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

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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
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
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

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

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

- 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!
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!

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

**Stress–Strain**

\[
F = \frac{YA_0}{L_0} \Delta L = \ddot{k} \Delta L
\]

\[
\therefore k = \frac{YA_0}{L_0}
\]
Example – Does it work?

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Calculated</th>
<th>Ab initio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tilde{\nu}$</td>
<td>$k$</td>
<td>$Y$</td>
</tr>
<tr>
<td>PP-I</td>
<td>66.6</td>
<td>1.9</td>
<td>4.9 ± 0.2</td>
</tr>
<tr>
<td>PP-II</td>
<td>98.1</td>
<td>3.8</td>
<td>9.6 ± 0.1</td>
</tr>
</tbody>
</table>
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)

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

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

NORMAL MODES - CARTESIAN DISPLACEMENTS

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIB</td>
<td>Frequency (cm⁻¹)</td>
<td>340.444852</td>
<td>1036.860333</td>
</tr>
<tr>
<td>VIB</td>
<td>Intensities</td>
<td>0.007659</td>
<td>0.005229</td>
</tr>
<tr>
<td>VIB</td>
<td>Red. Masses (a.u.)</td>
<td>1.067601</td>
<td>1.114971</td>
</tr>
<tr>
<td>VIB</td>
<td>Frc consts (a.u.)</td>
<td>0.000037</td>
<td>0.003299</td>
</tr>
</tbody>
</table>
Bad output! Negative modes!

Not in a global minimum!

| VIB| | NORMAL MODES - CARTESIAN DISPLACEMENTS |
|---|---|---|---|
| | 1 | 2 | 3 |
| VIB|Frequency (cm⁻¹) | -34.444852 | 1036.860333 | 1096.247495 |
| VIB|Intensities | 0.007659 | 0.005229 | 0.006011 |
| VIB|Red.Masses (a.u.) | 1.067601 | 1.114971 | 7.032618 |
| VIB|Frc consts (a.u.) | 0.000037 | 0.003299 | 0.026003 |
| ATOM | 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 |
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 won’t be accounted for.

  - **Anharmonicity**
  - **Thermal Effects**
  - MD can account for these!
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

New Data

**THz-TDS**

- 300 K
- 250 K
- 200 K
- 150 K
- 100 K

**Low-Frequency Raman**

- 300 K
- 250 K
- 200 K
- 150 K
- 100 K

DFT Can’t predict shift!
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

M. T. Ruggiero and J. A. Zeitler, *submitted* (2016)
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
&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

Figure 5. Experimental 78 K THz spectrum (grey) 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 4.40 cm⁻¹ was used in convolving Lorentzian line shapes for simulated spectra.

Table 7: Descriptions of Calculated Vibrational Modes (±10 cm⁻¹) for the Best-Fit Simulation (B3LYP-6-311+G(d,p)) of l-Serine-H2O

<table>
<thead>
<tr>
<th>mode</th>
<th>freq. cm⁻¹</th>
<th>mode description</th>
<th>% H2O contrib</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>61.0</td>
<td>serine: 100% ET along a-axis</td>
<td>18</td>
</tr>
<tr>
<td>b</td>
<td>72.9</td>
<td>H2O: 75% ET along b-axis, 25% ER about b-axis</td>
<td>20</td>
</tr>
<tr>
<td>c</td>
<td>80.1</td>
<td>serine: 75% ER about b- and c-axes, 25% Int (NH₃⁻ rotation)</td>
<td>16</td>
</tr>
<tr>
<td>d</td>
<td>82.3</td>
<td>H2O: 75% ET along c-axis, 25% ER about b- and c-axes, 50% Int (C₁⁻C₂⁻ C₃⁻O₂⁻ torsion)</td>
<td>16</td>
</tr>
<tr>
<td>e</td>
<td>91.5</td>
<td>serine: 100% ER about b-axis</td>
<td>15</td>
</tr>
<tr>
<td>f</td>
<td>98.9</td>
<td>H2O: 100% ET along c-axis, 50% Int (C₁⁻C₂⁻ C₃⁻O₂⁻ torsion)</td>
<td>19</td>
</tr>
<tr>
<td>g</td>
<td>101.5</td>
<td>serine: 75% ER about c-axis, 50% Int (C₁⁻C₂⁻ C₃⁻O₂⁻ torsion)</td>
<td>22</td>
</tr>
<tr>
<td>h</td>
<td>105.8</td>
<td>serine: 50% ER about a-axis, 50% Int (C₁⁻C₂⁻ C₃⁻O₂⁻ torsion)</td>
<td>26</td>
</tr>
<tr>
<td>i</td>
<td>107.6</td>
<td>H2O: 100% ET along b-axis, 75% ER about b- and c-axes, 25% Int (NH₃⁻ rotation)</td>
<td>10</td>
</tr>
</tbody>
</table>

ET = translation; ER = external rotation; Int = internal motion. *Percent of total atomic displacements due to motion of H2O molecules.
Investigating the Anharmonicity of Lattice Vibrations in Water-Containing Molecular Crystals through the Terahertz Spectroscopy of l-Serine Monohydrate

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|---|---|---|---|
| mode | freq. cm⁻¹ | mode description | % H2O contrib |
| a | 61.0 | serine: 100% ET along a-axis | 18 |
| b | 72.9 | H2O: 75% ET along b-axis, 25% ER about b-axis | 20 |
| c | 80.1 | serine: 75% ET along c-axis, 25% ER about c-axis | 16 |
| d | 82.3 | H2O: 75% ET along c-axis, 25% ER about c-axis, 50% Int (C–C, C–O–H torsion) | 16 |
| e | 91.5 | serine: 100% ER about a-axis | 15 |
| f | 98.9 | H2O: 100% ET along a-axis | 19 |
| g | 101.5 | serine: 75% ER about a-axis, 25% Int (C–C, C–O–H torsion) | 22 |
| h | 105.8 | H2O: 100% ET along c-axis | 26 |
| i | 107.6 | serine: 75% ER about b-axis, 25% Int (C–C, C–O–H torsion) | 10 |

ET = translation; ER = external rotation; Int = internal rotation. * 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
Acknowledgements

Terahertz Applications Group

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Daniel Markl – Postdoctoral Fellow

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Marcin Krynski (Cambridge, UK)
Iain Bethune (EPCC, UK)
Alessandro Erba (University of Turin, IT)
Timothy Korter (Syracuse University, USA)

Email: mtr34@cam.ac.uk
Thank you for your attention!