Temperature Dependence of the Vibrational Spectrum of Porphycene

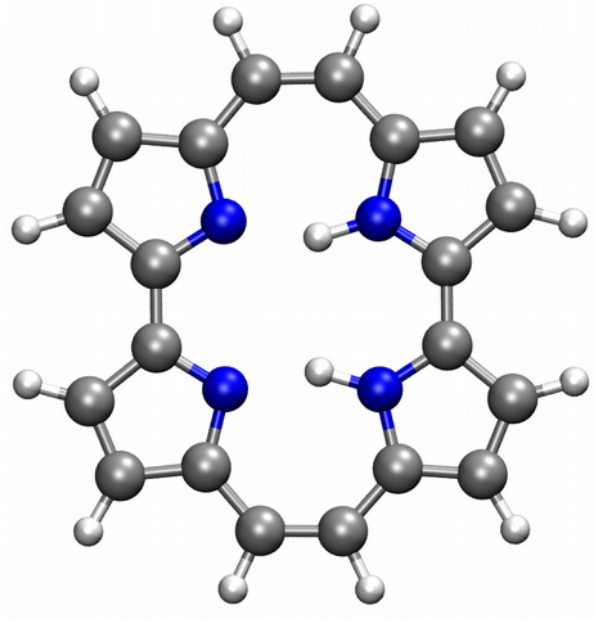
Yair Litman

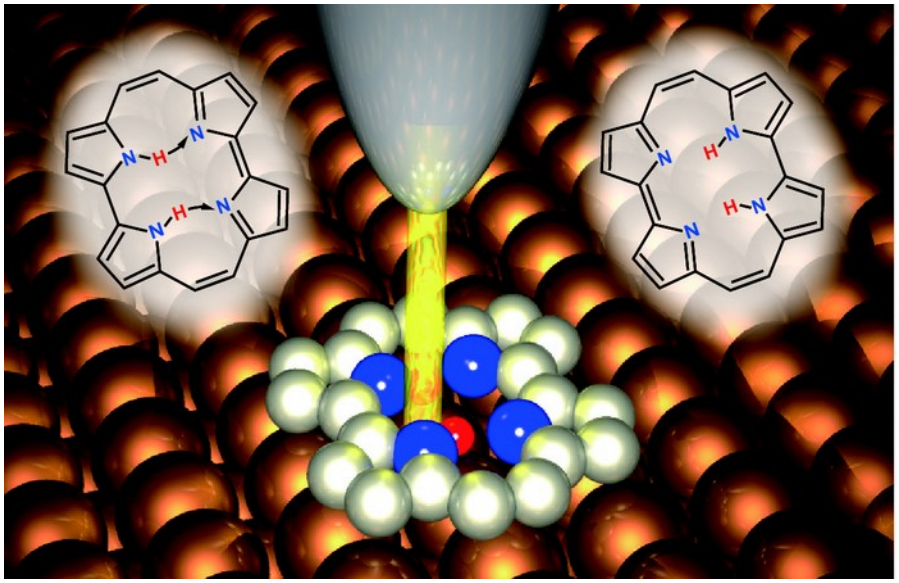
Fritz Haber Institute of the Max Planck Society
Berlin, Germany

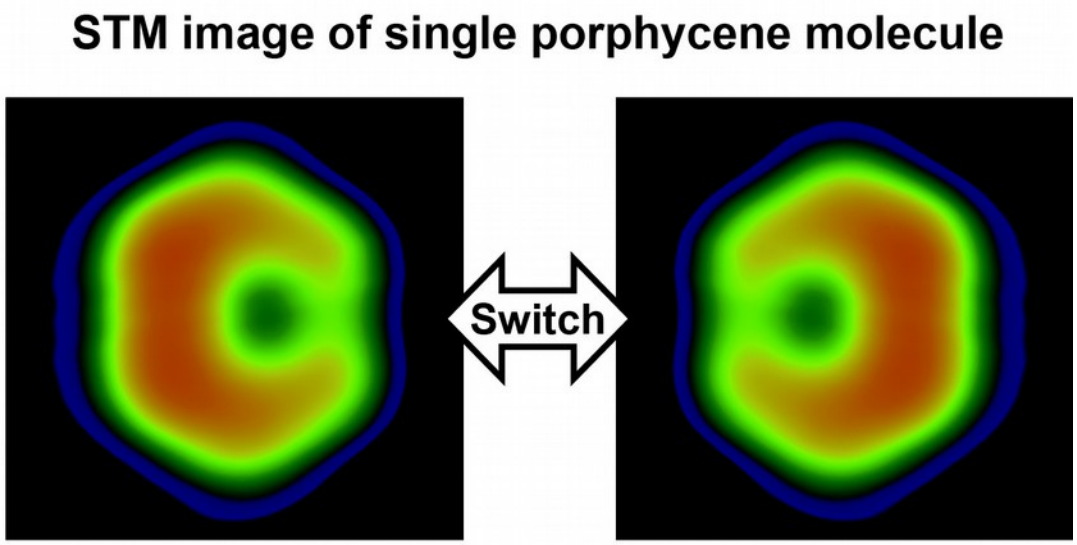
SAbIA
Simulations from
Ab Initio Approaches
Structure and Dynamics
from Quantum Mechanics

Porphycene Molecule

- Well studied model of intramolecular hydrogen transfer processes in both ground and excited electronic states
- Important due to its proton transfer properties and synthesis of derivatives
- Prototype of a molecular switch







Pictures taken from http://www.fhi-berlin.mpg.de/pc/kumagai/nsc_research.html

Previously on DPG:Porphycene IR spectra

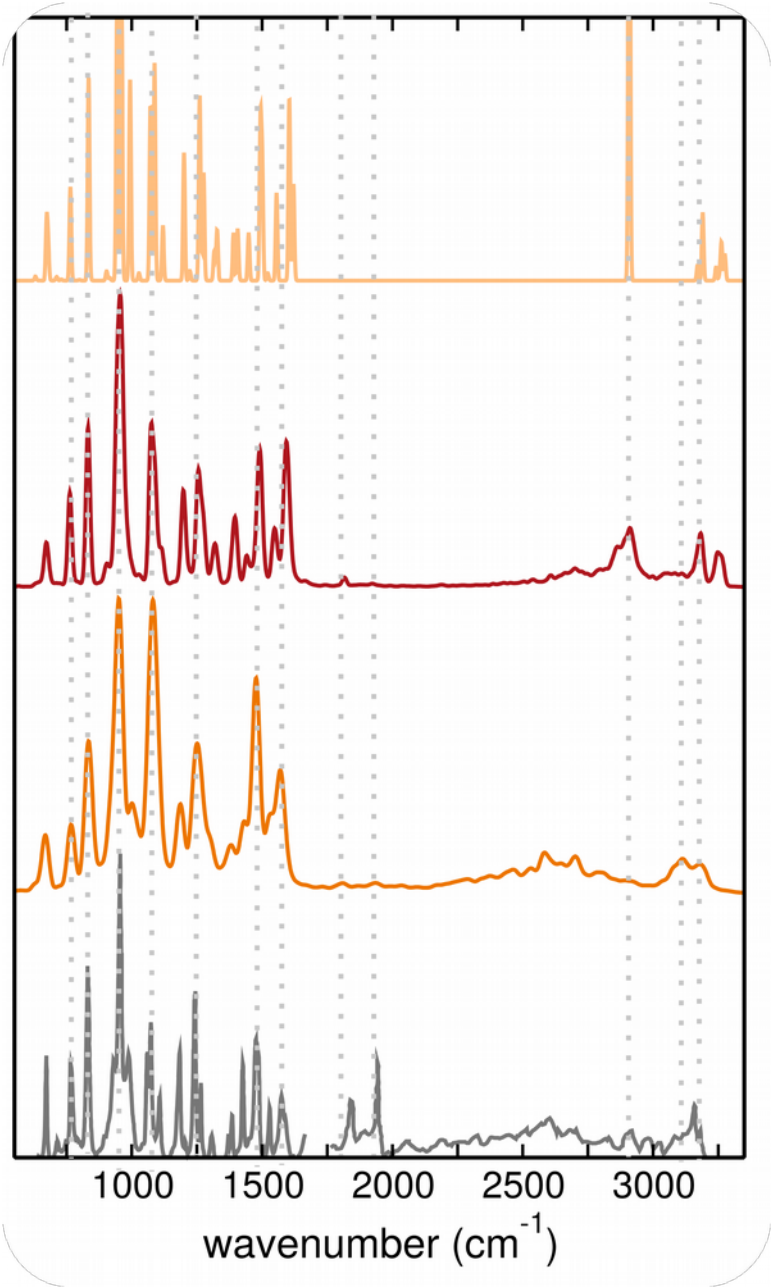
<u>Methodology</u>

Harmonic

Classical nuclei

Quantum nuclei

Experiment (KBr)



<u>Result</u>

Strong NH signal

Small broadening and not peak shift

Huge broadening and peak shift

Gawinkowski, S.; et al. Phys. Chem. Chem. Phys., 14, 5489 (2012)

Litman, Y.; et al. J. Am. Chem. Soc. 141, 2526-2534 (2019)

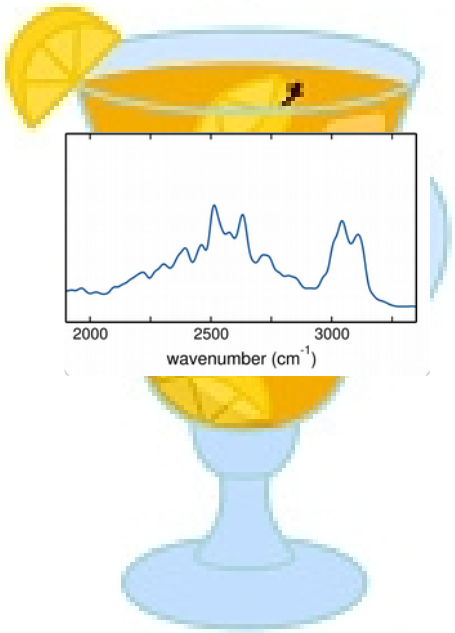
Ingredients

Quantum Nuclear dynamics

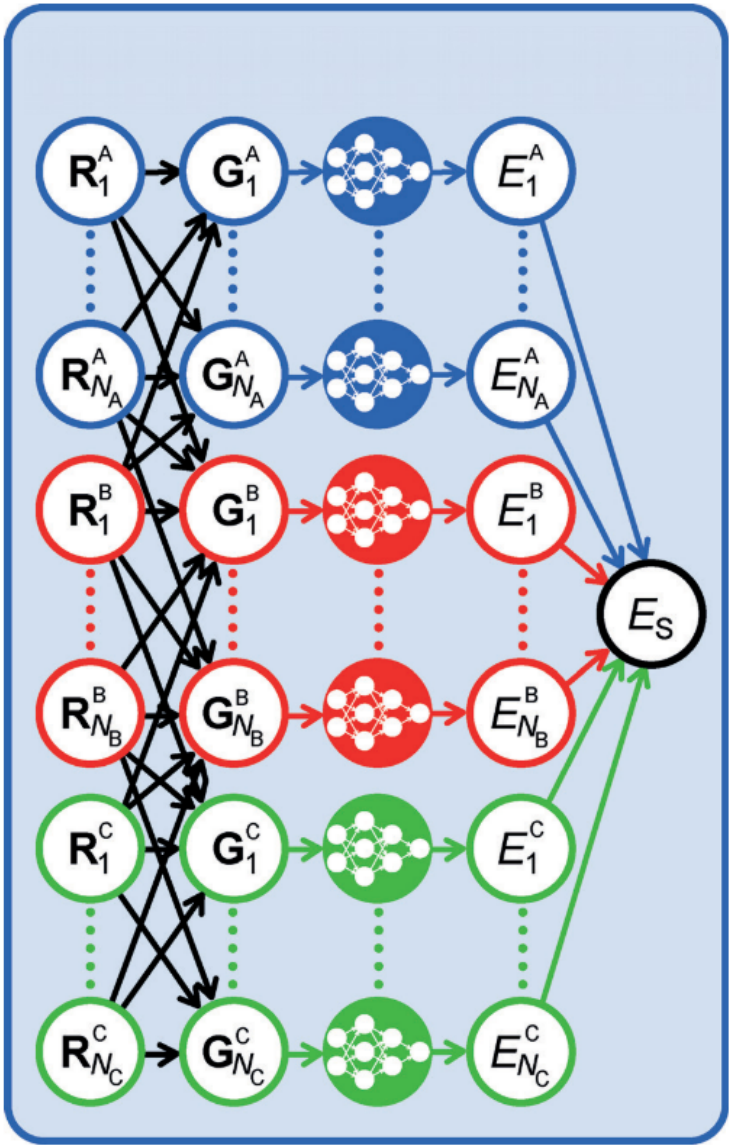
Reliable PES

Really good statistics

Manpower



High Dimensional Neural Network Potential (HDNNP)



Atomic coordinates

Symmetry functions

Atomic NN

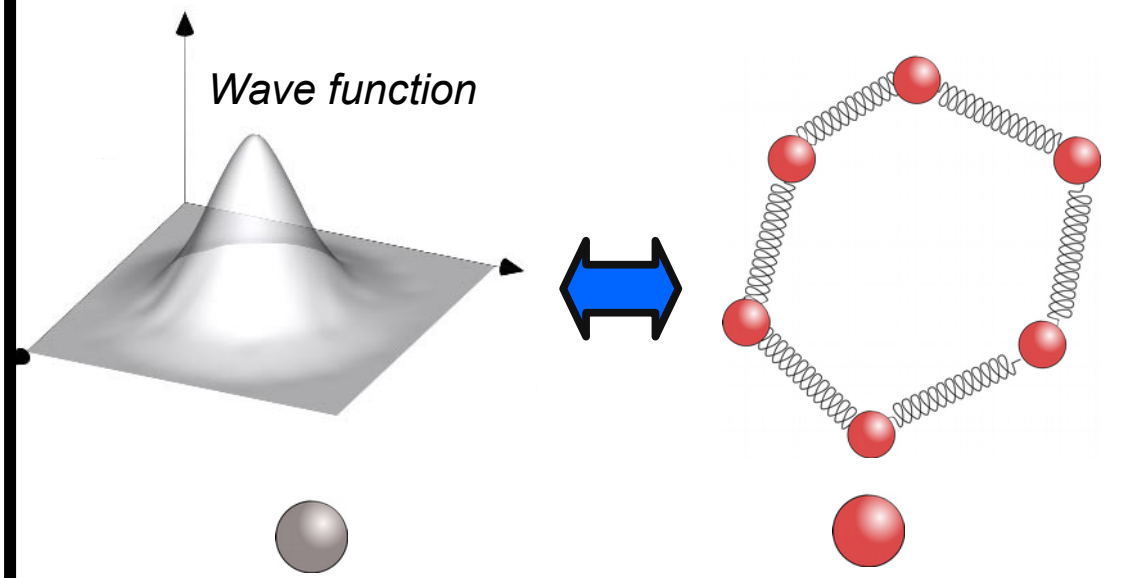
Atomic energies

Short range energy

HDNNP: J. Behler, M. Parrinello. Phys. Rev. Lett. 98, 146401 (2007) Picture from: J. Behler, M. Parrinello. Phys. Rev. Lett. 98, 146401 (2007)

IR spectra

- Path integral formulation of quantum mechanics:

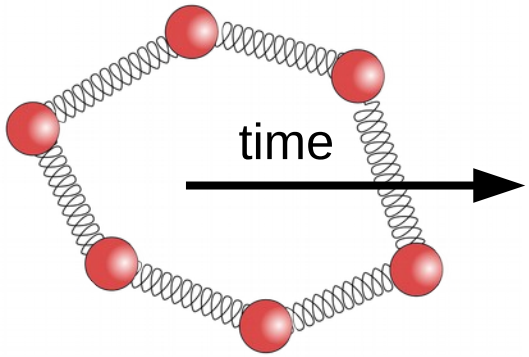


Quantum particle

Ring polymer made of classical particles

Exact for equilibrium properties

Approximation to quantum dynamics



✔ Conserves QM equilibrium distribution

✔ Includes ZPE and tunneling

✘ Neglects quantum coherence effects

TRPMD Rossi, M.; et al. J. Chem. Phys.,148, 102301 (2018)

I-PI code: Kapil, V.; et al., Com. Phys. Comm. 236, 214-223 (2018)

Technical Slide

Reference method: DFT B3LYP + vdW

Number of points ~ 100.000 (but it can be done with much less)

Ensemble of 6 different HDNNP to check consistency

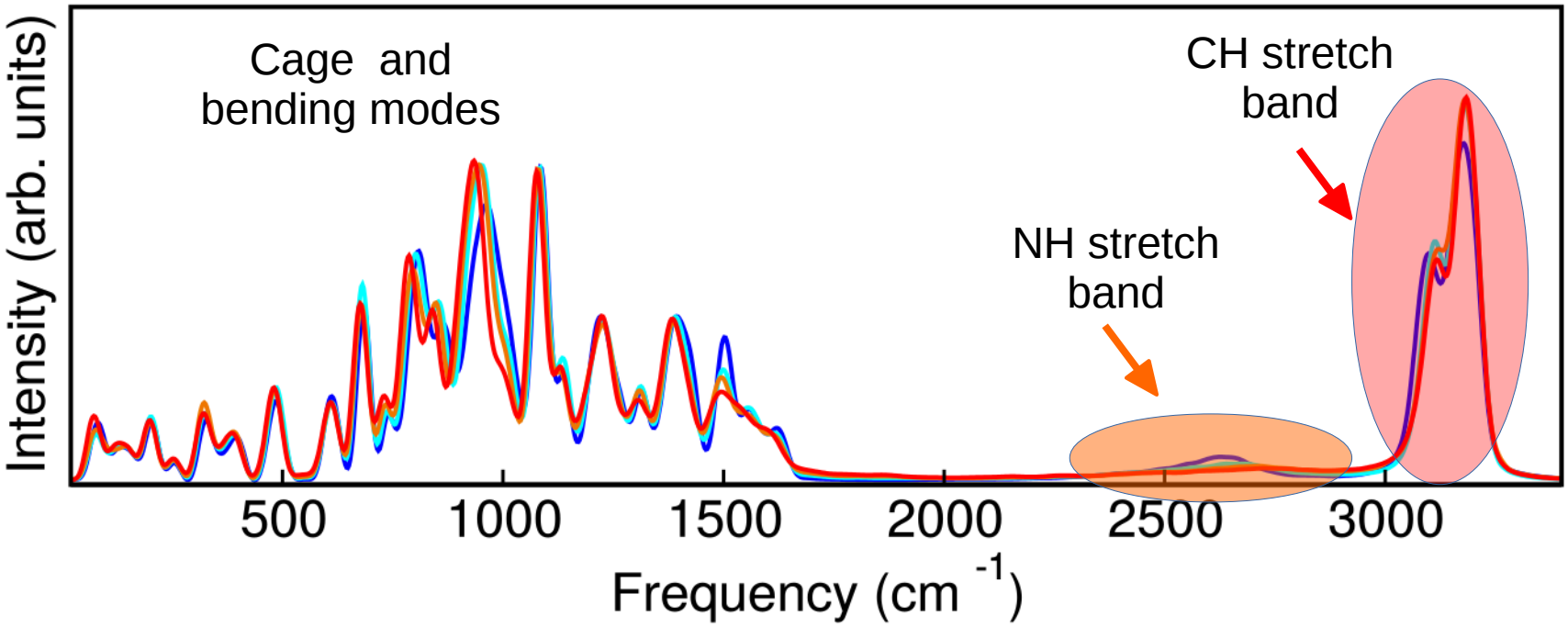
HDNNP overall accuracy: RMSE Energies ~1meV/atom , RMSE forces ~80 meV/bohr

100 TRPMD trajectories of 10 ps each

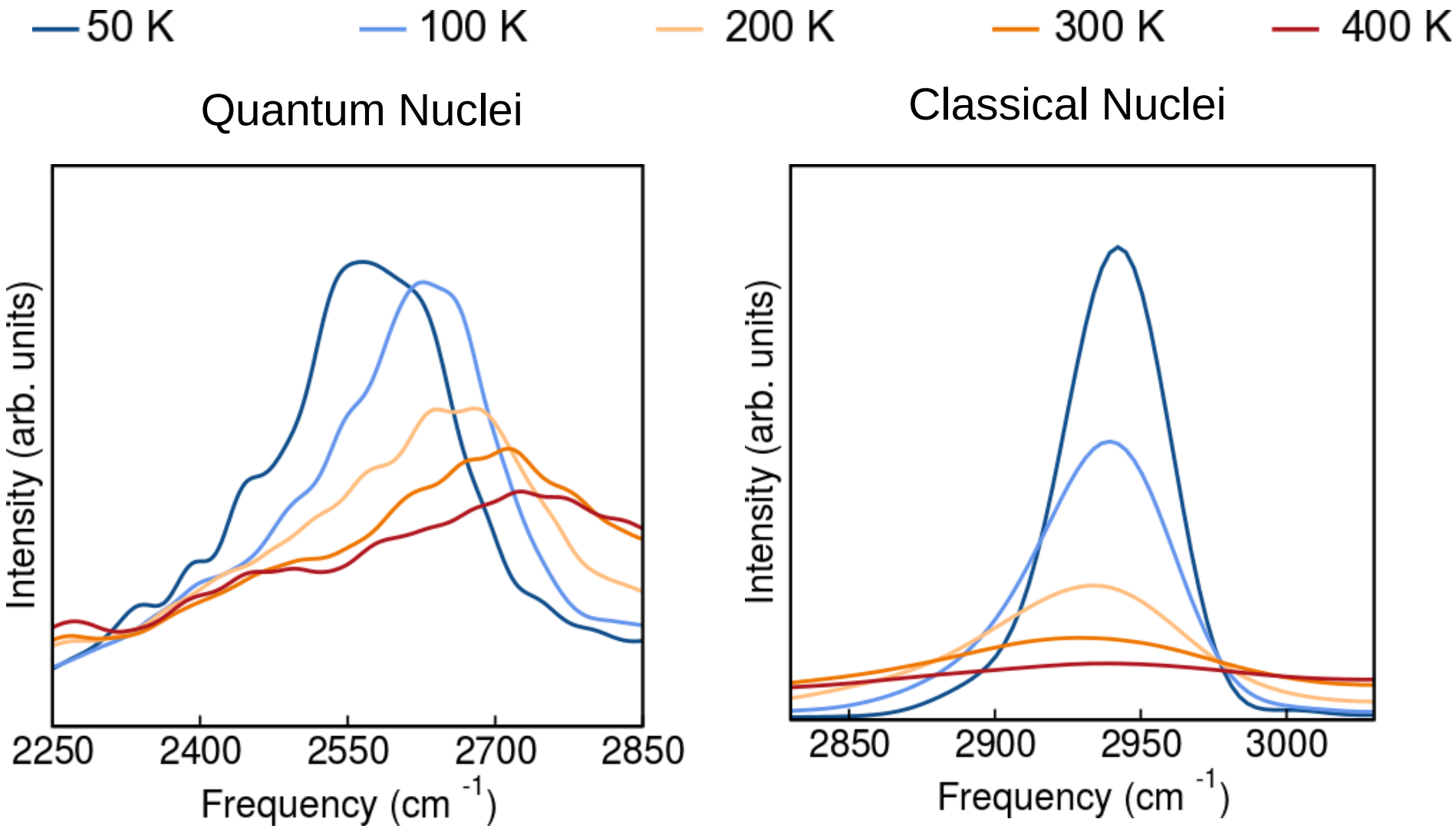
KRR model to predict IR (not shown in this talk)

Temperature dependence

Velocity density of states (VDOS)

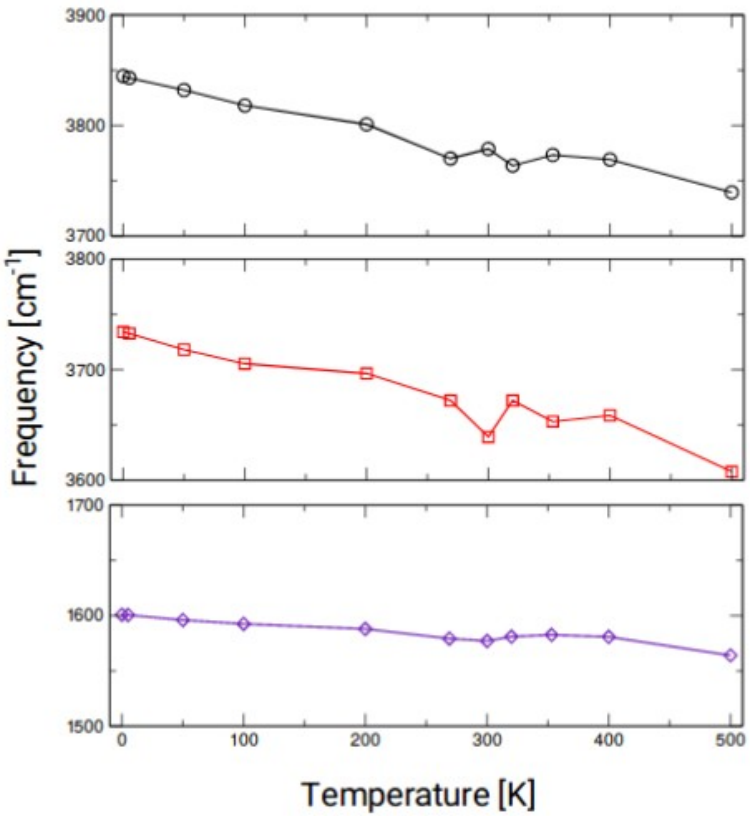


Temperature dependence

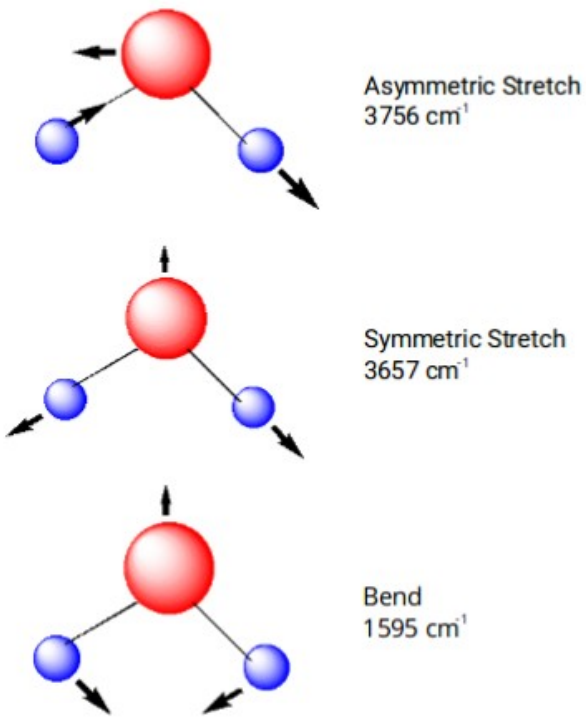


This reminds me something ...

26 March	*Florian Knoop*	*A Linear Algebra Approach towards Symmetry in Physical Problems*

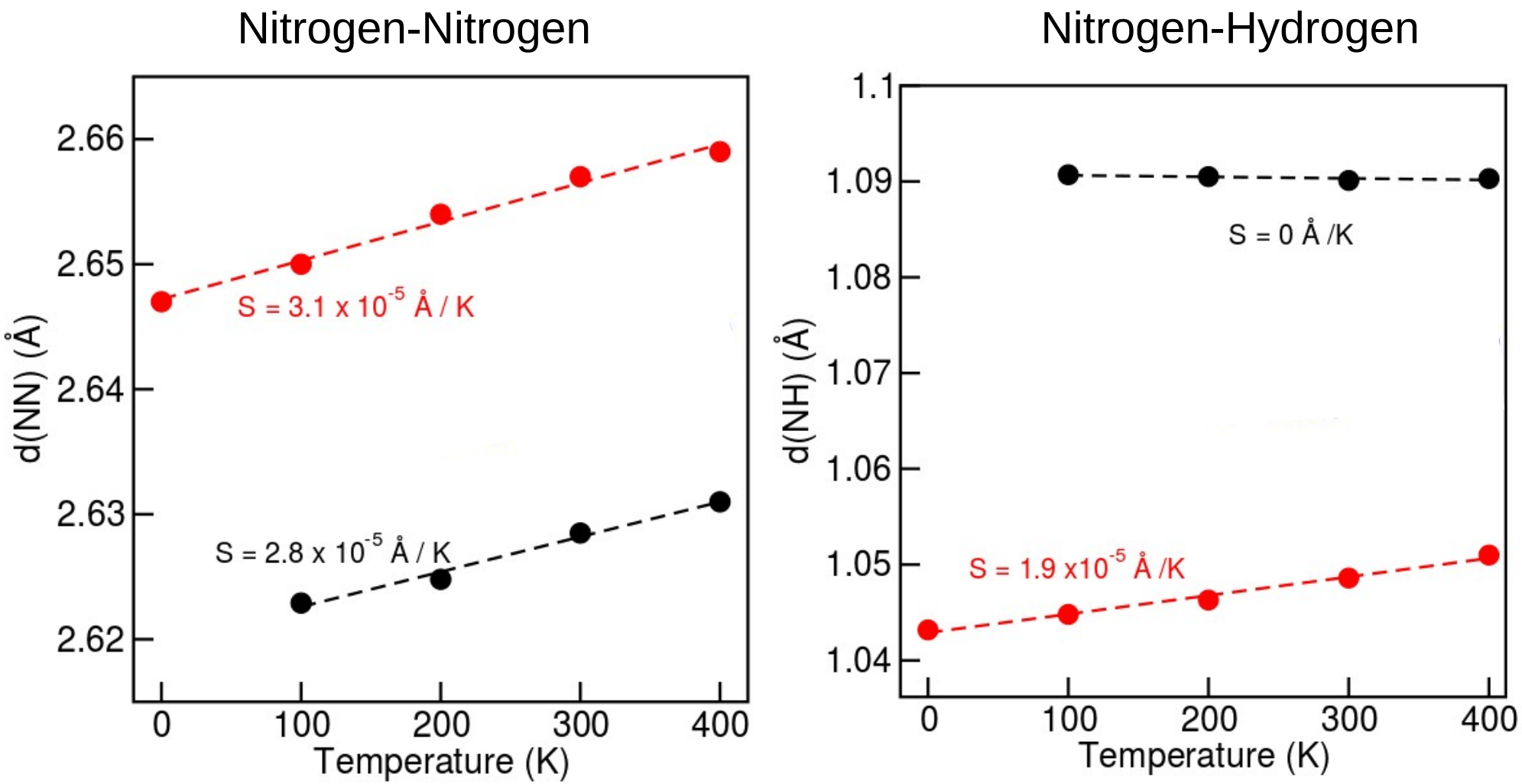


Change of vibrational frequencies with temperature



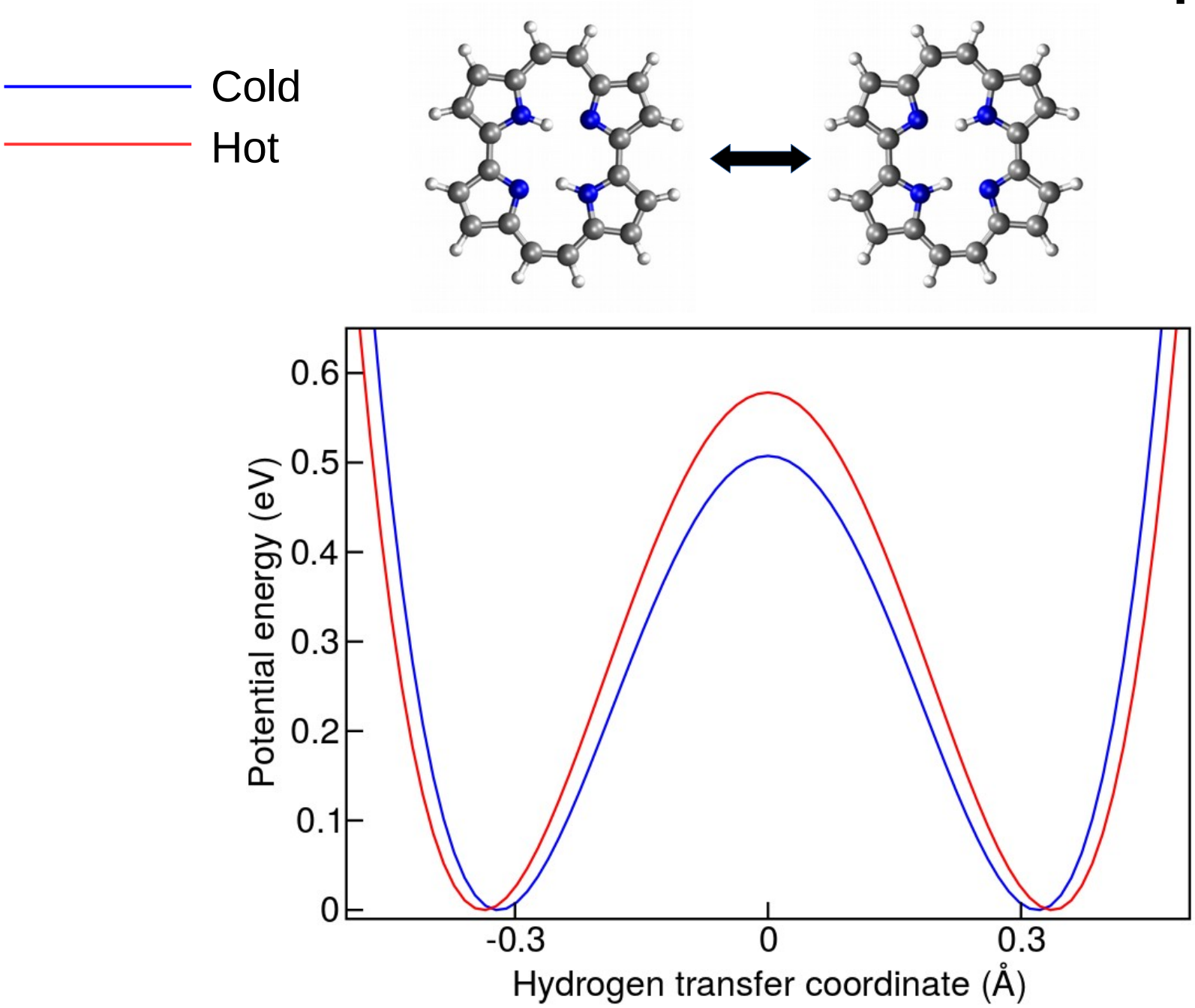
Sketch of Vibrational modes
physics.stackexchange.com/a/153091

Red or Blue Shift, that is the question

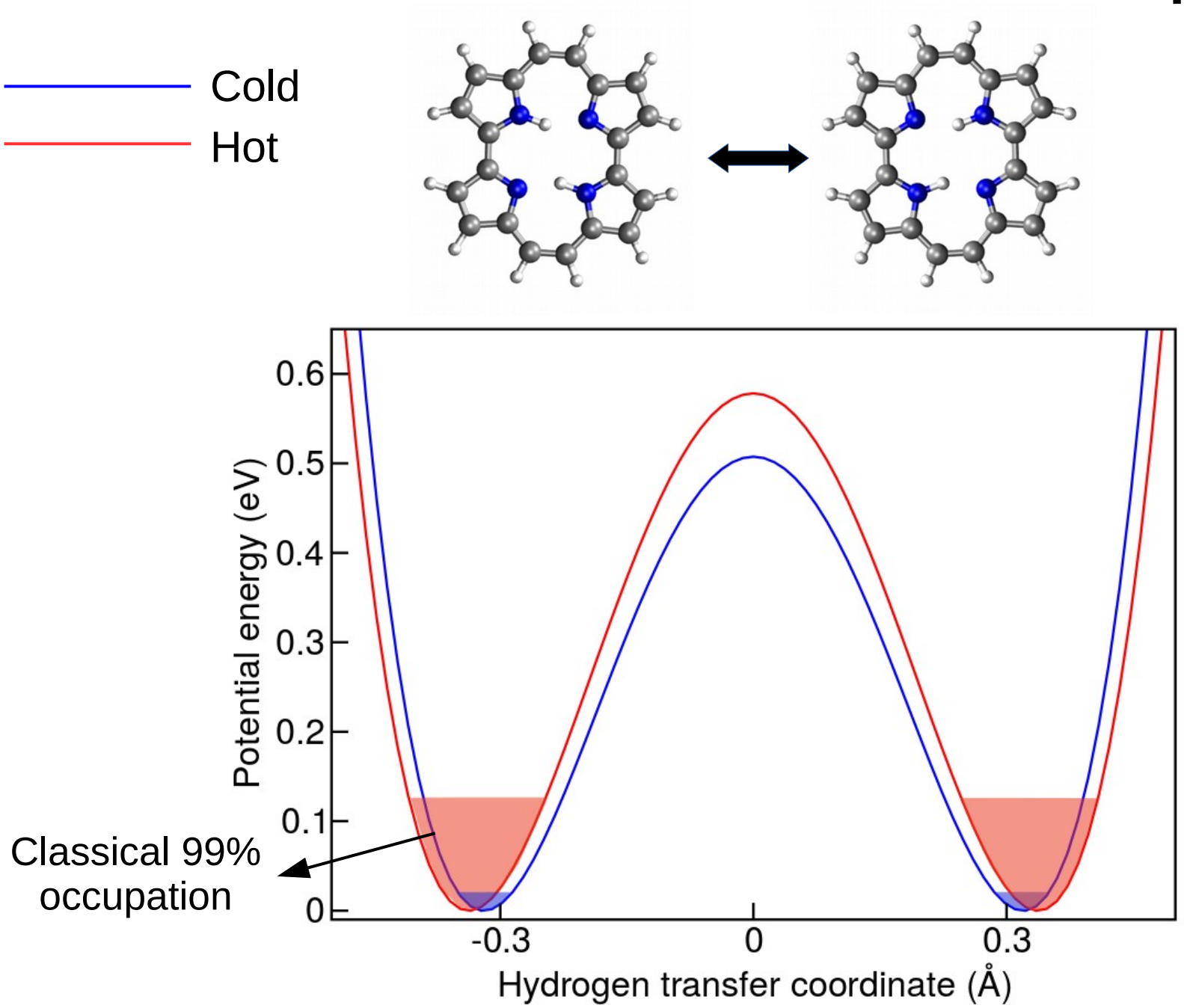


Quantum nuclei Classical nuclei

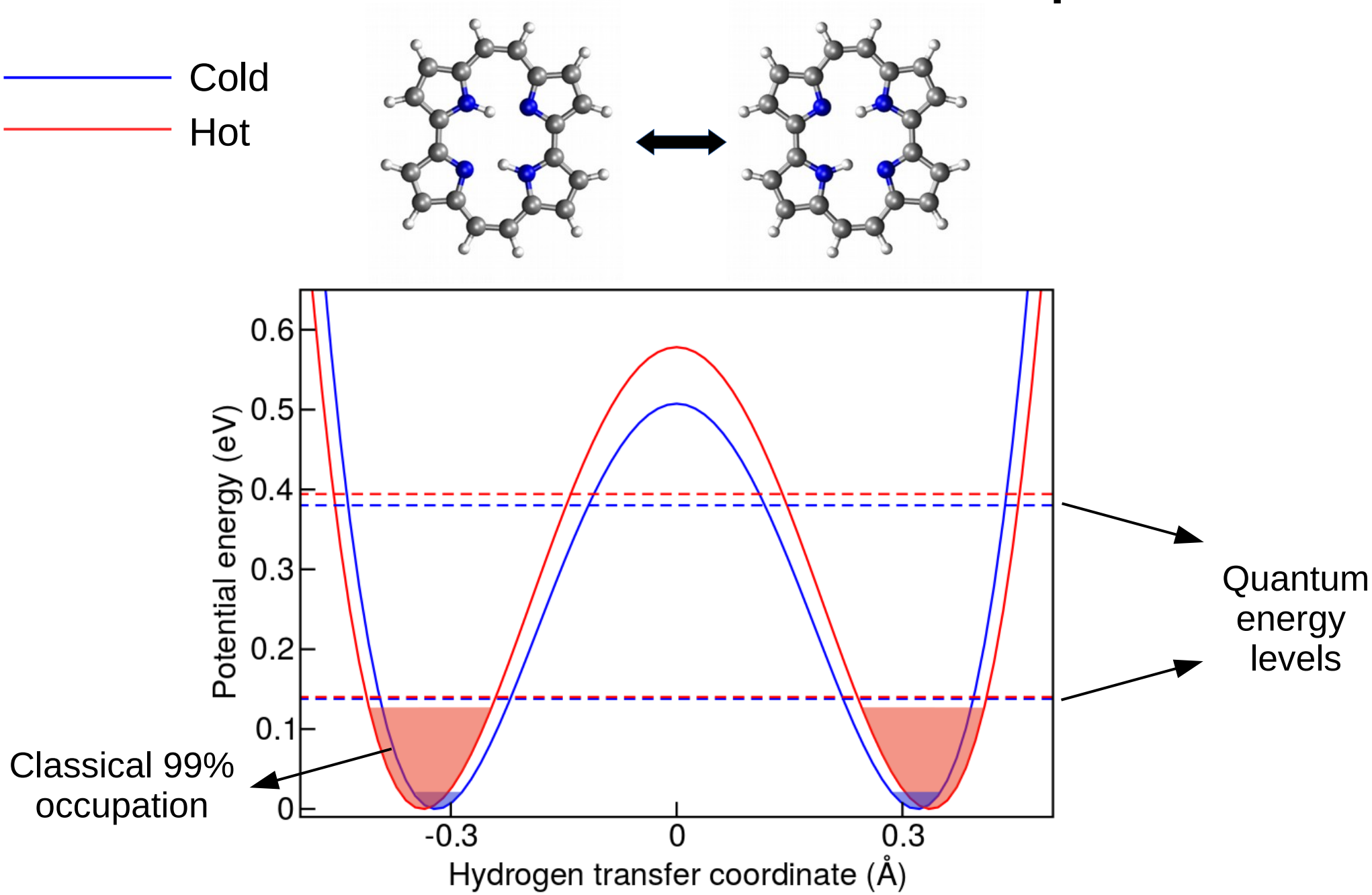
Red or Blue Shift, that is the question



Red or Blue Shift, that is the question



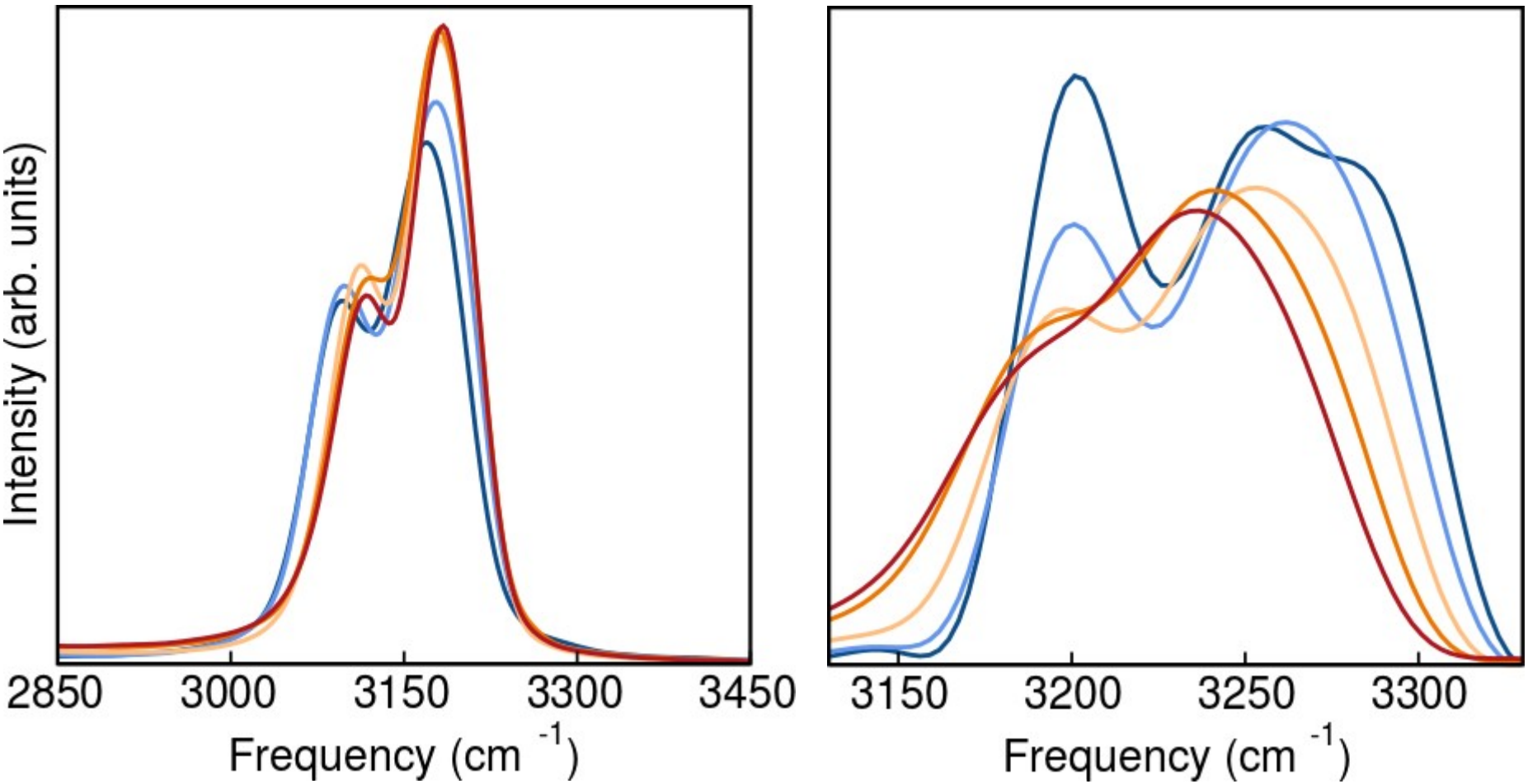
Red or Blue Shift, that is the question



Still trying to fully understand ...

The CH band presents similar behavior

Is there any 1D model that can explain the physics in this case?



Take Home Messages

Nuclear quantum effects and full-multidimensionality are decisive to predict the temperature dependence of the vibrational spectra

HDNNP and KRR methods provide an useful framework to re-purpose the data, and allows to converge statistics without sacrificing the accuracy of the PES

Acknowledgement

M. Rossi

J. Behler

Computational time:

MPCDF Max Planck Computing & Data Facility