

Phonopy-Spectroscopy: A computational spectroscopy modelling package



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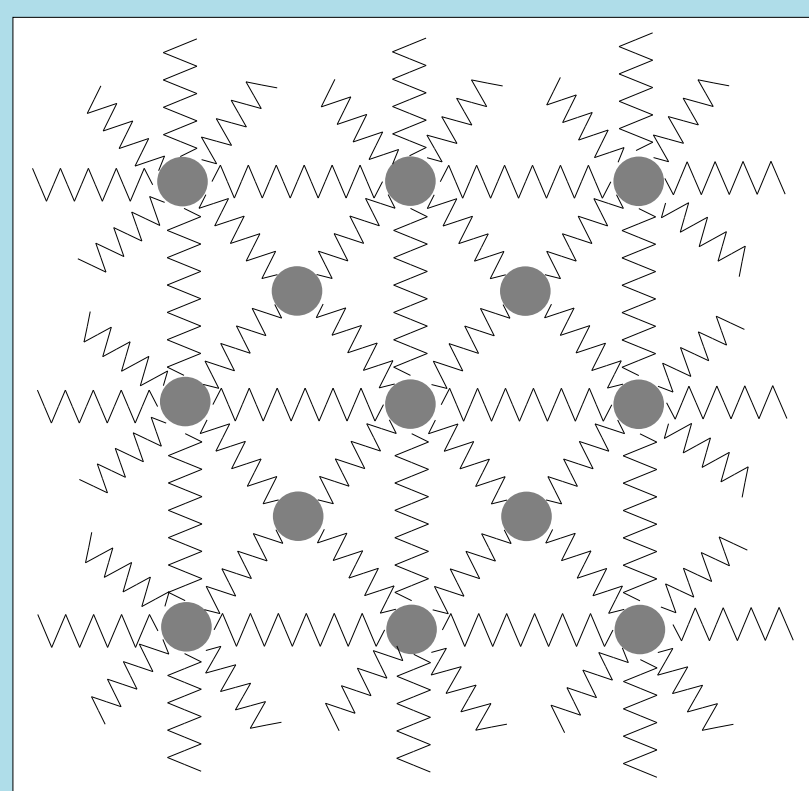
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1. Introduction

Vibrational properties are used to predict several physical phenomena of a system, which are comparable against experiment.¹



- Dynamic stability
- Heat capacity
- Thermodynamic free energies
- Thermal conductivity
- IR and Raman spectral signatures

$$E(R_0 + \Delta R) \approx E(R_0) + \sum_i \frac{\partial E}{\partial R_i} \Delta R_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 E}{\partial R_i \partial R_j} \Delta R_i \Delta R_j$$

Atomic motion at small amplitudes is usually well described by the harmonic approximation. This approximation provides the IR and Raman peak positions.

To predict peak widths, higher order anharmonic terms are required.

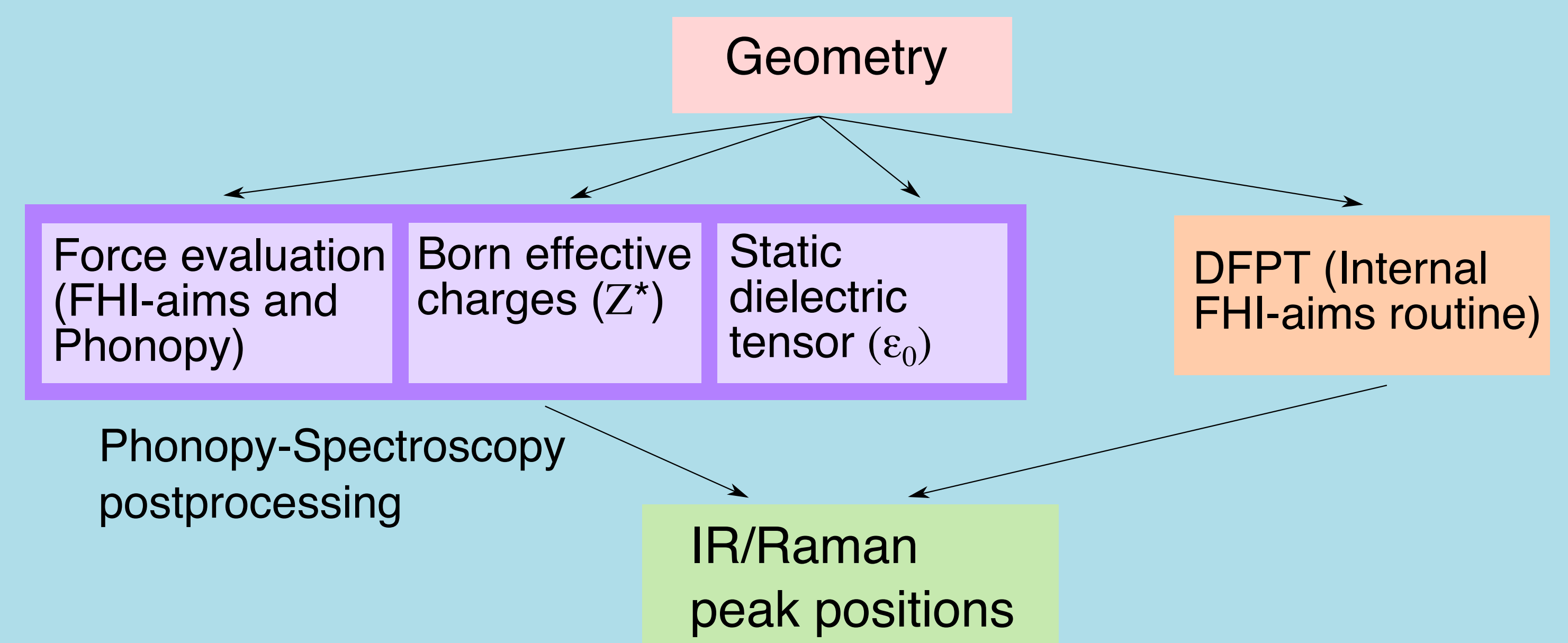
Phonopy-Spectroscopy² analyses Phonopy³ output to produce DFT-based IR and Raman spectra for molecules and materials.

It is tested with VASP and FHI-aims as the force calculator, however the modular structure of the code makes it extensible to other DFT codes.

2. Methods and workflow

A well converged geometry is a requirement of any lattice dynamics calculation. The force constant matrix can be evaluated using finite difference (FD) or density functional perturbation theory (DFPT).

In this work, we benchmark results from FD and Phonopy-Spectroscopy against the internal DFPT and IR/Raman routine⁴ in the FHI-aims code.



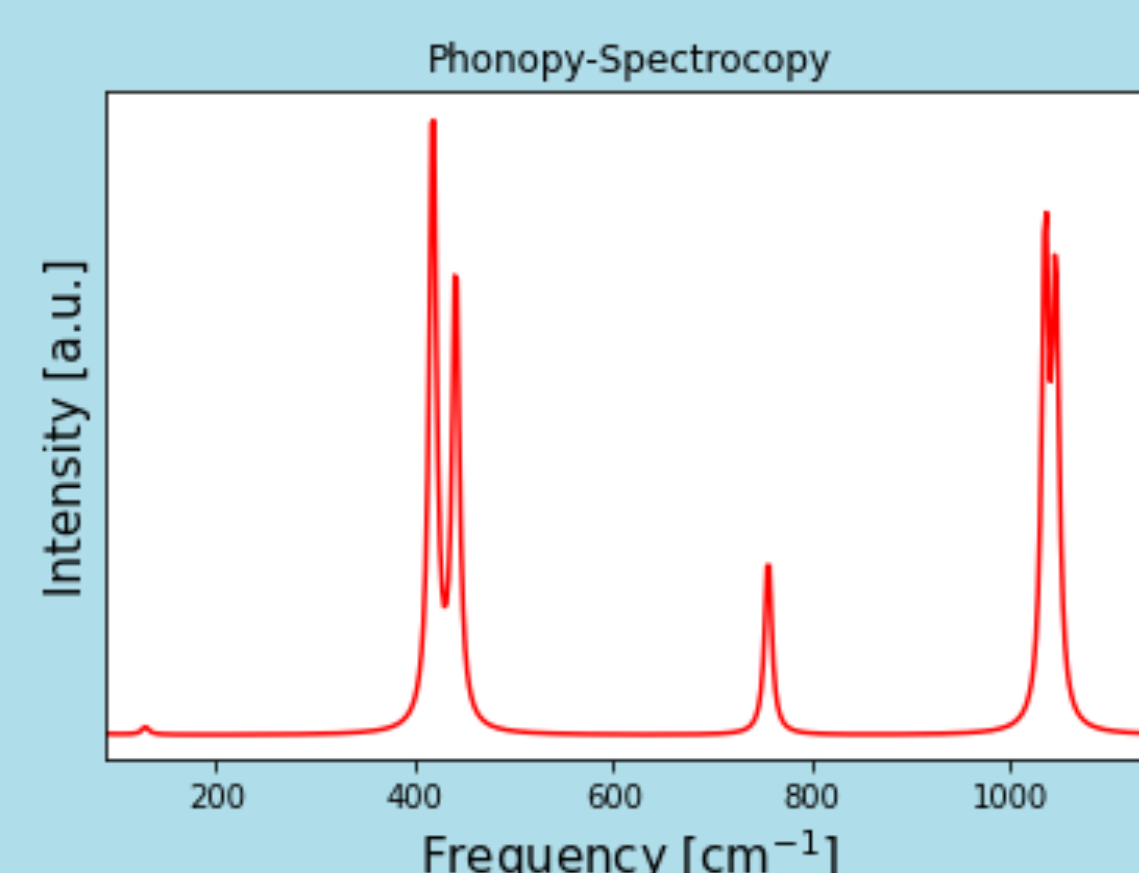
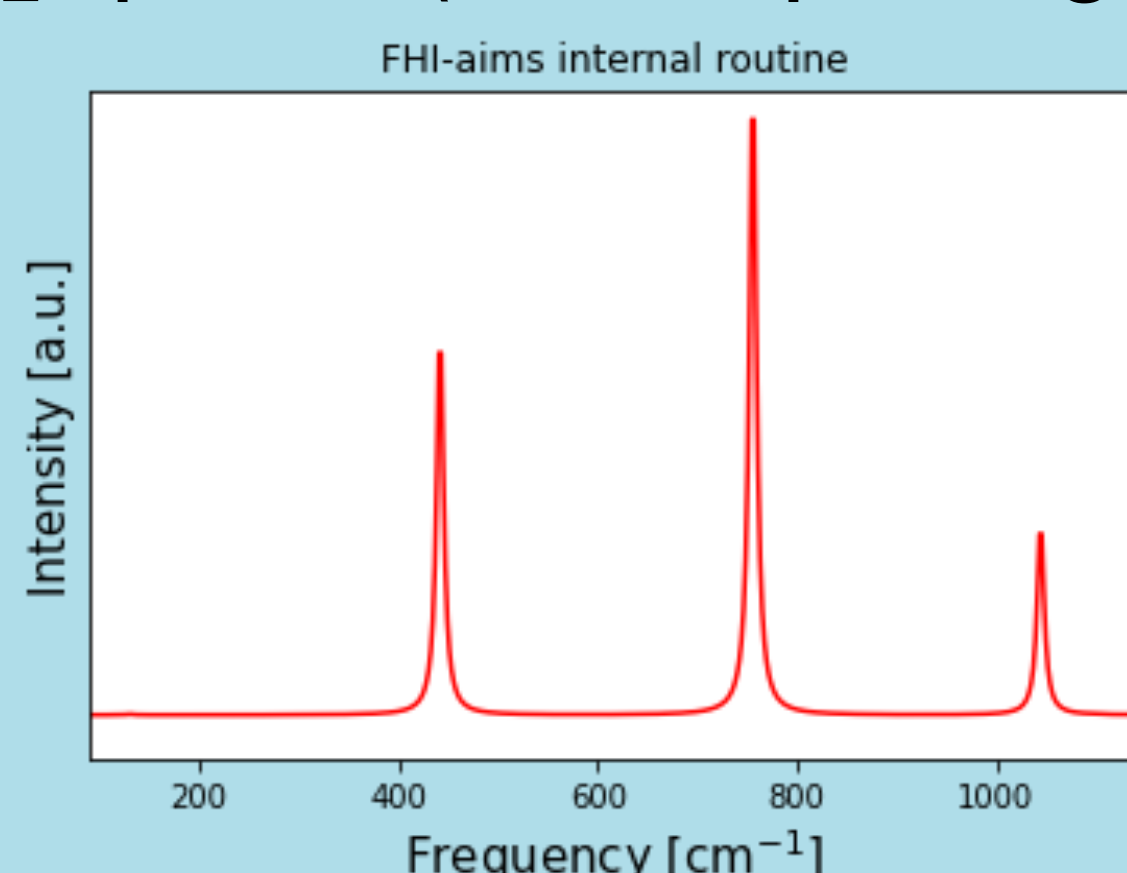
Z^* are the changes in polarization as a response to perturbations created by an electric field.

ϵ_0 is the response of a material to a low frequency or constant electric field.

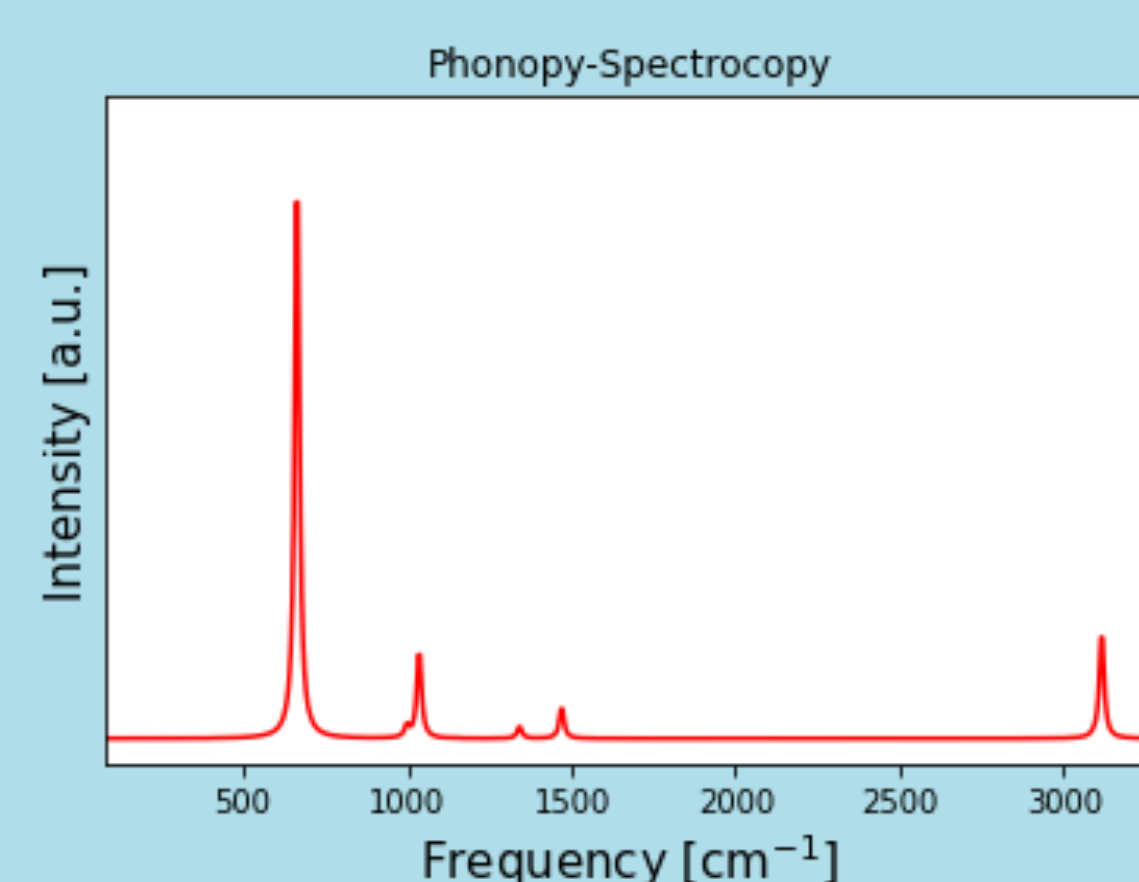
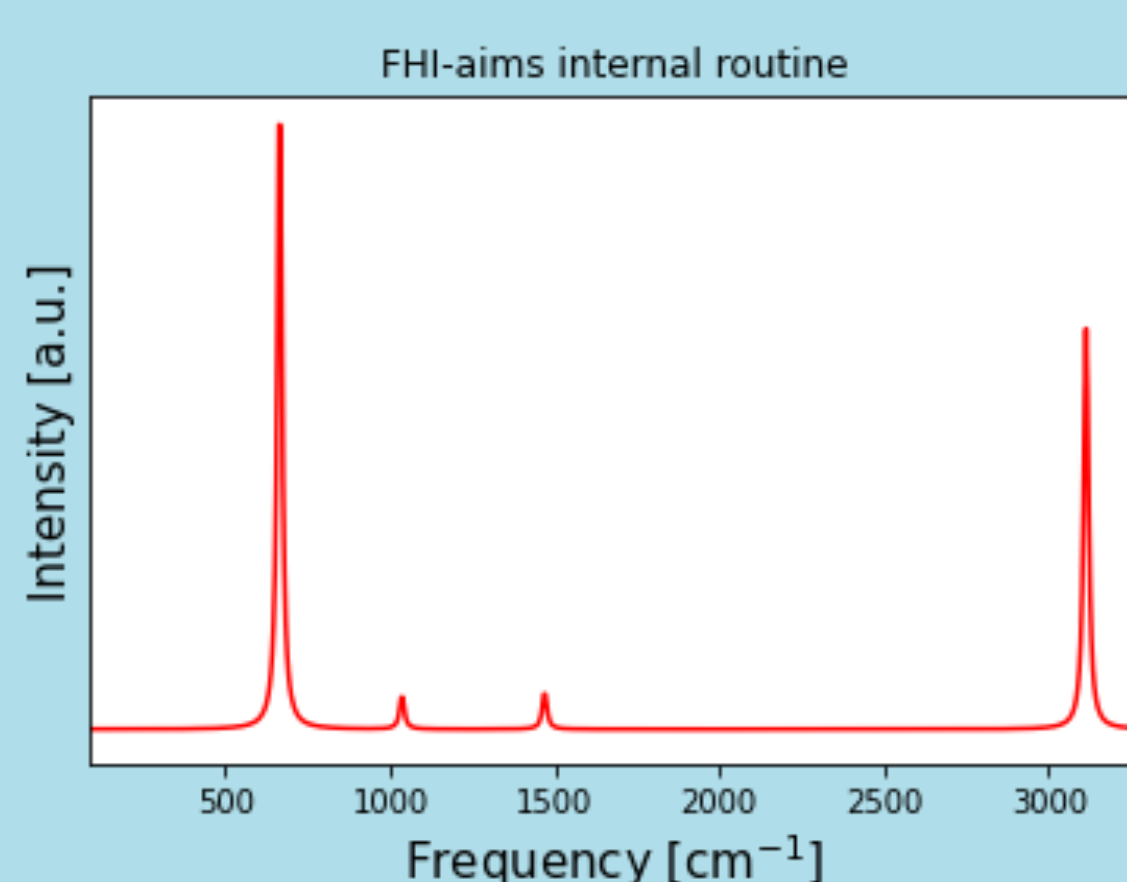
3. Results

All calculations were performed with the tight tier-2 basis set in FHI-aims with the PBE functional for geometry relaxation and postprocessing. Tighter convergence settings employed for molecules. Initial geometries for materials are taken from the AFLOW⁵ database and CCCBDB⁶ database for molecules.

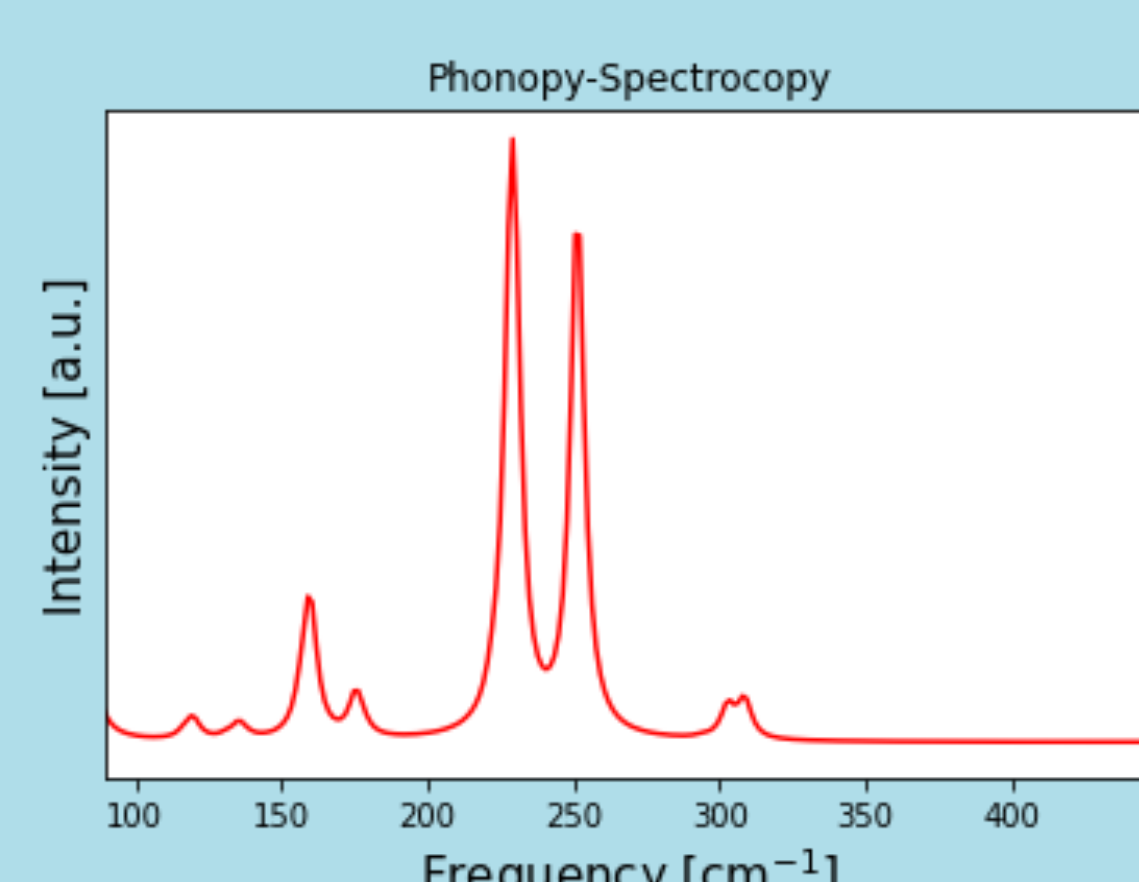
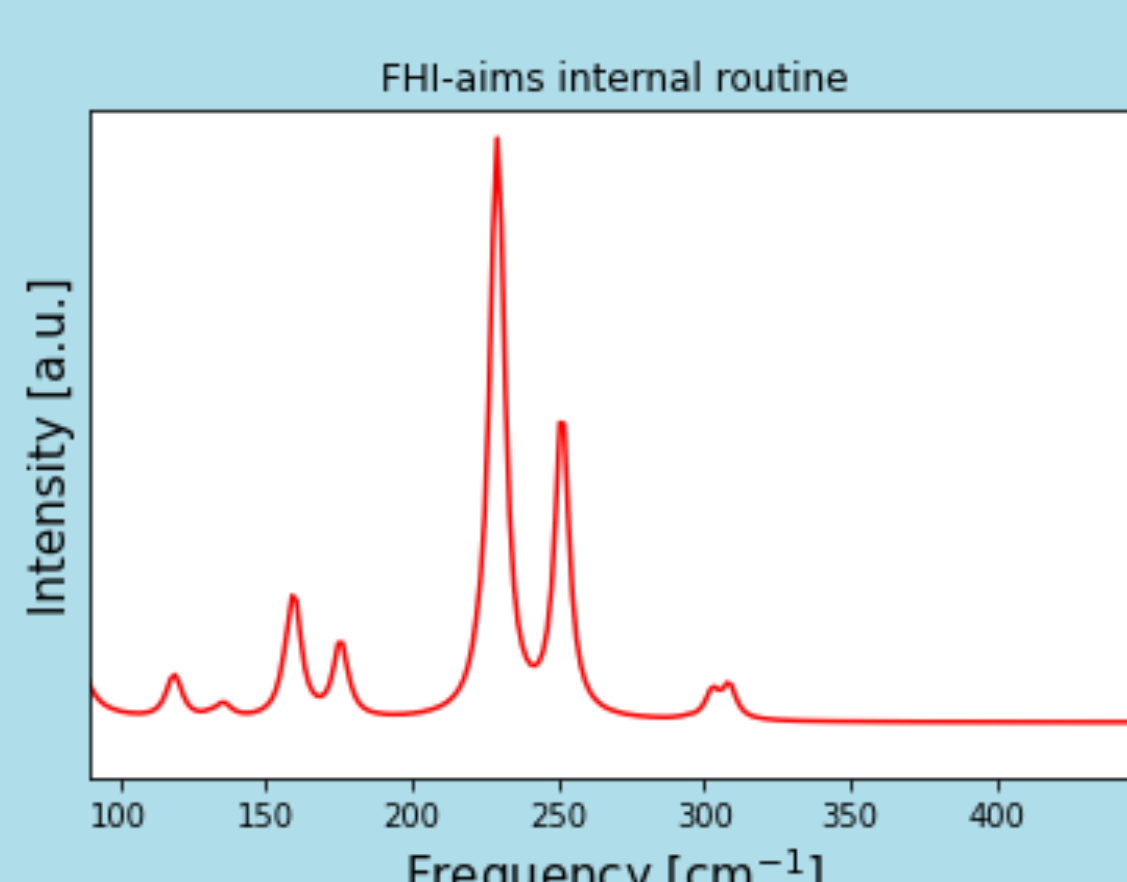
SiO₂ quartz (*I4-2d* space group)



Benzene (molecular relaxation followed by phonon calculation by adding 15A vacuum unit cell)



BaZrS₃ perovskite (*Pnma* space group)



5. Discussions

Phonopy-Spectroscopy is able to resolve spectral peaks better compared to the FHI-aims routine.

Peak heights are more realistic with Phonopy-Spectroscopy when compared to experiment.

Experimental results for the perovskite system need to be verified. Results from this work will aid in following the reaction for experimental synthesis.

With Phonopy-Spectroscopy additional dielectric constant calculations need to be performed to obtain the Raman spectra.

6. Software challenges

1. Software specificity is the devil:

Many analysis methods are software specific. Having modular codes to integrate outputs from several DFT programs can aid in having the same underlying postprocessing routines.

2. What numbers are good enough?

Few benchmark studies comparing settings to understand convergence across codes/methods. Lack of acceptable error bars with respect to experiment can help avoid running large calculations for little gain.

3. Documentation and version control:

Under-documentation of codes without general examples can hinder usability. Lack of an inclusive forum to raise, discuss, update and upgrade issues.

7. Outlook

- PYPI upload
- API documentation
- Unit testing
- Integration with other DFT codes

8. References

- ¹ Gold-Parker *et al.*, 2018 PNAS **115** 11905
- ² Skelton *et al.*, 2017 PCCP **19** 12452
- ³ Togo *et al.*, 2015 Scr. Mater. **108** 1
- ⁴ Shang *et al.*, 2017 Comp. Phys. Comm. **216** 46
- ⁵ Curtarolo *et al.*, 2012 Comp. Mat. Sci. **58** 218
- ⁶ <http://cccbdb.nist.gov/>

9. Links

Project repository hosted at:

<https://github.com/JMSkelton/Phonopy-Spectroscopy>

To reproduce results on this poster, scan:

