ABSTRACT

Title of Dissertation:	PHONON TRANSPORT AND NONEQUILIBRIUM KINETICS WITH STIMULATION MODELING IN MOLECULAR CRYSTALS
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An important family of materials known as molecular crystals has been used extensively in fields such as organic semiconductors, energy, optoelectronics, and batteries. Due to their periodic crystal structure, phonons are the predominant heat and energy carriers. Phonons and their transport behaviors are crucial to the performance of semiconductors, the figure of merit of thermoelectrics, shock-induced properties of molecular crystals, and light-matter interactions of materials. Recent decades have seen significant advancements in the understanding of the phonon transport behaviors in inorganic crystals. However, a comprehensive understanding of phonon properties in molecular crystals is still lacking. While various theoretical models and computational simulations have been developed to study vibrational energy transfer in molecular crystals and to correlate vibrational structure with the stability of materials , these approaches often suffer from limitations. Many of these studies either neglect anharmonic scattering entirely or rely on simplified representations of phonon scattering.

In this dissertation, we focus on investigating the phonon transport and nonequilibrium kinetics in molecular crystals. In the first work, we study the harmonic phonon properties of cellulose Iβ using tapered reactive force fields (ReaxFF). While geometry optimization with the original ReaxFF potential often results in structures with negative eigenvalues, indicating structural instability, the modified potential with a tapering function yields structures with no associated negative eigenvalues. Three ReaxFF parameterizations are evaluated by comparing lattice properties, elastic constants, phonon dispersion, temperature-dependent entropy, and heat capacity with experimental results from the literature.

In the second study, we study the phonon transport behavior of Si, $Cs_2PbI_2Cl_2$, cellulose Iβ, and α-RDX by calculating the thermal conductivity using different thermal transport models including the Phonon gas model, Cahill-Watson-Pohl, and the Allen-Feldman model and the Wigner formulation. By comparing the calculated thermal conductivity with experimental values, we highlight the significant contributions of wave-like heat carriers in cellulose Iβ and α-RDX. We show how different phonon properties influence particle-like and wave-like behavior in various materials and reveal unusual mechanisms present in molecular crystals.

Lastly, we investigate nonequilibrium phonon kinetics resulting from direct vibrational excitations by employing the phonon Boltzmann transport equations. The results of our mid-IR pump-probe spectroscopy simulations align closely with experimental data from the literature. Additionally, by exciting different phonon modes at varying frequencies, we uncover distinct stages and pathways of vibrational energy transfer. To gain insights into the decomposition mechanism of RDX under excitation, we further calculate the bond activities of the N-N and N-O bonds, identifying possible stimuli that could trigger bond cleavage.