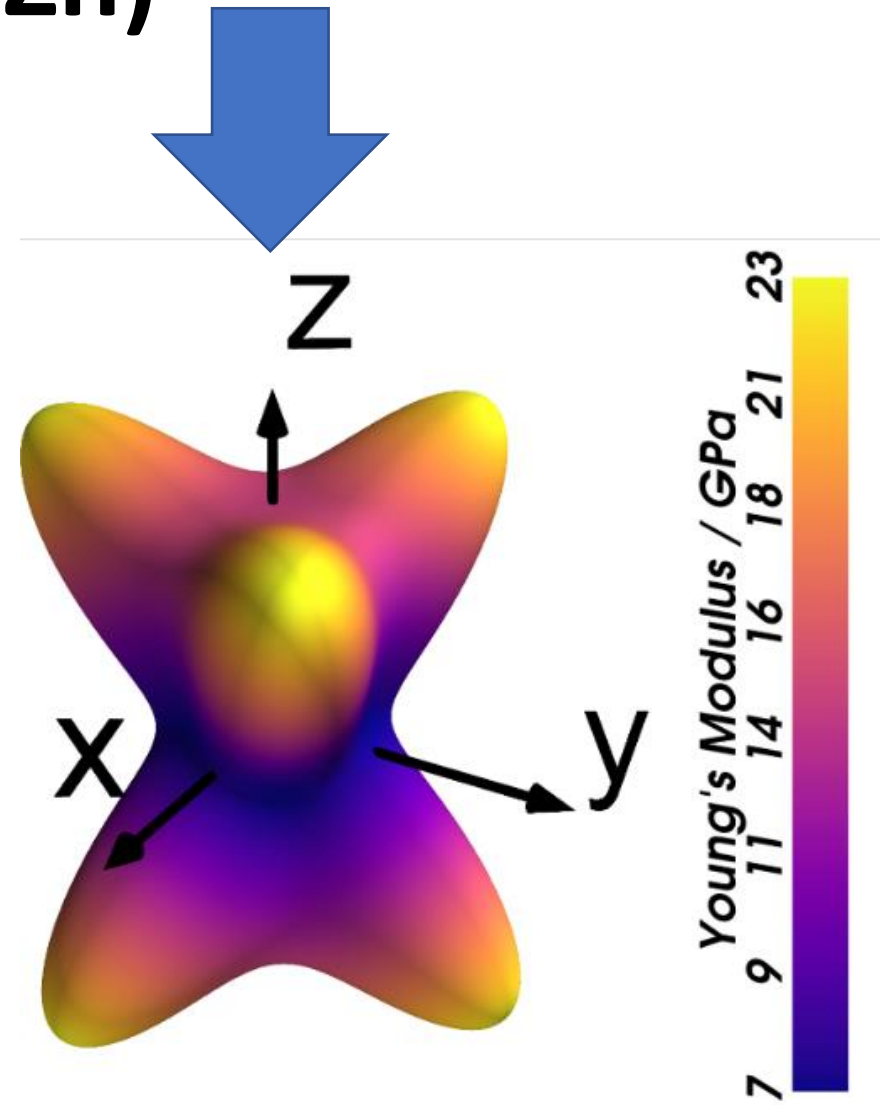




2 Lattice Paramters (*a*,*c*), rhombohedral Bravais lattice

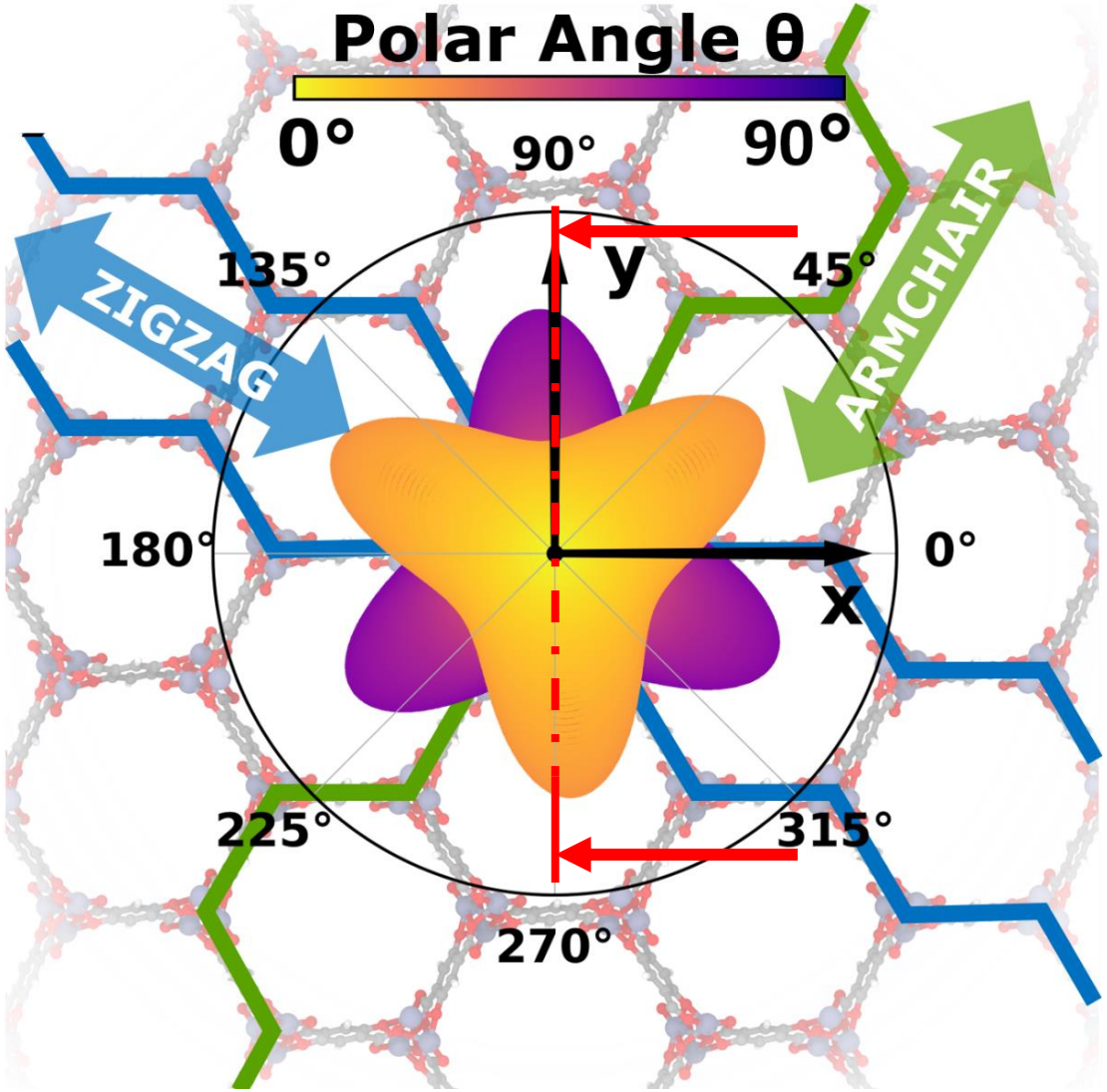
Young's Modulus in MOF-74(Zn)

= mechanical resistance to uniaxial strain



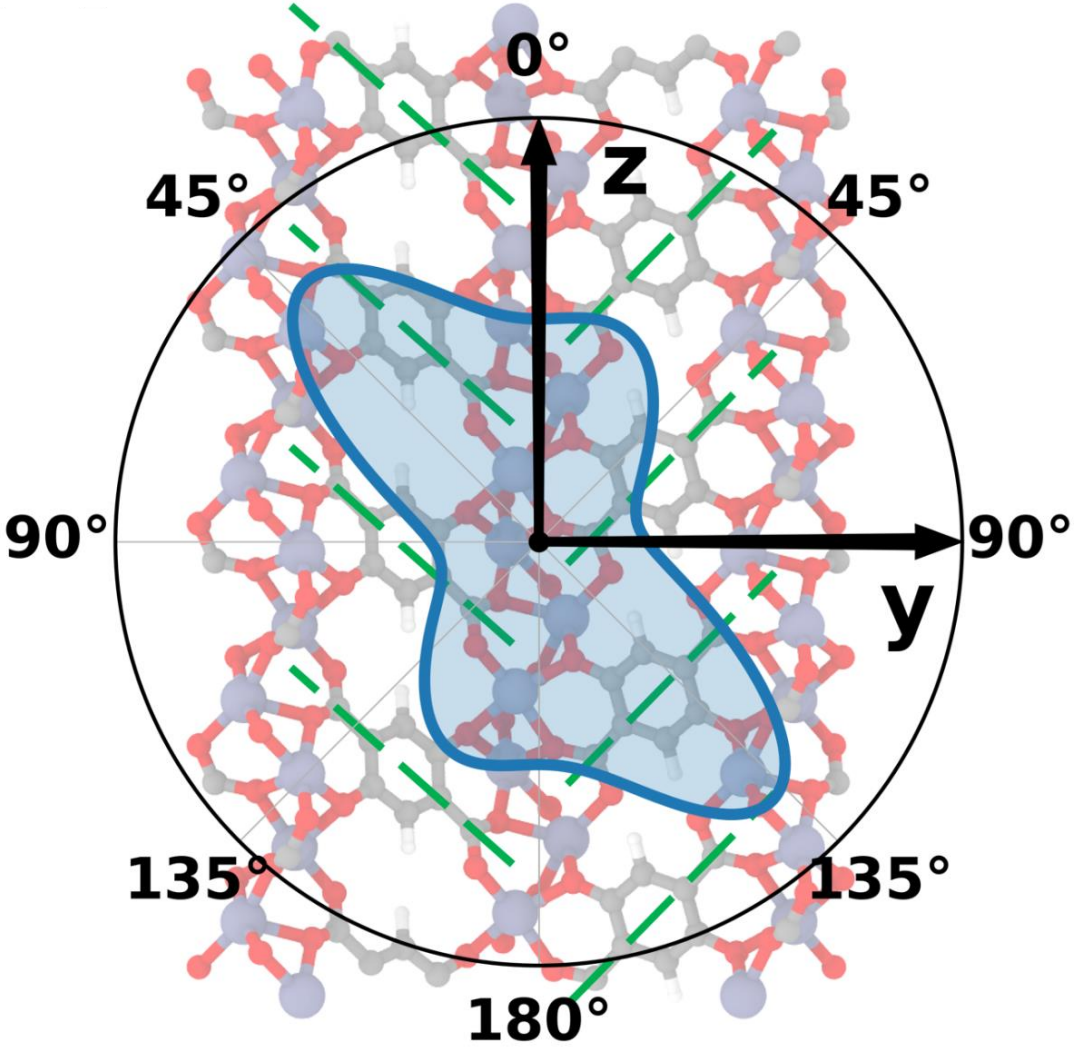
- Local minimum in *z*-direction
- Smaller in *xy*-plane
- 3 pronounced lobes
  (±48° inclined with respect to *xy*-plane)

Young's Modulus in MOF-74(Zn) (top view)



Young's Modulus in MOF-74(Zn) (side view)

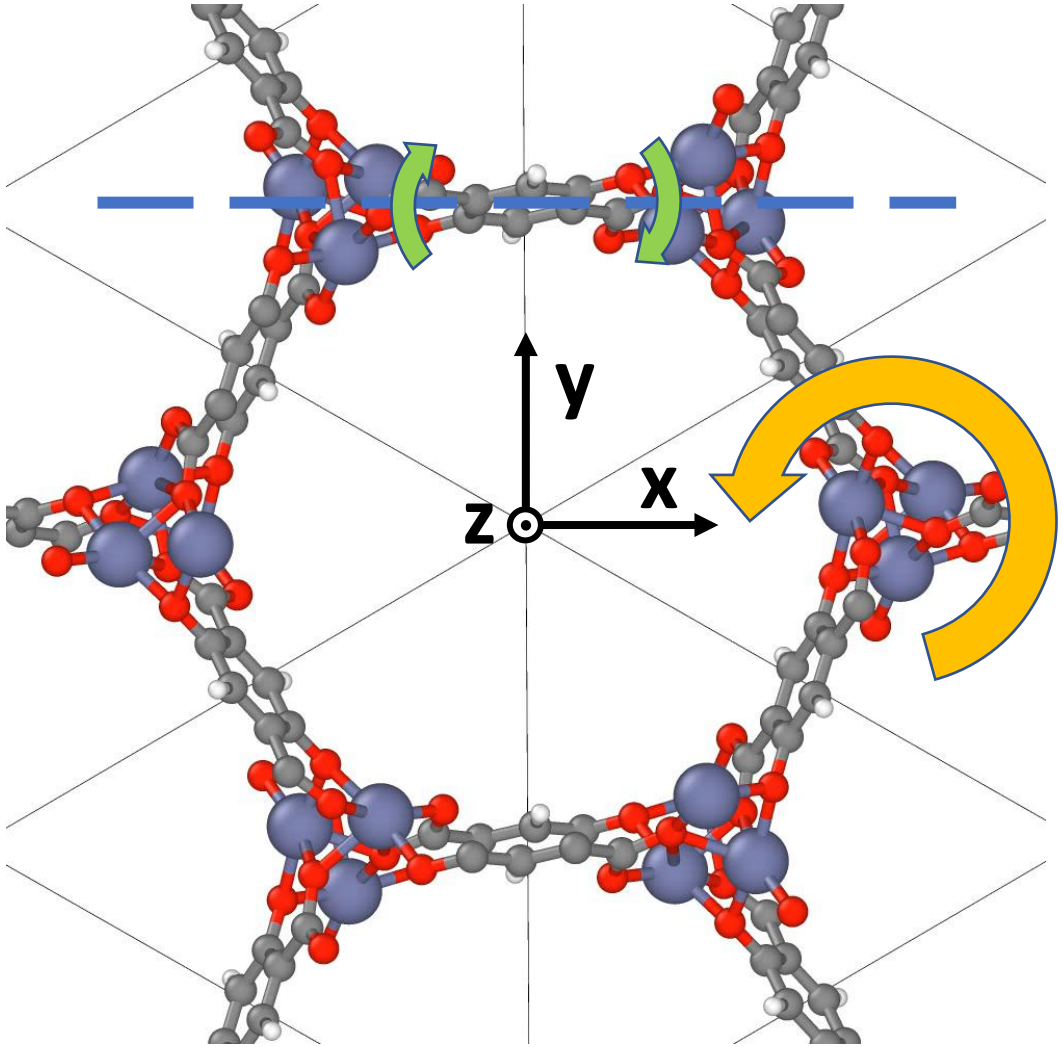
- Maxima nearly aligned with the long molecular axes of the linkers (~5° difference)
- Linker backbone: strong covalent C-C bonds



Mechanisms at the Microscopic Level

- Applying compressive stress in *z*-direction
  - Shrinkage along channel
  - Lateral expansion

- Nodes grow laterally
- Nodes rotate
- Linker inclination increases



Structure-to-Property: Microscopic Changes to Macroscopic Properties

Adsorbates	Metal Ions	Linker Molecules
• Water	• Zn^{2+} • Ca^{2+} • Mg^{2+} • Be^{2+} • Mixtures	• 1 Phenylene ring • 2 Phenylene rings • 3 Phenylene rings

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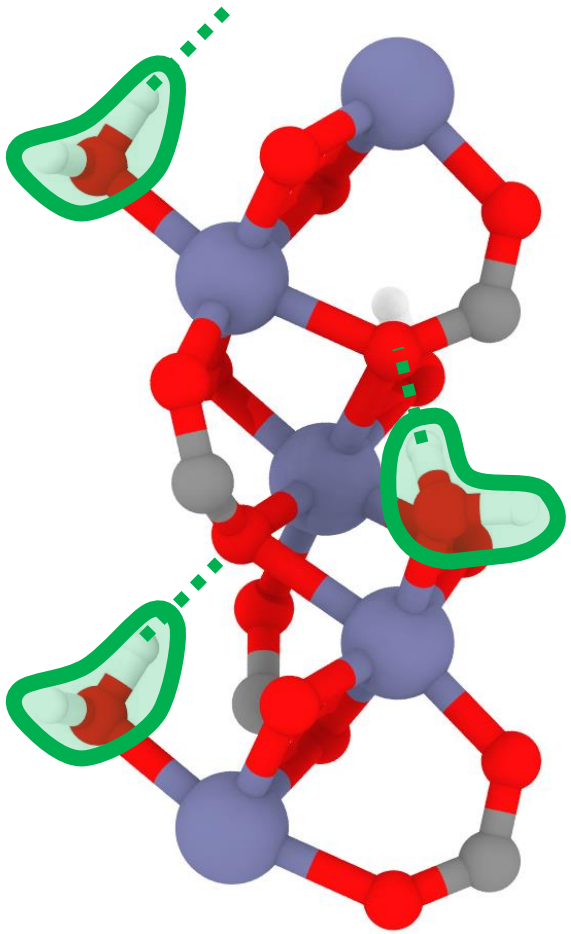
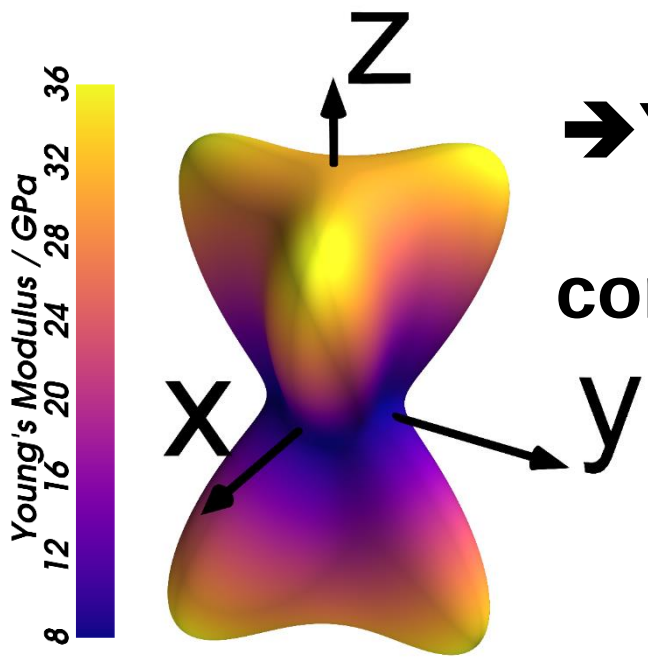
Effect of Adsorbed Water



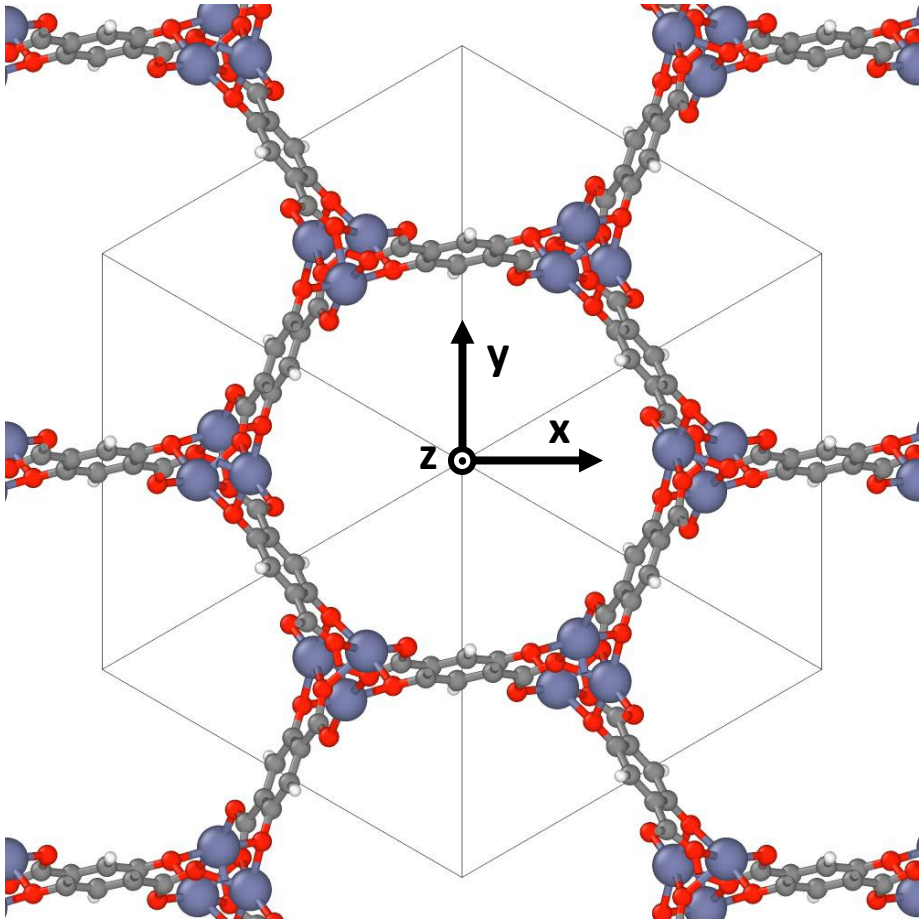
- Water at uncoordinated metal sites
- H-bridges
- Stabilize the node



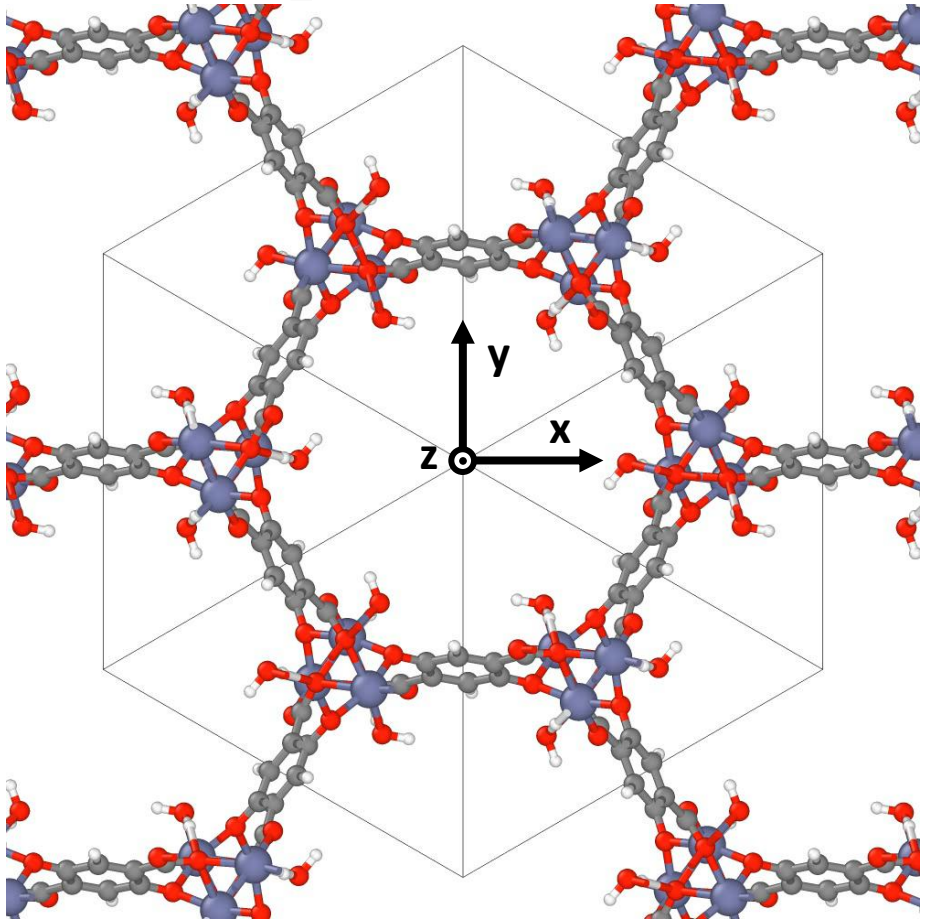
➔Young‘s Modulus in *z*-direction increases compared to dehydrated system

Hydrogen bridges make lateral expansion of nodes more difficult

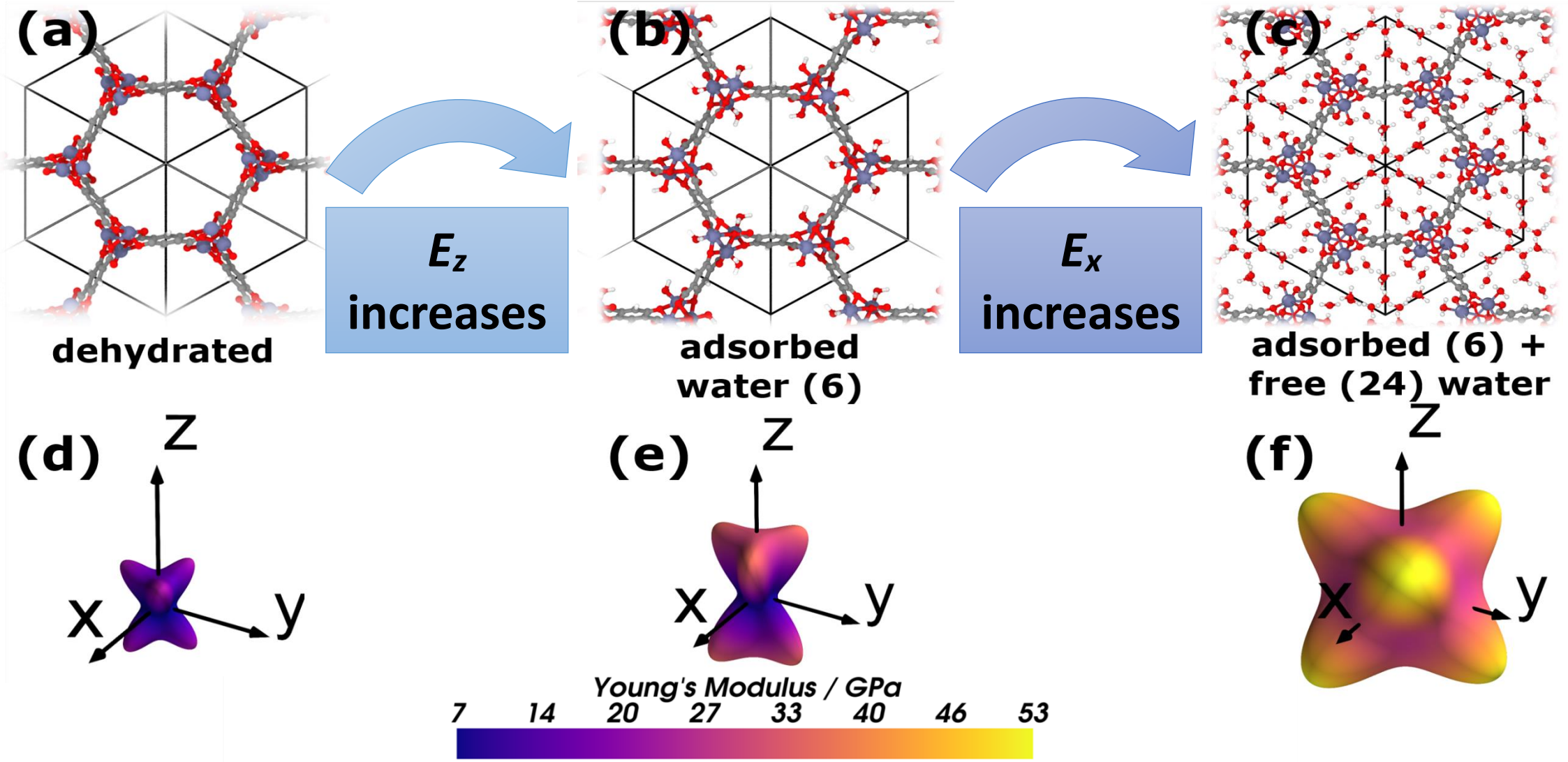
Dehydrated



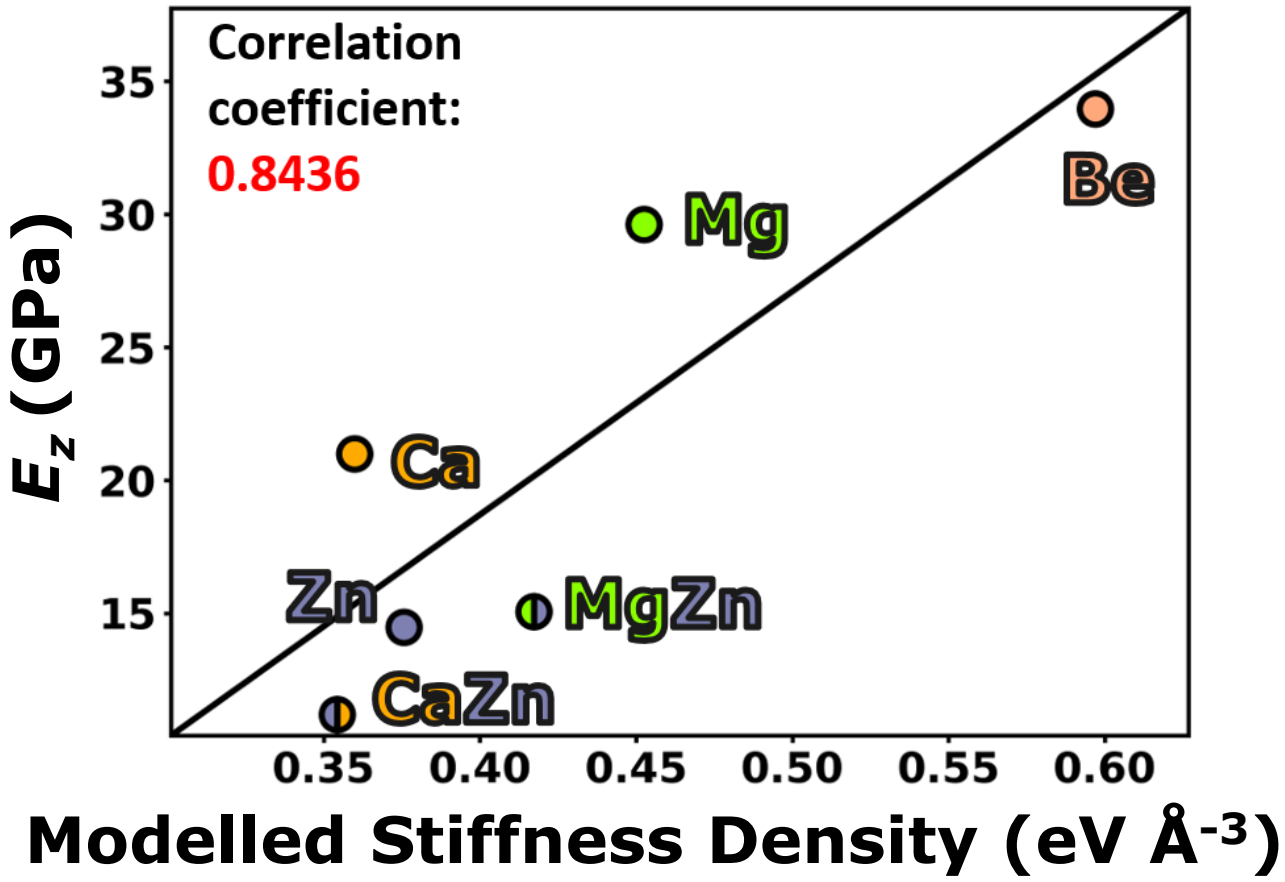
+6 H_20 per unit cell



Water increases E_z and after first layer also E_x



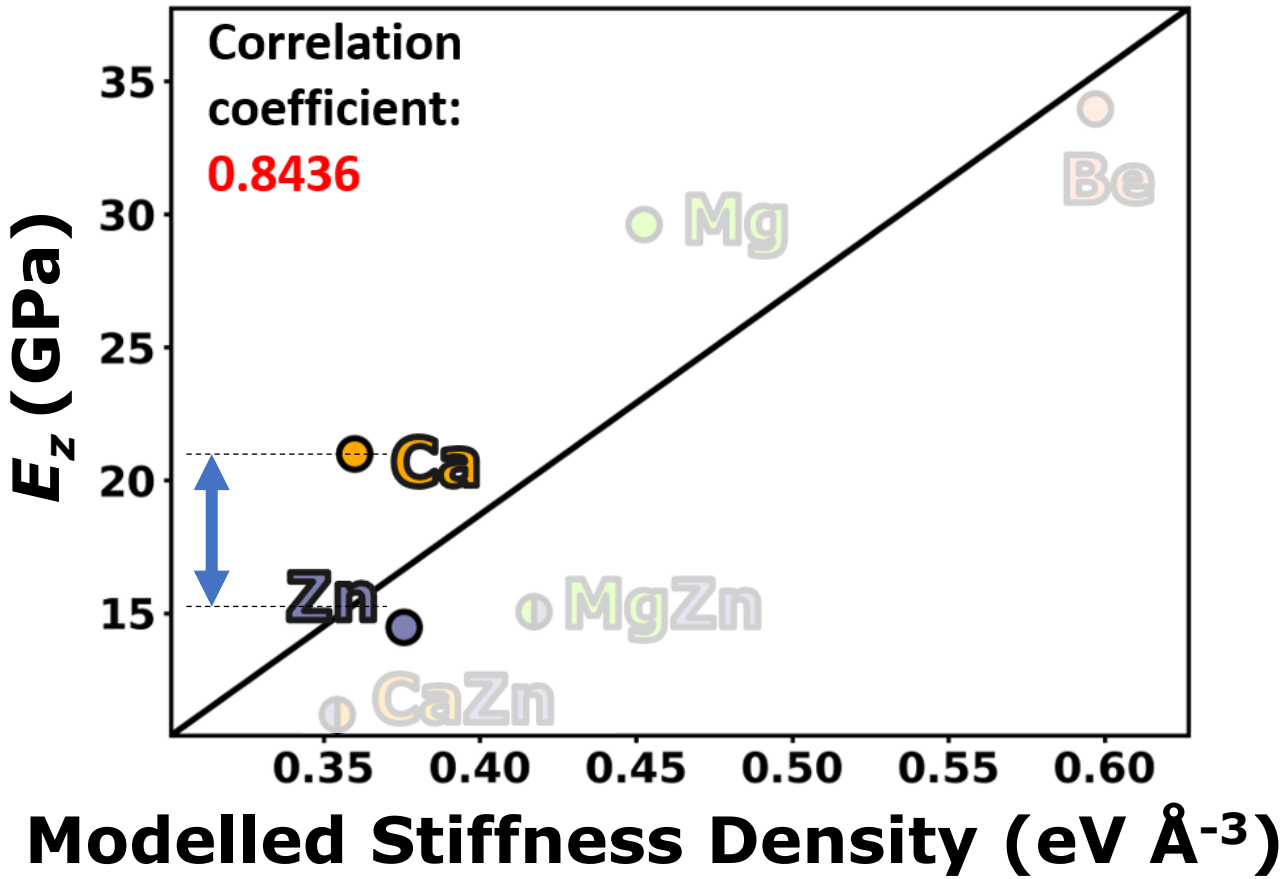
Metal Exchange: General Trends but Individual Deviations



Considering:

- **Porosity** (Lattice Constants)
- Metal-Oxygen **Interaction Strength** (Force Constants)

Metal Exchange:
General Trends but Individual Deviations



Considering:

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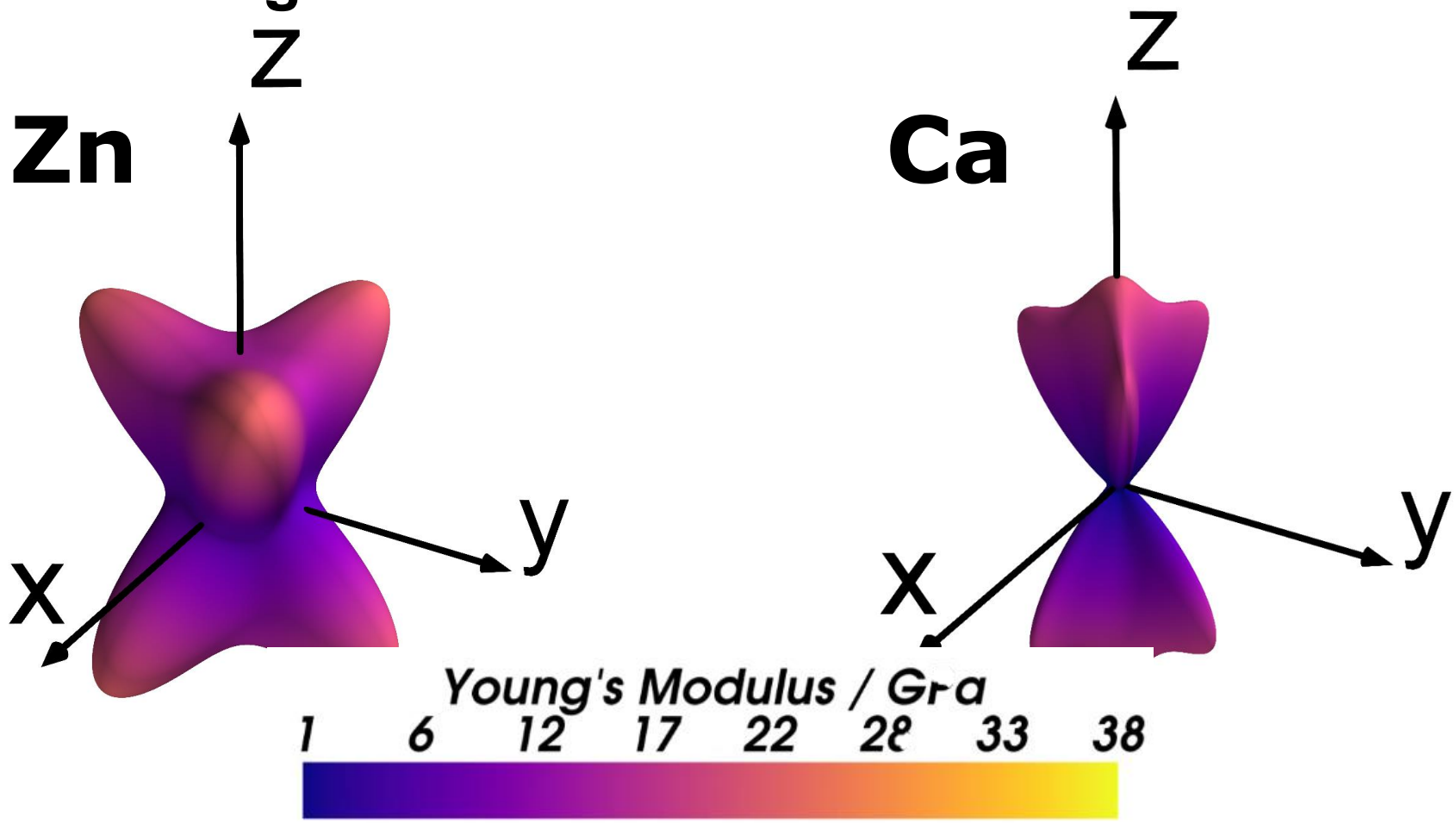
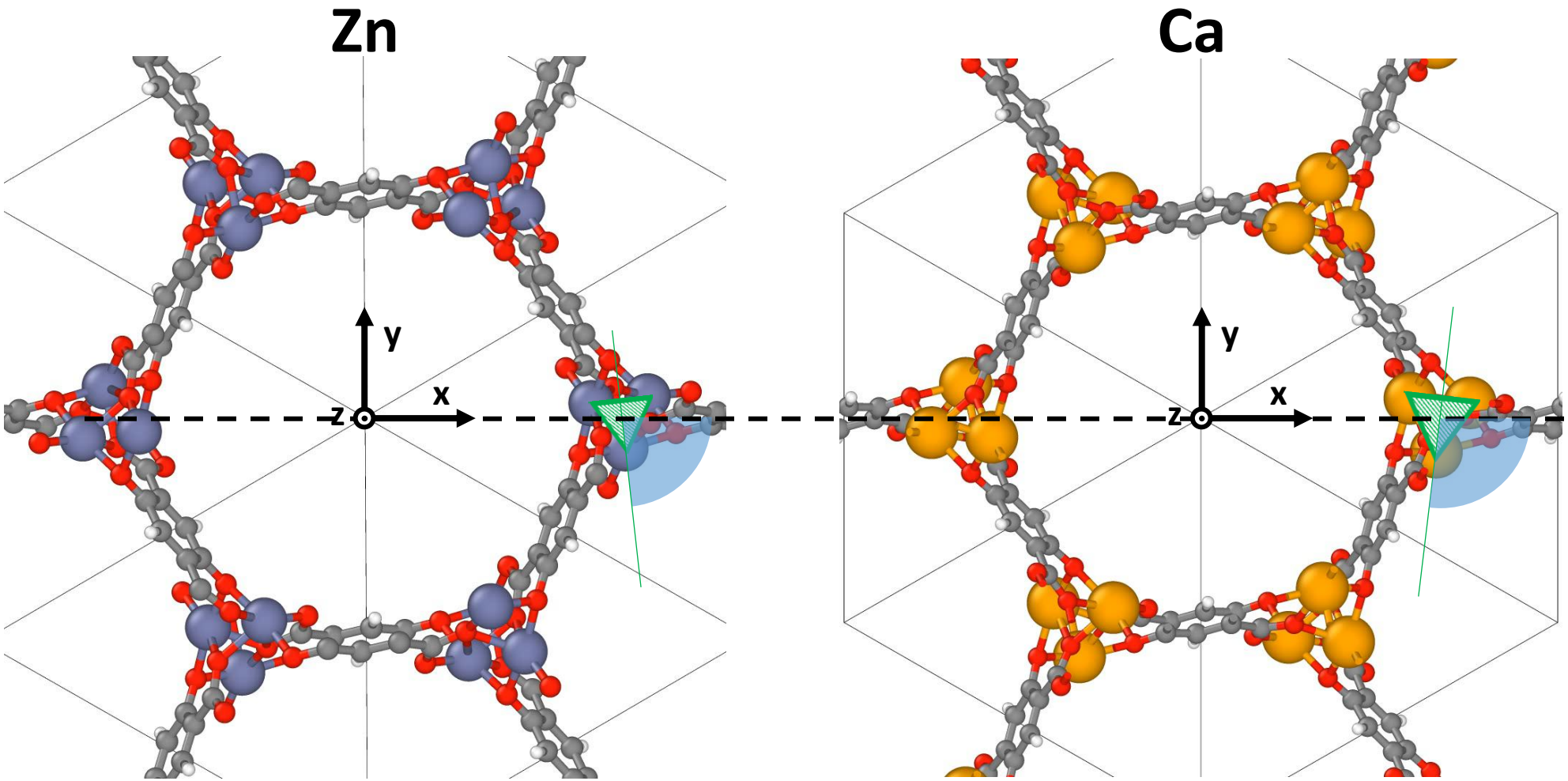
Metal Exchange:
Young‘s Modulus Changes Also Qualitatively

Ca: Young‘s modulus in *z*-direction is a maximum



Different Deformations upon *z*-Stress



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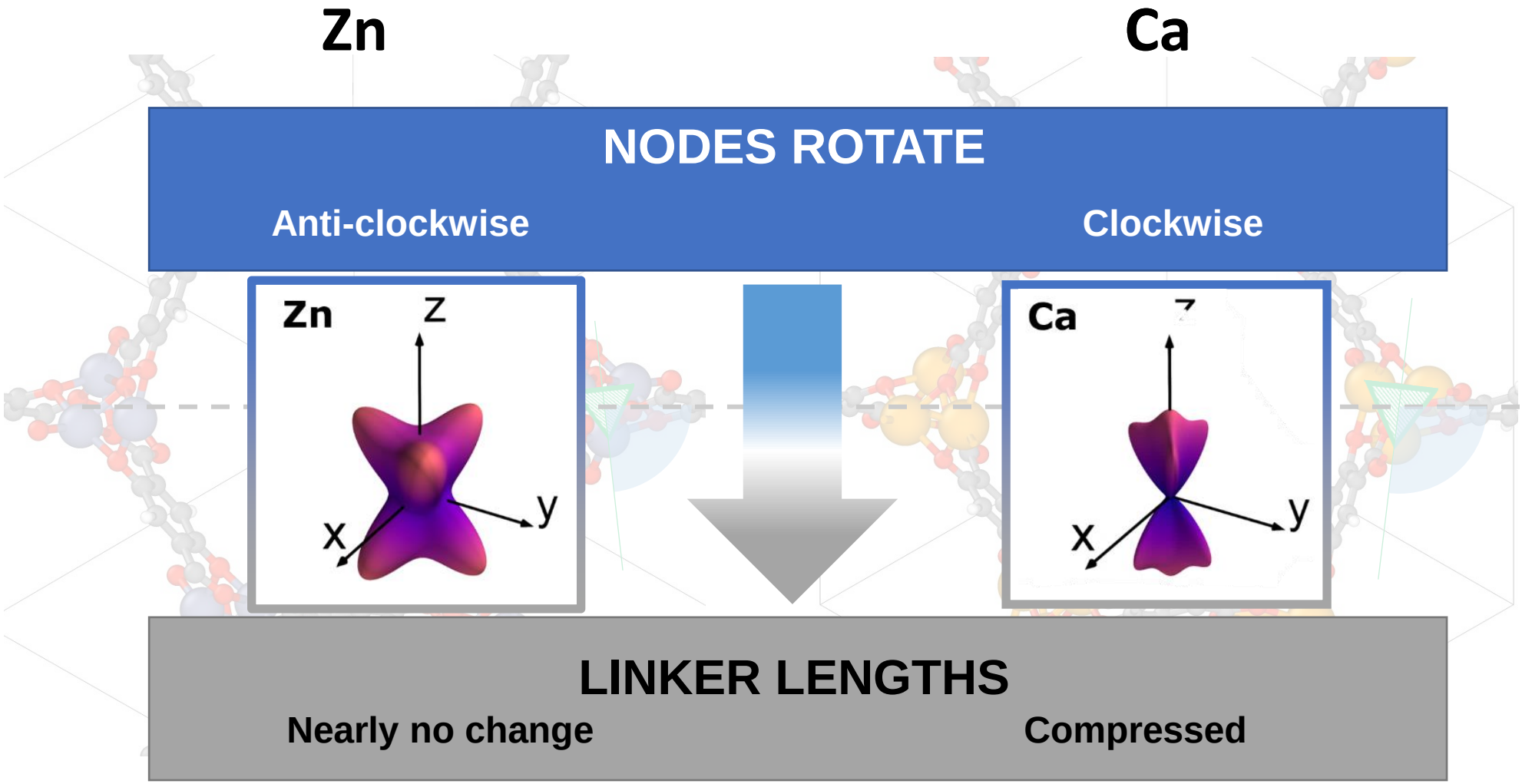
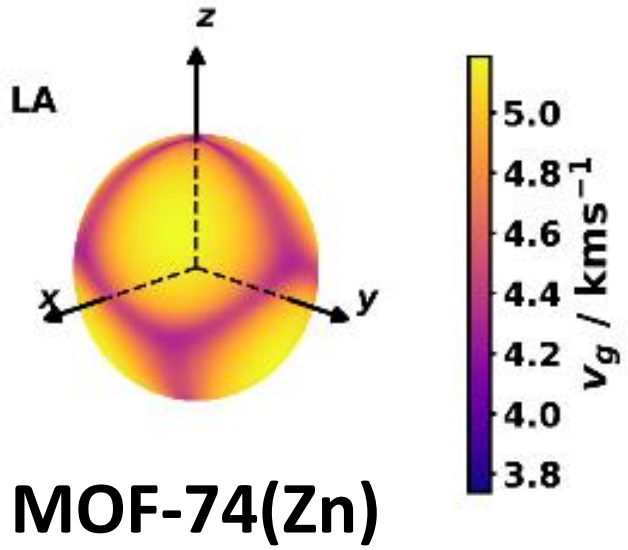
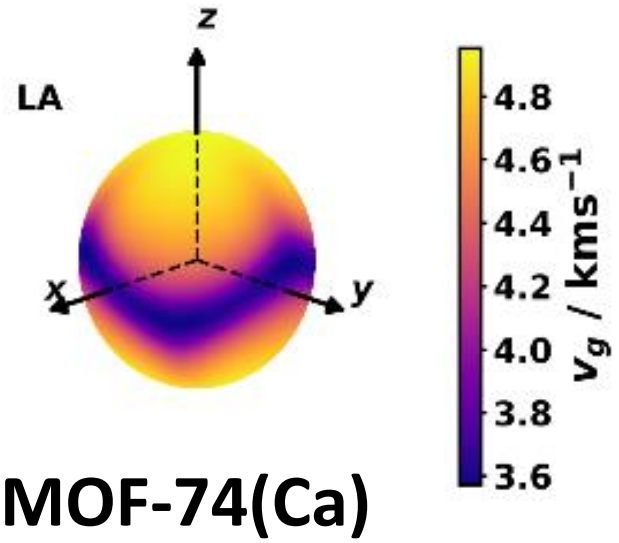


Sound Velocity Distributions Change

Elastic Properties ⟷ Sound Velocities (Christoffel Equations)



MOF-74(Zn)



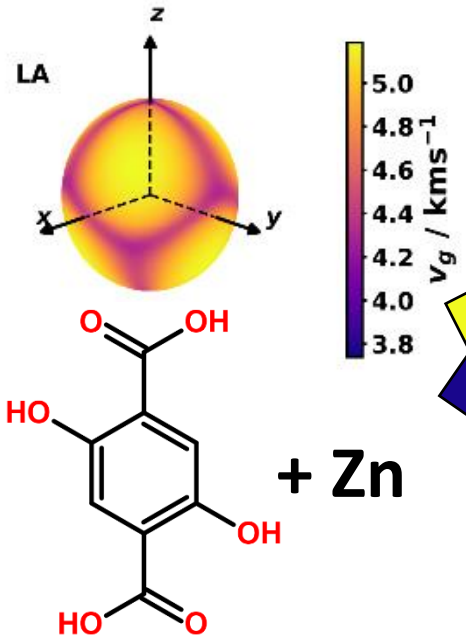
MOF-74(Ca)

Longitudinal Acoustic Sound Velocities (Long Wavelength Limit)

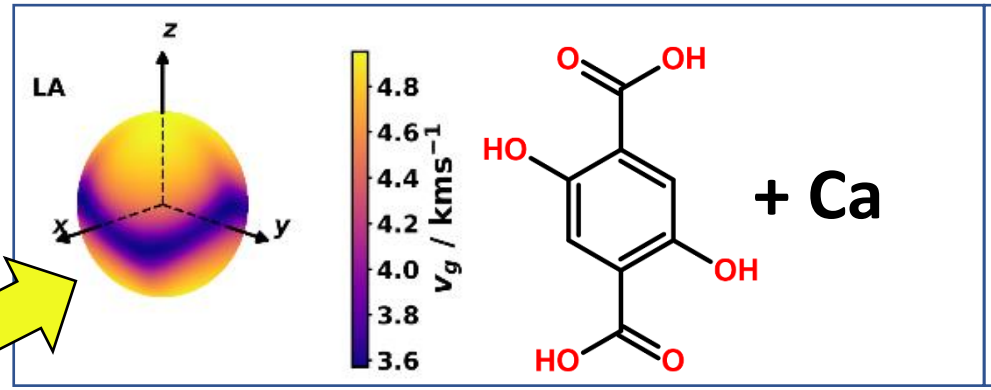
Manipulation of Sound Velocity Distributions

Longitudinal Acoustic Sound Velocities (Long Wavelength Limit)

Elastic Properties ⟷ Sound Velocities (Christoffel Equations)



+ Zn



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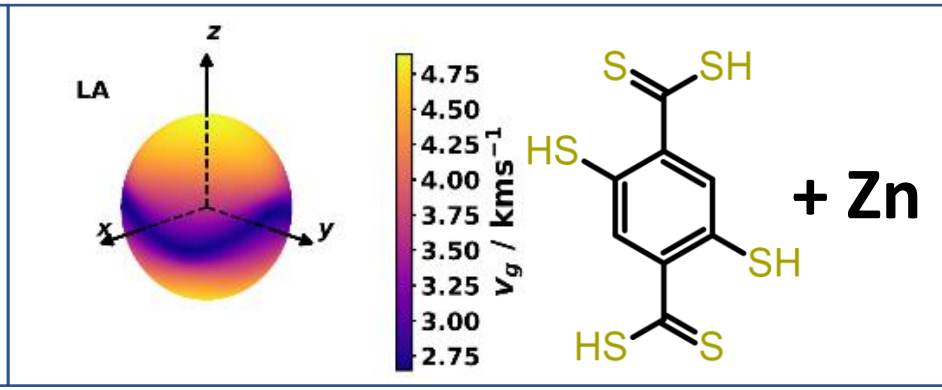
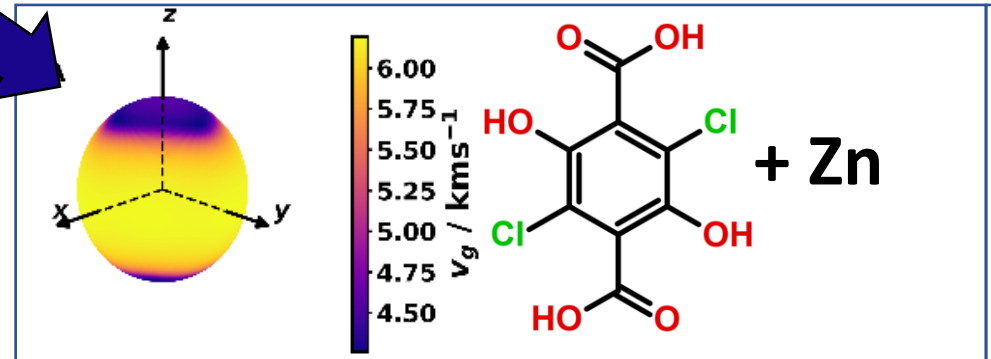
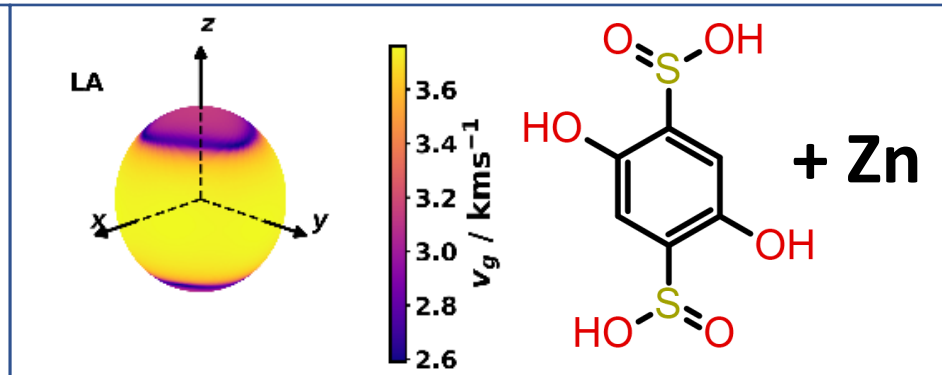


+ Zn



+ Zn



+ Zn

Thermal Expansion and Anharmonic Properties in MOF-74

Kamencek and Zojer; *in preparation*

Thermal Expansion and Anharmonic Properties in MOF-74

Goals and Motivation

DFT: PBE/D3-BJ

- Thermal expansion is an anharmonic effect
- Thermal expansion ➔ thermal mismatch (heteroepitaxy)
- Origin of thermal expansion in MOFs not fully clear (different hypotheses)
- High level of insight: Grüneisen theory of thermal expansion

Grüneisen Theory of Thermal Expansion

Cubic Crystals

$$\alpha_V = \frac{C_V \langle\gamma\rangle}{V B} \qquad \gamma_\lambda = -\frac{V}{\omega_\lambda}\frac{d\omega_\lambda}{dV}$$

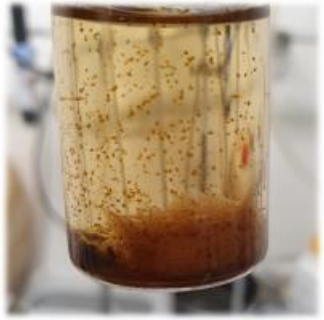
Anharmonic Effect!

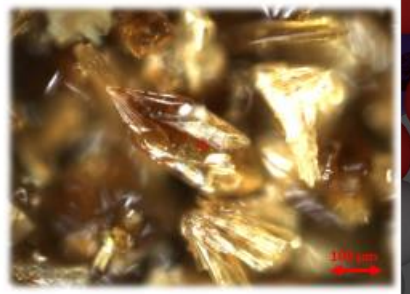
Non-Cubic Crystals

$$\alpha_{ij} = \frac{C_V}{V} S_{ijkl} \langle\gamma_{kl}\rangle \qquad \gamma^\lambda_{kl} = -\frac{1}{\omega_\lambda}\frac{d\omega_\lambda}{d\varepsilon_{kl}}$$

Anharmonic Effect!

Real-Life MOF-74(Zn)





Large mass mismatch between metals and linkers leads to complex phonon properties

Heavier metals shift phonons to lower frequencies

More complex linkers introduce more low-lying linker deformation modes

Inter-system trends of Γ-phonon frequencies can be observed based on classical arguments

Phys. Rev. Mater. **2019**, 3, 116003

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J. Phys. Chem. C **2021**, in press

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Most relevant contributions to the thermal expansion can be found for phonons < 3 THz

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In preparation

Acknowledgements

- Supervisors: Paolo Falcaro and Egbert Zojer
- Falcaro Group @ IPTC and
- Advanced Modelling Team @ IF

- Austrian Academy of Sciences: DOC Fellowship
- Lead Project (LP-03) Porous Materials @ Work

ÖAW ÖSTERREICHISCHE AKADEMIE DER WISSENSCHAFTEN

Grant No. 25783

- Computational Resources: VSC, High-Performance Computing TU Graz (dCluster, aCluster)

VSC VIENNA SCIENTIFIC CLUSTER

TU Graz

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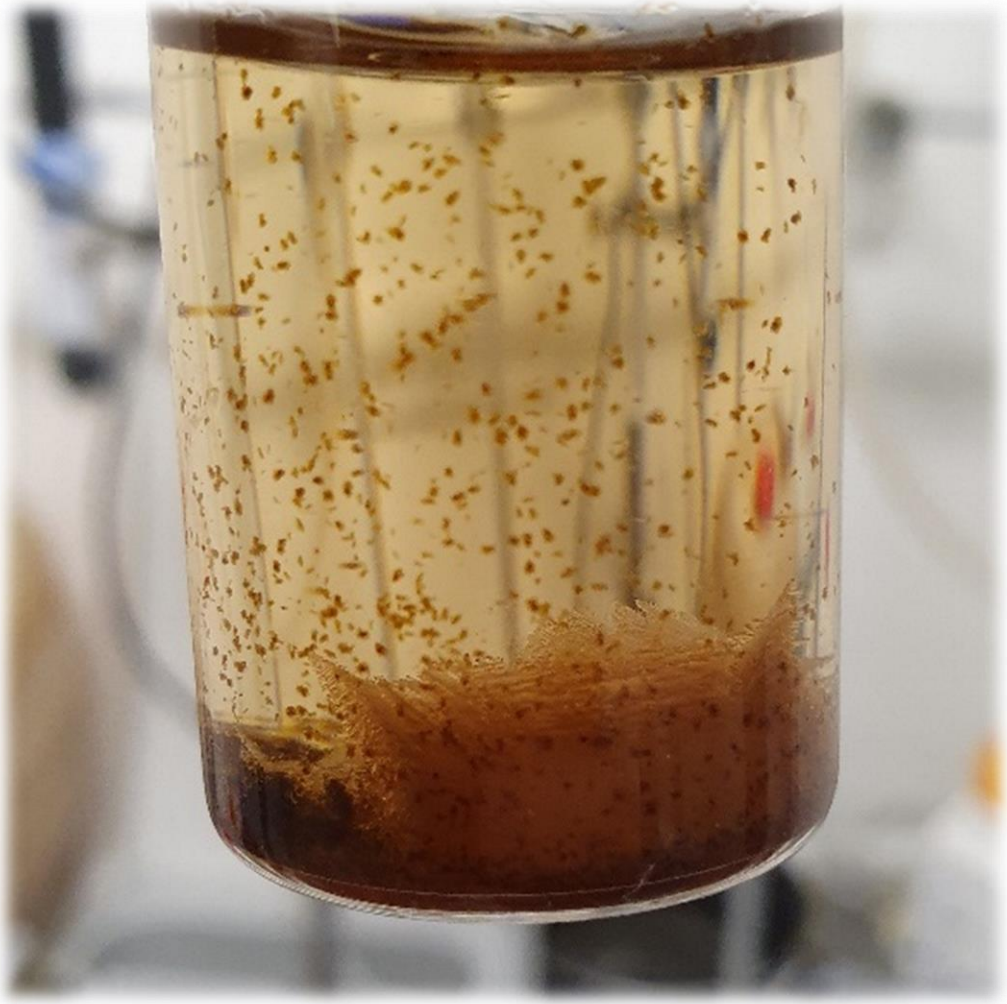

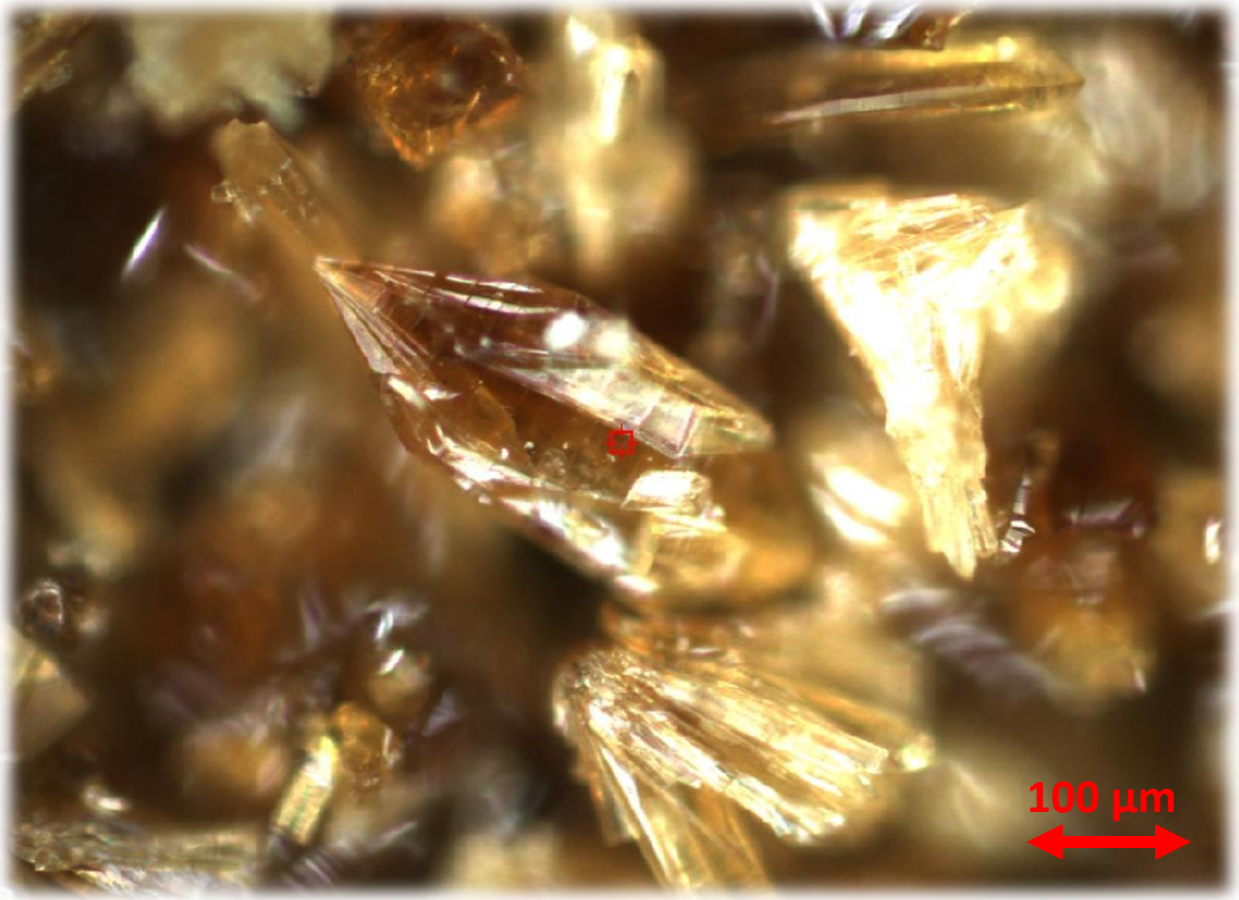

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