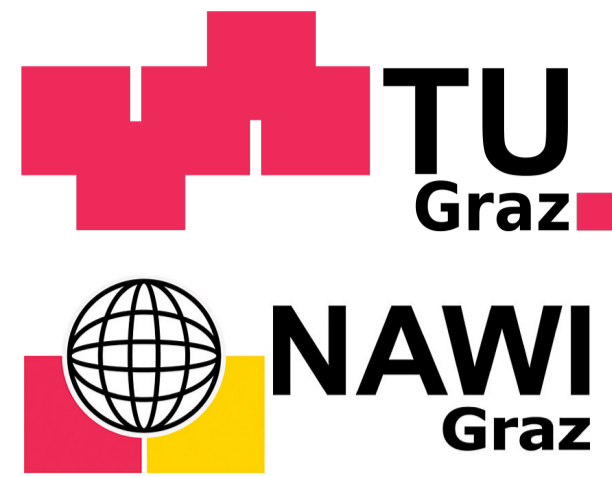# HOW ACCURATE CAN MACHINE-LEARNED FORCE FIELDS DESCRIBE SPIN-POLARIZATION DEPENDENT VIBRATIONS OF HKUST-1 COMAPRED TO DENSITY FUNCTIONAL THEORY?
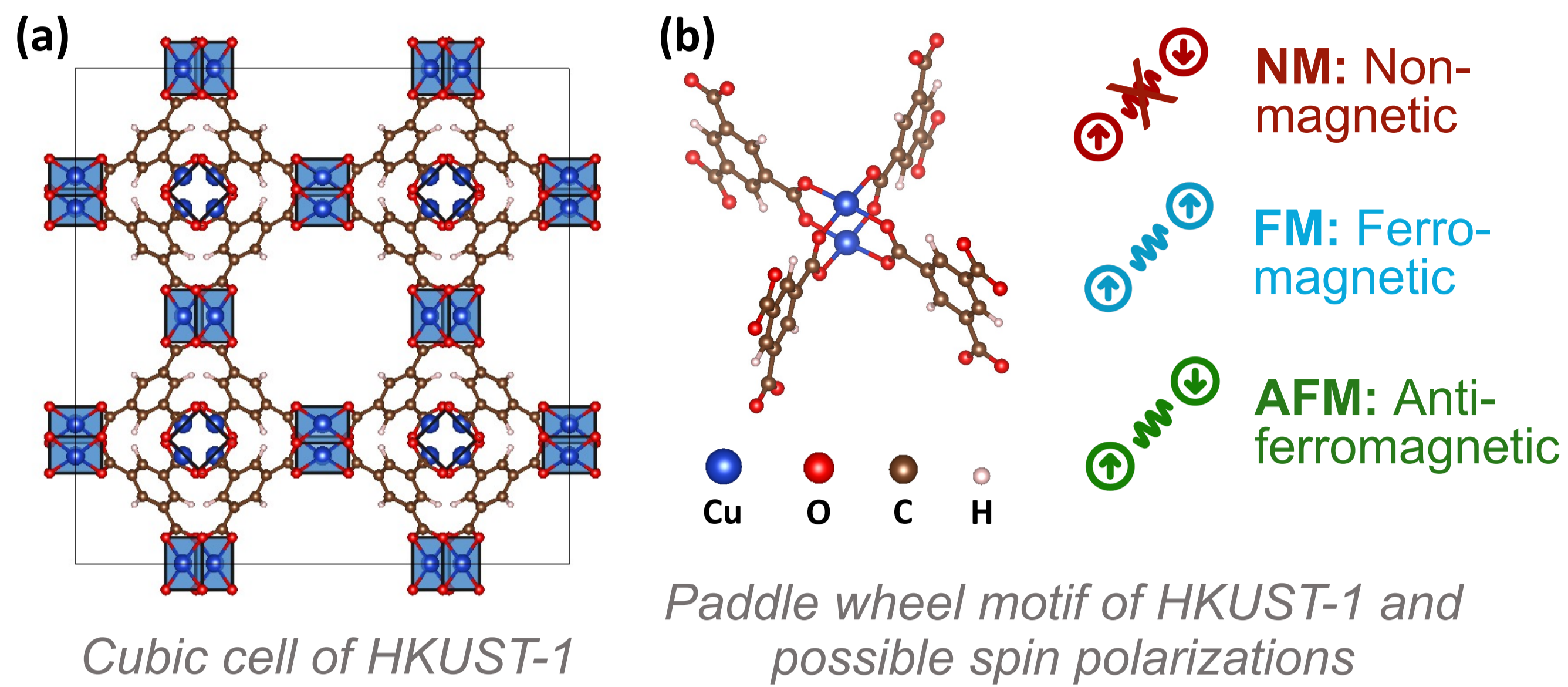
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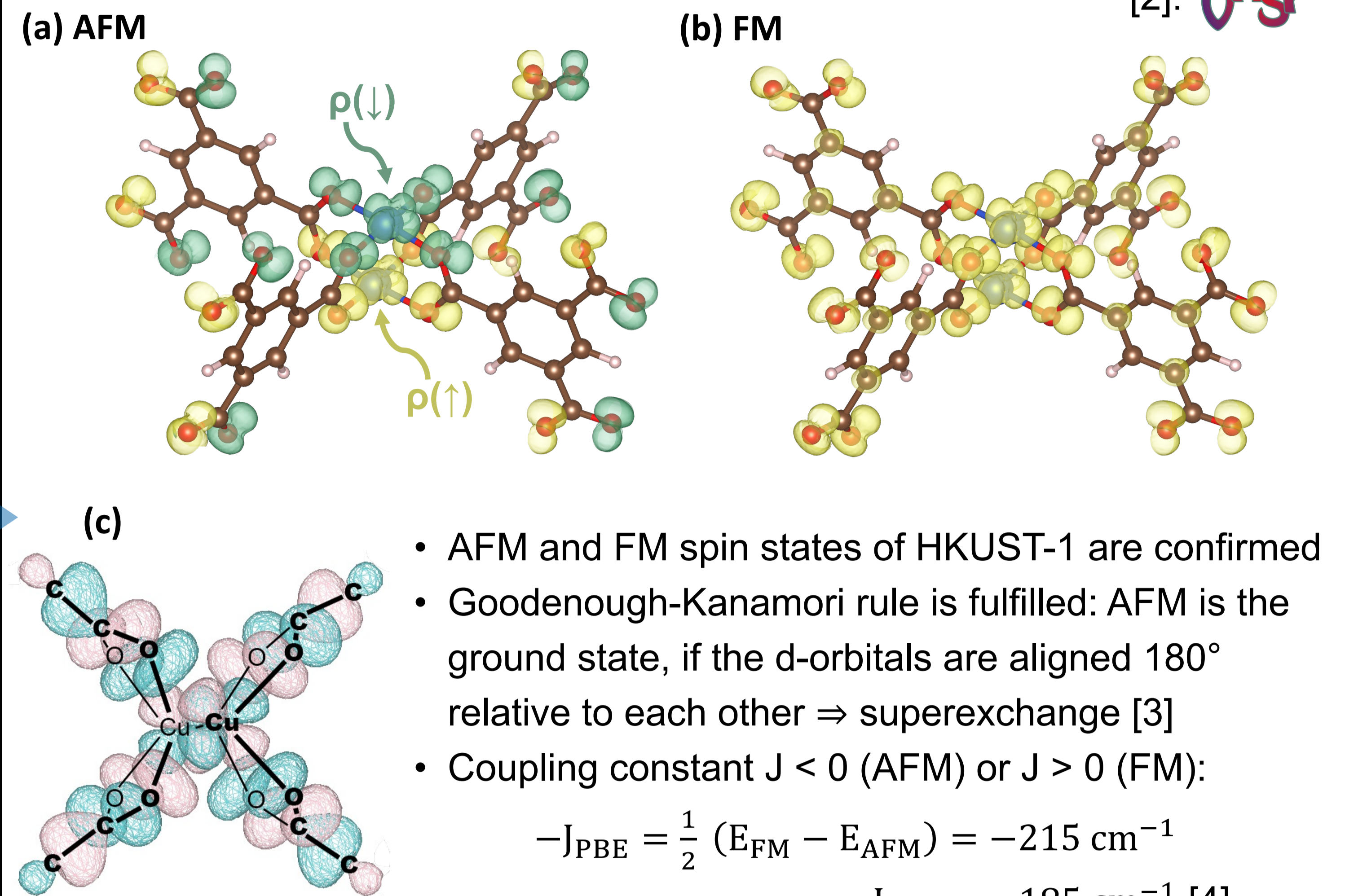
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Geometry and Spin States of HKUST-1

(a) Cubic cell of HKUST-1

(b) Paddle wheel motif of HKUST-1 and possible spin polarizations

NM: Non-magnetic
FM: Ferro-magnetic
AFM: Anti-ferromagnetic

Cu O C H

- HKUST-1 has unpaired electrons on Cu(II) ions
- Different possibilities for spin coupling within the paddle wheel
- Application: removal of pharmaceuticals from waste water [1]

**Question #1** What is the ground state of HKUST-1? How can these spin states be validated in DFT?

Spin Densities of HKUST-1

[2]: VASP

(a) AFM $\rho(\downarrow)$ $\rho(\uparrow)$

(b) FM

(c)

- AFM and FM spin states of HKUST-1 are confirmed
- Goodenough-Kanamori rule is fulfilled: AFM is the ground state, if the d-orbitals are aligned 180° relative to each other ⇒ superexchange [3]
- Coupling constant J < 0 (AFM) or J > 0 (FM):

$$-J_{PBE} = \frac{1}{2}(E_{FM} - E_{AFM}) = -215 \text{ cm}^{-1}$$

$$J_{EXP} = -185 \text{ cm}^{-1} \text{ [4]}$$

Question #2 Does the spin state influence phonon properties?

Benchmarking of MTPs Against DFT Reference Data

- Excellent agreement between MLIP and DFT (RMS error of 6 cm^{-1})

(d) PBE

(e) MTP
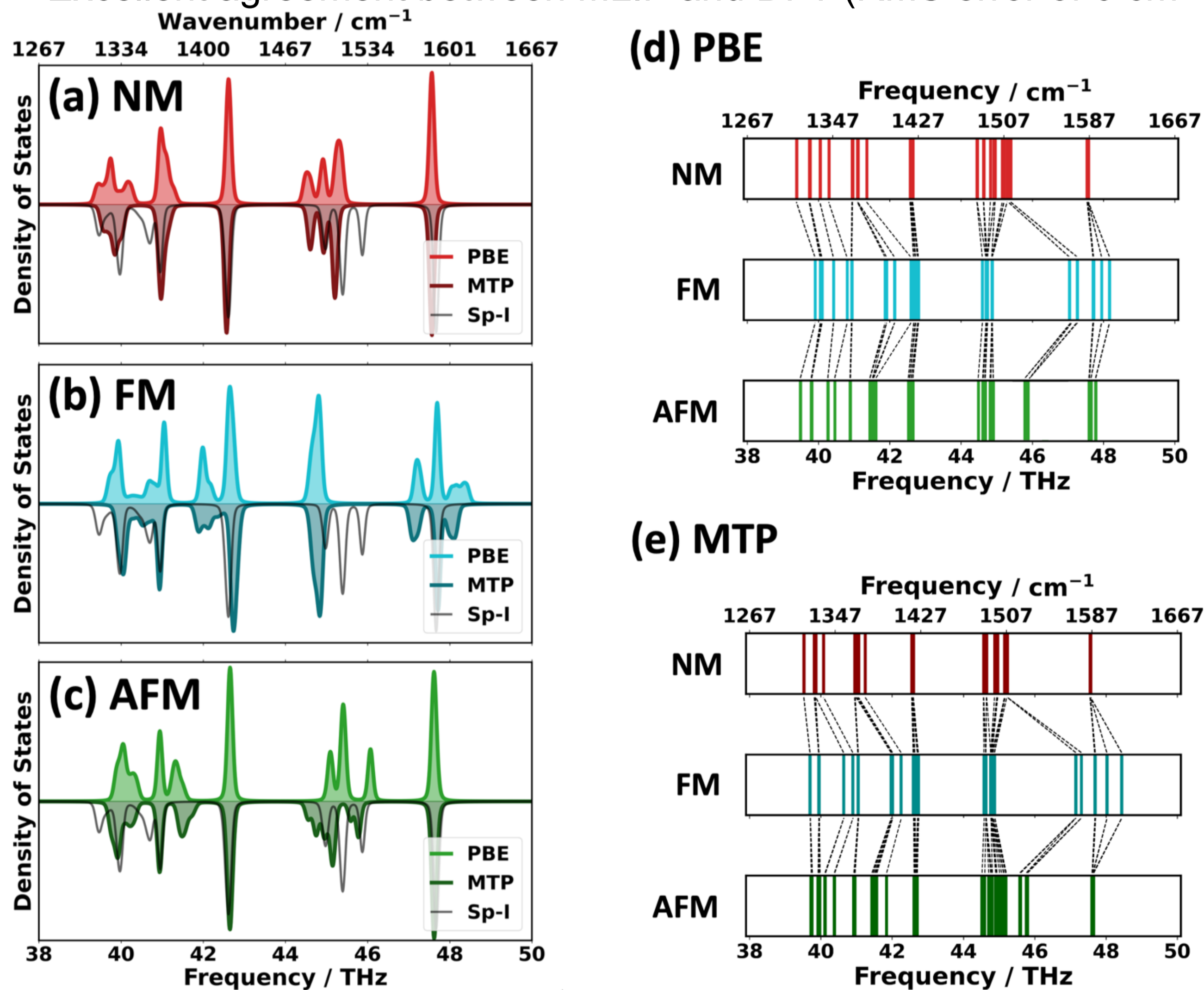
Question #4 How well does the IR spectrum agree with experiments?

Influence of Spin States on IR Spectra

- Density functional theory (DFT) shows differences between AFM, FM and NM state in the IR spectral region of 1400–1600 cm^{-1}


① - ③ $\nu_{as}(COO)$
④ $\nu_s(COO)$
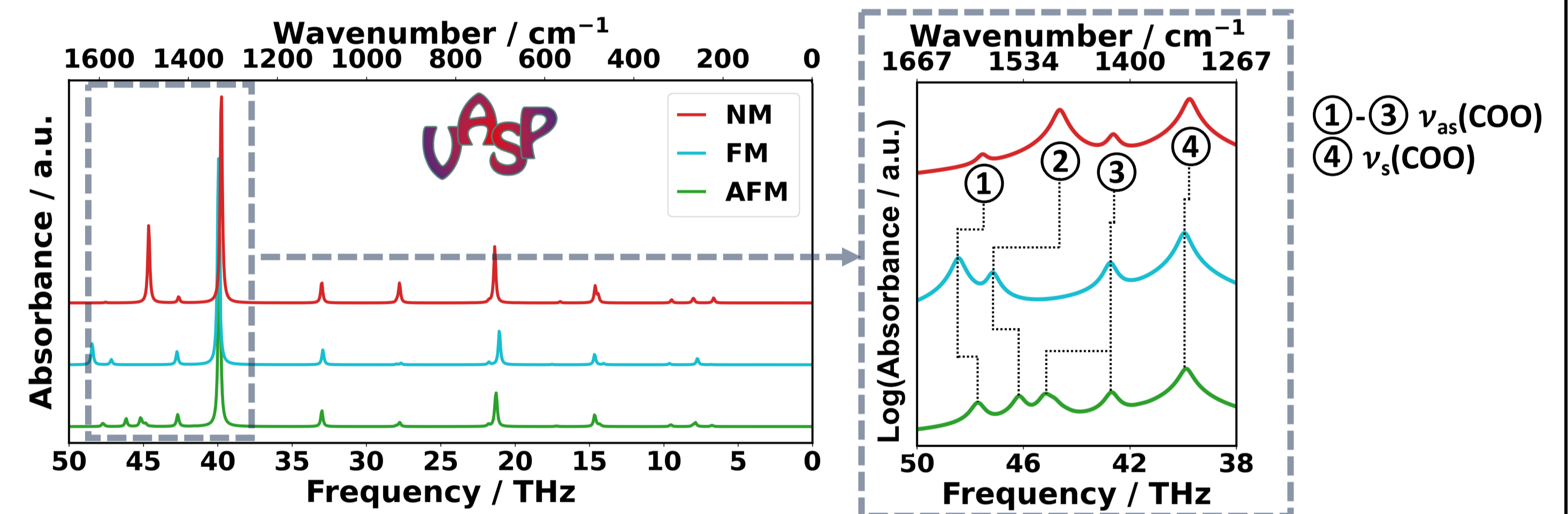
Simulated IR spectrum for HKUST-1 using PBE in various spin states

- Training of moment tensor potentials (MTPs) based on 500 configurations obtained from a combined *ab initio* and molecular dynamics run [5]

Question #3 Can MTPs that are parametrized against spin-dependent training data reproduce these differences? [6]: MLIP

Agreement with Experiment

FHI-aims + VASP

[7]: IR Spectra — Collective Vibrations
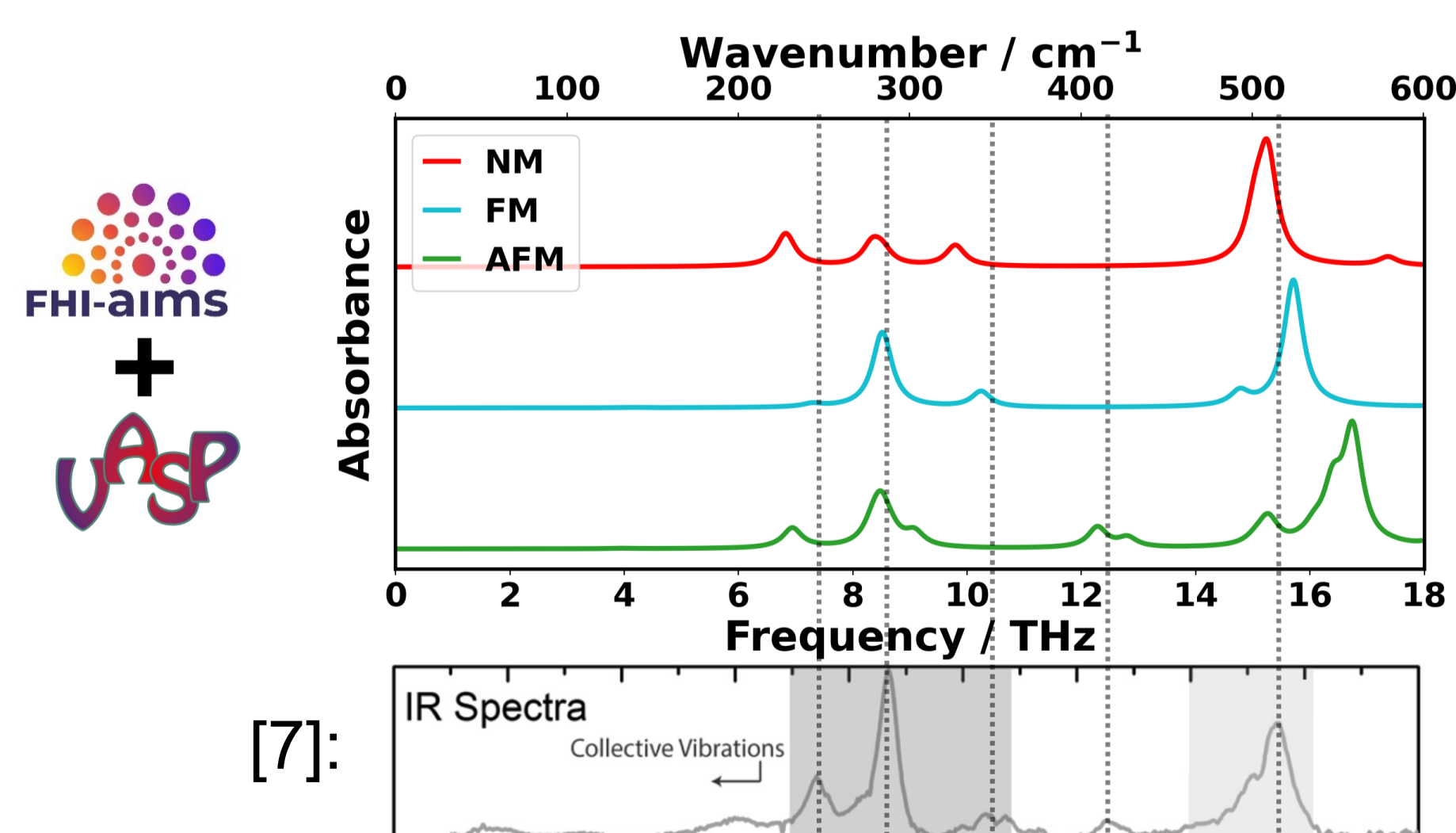
Computed IR spectrum of HKUST-1 using PBE0 agrees very well with experiment

- PBE underestimates the IR frequencies by approximately 9 % compared to experiment

- Hybrid functionals are accurate enough for a reliable prediction of the IR spectra, but overestimate the C-H vibration

- Anharmonic effects also play a role

Conclusion

- Different spin states of HKUST-1 have been validated using spin densities in DFT
- Confirmation of AFM as a ground state for HKUST-1
- Different spin configurations result in different IR spectra → asymmetric COO vibration is affected
- MTPs are able to reproduce these deviations in the phonon band structure
- MTPs agree with DFT frequencies within ~6 cm^{-1}
- MTPs can give access to other relevant quantities (e.g. thermal expansion and heat transport) of MOFs that are otherwise too expensive to compute

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