Modelling Vibrations and Phonons
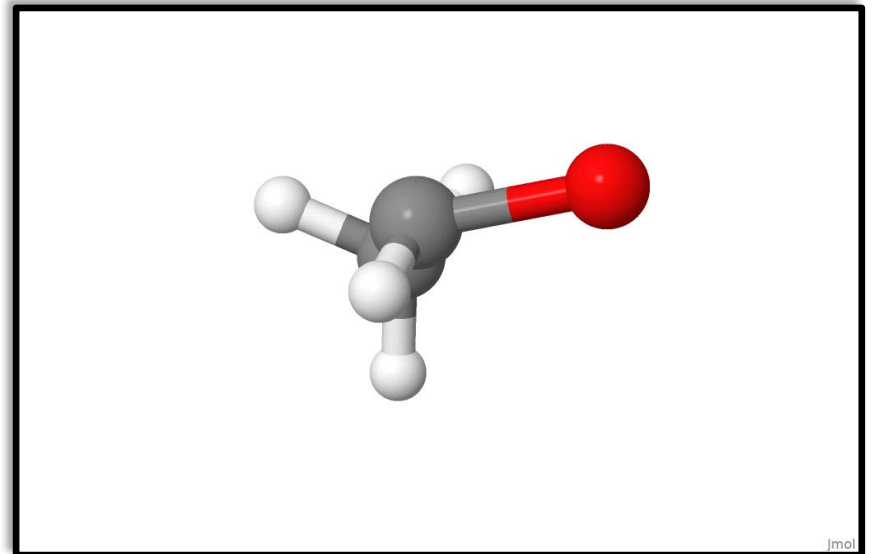

some slides based on talks by Oliver T. Hofmann an a short script by Peter Puschnig

Why calculating vibrations?

➢ **Classification of stationary points (minimum / saddle point)**

➢ **If saddle-point: search direction**

➢ **Thermodynamic data**
   Zero-point energy (contributes to total energy also at 0K !), partition sums, finite temperature effects

➢ **Connection to experiment:**
   Infra-red intensities: derivative of dipole moment
   Raman intensities: derivative of polarizabilty

Practical relevance of vibrations

- Identification of chemical species and polymorphs

- Identification of relative orientation of sub-systems (e.g., in TMDs)

- Identification of charged states (fingerprints)

- Understanding interaction between sub-systems

- Determining heat transport (anharmonic effects)

- Dynamic disorder crucially impacting charge transport

- …….

Expand total energy in Taylor (power) series:

$$E\left(\vec{R}\right) = E\left(\vec{R}_0\right) + \sum_i \left(\frac{\partial E}{\partial R_i}\right)_0 \Delta R_i + \sum_{i,j} \left(\frac{\partial^2 E}{\partial R_i \partial R_j}\right)_0 \Delta R_i \Delta R_j + \ldots.$$

vanishes at extremum

Hessian (needs to be diagonalized to get "force constants")

Hessian from geometry optimization not sufficent

○ **Analytic second derivative using perturbation theory [1]**

○ **Numerical differentiation (displace all atoms)**

– **Computationally very expensive**

– **Contains parameter (displacement), needs to be converged carefully**

– **Often single displacement problematic to sample all vibrations (different harmonic range)**

[1] S. Baroni et al. , Rev. Mod. Phys. 73 , 515 (2001).

How good is the harmonic approximation?

Morse-potential: $E = U_0 \left(e^{(2a(r-r_0))} - 2e^{a(r-r_0))} \right)$

Harmonic oscillator: $E = U_0 + \frac{1}{2}\gamma(r - r_0)^2$
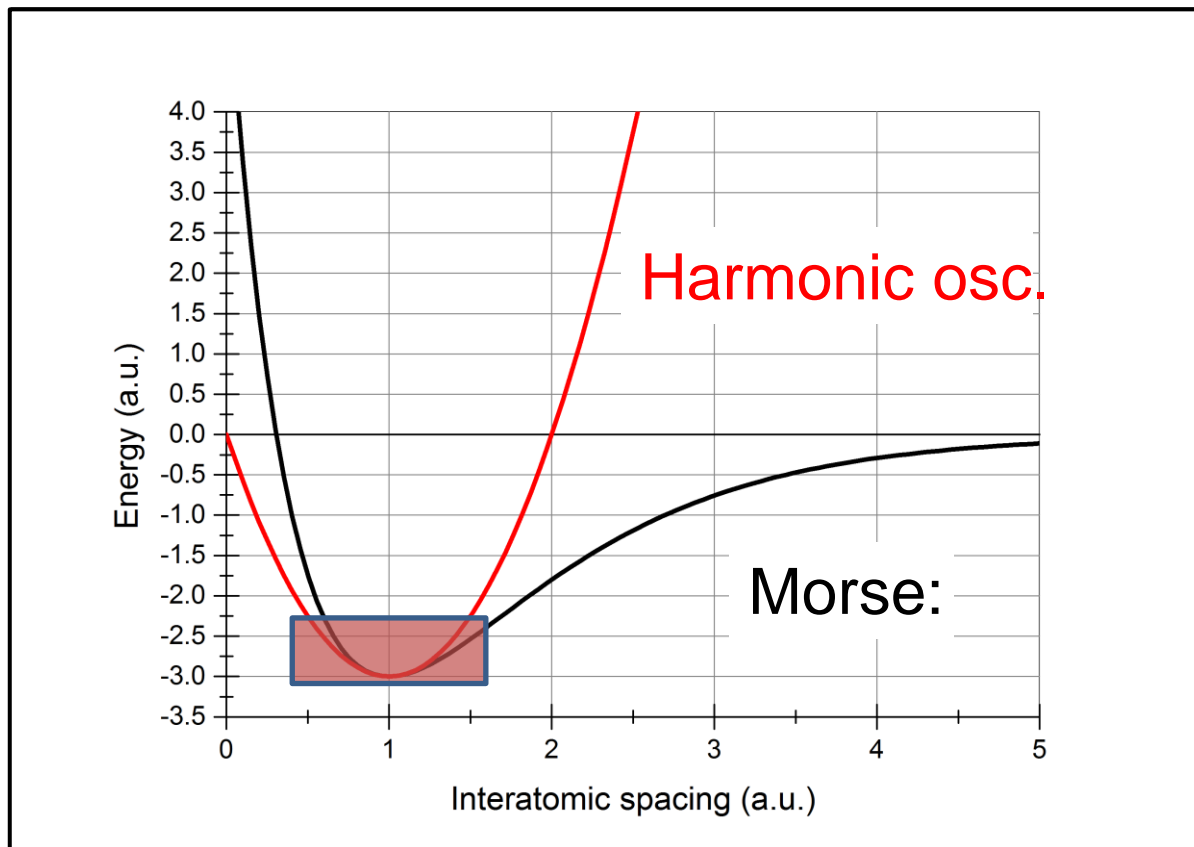
Morse-potential: $E = U_0 \left(e^{(2a(r-r_0))} - 2e^{a(r-r_0))} \right)$

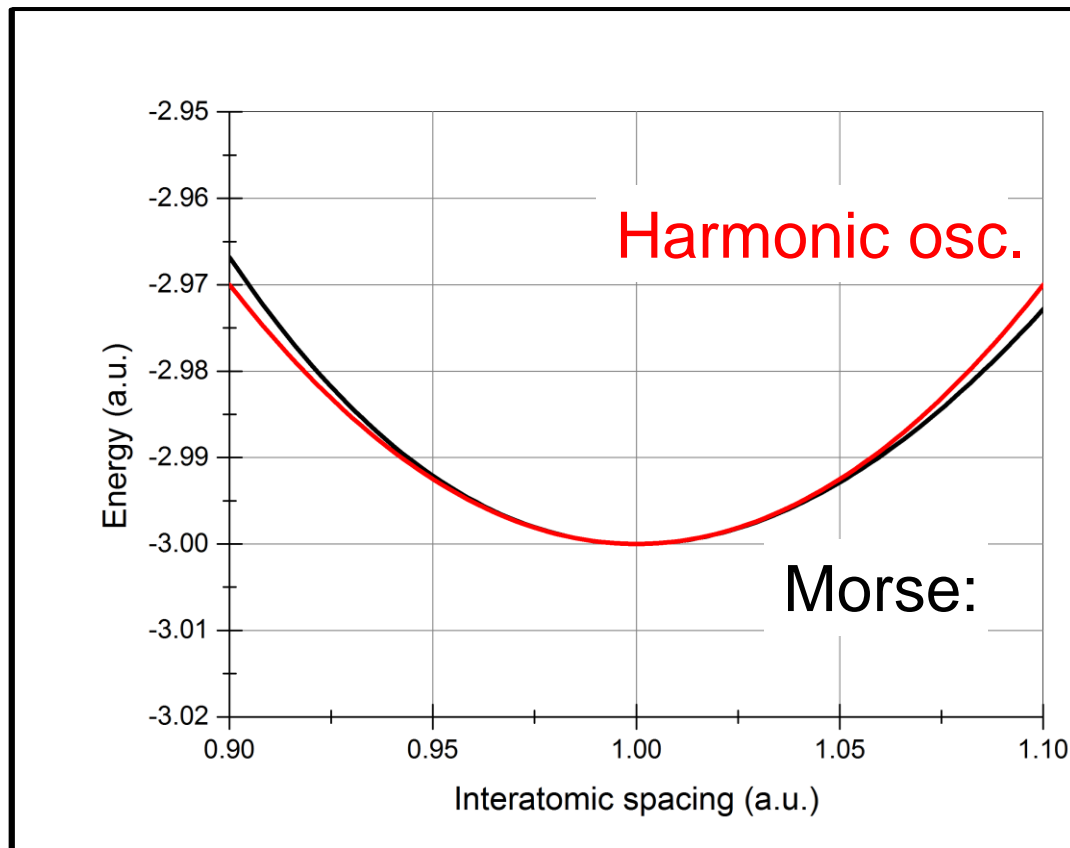**Harmonic oscillator:** $E = U_0 + \frac{1}{2}\gamma(r - r_0)^2$

Maximum displacement:

$A = max(x) = \sqrt{\dfrac{2k_B T}{\gamma}}$

ca. 0.1Å at room temperature

Typical displacement in actual calculation: 0.01 Å

too large: anharmonicities too small: numerical noise

Harmonic osc.

Morse:

The following consideration on how to "diagonalize the Hessian" are inspired by:

Vibrational Analysis in *Gaussian*

Joseph W. Ochterski, Ph.D.
help@gaussian.com

October 29, 1999

available at: http://gaussian.com/wp-content/uploads/dl/vib.pdf

which is in turn inspired by „Molecular Vibrations" by Wilson, Decius and Cross

➢ **Following considerations valid only, when geometry is at a stationary point (first derivatives of energy wrt. displacement vanish)**

➢ **Geometry optimization and frequency calculation must be done at the same level of theory (method, basis set, k-point grid, etc.)**

How to get frequencies and normal modes from Hessian ?

o **Starting point: Hesse matrix (= force-constant matrix) in Cartesian coordinates**

$$H_{cart,ij} = \left(\frac{\partial^2 E}{\partial R_i \partial R_j} \right)_0$$

o **1st step: conversion to mass-weighted Cartesian coordinates (might be used in the output of the eigenmodes)**

$$H_{MW,ij} = \frac{H_{cart,ij}}{\sqrt{m_i m_j}} = \left(\frac{\partial^2 E}{\partial Q_i \partial Q_j} \right)_0 \quad \text{with} \quad Q_i = \sqrt{m_i} R_i$$

o **2nd step: identify center of mass and principle axes of inertia (from diagonalizing the moment of inertia tensor)**

o **3rd step:** **Use these to generate the transformation matrix D from 3N mass-weighted cartesian coordinates to a system where 5 (6) translational and rotational degrees of freedom can be easily separated from the vibrations (for details see: https://gaussian.com/vib/)**

  ➢ **determine translation vectors**

  ➢ **using the normalized eigenvectors of tensor of inertia produce rotation vectors**

  ➢ **generate the eigenvectors that are orthogonal to them**

This yields: internal coordinates
$$\vec{S} = \overleftrightarrow{D}\vec{Q}$$

o **4th step: transform Hessian to internal coordinates**

$$\overleftrightarrow{H}_{INT} = \overleftrightarrow{D}^T \overleftrightarrow{H}_{MW}\overleftrightarrow{D}$$

o **5th step: diagonalize H_{INT} to obtain eigenvalues λ_i and eigenmodes**

Obtain wavenumbers via: $\tilde{\nu}_i = \sqrt{\dfrac{\lambda_i}{4\pi^2 c^2}}$

➢ **In case you are at a saddle point, you obtain imaginary frequencies (often printed out as negative frequencies)**

➢ **The first six non-immaginary frequencies should be very close to zero**

How close depends on the numerical settings

Table 1: The effect of optimization criteria on the low frequencies of water using HF/3-21G*. The frequencies are sorted by increasing absolute value, so that it's easier to distinguish rotational modes from vibrational modes.

Criteria	Low frequencies					
Opt	−0.0008	0.0003	0.0013	40.6275	59.3808	66.4408
Opt=Tight	0.0011	0.0013	0.0015	4.1908	−6.8779	12.4224
Opt=VeryTight	−0.0011	0.0014	0.0015	−0.9207	−1.1831	−1.6023

from Ochterski whitepaper

➢ **Tradeoff between accuracy and computational effort**

➢ **Often, significantly tighter numerical setting are needed when calculating vibrations compared to geometry optimizations**
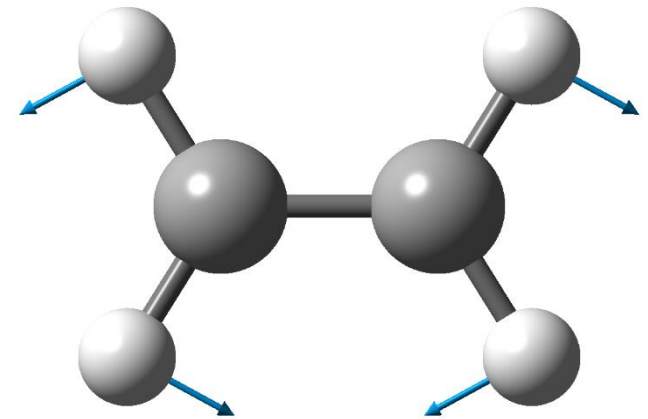
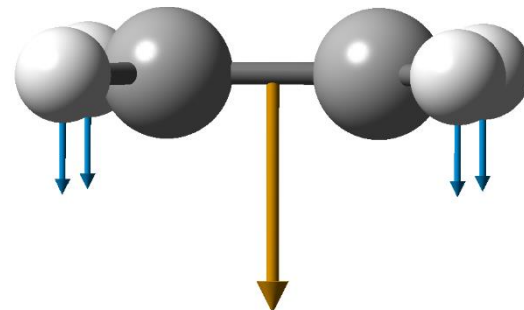**Note: Eigenmodes are typically very different from cartesian displacements ! = coupled motion of atoms**
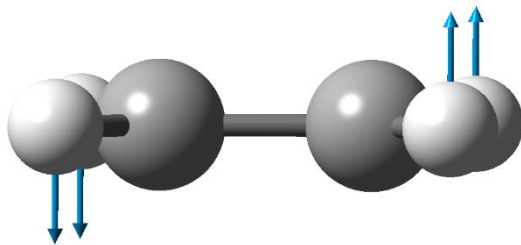
830 cm⁻¹

961 cm⁻¹
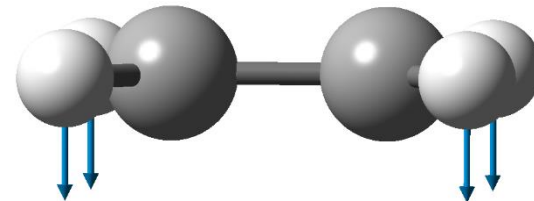
977 cm⁻¹

Which of the modes is infrared active, which one is Raman active ?

Plot dipole-derivative vector

How strongly do the frequencies depend on the used method?

There exist various sets of empirical scaling factors !

e.g.:

J. Phys. Chem., Vol. 100, No. 41, 1996

Both, theoretical approach and basis set count !

TABLE 1: Frequency Scaling Factors Suitable for Fundamental Vibrations and rms_{ov} (cm^{-1}) Derived from a Least-Squares Fit of Frequencies[a]

method	scale factor[b]	rms_{ov}[c]
AM1	0.9532	126
PM3	0.9761	159
HF/3-21G	0.9085	87
HF/6-31G(d)	0.8953	50
HF/6-31+G(d)	0.8970	49
HF/6-31G(d,p)	0.8992	53
HF/6-311G(d,p)	0.9051	54
HF/6-311G(df,p)	0.9054	56
MP2-fu/6-31G(d)	0.9427	61
MP2-fc/6-31G(d)	0.9434	63
MP2-fc/6-31G(d,p)	0.9370	61
MP2-fc/6-311G(d,p)	0.9496	60
QCISD-fc/6-31G(d)	0.9537	37
B-LYP/6-31G(d)	0.9945	45
B-LYP/6-311G(df,p)	0.9986	42
B-P86/6-31G(d)	0.9914	41
B3-LYP/6-31G(d)	0.9614	34
B3-P86/6-31G(d)	0.9558	38
B3-PW91/6-31G(d)	0.9573	34

What about solids ?

➢ **Necessary to be in minimum structure w.r.t. atomic positions**

➢ **Not nescessary to be in minimum w.r.t. lattice constants (= corresponds to material exposed to stress and strain)**

➢ **Correct description of inter-molecular interactions sizable challenge (van der Waals interactions)**

➢ **In solids, we are interested in phonon bands → we need to calculate off Γ-point !**

Situation more complex than in finite-size system, as in a solid we are dealing with an infinite number of interacting atoms !

Exploit periodic boundary conditions !

Instructive compilation of the theoretical background by Peter Puschnig

http://physik.uni-graz.at/~pep/Lehre/PP/DynMat.pdf (13.5.2019)

Taylor series expansion of potential energy
(truncated after harmonic term)

$$W(s_{n\alpha i}) = W(\mathbf{R}_{n\alpha}) + \sum_{n\alpha i} \left[\frac{\partial W(\mathbf{x})}{\partial s_{n\alpha i}} \right]_{\mathbf{x}=\mathbf{R}_{n\alpha}} s_{n\alpha i}$$

$$+ \frac{1}{2} \sum_{n\alpha i} \sum_{n'\alpha'i'} \left[\frac{\partial^2 W(\mathbf{x})}{\partial s_{n\alpha i} \partial s_{n'\alpha'i'}} \right]_{\mathbf{x}=\mathbf{R}_{n\alpha}} s_{n\alpha i} s_{n'\alpha'i'} + O(s^3)$$

unit cell　　**atom in basis**　　**coordinate direction**　　**displacements**

sum over all pairs of atoms in entire crystal

Force constant matrix
$$\Phi_{n\alpha i}^{n'\alpha'i'} = \left[\frac{\partial^2 W(\mathbf{x})}{\partial s_{n\alpha i} \partial s_{n'\alpha'i'}} \right]_{\mathbf{x}=\mathbf{R}_{n\alpha}}$$

In practice: displace one atom, calculate change in forces on all the other atoms

Equation of motion:

$$M_\alpha \frac{d^2 s_{n\alpha i}}{dt^2} = -\sum_{n'\alpha'i'} \Phi^{n'\alpha'i'}_{n\alpha i} s_{n'\alpha'i'}$$

Harmonic oscillator ansatz:

$$s_{n\alpha i}(t) = \frac{1}{\sqrt{M_\alpha}} u_{n\alpha i} e^{-i\omega t}$$

Eigenvalue equation for all frequencies

$$\omega^2 u_{n\alpha i} = \sum_{n'\alpha'i'} \frac{\Phi^{n'\alpha'i'}_{n\alpha i}}{\sqrt{M_\alpha M_{\alpha'}}} u_{n'\alpha'i'}$$

Problem: We still need to sum over all atoms in the crystal !

exploit:

periodicity of the lattice $u_{n\alpha i} = c_{\alpha i} e^{i\mathbf{q}\mathbf{R}_n}$

force-constants only depend on difference between unit cells

$$\Phi_{n\alpha i}^{n'\alpha'i'} = \Phi_{\alpha i}^{\alpha'i'}(n - n')$$

final equations to solve:

Eigenvalue equation of dimension 3×number of atoms in unit cell

3×α solutions for every q!

q-dependence = phonon band structure

$$\sum_{\alpha'i'} D_{\alpha i}^{\alpha'i'}(\mathbf{q}) c_{\alpha'i'} = \omega^2(\mathbf{q}) c_{\alpha i}$$

with

$$D_{\alpha i}^{\alpha'i'}(\mathbf{q}) = \left[\sum_n \frac{\Phi_{\alpha i}^{\alpha'i'}(n)}{\sqrt{M_\alpha M_{\alpha'}}} e^{i\mathbf{q}\mathbf{R}_n} \right]$$

Dynamical matrix

$$D_{\alpha i}^{\alpha' i'}(\mathbf{q}) = \left[\sum_n \frac{\Phi_{\alpha i}^{\alpha' i'}(n)}{\sqrt{M_\alpha M_{\alpha'}}} e^{i\mathbf{q}\mathbf{R}_n} \right]$$

Fourier transform of mass-weighted force-constant matrix

one only needs force constants for atoms in the unit cell

BUT: dependence of Φ on n!

→ still, one has to calculate force constants for displacements of every atom in the crystal

In practise:
- **calculate supercells**
- **increase size of supercell until impact on force constants becomes negligible**
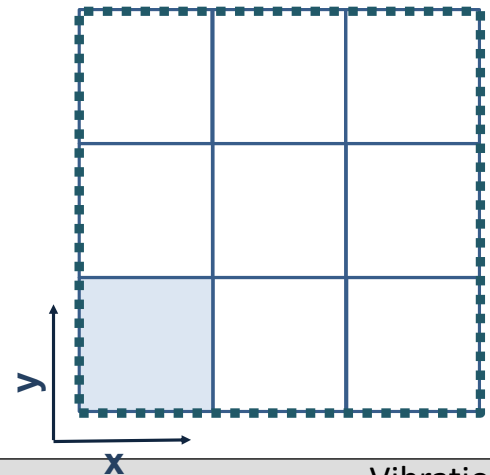
Density functional perturbation theory (DFPT)

aternative approach for obtaining the dynamical matrix

For a detailed discussion see:
Baroni et al., Review of Modern Physics, 73 (2001)

In essence:

Exploiting the Born-Oppenheimer approximation and the Hellman-Feynman theorem one can show that for getting the Hesse matrix one needs:

- **the ground state density** $n_{\mathbf{R}}(\mathbf{r})$ from DFT

- **its (linear) response to a distortion of the nuclear geometry**

$$\partial n_{\mathbf{R}}(\mathbf{r})/\partial \dot{\mathbf{R}}_I$$ from DFPT

perturbative treatment of response of electrons to external stimulus)

Example: Phonon band structure of Si.
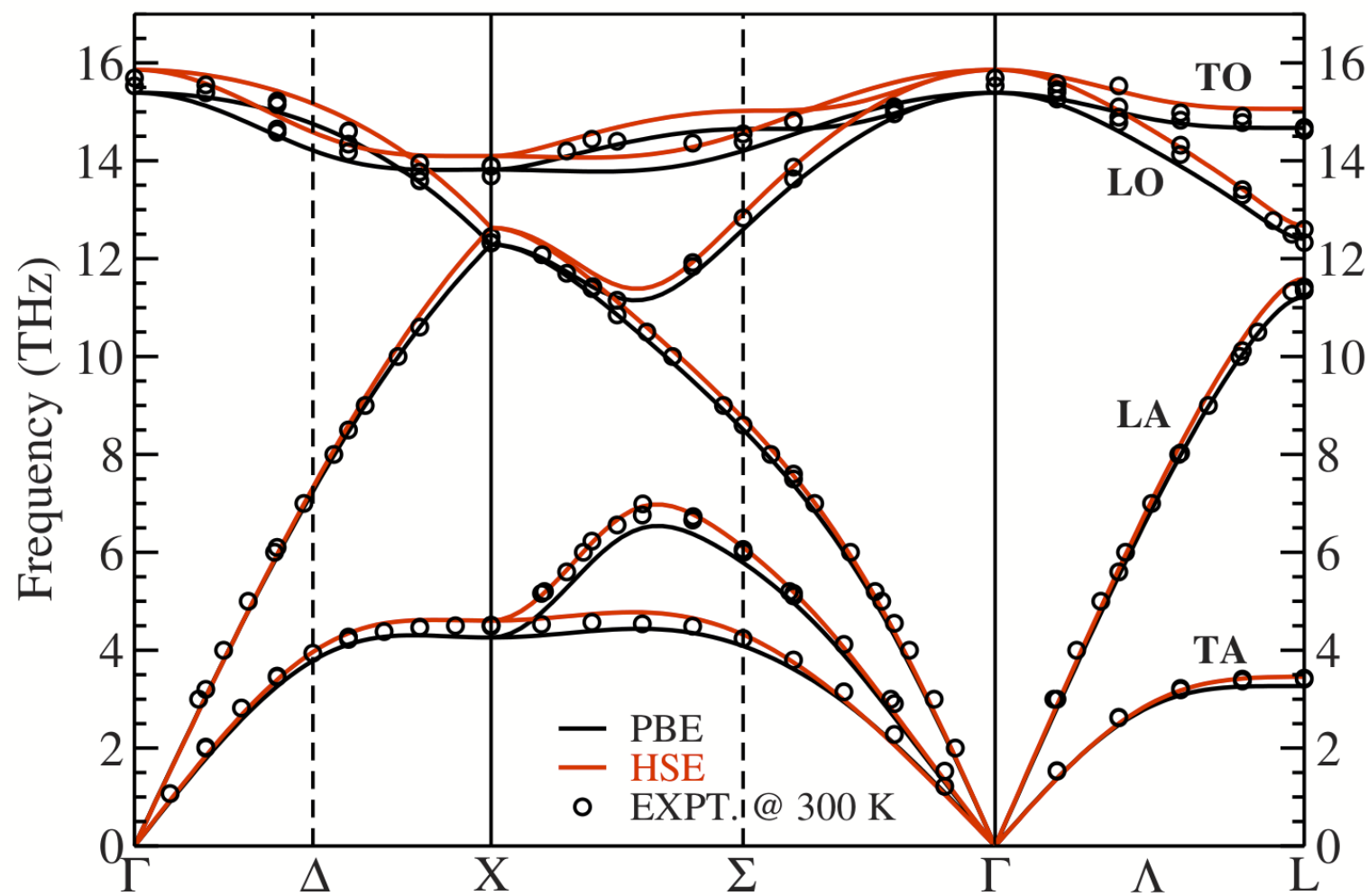
Hummer et al. Phys. Rev. B 80, 115205 (2009)

Example: Phonon spectra of prototypical MOFs

T. Kamencek et al., Phys. Rev. Mater., 3, 116003 (2019)
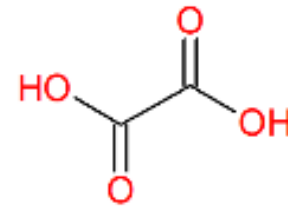
metal-organic frameworks

metal atoms (e.g., Zn, Mg, Ca, Cu …)

oxygen

Convergence of force constants: for supercells containing 64 metal nodes !

linker

here (very simple):

(a)

IRMOF-130(Mg/Ca)
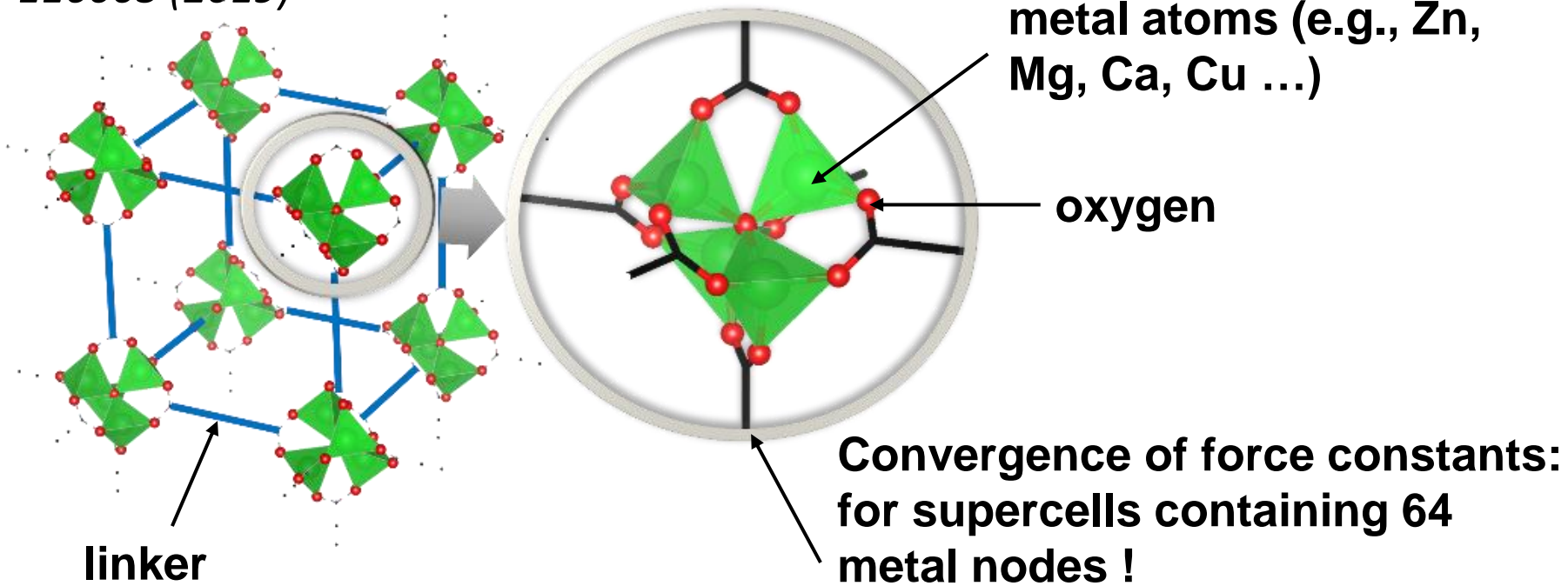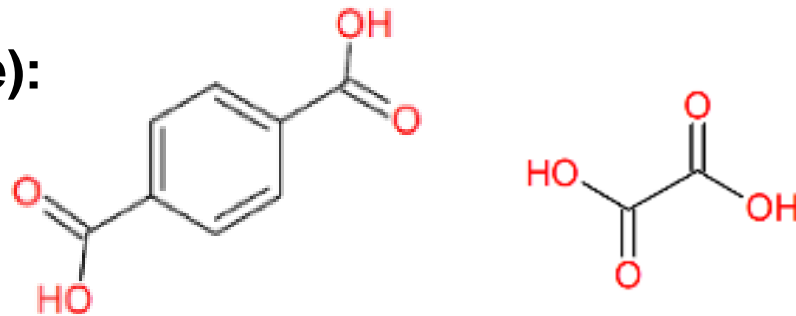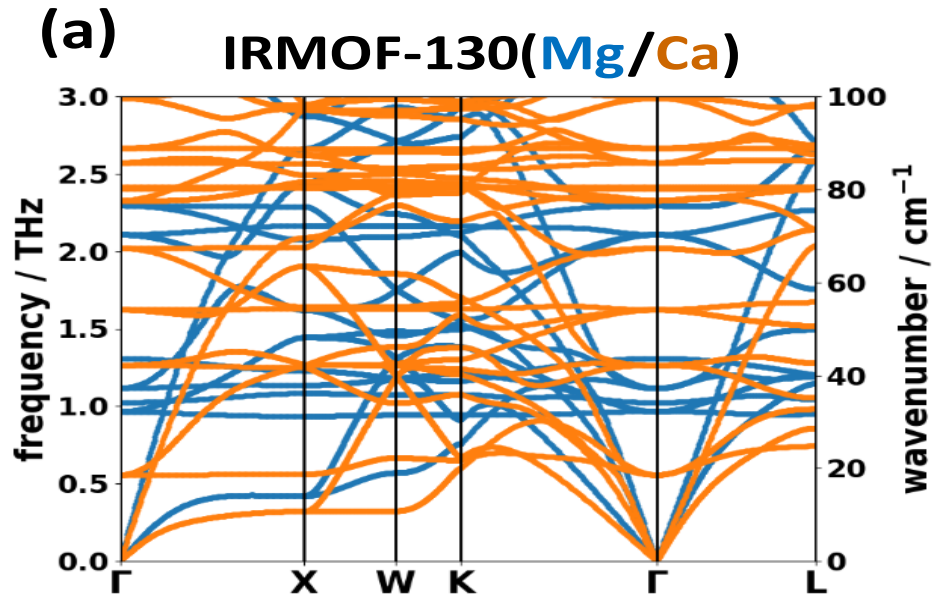
LOW ENERGY REGION
of the phonon bands

(b)

IRMOF-130(Mg)
IRMOF-1(Mg)
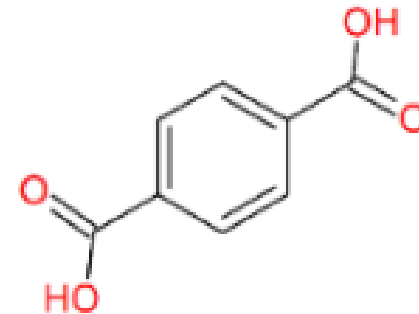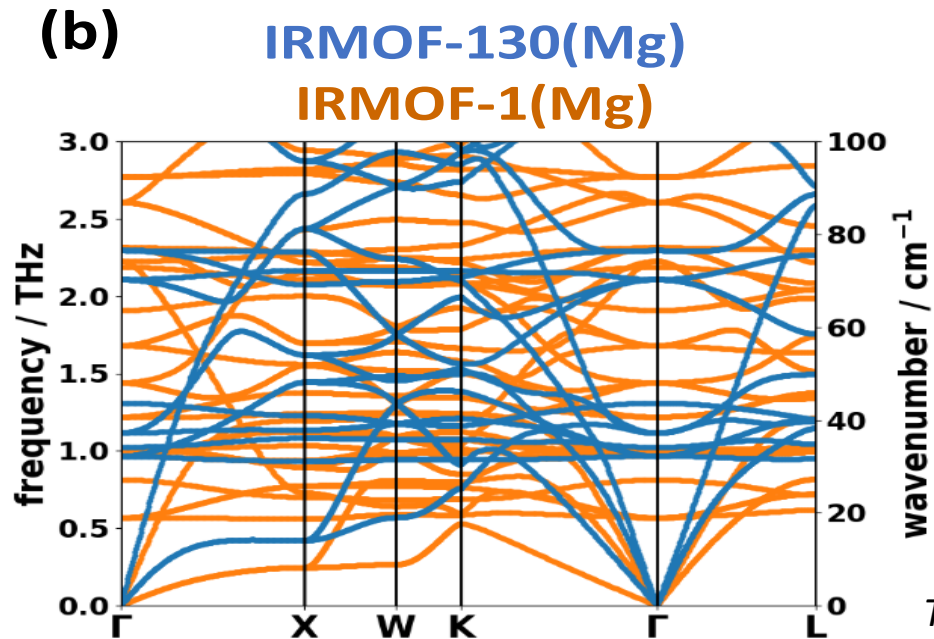
T. Kamencek et al., Phys. Rev. Mater., 3, 116003 (2019)

(Projected) density of states:

huge number of (optical) bands
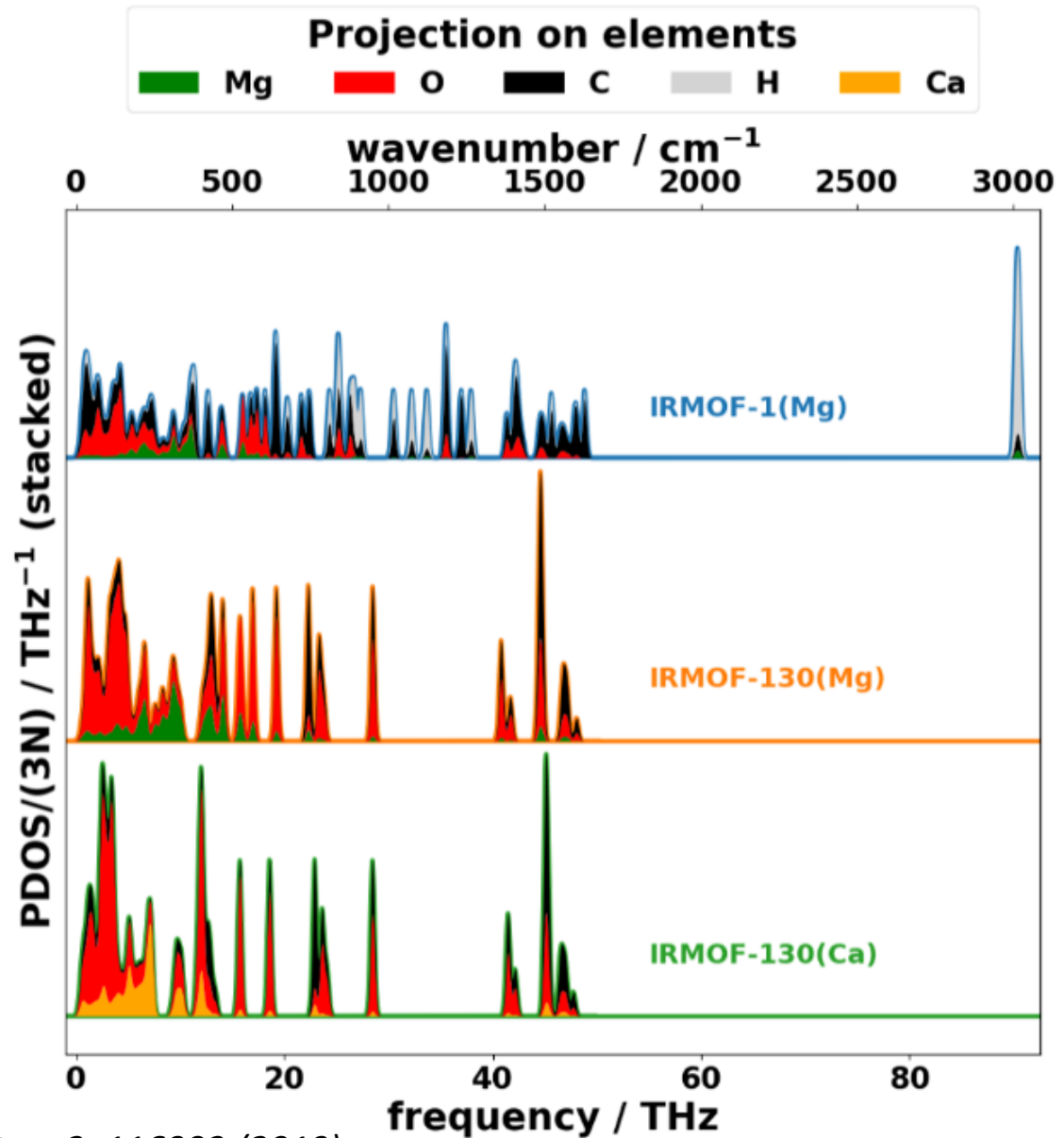
T. Kamencek et al., Phys. Rev. Mater., 3, 116003 (2019)

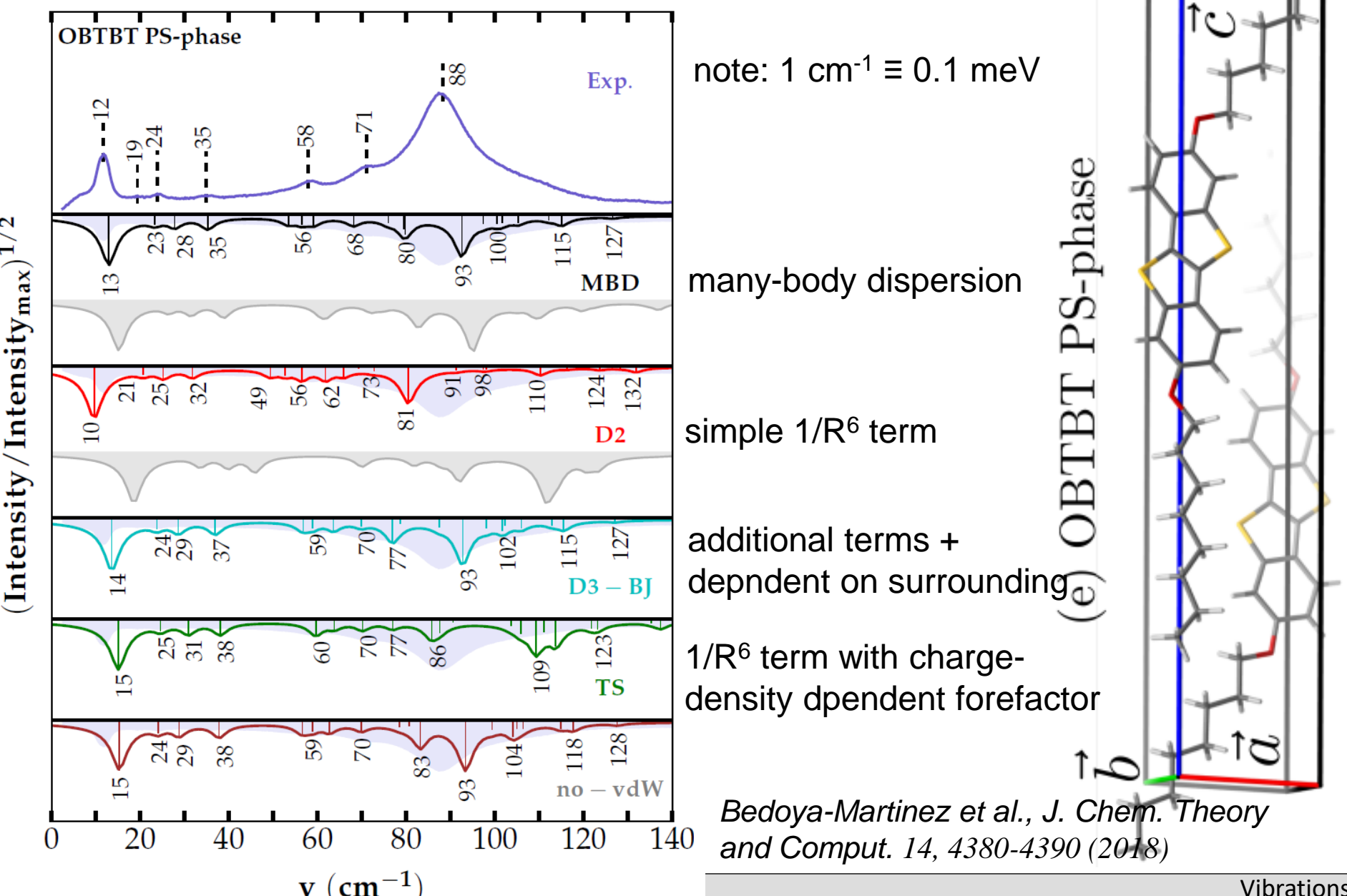# Analyze band structures in terms of group velocities
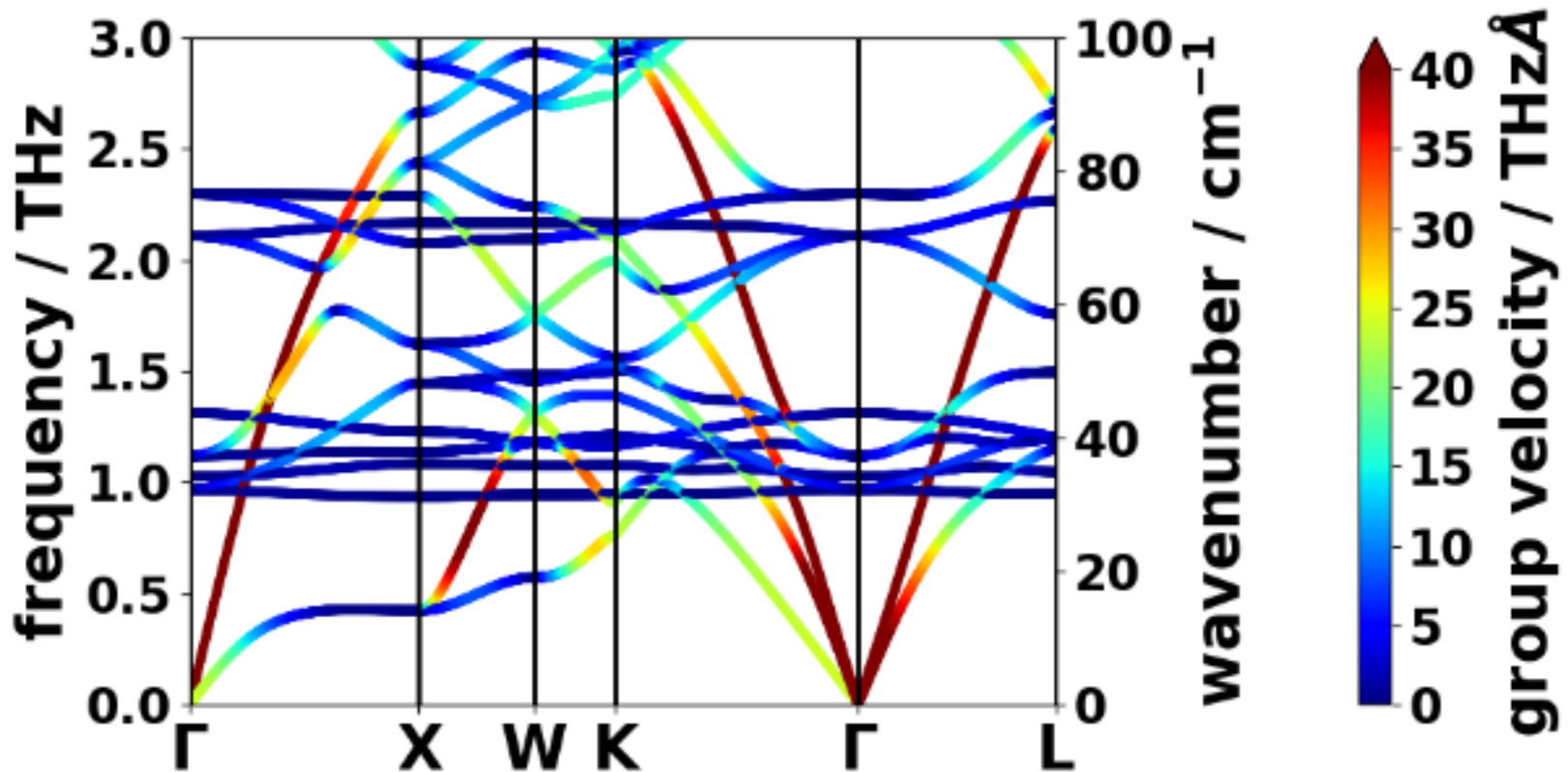
calculate thermal, elastic … properties

T. Kamencek et al., Phys. Rev. Mater., 3, 116003 (2019)

Challenge: How to get interaction energies right ?

Problem, e.g., long-range van der Waals interaction, which is not contained in (semi)local DFT.

Challenge, for example, when modelling molecular crystals!

Common approach to deal with vdW interactions:
# A posteriori corrections of the energy

note: $1\ \text{cm}^{-1} \equiv 0.1\ \text{meV}$

many-body dispersion

simple $1/R^6$ term

additional terms +
depndent on surrounding

$1/R^6$ term with charge-
density dpendent forefactor

*Bedoya-Martinez et al., J. Chem. Theory
and Comput. 14, 4380-4390 (2018)*

(e) OBTBT PS-phase

Vibrations

Low-wavenumer regime dominated by inter-molecular vibrations
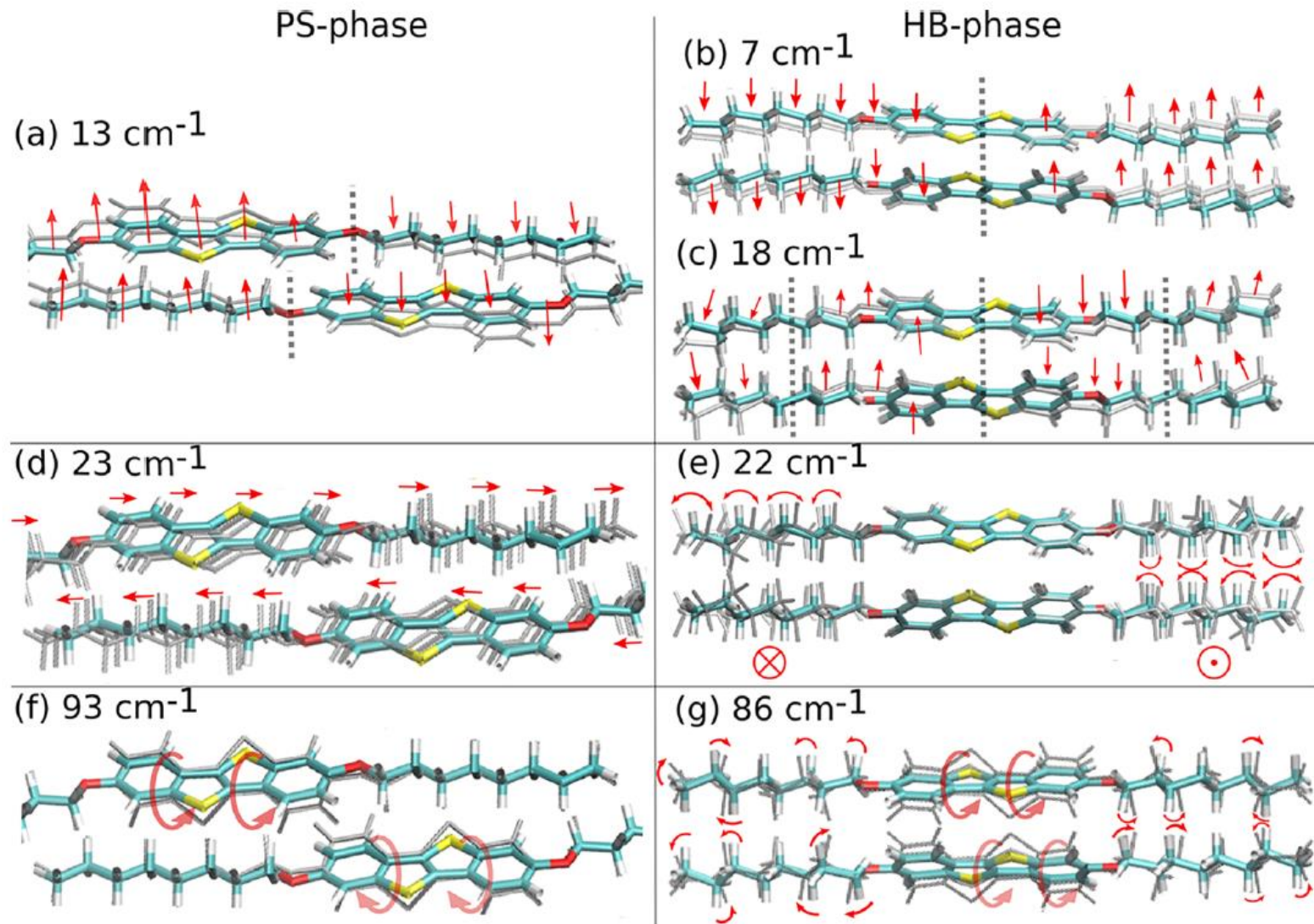
Bedoya-Martinez et al., J. Phys. Chem. Lett, 2017

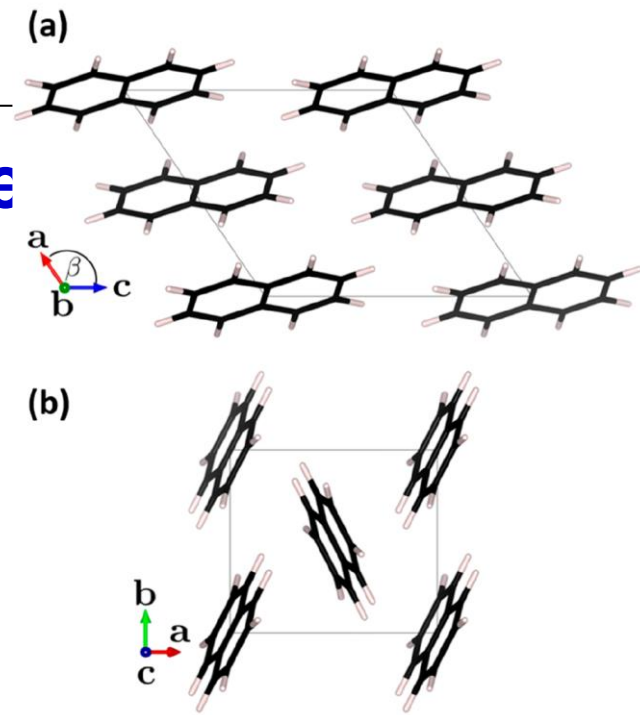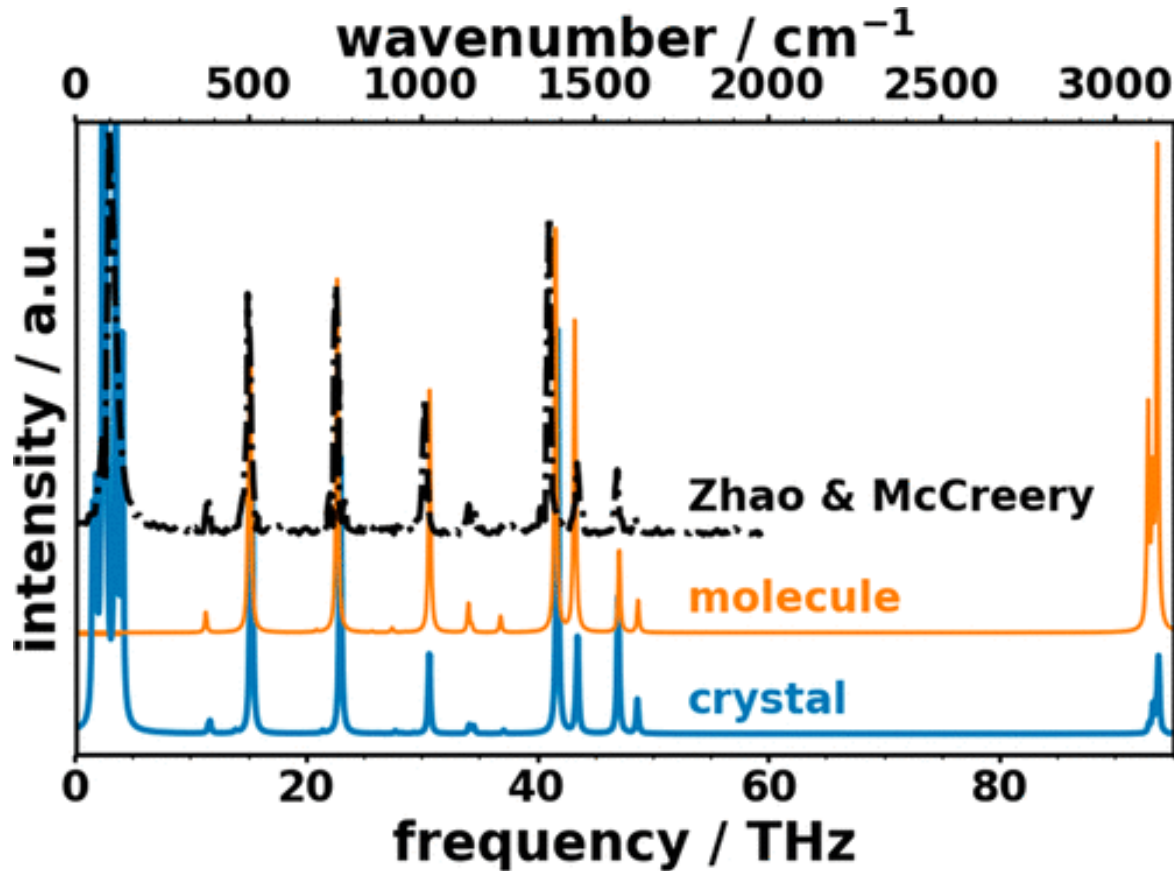# Advantage of simulation: Type of vibrations can be analyzed
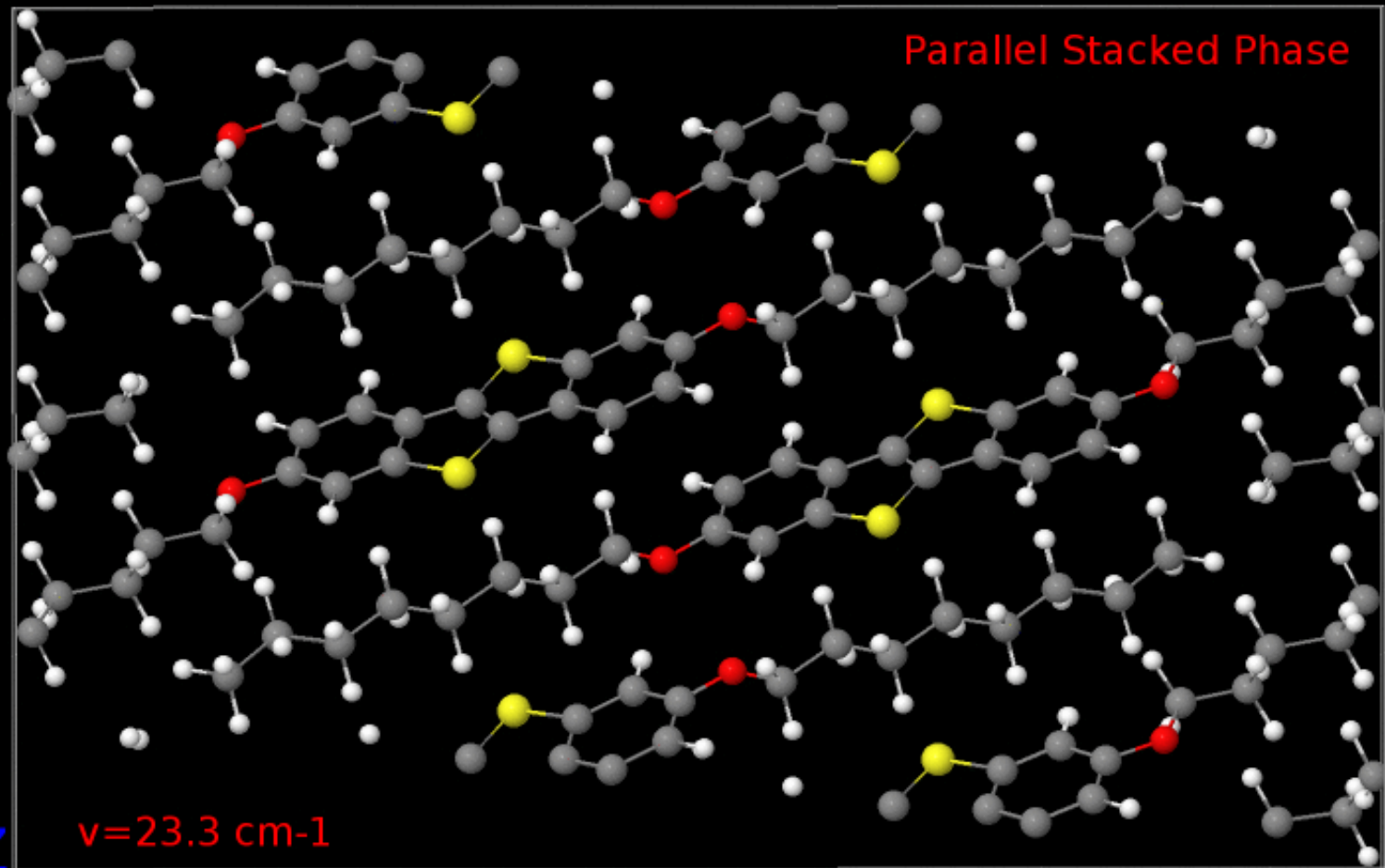
Herringbone Phase
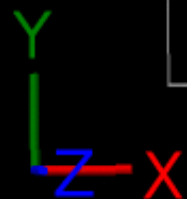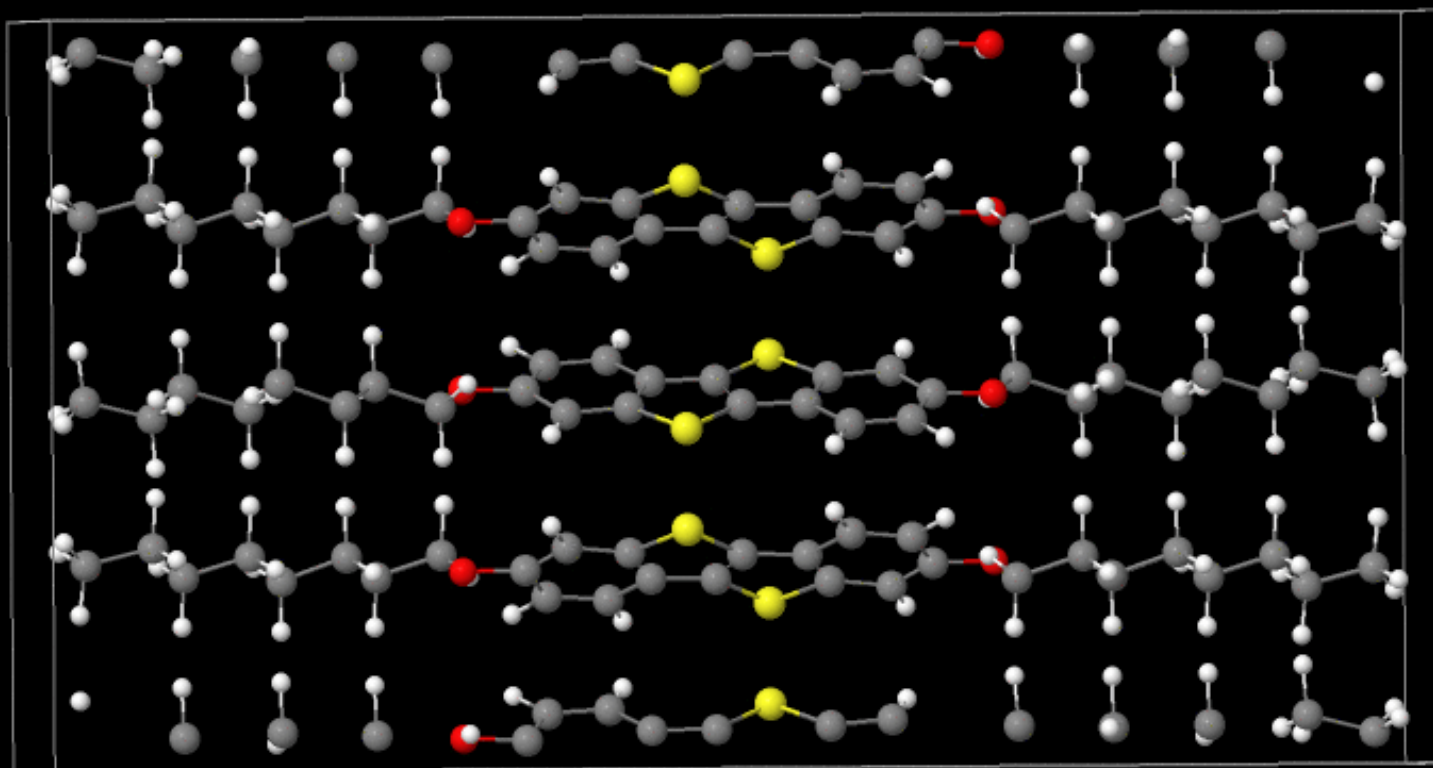
v= 86.3 cm-1

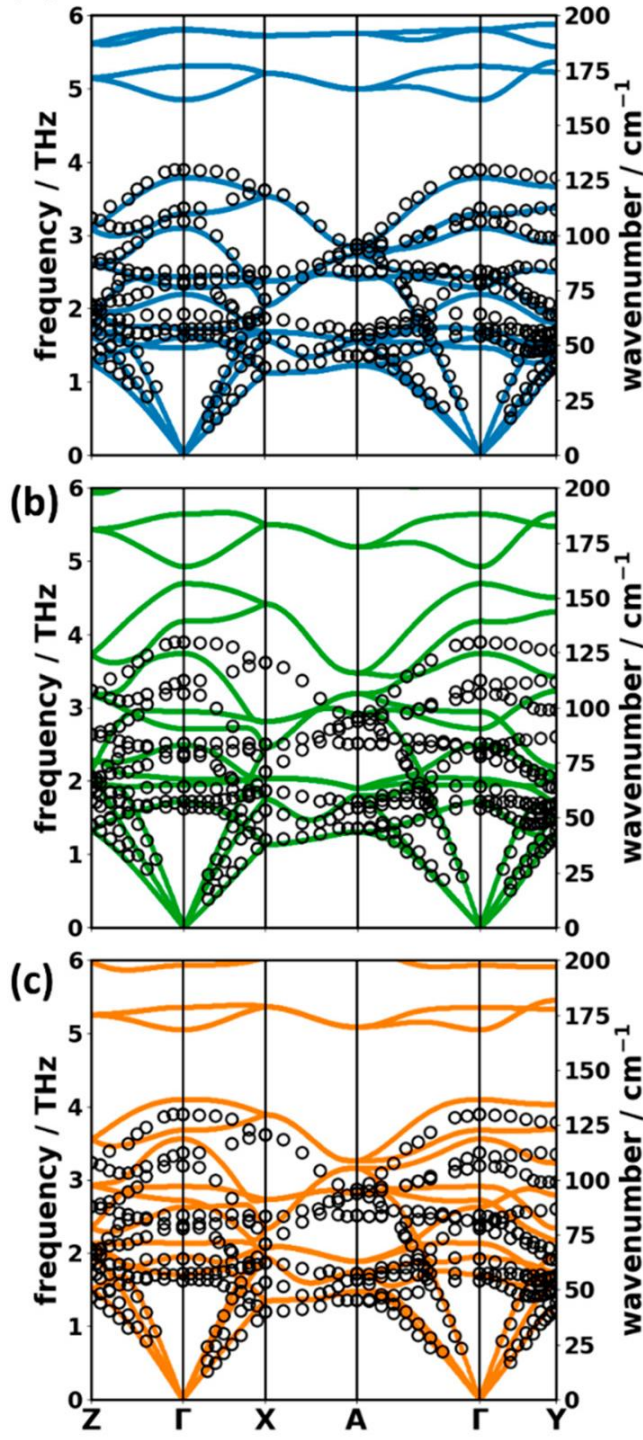# What about Phonon band structure

Experimental phonon BS exist for deuterated naphthalene!

(a)

(b)

Raman spectra

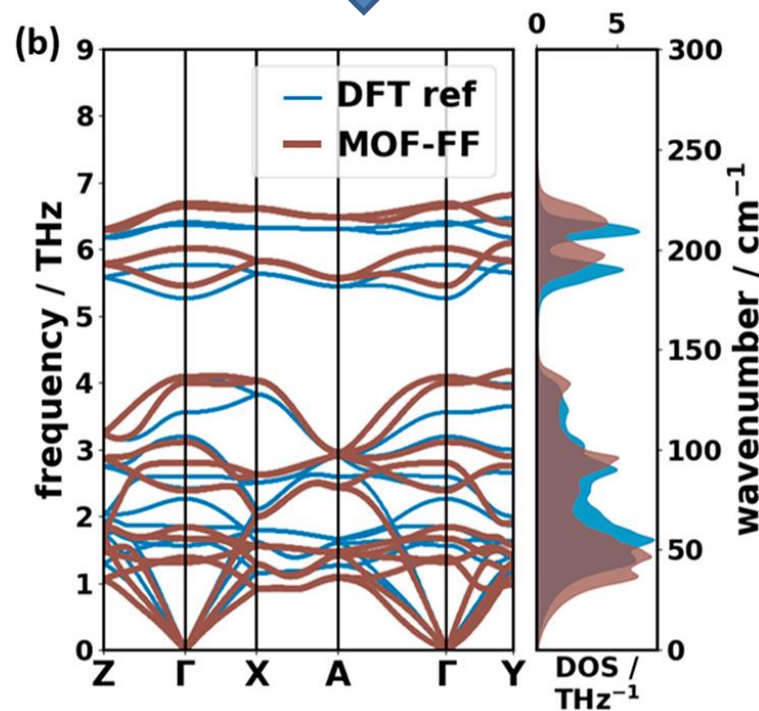*Tomas Kamencek, et al. The Journal of Chemical Theory and Computation 16, 2716-2735 (2020)*

PBE with (a) D3-BJ, (b) TS, and (c) D2 vdW correction

Sophisticated classical force field

Tomas Kamencek, et al. The Journal of Chemical Theory and Computation 16, 2716-2735 (2020)