

Probing the Origins of Intermolecular Vibrational and Relaxational Dynamics in Organic Solids with CP2K

Michael Ruggiero

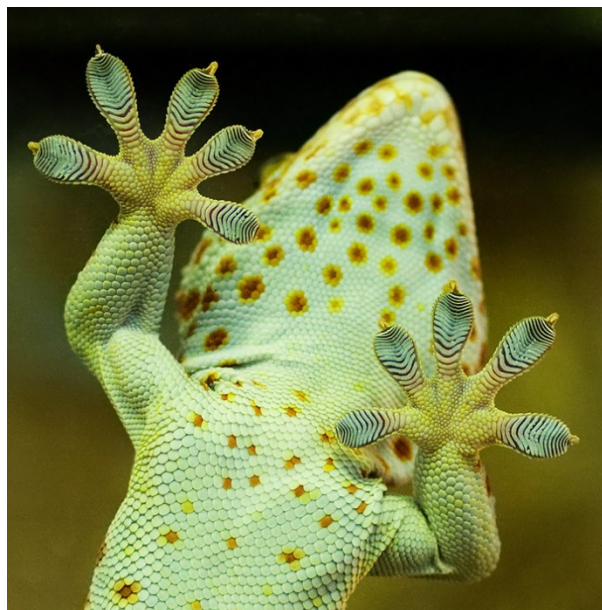
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Outline

- Introduction
 - Why do we care about vibrational dynamics?
 - Experimental and theoretical characterization
- Using CP2K to determine static (harmonic approx.) normal modes
- Using CP2K to determine vibrational spectra with molecular dynamics
 - The pros and cons of each
- Conclusions

Introduction

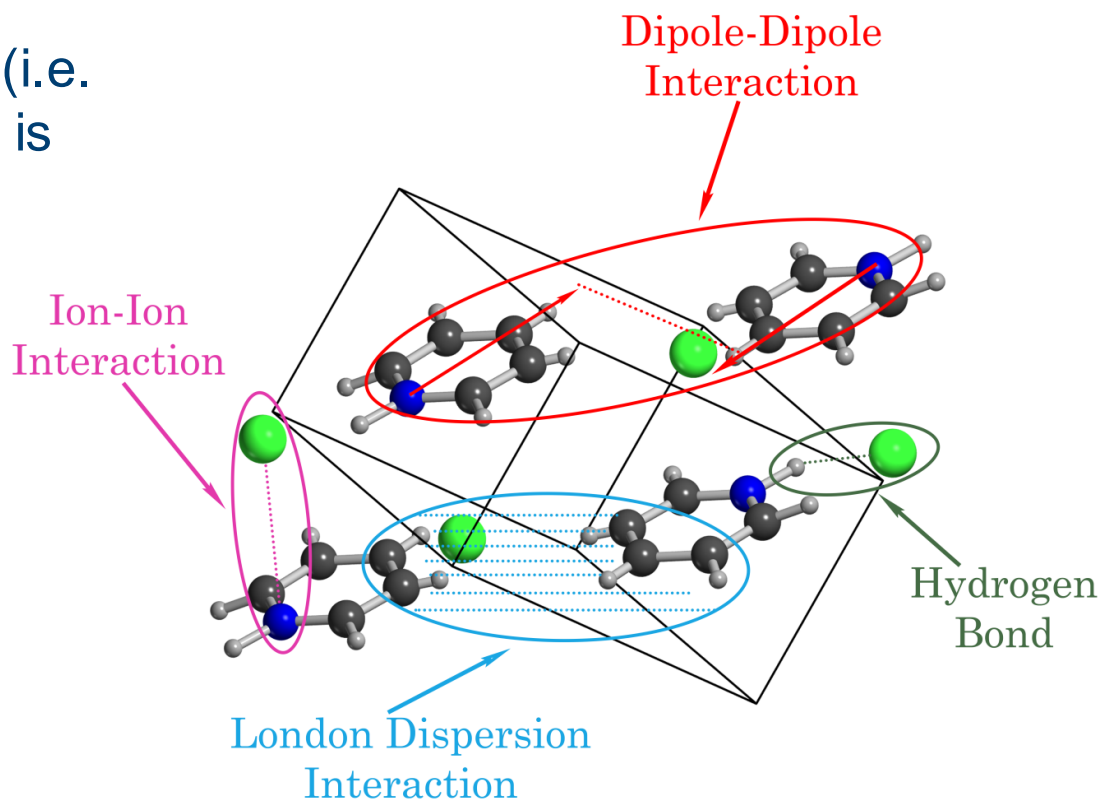
- Intermolecular forces (**IMFs**) are a critical for understanding physical properties
- IMFs are typically weak compared to covalent bonds
 - Hydrogen Bonds
 - van der Waals
- Understanding how and why IMFs form important for describing **physical observations**



Introduction

Vibrational Dynamics

- Structural information (i.e. X-ray crystallography) is useful for qualitatively understanding the interactions between molecules/atoms
- But doesn't yield a complete picture



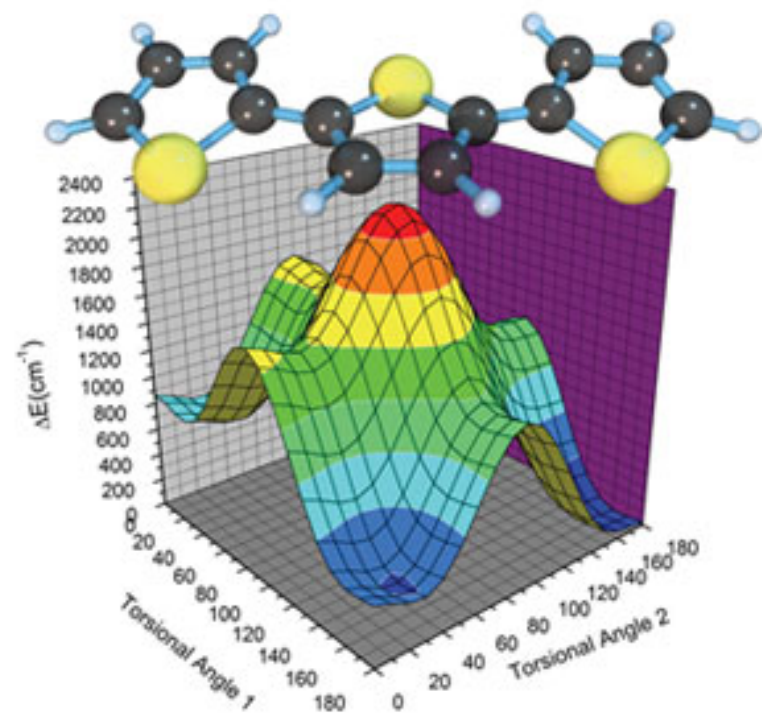
Introduction

- But because vibrations depend on the **Curvature** of the potential energy surface, they are powerful for understanding the interaction strengths and nature

- $F = ma = m \frac{\partial V^2}{\partial r^2} = -kx$

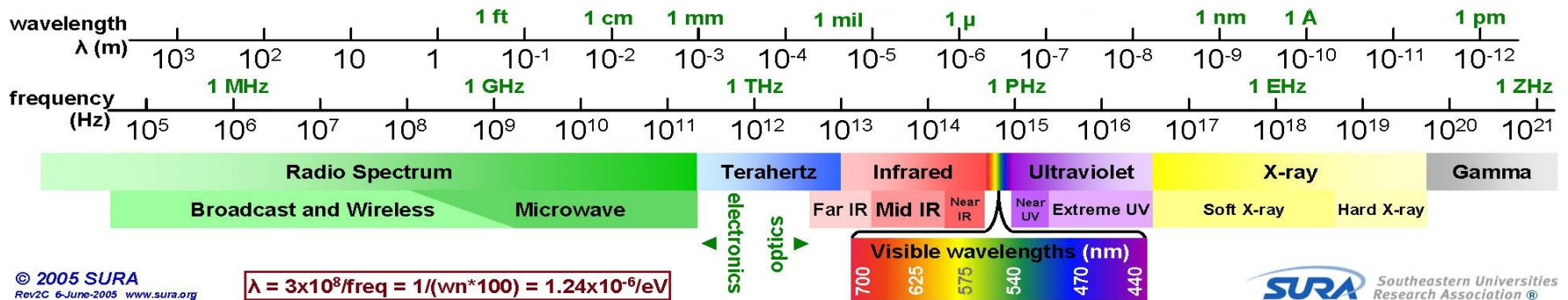
- Quantum mechanically, solving the Schrodinger equation yields the expression

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$



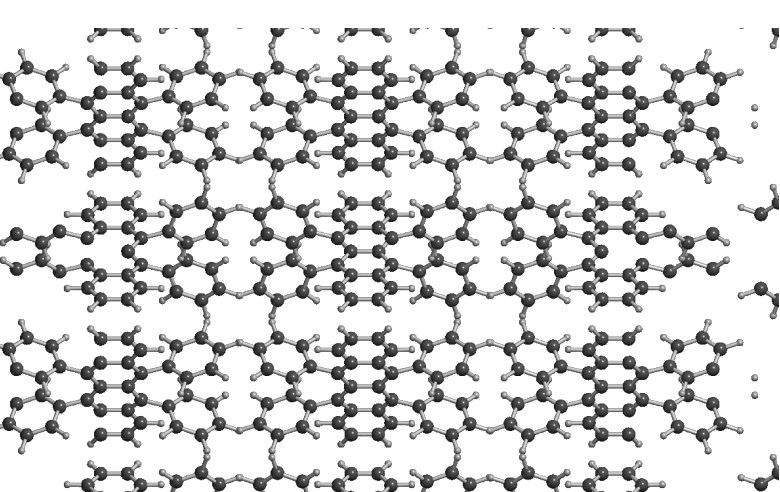
Introduction

- So experimentally, we can use **vibrational spectroscopy** to understand the interactions in materials
 - Mid-IR, Raman
- For solids, **terahertz time-domain spectroscopy** is a low frequency version of mid-IR and is powerful for looking at solids



Terahertz Vibrations

- Mode-types arise from the solution to the Schrödinger equation:



$$E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

$$\omega = \sqrt{\frac{k}{\mu}}$$

Force
Constant

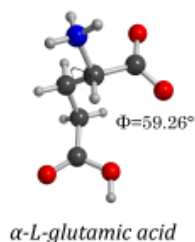
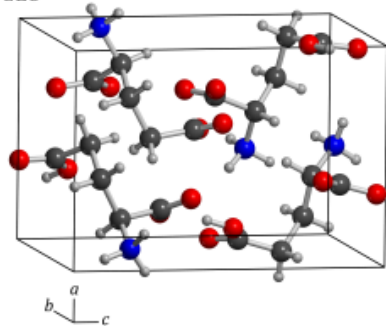
Reduced
Mass

- Large amplitude vibrations transverse large areas of the potential energy surface
- Therefore, both the **internal bond AND external intermolecular potentials** are sampled!

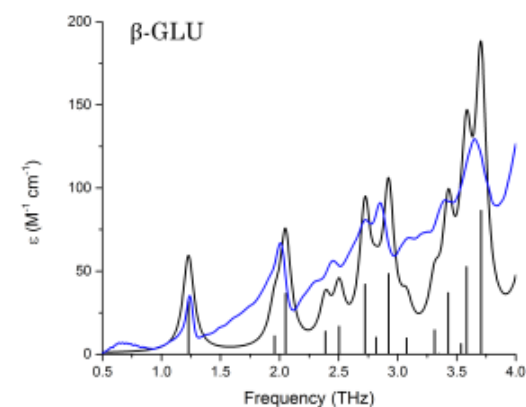
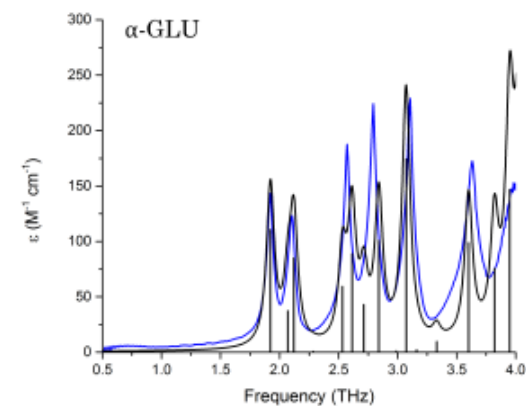
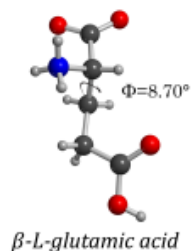
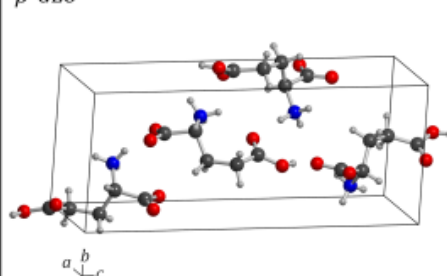
Introduction

- Unlike the mid-IR, there are no functional group specific vibrations at THz frequencies
- NEED a way of analyzing the spectra!
- DFT and AIMD!

α -GLU

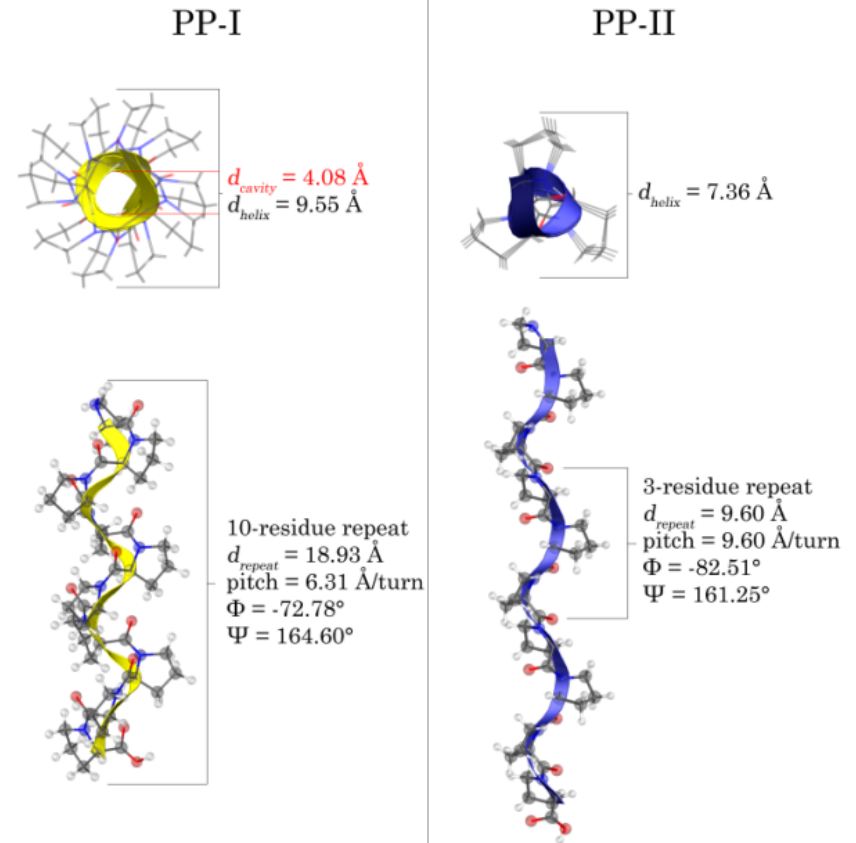


β -GLU



Quick Example of Usefulness

- Polyproline – ‘rigid’ peptide that has been used to as a standard in biochemistry due to its uniform length and size.
- Two forms – PP-I and PP-II, differ in their chirality
- Rigidity information not known nor easily obtained
 - AFM is v. difficult!

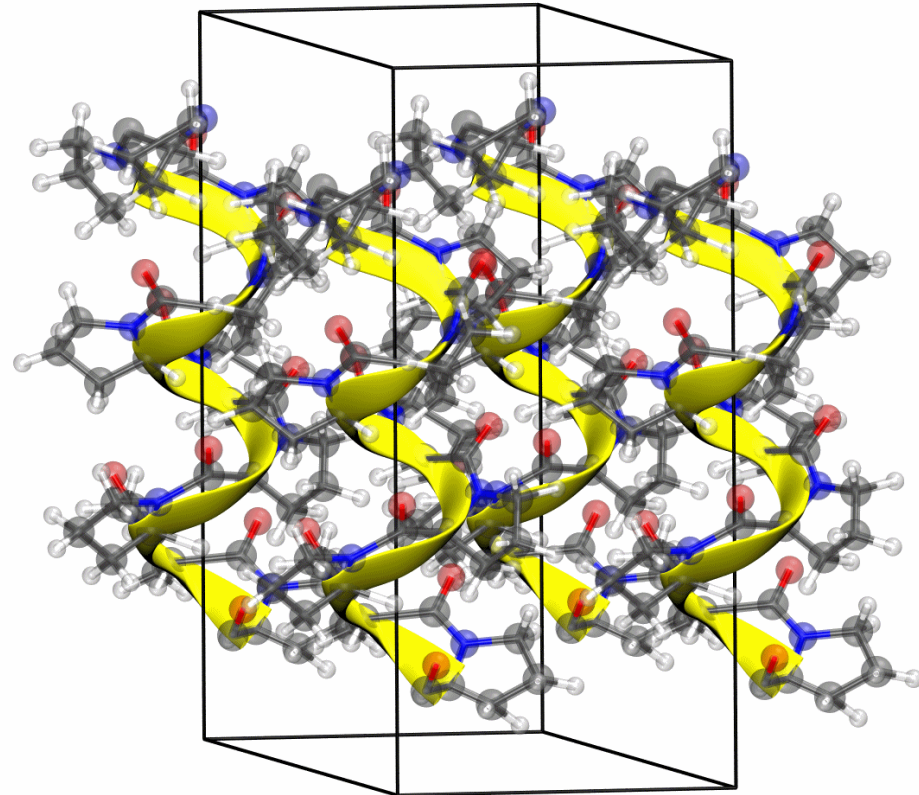


Example

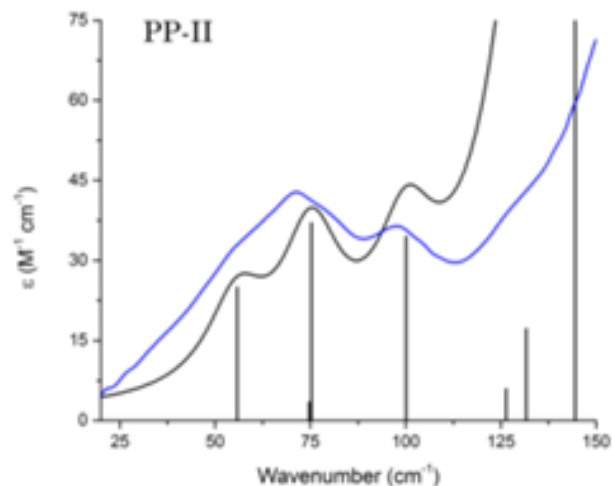
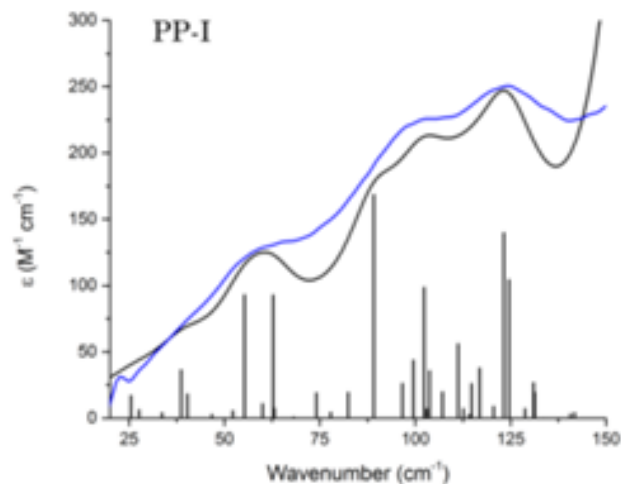
- Calculation of low-frequency vibrations show that the modes are very 'spring' like
- Can use vibrational force constants and reduced masses to determine Young's moduli!

$$Y = \frac{\sigma}{\varepsilon} = \frac{FL_0}{A_0\Delta L}$$

$$F = \overbrace{\frac{YA_0}{L_0} \Delta L}^{\text{Stress-Strain}} = \overbrace{k\Delta L}^{\text{Hooke's Law}}$$
$$\therefore k = \frac{YA_0}{L_0}$$

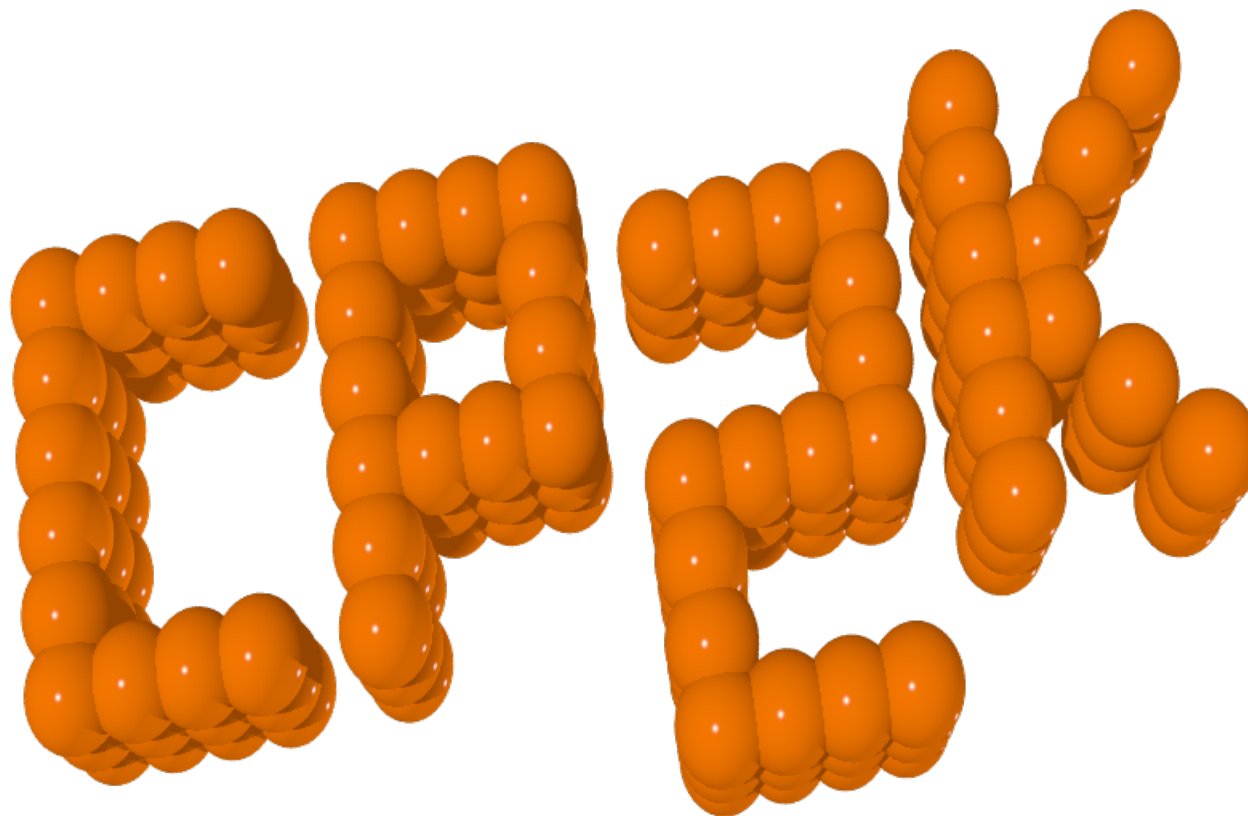


Example – Does it work?



	Experimental			Calculated				<i>Ab initio</i>
	$\tilde{\nu}$	k	Y	$\tilde{\nu}$	k	μ	Y	Y
PP-I	66.6	1.9	4.9 ± 0.2	68.15	1.94	7.08	5.04	5.06
PP-II	98.1	3.8	9.6 ± 0.1	100.1	3.91	6.62	9.82	10.57

So What Can We Do With CP2K?!



Using DFT Methods to Characterise Dynamics

Static DFT

- Harmonic approximation
- Gradient of P.E.S determined via finite differences (dx, dy, dz)
- **Yields very detailed information**
 - Normal mode frequencies, eigenvectors
- Integrated intensities can be easily determined with high accuracy

AIMD

- No explicit treatment of quantized vibrations
- Generates an overall vibrational spectra
- Yields lineshapes, intensities.
- No explicit normal mode treatment/calculation
- **Can include temperature effects!**

Static DFT

- Works by building a force constant matrix
 - Numerical displacements in all three coordinates for all atoms
 - 3N displacements

$$D_{IJ} = \frac{\partial^2 E}{\partial R_I \partial R_J}$$

- Force constant matrix (Hessian) is then diagonalized to yield eigenvectors and eigenvalues

So what does the INPUT look like?

- Very similar to normal CP2K INPUT, but with an additional block(s)

```
&VIBRATIONAL_ANALYSIS
  INTENSITIES
  NPROC_REP 16
  DX 0.001
  &PRINT
    &PROGRAM_RUN_INFO ON
  &END
&END
```

```
&DFT
  BASIS_SET_FILE_NAME ./BASIS_MOLOPT
  POTENTIAL_FILE_NAME ./GTH_POTENTIALS
  &PRINT
    &MOMENTS
    PERIODIC FALSE
  &END
&END
```

.....

Important considerations

- Vibrational analyses should only be performed on well-optimized structures!
 - If not at a minimum in the P.E.S this will lead to imaginary modes!
- Tighter convergence criteria should be used!
 - $EPS_SCF < 10^{-9}$ (or tighter!!) for best results
 - Especially for intensities! $Z^* = \frac{\partial \mu}{\partial R} = \frac{\partial^2 E}{\partial R \partial \epsilon} = \frac{\partial P}{\partial R}$
 - MAX_FORCE should also be checked to ensure convergence
 - $1.0E-4$ or smaller

Output from Static DFT

- Good output, no imaginary (negative) frequencies

```
VIB|
VIB|
VIB|
VIB|Frequency (cm^-1)
VIB|Intensities
VIB|Red.Masses (a.u.)
VIB|Frc consts (a.u.)
  ATOM  EL
    1  C
    2  O
    3  H
    4  H
    5  H
    6  H
```

NORMAL MODES - CARTESIAN DISPLACEMENTS

	1	2	3
Frequency (cm ⁻¹)	340.444852	1036.860333	1096.247495
Intensities	0.007659	0.005229	0.006011
Red.Masses (a.u.)	1.067601	1.114971	7.032618
Frc consts (a.u.)	0.000037	0.003299	0.026003

ATOM	EL	X	Y	Z	X	Y	Z	X	Y	Z
1	C	0.00	0.00	-0.00	0.08	-0.01	0.00	0.01	0.54	-0.00
2	O	-0.00	-0.00	0.06	-0.01	0.05	-0.00	0.00	-0.44	0.00
3	H	-0.00	-0.00	-0.30	-0.08	-0.58	-0.00	-0.10	0.09	0.00
4	H	0.00	-0.00	-0.88	-0.20	-0.59	0.00	0.05	-0.36	0.00
5	H	-0.22	0.04	0.10	-0.25	0.26	0.04	-0.07	0.42	0.05
6	H	0.22	-0.04	0.10	-0.25	0.26	-0.04	-0.07	0.42	-0.05

Bad output!

- Bad output! Negative modes!
- Not in a global minimum!

```
VIB|
VIB|
VIB|
VIB|Frequency (cm^-1)
VIB|Intensities
VIB|Red.Masses (a.u.)
VIB|Frc consts (a.u.)
  ATOM  EL
    1   C
    2   O
    3   H
    4   H
    5   H
    6   H
```

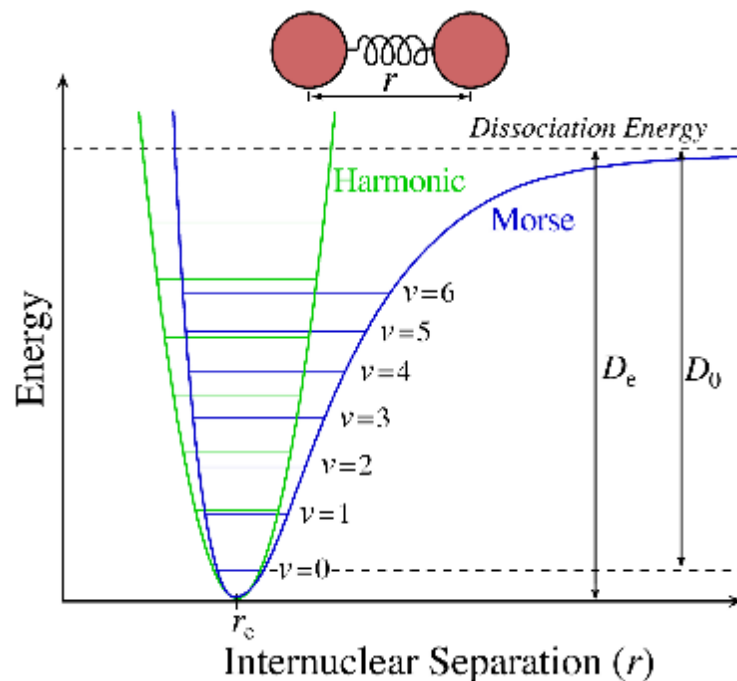
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5	H	-0.22	0.04	0.10	-0.25	0.26	0.04	-0.07	0.42	0.05
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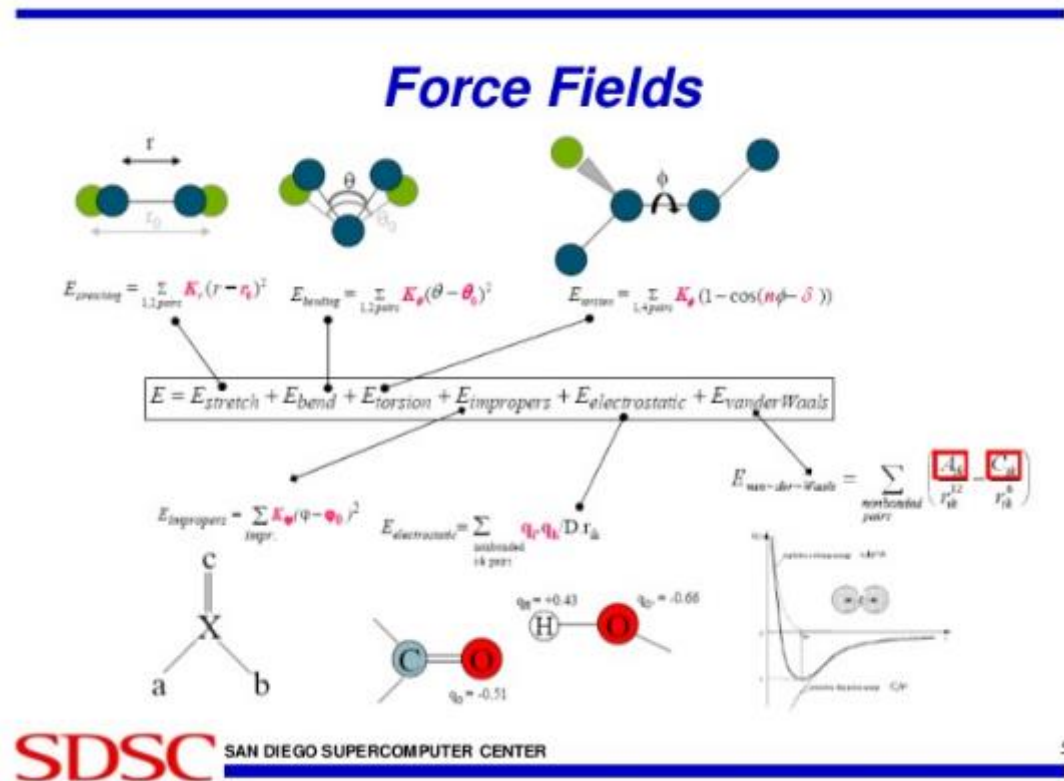
Ab initio MD

- The Harmonic Approx is great and has proven to give good results
- But it is only an approximation, and any deviations from harmonic behavior wont be accounted for
- **Anharmonicity**
- **Thermal Effects**
- MD can account for these!



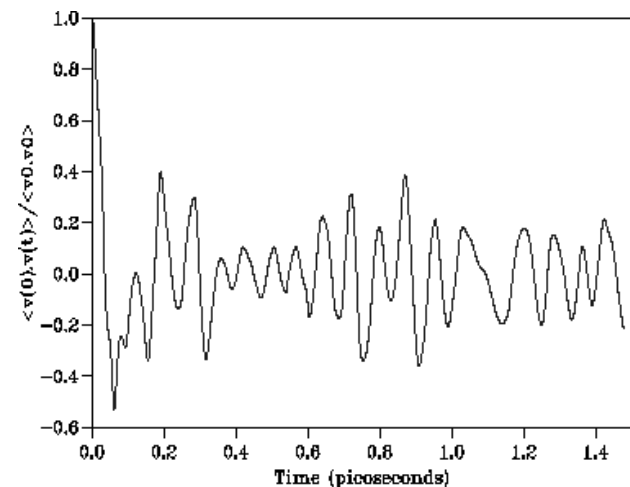
ab initio Simulations - Molecular Dynamics

- Molecular dynamics (MD) calculations can be applied to very large systems
- Proteins, 100,000s of atoms
- However traditional MD is a **classical** method
- Newtonian mechanics and pre-built atomic 'force-fields'
- Leads to biased vibrational results!



ab initio Simulations - Molecular Dynamics

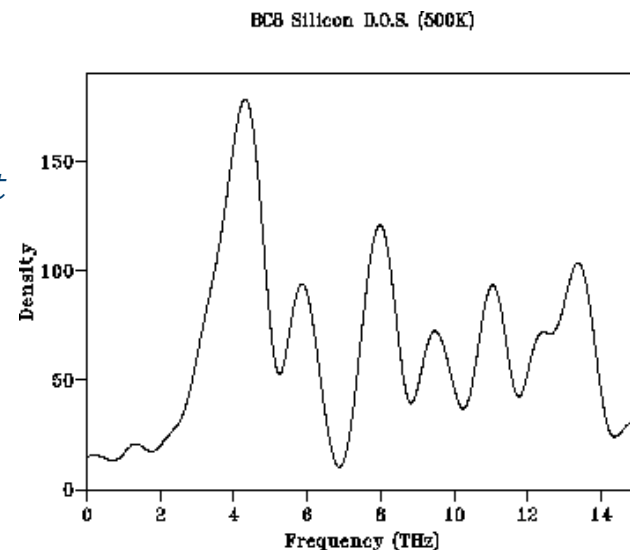
- The solution?
 - A dual DFT-MD approach (*ab initio* molecular dynamics, AIMD)
- Recalculate the **quantum** potential energy surface at each **classical** time-step
- MD results can be used to calculate IR spectra



$$A(\omega) \propto \int \langle \mu(\tau) \mu(t + \tau) \rangle_{\tau} e^{-i\omega t} dt$$

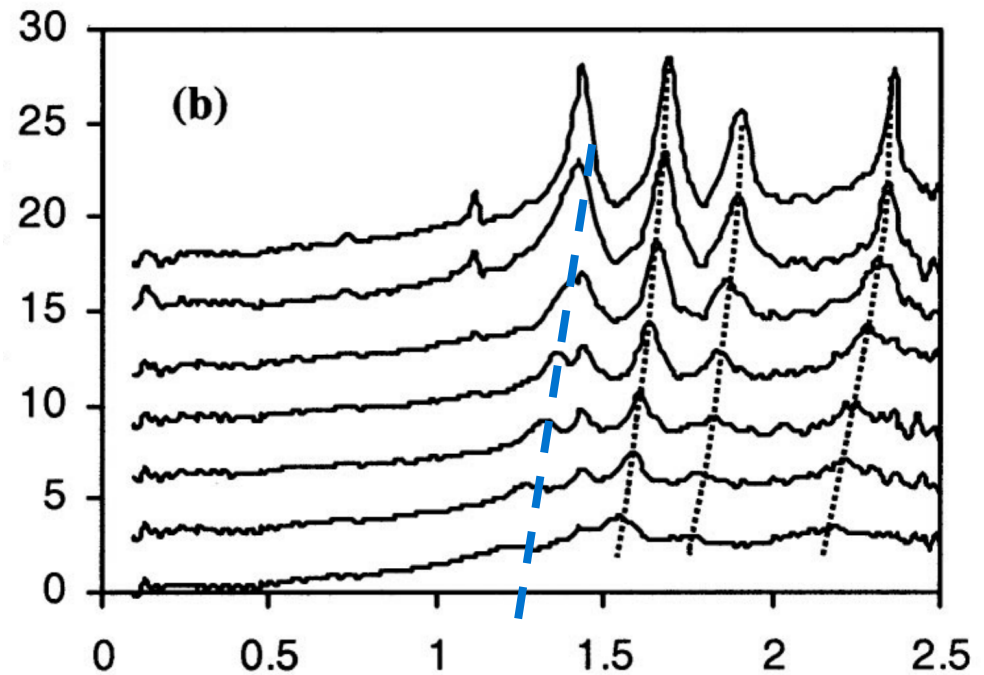
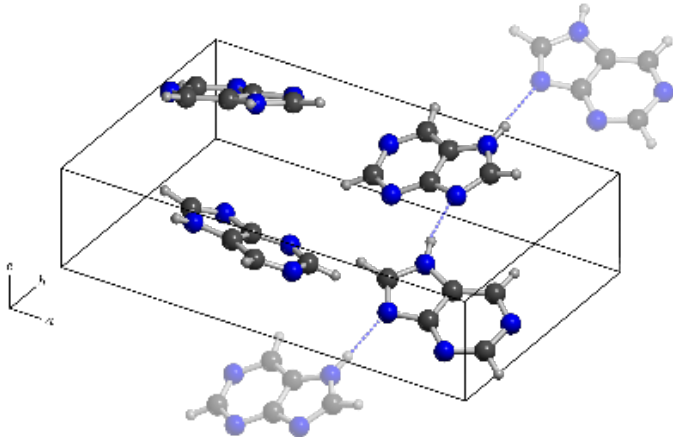


**Fourier Transforming the
dipole moment
autocorrelation function**



Example – Crystalline Purine

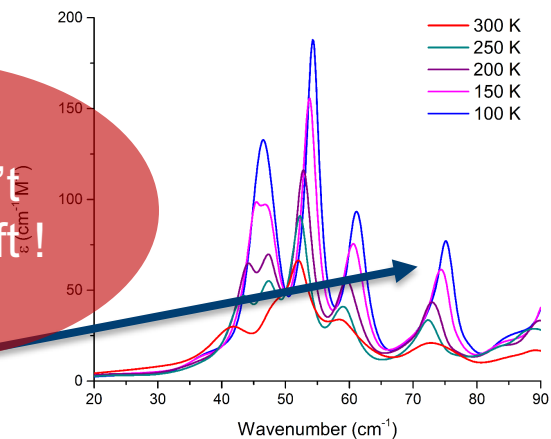
- Model system – Purine
- Large changes in THz-TDS spectra as a function of temperature
- Sign of anharmonicity



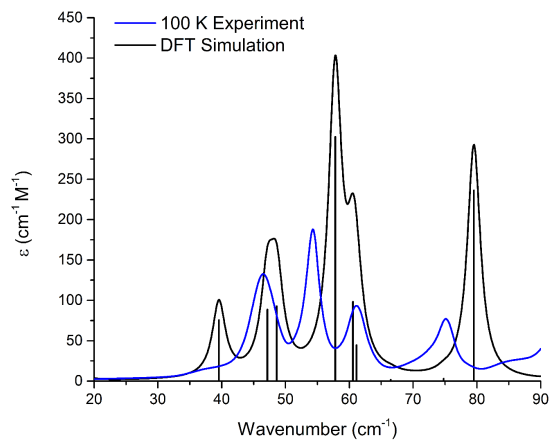
Shen, Y. C., P. C. Upadhyaya, E. H. Linfield, and A. Ga Davies. "Temperature-dependent low-frequency vibrational spectra of purine and adenine." *Applied Physics Letters* 82, no. 14 (2003): 2350-2352.

New Data

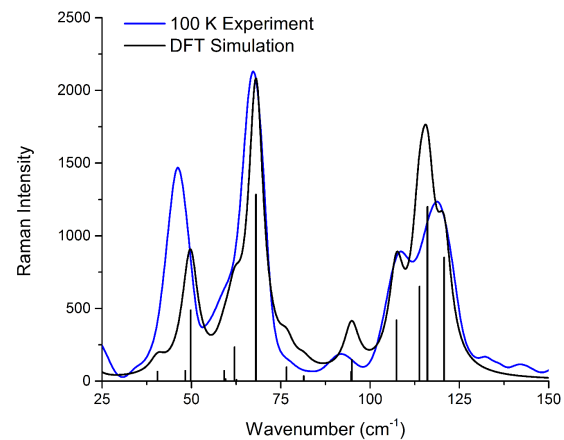
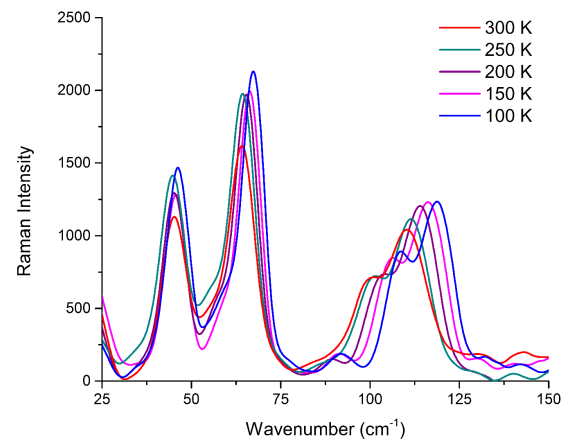
THz-TDS



DFT Can't predict shift!

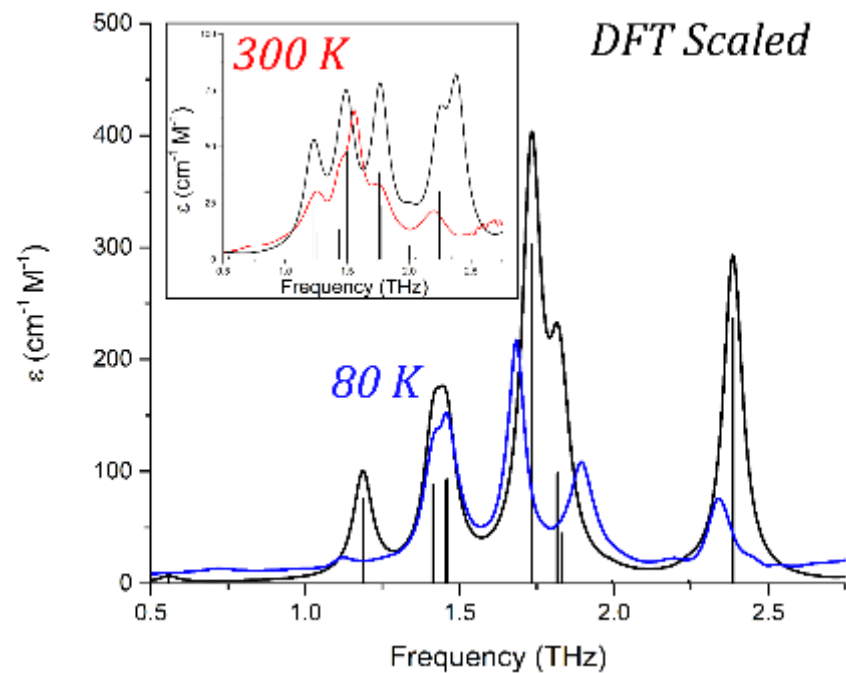
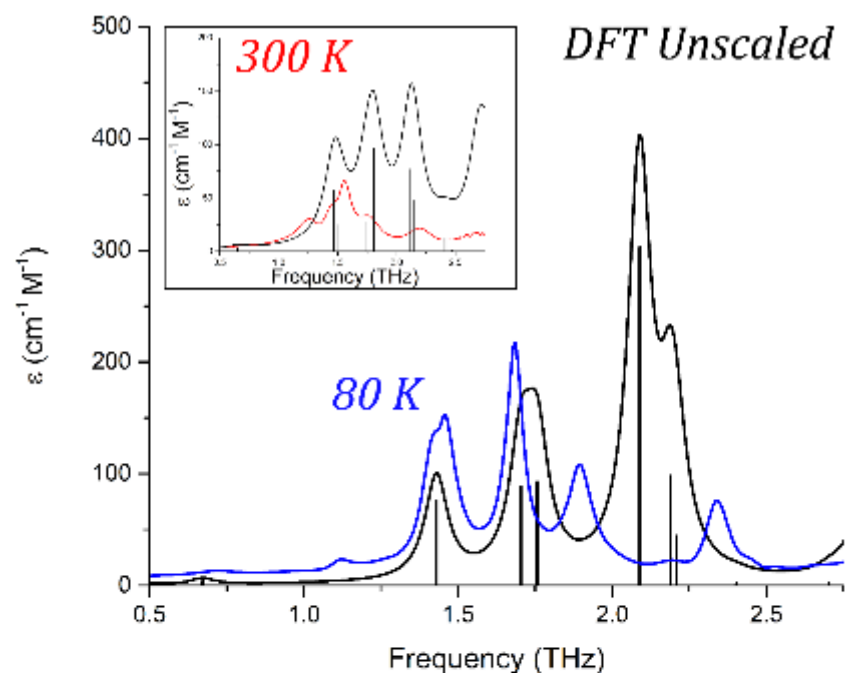


Low-Frequency Raman



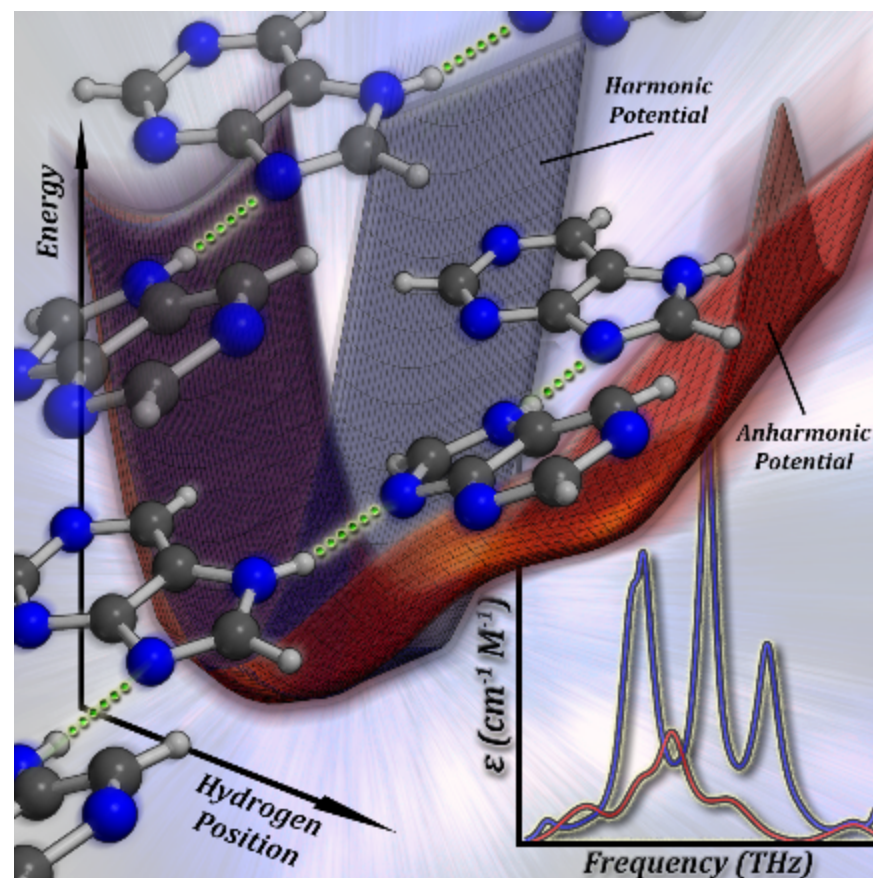
Is it reliable?

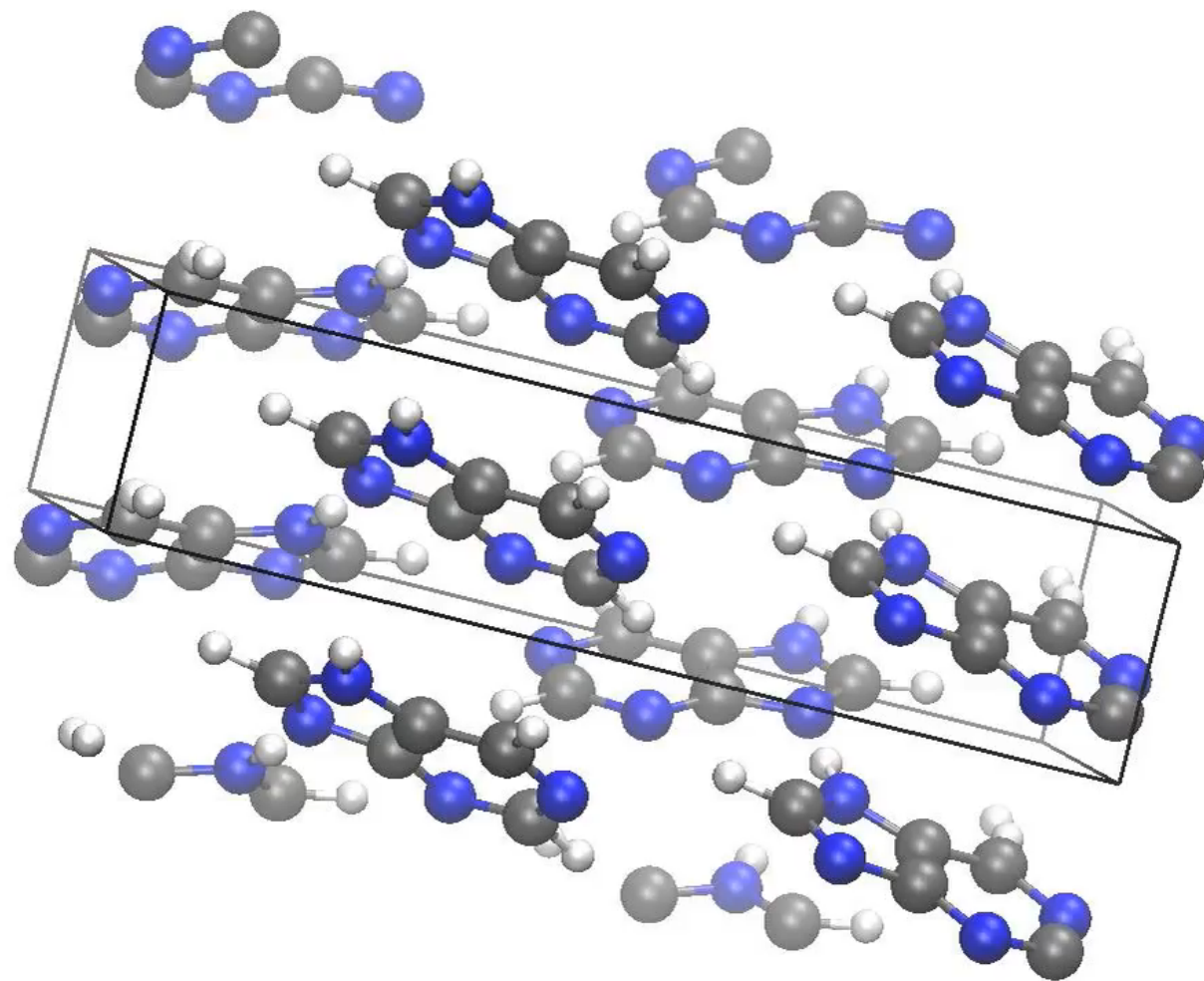
- Solid-state DFT results



Is it reliable?

- DFT is good, but requires scaling and not all peak shifting is reproduced
- Can account for *structural* anharmonicity, but not *vibrational* anharmonicity
- Solution: AIMD



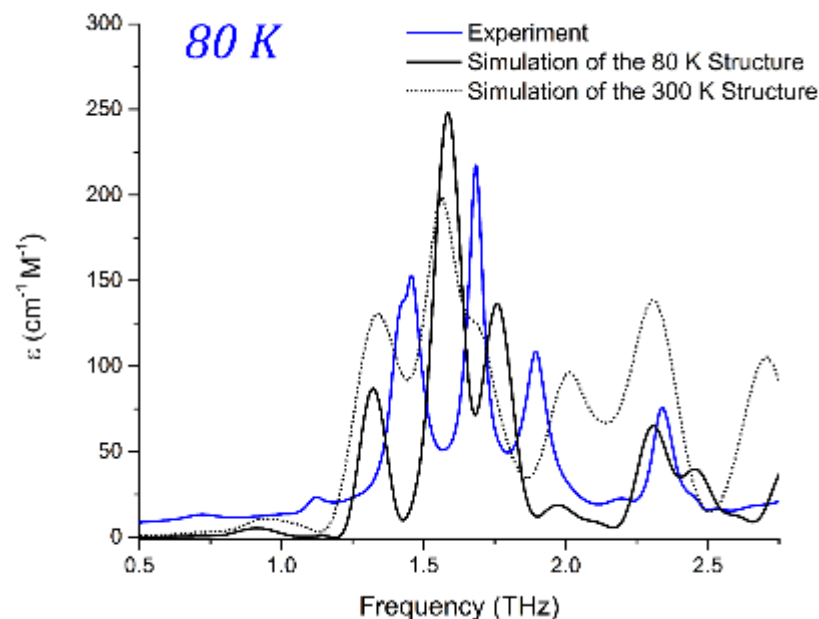
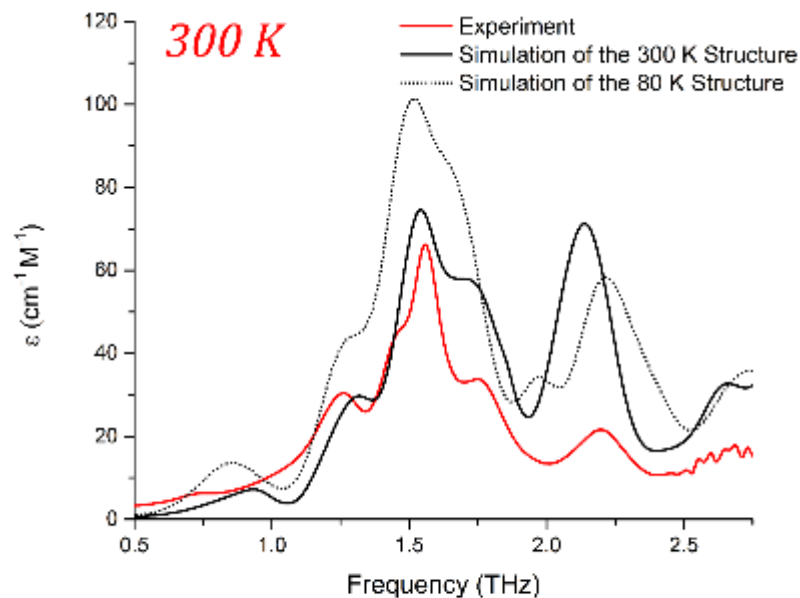


How To?

- NVT Simulation, with the calculation of Wannier Functions at various intervals
- Best is 0.5 fs time step, with WF calculation at every 5 steps (2.5 fs).

```
&LOCALIZE  
  METHOD CRAZY  
  MAX_ITER 2000  
  &PRINT  
  &WANNIER_CENTERS  
  IONS+CENTERS  
  FILENAME = wannierout.xyz  
  &EACH  
  MD 5  
  &END EACH  
  &END WANNIER_CENTERS  
  &END PRINT  
&END LOCALIZE
```

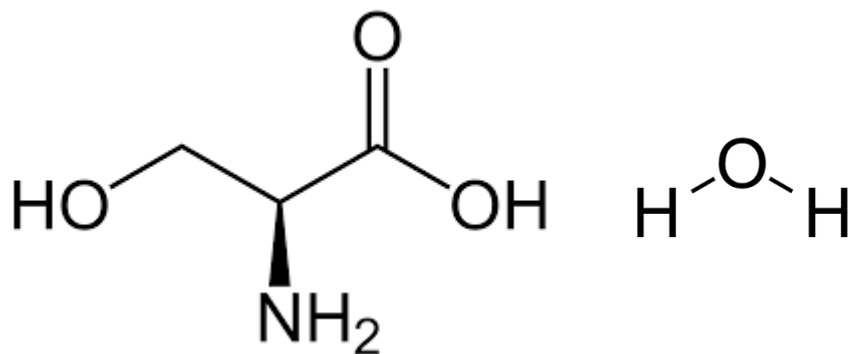
MD of Purine



- Temperature dependencies are resolved without any scaling!
- Origins of temperature changes probed by performing the MD simulations on the 'reciprocal' structures
 - 300 K structure simulated at 80 K, and *vice versa*

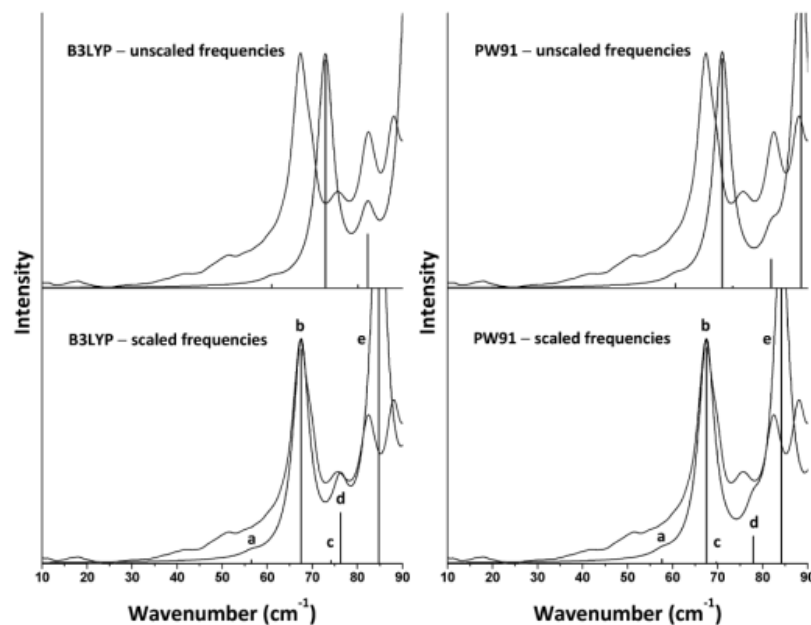
Contributions from Different Groups – Serine Monohydrate

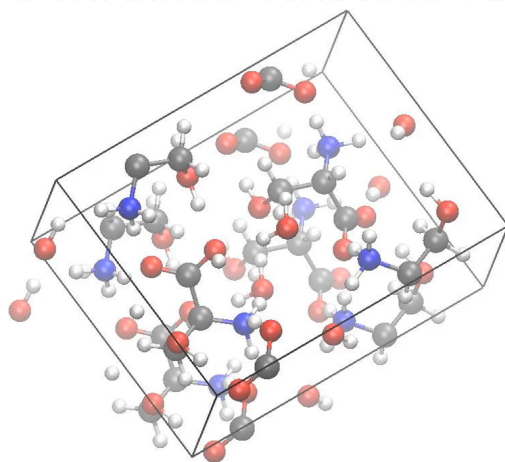
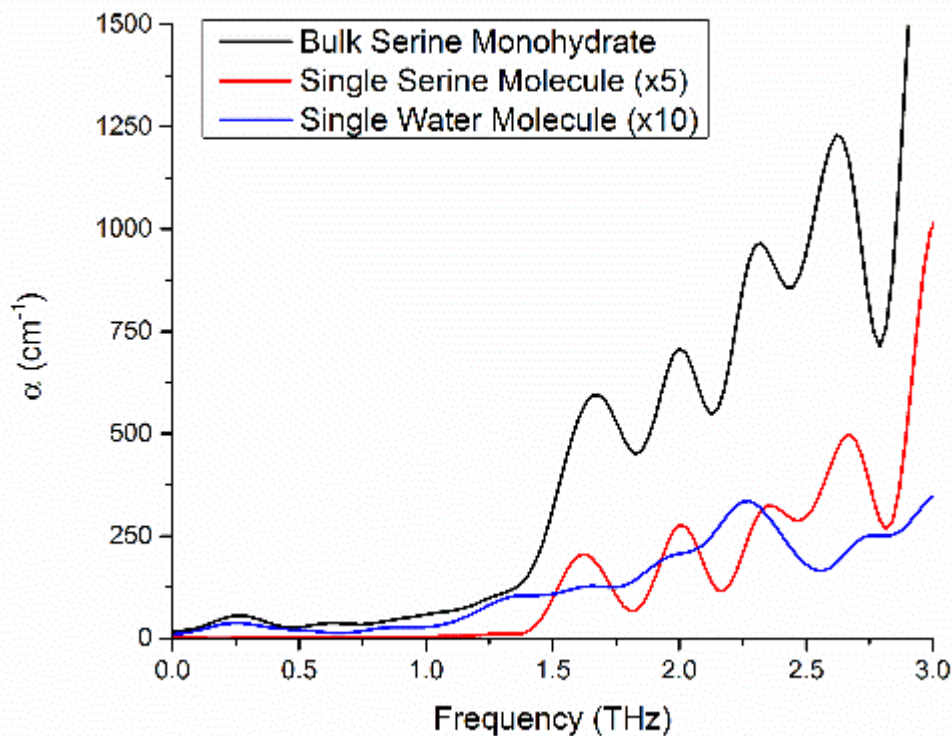
- Serine monohydrate is believed to exhibit anharmonicity
- DFT was shown to over-estimate vibrational frequencies by ~10%
- What specific atoms are contributing to the anharmonicity?



Investigating the Anharmonicity of Lattice Vibrations in Water-Containing Molecular Crystals through the Terahertz Spectroscopy of L-Serine Monohydrate

Matthew D. King, William D. Buchanan, and Timothy M. Korter*





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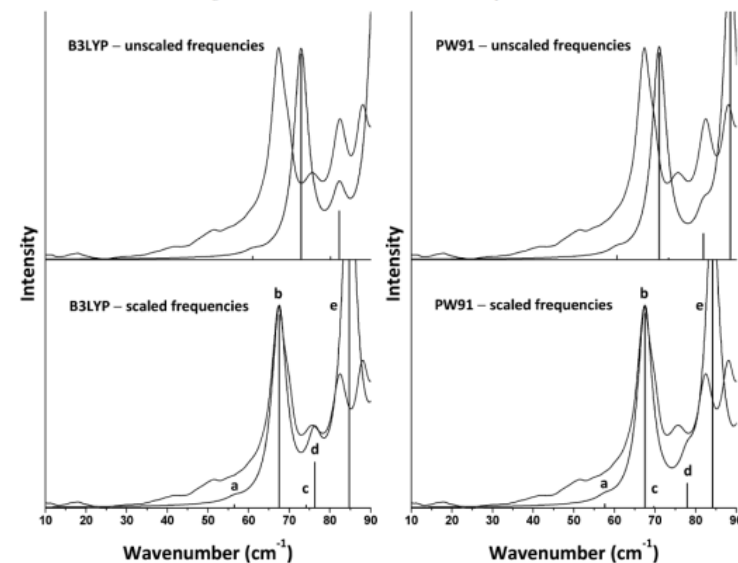


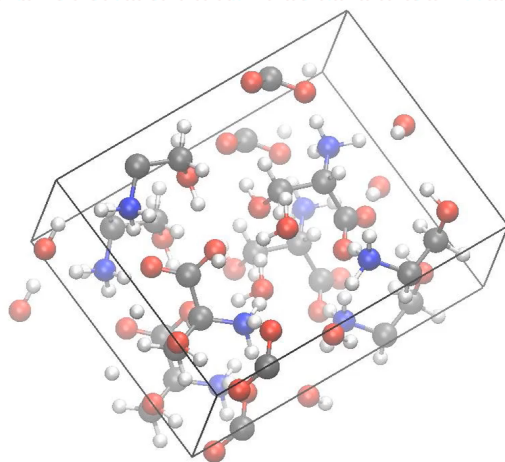
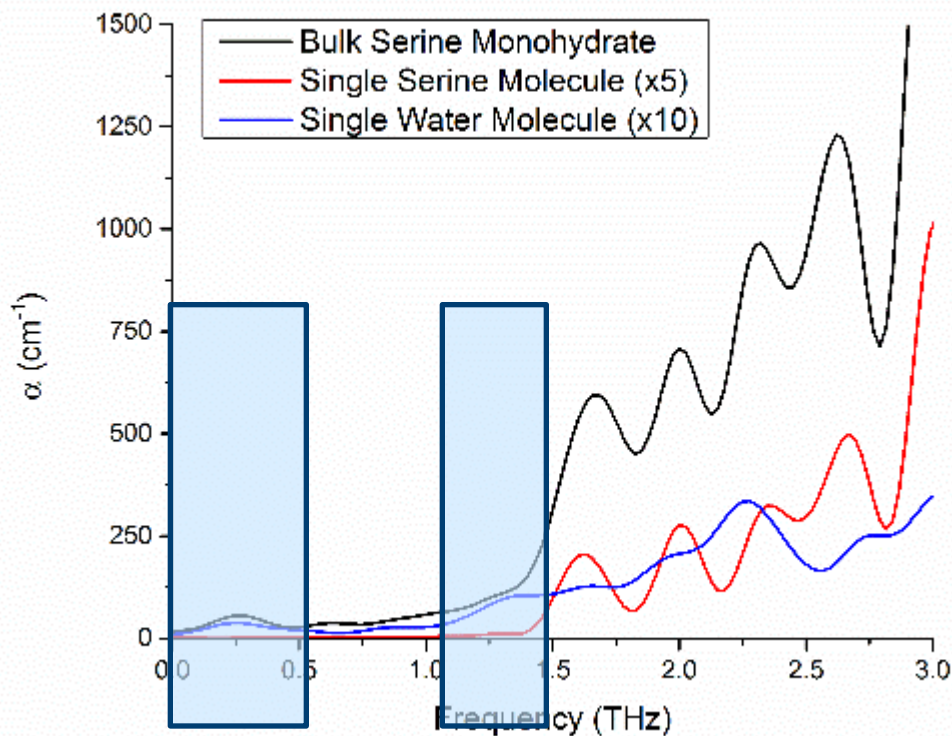
Figure 5. Experimental 78 K THz spectrum (gray) of L-serine·H₂O. The top figures are plotted with unscaled vibrational frequencies and the bottom with the applied frequency scalars of 0.925 for B3LYP and 0.950 for PW91. An empirical full-width-half-maximum value of 4.30 cm⁻¹ was used in convolving Lorentzian line shapes for simulated spectra.

TABLE 7: Descriptions of Calculated Vibrational Modes (<110 cm⁻¹) for the Best-Fit Simulation (B3LYP/6-311G(d,p)) of L-Serine·H₂O

mode	freq, cm ⁻¹	mode description ^a	% H ₂ O contrib ^b
a	61.0	serine: 100% ET along <i>a</i> -axis H ₂ O: 75% ET along <i>b</i> -axis, 25% ER about <i>b</i> -axis	18
b	72.9	serine: 75% ER about <i>b</i> - and <i>c</i> -axes, 25% Int (-NH ₃ ⁺ rotation) H ₂ O: 100% ET along <i>a</i> -, <i>b</i> -, and <i>c</i> -axes	20
c	80.1	serine: 75% ET along <i>c</i> -axis, 25% ER about <i>b</i> -axis H ₂ O: 75% ET along <i>c</i> -axis, 25% ER about <i>b</i> - and <i>c</i> -axes	16
d	82.3	serine: 25% ET along <i>c</i> -axis, 25% ER about <i>a</i> - and <i>c</i> -axes, 50% Int (C ₁ -C ₂ , C ₃ -O ₃ torsions) H ₂ O: 50% ET along <i>a</i> - and <i>c</i> -axes, 50% ER about <i>b</i> -axis	16
e	91.5	serine: 100% ER about <i>b</i> -axis H ₂ O: 100% ET along <i>a</i> -axis	15
f	98.9	serine: 75% ER about <i>a</i> -axis, 25% Int (C ₂ -C ₃ torsion) H ₂ O: 100% ET along <i>a</i> - and <i>b</i> -axes	19
g	101.5	serine: 50% ER about <i>c</i> -axis, 50% Int (C ₁ -C ₂ , C ₃ -O ₃ torsions) H ₂ O: 100% ET along <i>b</i> -axis	22
h	105.8	serine: 50% ER about <i>a</i> -axis, 50% Int (C ₁ -C ₂ , C ₃ -O ₃ torsions) H ₂ O: 100% ET along <i>b</i> -axis	26
i	107.6	serine: 75% ER about <i>b</i> - and <i>c</i> -axes, 25% Int (C ₂ -C ₃ torsion) H ₂ O: 75% ET along <i>a</i> -, <i>b</i> -, and <i>c</i> -axes, 25% ER about <i>a</i> -, <i>b</i> -, and <i>c</i> -axes	10

^a ET = translation; ER = external rotation; Int = internal motion. ^b Percent of total atomic displacements due to motion of H₂O molecules.





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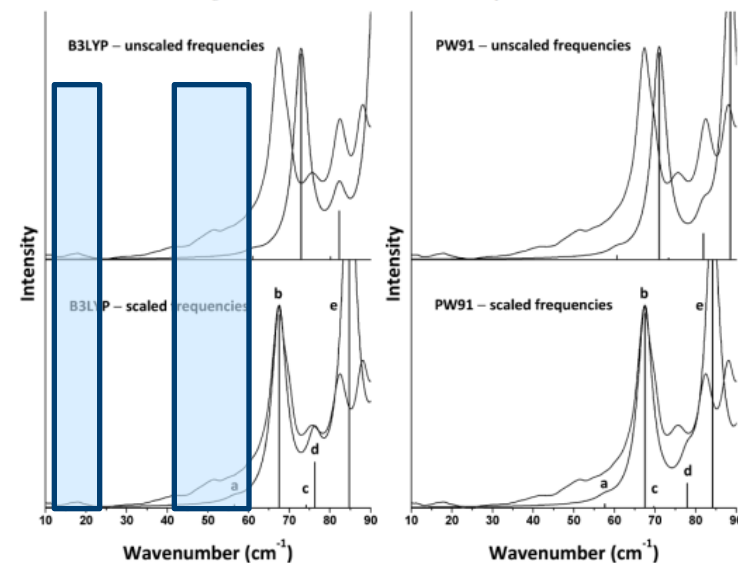


Figure 5. Experimental 78 K THz spectrum (gray) with overlaid simulated spectra (black) of L-serine·H₂O. The top figures are plotted with unscaled vibrational frequencies and the bottom with the applied frequency scalars of 0.925 for B3LYP and 0.950 for PW91. An empirical full-width-half-maximum value of 4.30 cm⁻¹ was used in convolving Lorentzian line shapes for simulated spectra.

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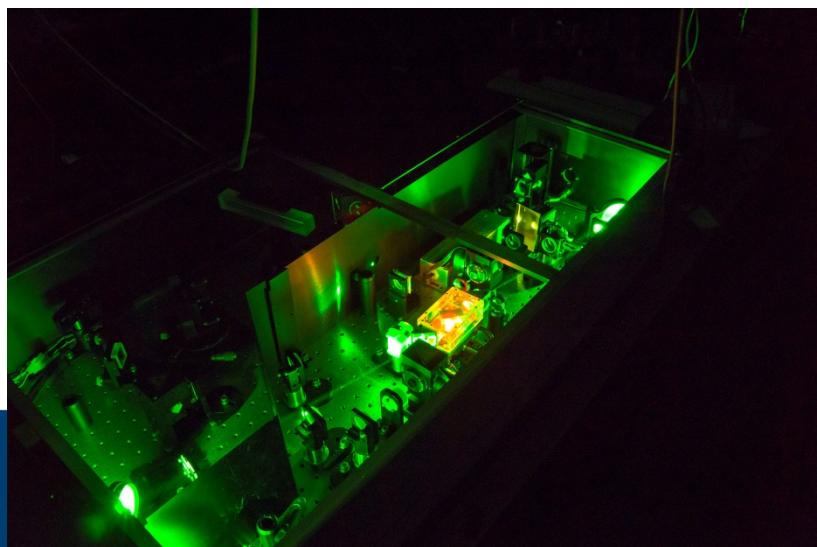
mode	freq, cm ⁻¹	mode description ^a	% H ₂ O contrib ^b
a	61.0	serine: 100% ET along <i>a</i> -axis H ₂ O: 75% ET along <i>b</i> -axis, 25% ER about <i>b</i> -axis	18
b	72.9	serine: 75% ER about <i>b</i> - and <i>c</i> -axes, 25% Int (-NH ₃ ⁺ rotation) H ₂ O: 100% ET along <i>a</i> -, <i>b</i> -, and <i>c</i> -axes	20
c	80.1	serine: 75% ET along <i>c</i> -axis, 25% ER about <i>b</i> -axis H ₂ O: 75% ET along <i>c</i> -axis, 25% ER about <i>b</i> - and <i>c</i> -axes	16
d	82.3	serine: 25% ET along <i>c</i> -axis, 25% ER about <i>a</i> - and <i>c</i> -axes, 50% Int (C ₁ -C ₂ , C ₃ -O ₃ torsions) H ₂ O: 50% ET along <i>a</i> - and <i>c</i> -axes, 50% ER about <i>b</i> -axis	16
e	91.5	serine: 100% ER about <i>b</i> -axis H ₂ O: 100% ET along <i>a</i> -axis	15
f	98.9	serine: 75% ER about <i>a</i> -axis, 25% Int (C ₂ -C ₃ torsion) H ₂ O: 100% ET along <i>a</i> - and <i>b</i> -axes	19
g	101.5	serine: 50% ER about <i>c</i> -axis, 50% Int (C ₁ -C ₂ , C ₃ -O ₃ torsions) H ₂ O: 100% ET along <i>b</i> -axis	22
h	105.8	serine: 50% ER about <i>a</i> -axis, 50% Int (C ₁ -C ₂ , C ₃ -O ₃ torsions) H ₂ O: 100% ET along <i>b</i> -axis	26
i	107.6	serine: 75% ER about <i>b</i> - and <i>c</i> -axes, 25% Int (C ₂ -C ₃ torsion) H ₂ O: 75% ET along <i>a</i> -, <i>b</i> -, and <i>c</i> -axes, 25% ER about <i>a</i> -, <i>b</i> -, and <i>c</i> -axes	10

^a ET = translation; ER = external rotation; Int = internal motion. ^b Percent of total atomic displacements due to motion of H₂O molecules.



Conclusions

- Analysing spectroscopic data, especially low-frequency spectra, via DFT methods
- Generates a picture of intermolecular energy landscape
- Static DFT calculations (in the harmonic approx.) give very detailed info, but lack temperature/anharmonic information
- MD calculations fill in the gaps



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Thank you for your
attention!