

The good, the bad, and the ugly: when do harmonic models go wrong for molecular materials ?

Re-interpreting molecular crystals through phonon anharmonicities

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In Short

- Correlate molecular features with vibrational structure of molecular materials
- Compute anharmonic corrections to molecular crystal vibrational spectra
- Investigate how physical features alter anharmonic contributions to molecular materials
- Explore the magnitude of anharmonic corrections to physical properties of molecular materials

The motion of atoms and molecules within the crystal lattice is indicative of many of the underlying physical properties, Figure 1. For example, the thermal expansion and mechanical properties of a material are both dependent on the vibrational dynamics. These thermo-mechanical properties find technological applications in areas including the development of construction materials and for ensuring the integrity of tableted powders (e.g. pharmaceuticals and explosive material compositions). More sophisticated functional properties such as charge transport^[1] and thermal conductivity^[2] are also strongly dependent on how atoms and molecules move within the lattice. Correspondingly, understanding the dynamics which comprise a crystalline material are of significant importance to the study and design of new materials.

The selective engineering of vibrations in inorganic materials has proved successful.^[3] This has allowed, for example, the targeted design of new thermo-electric materials.^[4] Strategies have not yet been developed for selectively modifying the vibrations in molecular materials. There exist routine strategies to model the vibrational properties of molecule and materials at the atomic level, upon which systematic analysis of molecular materials could be undertaken. However, these approaches are all based within the so-called harmonic approximation. Theoretical approaches to move beyond the harmonic approximation, including (i) the stochastic self-consistent harmonic approximation (SSCHA)^[5] and (ii) perturbative approaches to extracting high-order force constants.^[6] These approaches have been used to study inorganic crystals and the role

of anharmonicity in e.g. superconducting materials, Figure 2.^[5] Molecular materials are known to be mechanically soft, exhibit large and anisotropic thermal expansion, and comprise light atoms which undergo significant vibrational displacements. All of these features indicate marked deviation from the harmonic model.

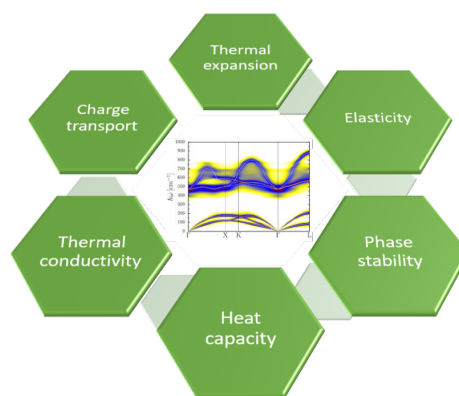


Figure 1: The vibrational structure of solids (centre) play a significant role in determining many of their physical properties, including thermal, physical, and opto-electronic properties.

The need to consideration lattice anharmonicity in molecular materials has been recognised previously. For example, Erba *et al* explored the effects of thermal expansion on thermodynamic and elastic properties of urea using the quasi-harmonic approximation (QHA).^[7] Moreover, the QHA approach has proved successful to explore corrections to energy landscapes of potentially polymorphic molecular materials.^[8] More commonly, anharmonic vibrational effects in molecular materials have been accounted for by *ab initio* molecular dynamics. Morrison and co-workers^[9] demonstrated anharmonic corrections to the lattice dynamics of solid ammonia in this way. It has been also demonstrated how temperature driven polymorphic transitions can be captured using these *ab initio* dynamics approaches.^[10] Although it is recognised that anharmonic effects in molecular materials are significant, there remains little understanding of when and by how much these effects contribute to molecular material properties. Exploring these correlations in more detail forms the base of this project.

Motivated by a growing interest in the rational design of functional molecular materials, this project

will take steps towards developing a detailed understanding of the anharmonic lattice contributions in molecular materials. Through use of a combination of advanced *ab initio* DFT, *ab initio* molecular dynamics, and machine learning approaches, we plan to explore systematically the origin and magnitude of lattice anharmonicity in our model systems. Together, these approaches will provide systematic analysis of the intrinsic and thermal anharmonic contributions to our model systems.

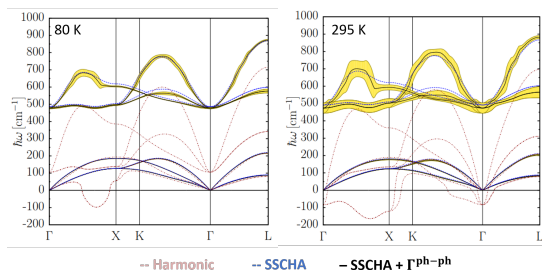


Figure 2: Effect of vibrational anharmonicity on the phonon dispersion curves for PdH₂. The QHA-corrected harmonic phonons are shown (pink) alongside those corrected by the SSCHA (blue) and SSCHA + phonon-phonon scattering (black). Figure adapted from Ref [5]

The main objectives driving this project are to (i) identify how structural features affect the vibrational properties of model molecular materials, and (ii) correlate these same structural features to the magnitude of anharmonic corrections to molecular material vibrations. To achieve these goals we will explore a series of small molecule organic crystalline structures. Our selected model systems allows us to explore vibrational properties across the entire Brillouin zone. This differs significantly from conventional experimental investigations which are often limited to Γ -point vibrational structure. At DFT level, the harmonic phonon dispersion structures will be systematically analysed for our model systems. Subsequently, anharmonic corrections to the harmonic phonon dispersions will be calculated, and their contributions to re-normalising vibrational properties will be assessed. These anharmonic corrections will be generated through a series of approaches, thereby allowing us to identify the most suitable approaches to describe molecular material anharmonicity.

Anharmonic effects contribute significantly to the design and properties of inorganic materials. A similar impact of is expected for molecular materials, but can only be assessed through more detailed investigation. It is our intention that this project will stimulate a more thorough understanding of molecular materials and their structure-property relations. Through our systematic exploration of vibrational an-

harmonicity, we aim to ultimately develop guiding principles to rationalise, identify, and design new molecular materials with tuned functional properties.

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More Information

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