Phonons and Thermal Transport in Organic Semiconductors

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Motivation

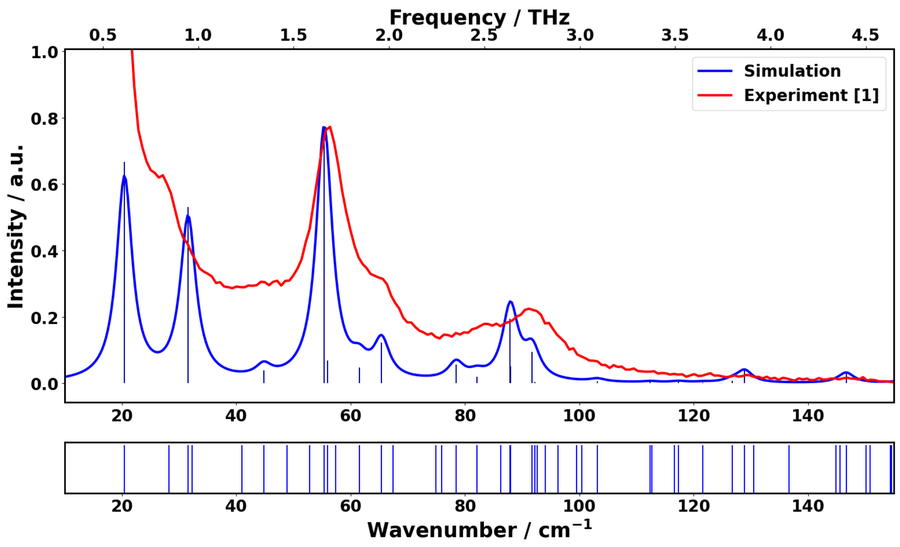
Organic semiconductors have a multitude of applications: OLED displays, transistors, organic solar cells and thermoelectric devices. However, still little is known about how one can tune their thermal properties, like their thermal conductivity.

Goals

How can one tune the thermal conductivity of organic semiconductors by changing their structure?

- Further Goals:
  - Improving the state-of-the-art methodology by benchmarking different methods against each other. What is the best method to reliably calculate phonon band structures and phonon lifetimes?
  - After successfully calculating phonons, thermal properties like the heat capacity can be calculated relatively easily.
- The goals will be reached by investigating materials with increasing complexity. First Polymers, then more complex organic semiconductors.

Validation by Experiment: Raman Spectra



The simulated Raman spectrum of the FD44 crystal is compared to the experiment performed at the University of Cambridge [1]. The low frequency region, that is shown here, is dominated by intermolecular modes. The lower bar shows the wave number of all Γ-phonon modes, including the Raman active and inactive ones. Note that in experiment there is strong noise for very low wave numbers, therefore this region was cut out of the plot.
The used methodology allows us to correctly predict phonon frequencies, as was extensively shown by our group in the past [2, 3].

Thermal Conductivity

- The thermal conductivity κ will be calculated via the **Boltzmann transport equation** within the relaxation-time approximation**:**

$$\kappa = \frac{1}{V}\sum_{modes} \textbf{Group velocities}^2 \cdot \textbf{Mode heat capacity} \cdot \textbf{Phonon lifetime}$$

slope in band structure — from density of states — from phonon scattering

- Group velocities and mode heat capacities can be easily obtained once the phonons are calculated.
- To calculate the phonon lifetimes, significantly more computational resources are necessary. Different methods will be evaluated, to find the best possible way to calculate phonon lifetimes.
- These calculations will be complemented by the results of a 2nd PhD student, **Lukas Legenstein**, who will perform molecular dynamics simulations.

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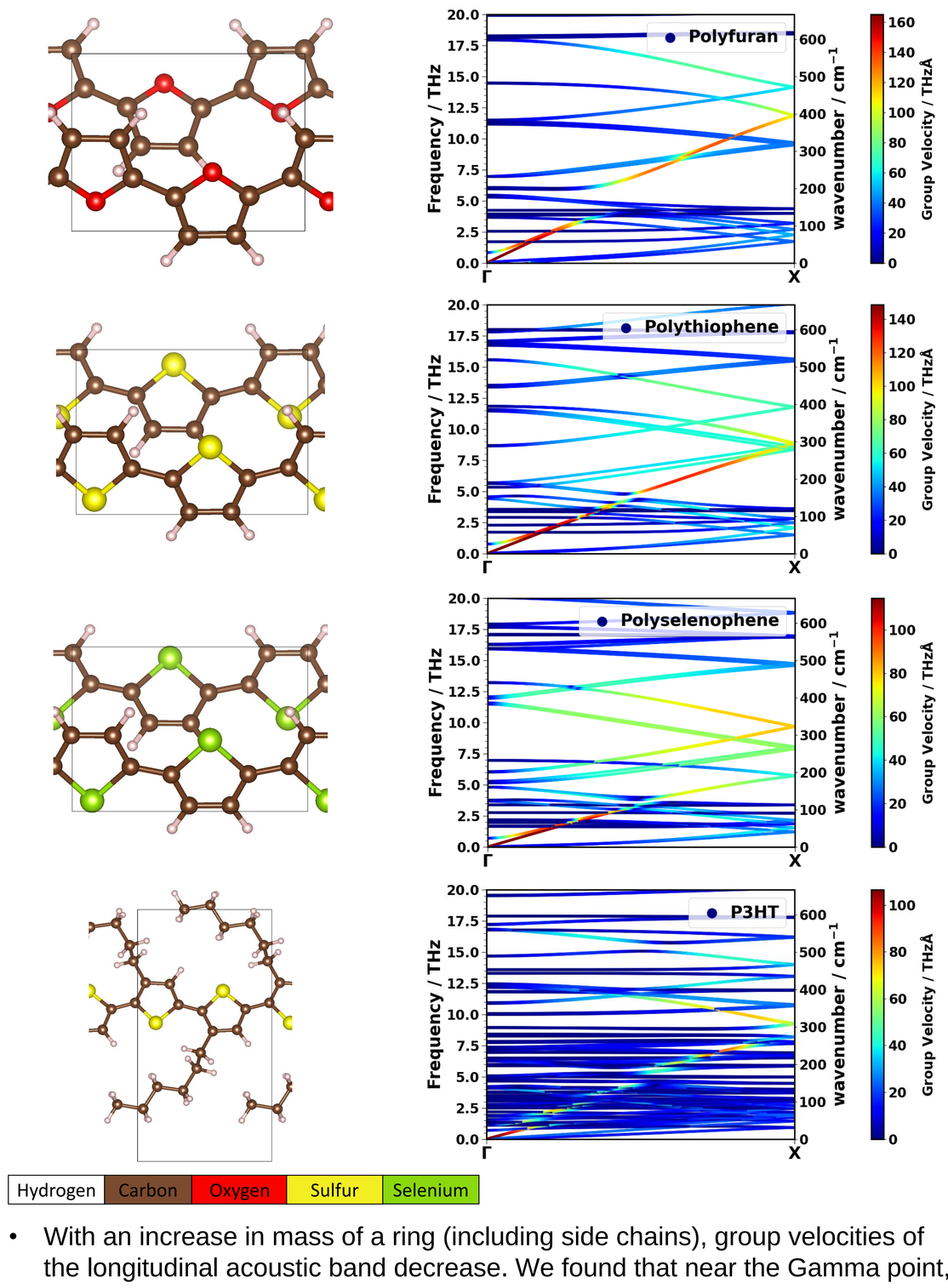
Phonon Band Structures



- With an increase in mass of a ring (including side chains), group velocities of the longitudinal acoustic band decrease. We found that near the Gamma point, they follow the trend one would expect from a 1D monoatomic chain

$$\lim_{k\to 0} v_g \sim \sqrt{\frac{1}{M}}$$

Methodology

- Two ways of calculating Phonons were employed so far:
  1. Phonons have been mainly calculated by employing the finite differences approach as implemented in Phonopy [4]. VASP [5] and FHI Aims [6] have been used as Density Functional Theory (DFT) codes.
  2. Density Functional Perturbation Theory (DFPT) as implemented in Quantum Espresso [7] has been tested.
- The DFT functional of choice is **PBE**, since it is still applicable to relatively large systems.
- The choice of the vdW-correction is crucial. Our group showed for the low frequency phonons of Naphthalene [2] and C_8-OBTBT-C_8 [3], that the D3 correction by Grimme [8] (implemented in VASP) as well as the MBD-NL correction [9] (implemented in FHI Aims) give excellent agreement to experiment.

References & Acknowledgements

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