ABSTRACT

COMPUTATIONAL MODELING OF
NANOSCALE VIBRATIONAL ENERGY
TRANSFER IN CRYSTALLINE RDX
Gauray Kumar

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Professor Peter W. Chung Department of Mechanical Engineering

Energetic materials appear in a wide range of industrial and defense applications such as mining, construction, rocket propellant, design of munitions, etc. Understanding the physical and chemical processes that result in phenomena leading to initiation is critical for the safe development, usage, transport, and storage of high-performance energetics.

A long held belief is that shock energy induces initiation of an energetic material through an energy up-pumping mechanism involving phonon scattering through doorway modes. In Chapters 4 and 6, a 3-phonon theoretical analysis of vibrational energy up-pumping in RDX is presented that considers possible doorway pathways through which energy transfer occurs. The vibrational energy transfer is modeled via 3-phonon scattering processes based on Fermi's Golden Rule. Our results indicate that the low frequency vibrational modes (below ~100 cm⁻¹) scatter less than 0.5% of the vibrational energy directly to the critical high frequency intramolecular vibrations. In contrast, the mid-frequency modes between 457 and 462 cm⁻¹ and

between 831 and 1331 cm⁻¹ are the most critical for vibrational heating of the critical intramolecular vibrations such as N-N stretching.

In Chapters 3 and 5, we examine the nature of thermal transport and how bond strain and rotation carry heat in RDX. To draw the distinction between propagating and diffusive carriers of heat, we compare the thermal conductivity estimates from three microscale models: Phonon Gas Model, Cahill-Watson-Pohl formula, and Allen-Feldman harmonic theory. We observed that due to a strong crystal anharmonicity, diffusive carriers contribute to over 95% of the thermal conductivity in RDX. These results indicate that van der Waals bonded organic crystalline solids conduct heat in a manner more akin to amorphous materials than simple atomic crystals.

In Chapter 7, we perform a numerical experiment to investigate the effects of stimulating different IR active vibrational modes on change in scattering rates, thermal diffusivity, and conductivity in RDX. The stimulation of the vibrational modes is performed one mode at a time using six different optical energy inputs (3 high intensity: few eV, and 3 low intensity: tens of meV). Based on the results of this study, we identify several vibrational modes stimulating which may lead to a substantial enhancement or frustration of the heat transport properties in RDX.

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by

Gaurav Kumar

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Advisory Committee: Professor Peter W. Chung, Chair/Advisor Professor Oded Rabin, Dean's Representative Professor Bao Yang Professor Abhijit Dasgupta Professor Yifei Mo © Copyright by Gaurav Kumar 2021

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List of Abbreviations

- EM Energetic Material
- SMRTA Single Mode Relaxation Time Approximation
- pDOS Phonon Density of States
- DOS Density of States
- FGR Fermi's Golden Rule
- NMD Normal Mode Decomposition
- MD Molecular Dynamics
- LD Lattice Dynamics
- ALD Anharmonic Lattice Dynamics
- QHLD Quasi-Harmonic Lattice Dynamics
- PGM Phonon Gas Model
- CWP Cahill-Watson-Pohl
- AF Allen-Feldman
- GK-MD Green-Kubo Molecular Dynamics
- 3D three dimensional
- 1D one dimensional
- BZ Brillouin Zone
- BE Bose-Einstein
- SE Secondary explosive
- **BTE** Boltzmann Transport Equation

TDSE - Time-Dependent Schrödinger Equation

LAMMPS - Large Scale Atomic/Molecular Massively Parallel Simulator

- GULP General Utility Lattice Program
- IFC Interatomic Force Constant
- SED Spectral Energy Density
- NVT statistical ensemble with a constant no. of particles, volume and temperature
- NPT statistical ensemble with a constant no. of particles, pressure and temperature
- NVE statistical ensemble with a constant no. of particles, volume and total energy
- DFT Density Functional Theory
- MFP Mean Free Path
- IR Infrared
- SHG Second Harmonic Generation
- TEA Transversely Excited Atmospheric
- EMR Electromagnetic Radiation
- CW Continuous Wave
- Eq. Equation
- No. Number
- RMS Root Mean Square
- FEL Free-electron Laser

Chapter 1: Introduction

1.1 Introduction to Energetic Materials

Energetic Materials (EMs) are a class of materials that can release a large amount of chemical energy per unit mass, stored in their molecular structure, upon external stimulations such as heat, shock, or electric current [1, 2, 3, 4, 5, 6, 7, 8]. EMs generally are organic compounds whose molecular structure comprises nitro, azide, hydrazide, etc., functional groups [9]. Examples of energetic materials are Cyclotrimethylene-trinitramine Triamino-trinitro-benzene (RDX), (TATB), Octahydro-tetranitro-tetrazocine (HMX), Trinitro-toluene (TNT), Nitrocellulose-based powders, etc. EMs appear in a wide range of industrial and defense applications such as mining, construction, rocket propellant, design of munitions, etc. [10, 11, 12, 13, 14, 15, 16, 17, 18, 9]. Based on their application, energetic materials can be categorized as explosives, propellants, and pyrotechnics. Explosives are materials that can release a large amount of energy and exhibit large volume expansion in a short span of time (μs timescale). The large amount of energy output is achieved via a rapidly propagating reaction through the whole material which is referred to as detonation. During detonation, a shockwave propagates through the material resulting in compression of material at the wave front, followed by an increase in temperature which further leads to exothermic chemical reactions. The chemical reactions, in turn, result in an increase in temperature and pressure that can provide enough energy to sustain the propagation of the shock through the material at supersonic speed. In propellants, the chemical reactions result in a reaction wave propagating through the material at sub-sonic speed, a few cm/s or m/s. They are also called low-explosives and the reaction process is referred to as deflagration. In pyrotechnics, the chemical reactions produce light, color, heat, smoke, and sound, and are often the ingredient for fireworks, airbags, etc. The reaction propagation rate in pyrotechnics is slower, on the order of mm/s [19].

Understanding the physical and chemical processes that result in phenomena leading to initiation is critical for the safe development, usage, transport, and storage of high-performance energetics. However, the extreme reaction conditions, the small length scale of reaction zones (nanometer to micrometer), and ultrafast reaction rate (sub-picosecond to microsecond) make the experimental investigation difficult and expensive. Computer simulations can offer a safe and convenient route for developing an accurate understanding of the physical and chemical processes and can provide essential information that is useful to experimentalists and engineers. In this thesis, quantum mechanical calculations such as perturbation theory, and normal mode decomposition, lattice dynamics, and molecular dynamics simulations are used to investigate the role of phonons in nanoscale vibrational energy transfer from the low frequency molecular translation modes to the high frequency intramolecular vibrations which may result in phenomena leading to initiation in crystalline RDX.

1.2 Motivation¹

Considerable efforts have studied the initial decomposition and initiation mechanisms in EMs where mechanical energy input creates conditions in the material that make it more susceptible to bond rupture and possible self-sustaining chemical reactions. Early efforts to study the thermal decomposition route by Robertson suggested that the primary reaction step involved the transfer of an oxygen atom from the nitro group to a neighboring carbon atom followed by the elimination of CH₂O and N₂O [20]. Based on the rapid initial production of NO₂, Rauch et al. suggested that the first step in the gas phase decomposition of RDX is the homolytic fission of the N-N bond [21]. Other works have also suggested N-N cleavage and HONO elimination to be more likely than other reaction routes such as C-N β -scission, oxygen insertion, nitro-nitrite isomerization, etc. [22, 23, 24, 25, 26, 27, 28, 29, 30]. Based on electronic structure calculations, barriers to N-N fission and HONO elimination are estimated to be significantly lower than other mechanisms [31, 32, 33]. Between N-N fission and HONO elimination, fission proceeds via a so called loose transition structure and is entropically favored [34]. In a recent study by Schweigert who performed a unimolecular dynamics simulation of RDX for a sampling temperature of 2000 K, N-N fission was found to be the dominant reaction mechanism, especially above ~1250 K [35]. Bowden and Yoffe [36, 37, 38] showed that the bulk heating of the material in shocked energetic crystals is insufficient to describe the initiation processes. As a

¹ Portions of this chapter appear in the preprint: G. Kumar, F. G. VanGessel, L. B. Munday, P. W. Chung, "3-phonon scattering pathways for vibrational energy transfer in crystalline RDX", *J. Phys. Chem. A*, 2021 [76]

result, the concept of localization of energy into microscale regions, called hotspots, near crystal defects and grain boundaries was developed [37, 39, 40, 41]. If the energy generated at these hotspots due to the exothermic decomposition of the material exceeds the energy that is dissipated due to thermal conductivity, then the decomposition of the material continues. Subsequently, to explain the initial thermal decomposition and the localization of energy, a mechanism of energy transfer via multi-phonon up-pumping was postulated [42, 43, 44, 45]. This model assumed that mechanical energy from the shock excites the low frequency phonons which results in a rapid increase in their population. The energy from these low frequency modes is then scattered into the mid-frequency modes, referred to as doorway modes, via phononphonon scattering. The energy from the doorway modes is, in turn, transferred into the high frequency intramolecular vibrations which are believed to increase the population and energy of internal molecular vibrations beyond bond dissociation limits. This picture of energy transfer meant that the mid frequency doorway modes are critical for phenomena leading to initiation in energetics. The model was further extended by Dlott and co-workers who studied terahertz excitation in molecular solids, measured by ps timescale vibrational spectroscopy, and included a description of localization of energy at crystal defects [46, 47, 48, 49]. Dlott et al. concluded that the rate of up-pumping of energy depends on the number of doorway modes and the Gruneisen parameter values which are indicative of the strength of anharmonic coupling between the modes [50].

For the up-pumping model for initiation to work, strong scattering must occur among a) modes at the low frequencies close to the frequencies associated with mechanical shock, b) the frequencies of the modes believed to serve as the doorway modes, and c) the modes associated with the largest distortions of the bonds, so-called vibrons, likely to possess dissociation energies which, when released, can sustain exothermic reactions. Aubuchon et al. [51], in their work on modes that result in asymmetric stretching of the nitro functional group (NO_2) in TNAZ, RDX, HMX, and CL-20, suggested that the relaxation of the intra-molecular vibrons occurs through a pathway involving a combination of high frequency (> 400 cm⁻¹) modes. Other works have also posited that the energy transfer process may occur through a direct route simply due to the NN activity found in low frequency eigenmodes without intermediate energy transfer or the involvement of doorway modes [52]. A definitive understanding of multi-phonon mechanisms in energetic materials, therefore, is needed. It requires a detailed determination of vibrational energy transfer of not only the relaxation behavior of individual modes, but a complete picture of mode-to-mode scattering that may drive energy through the intrinsic scattering network.

Much progress has occurred toward this goal motivated by early interest in the relationship between vibrational energy transfer and sensitivity. To calculate the total energy transfer rate into vibron bands, Fried and Ruggiero [53] derived a simple formula in terms of the density of vibrational states and the vibron-phonon coupling, which were calculated using existing inelastic neutron scattering data. They studied TATB, γ and β -HMX, RDX, Pb-styphnate, Styphnic acid, and Picric acid, and observed that the estimated energy transfer rates in pure unreacted material are several times greater in sensitive explosives than in insensitive explosives. Following Fried and Ruggiero's formula, Koshi and co-workers investigated a broad range of EMs including PETN, HMX, RDX, Tetryl, TNT, FOX-7, ANTA, PN, NQ, and DMN, and

observed a good correlation of the energy transfer rates with the impact sensitivity [54, 55, 56]. Similar observations were made by Bernstein [57], Joshi et al. [58], and McNesby et al. [59] who investigated the rate of energy transfer from the low frequency phonons to the higher frequency vibrons. Aubuchon et al. used IR pump-probe spectroscopy to show rapid relaxation (2 to 6 ps time scale) of the asymmetric stretching mode of the nitro functional group (NO_2) of several molecules used in TNAZ, RDX, HMX, and CL-20 [51]. Ostrander et al. also used IR pump-probe spectroscopy to study the asymmetric stretching of the nitrate ester groups in PETN thin films and observed a 3.7 ps decay, attributing this decay to rapid energy transfer due to intermolecular vibrational coupling [60]. Numerous other works have explored the role of various crystal distorting modes in the transfer of energy in EMs [52, 61, 62, 63, 64, 65, 66, 67]. These works provide useful insights into the phonon modes which can be critical in phenomena leading to initiation and have motivated investigation of the critical bond stretching and bending modes.

A significant challenge in the development of a complete phonon picture of uppumping has been the lack of a quasiparticle model that accurately accounts for third (and higher) order terms in the Hamiltonian vis-à-vis Fermi's Golden Rule [68] across a larger range of the Brillouin zone. But with the perpetual development of advanced computational architectures, efforts have been made to calculate the anharmonic phonon properties more accurately to model the energy transfer between the vibrational modes. Early efforts were based on approximations to the anharmonic terms that made it possible to overcome the computational costs at the expense of making it difficult to generalize the consideration of distinct phonon modes. Hooper developed a parametric expression for transition probabilities for nitromethane, RDX, and HMX that require assumptions including the Single Mode Relaxation Time Approximation (SMRTA), the applicability of Debye's model for the pDOS (phonon Density of States), the occupation numbers being independent of frequency, and that only modes of equal frequency can scatter [69]. Long and Chen calculated phonon-phonon scattering rates in TATB by developing a stress-frequency relationship as a means of representing anharmonic effects without the high computational cost of a 3-phonon scattering Hamiltonian [70]. Michalchuk et al. studied the sensitivity of a wide range of EMs using a 3-phonon scattering model derived from Fermi's Golden Rule (FGR) [71]. This work was built on the so-called average anharmonic approximation [72], which reduces computational cost by assuming that all elements of the cubic anharmonic matrix $V^{(3)}$ are equal. Recently, however, estimates of thermal properties based on quasiparticle models have shown that a more complete representation of carriers in the Brillouin zone may be necessary for the accurate modeling of phonon mechanisms. Kumar and coworkers showed that the thermal conductivity of energetic crystals like RDX can be dominated by non-acoustic carriers, which constitute the majority of the phonon modes [73], and that modes outside of the acoustic bands can contribute substantially to NN and other intramolecular bond distortions [74, 75]. These observations suggest that the use of approximations that otherwise reduce the complexity of the rich set of optical modes in these materials may omit important contributions from a large number of modes to the transfer of vibrational energy.

1.3 Research Outline

In this dissertation, we present a computational investigation of the role played by phonons in determining important thermodynamic properties such as thermal diffusivity, conductivity, rate of vibrational energy transfer to the high frequency intramolecular vibrations, etc. in RDX. An accurate understanding of these properties can reveal the key physics necessary for the safe development of energetics and can provide insights into controlling the behavior of these highly sensitive materials. The results of this study were published in [75, 73, 74, 76].

In Chapter 3, we present the computational details for obtaining the minimum free energy structure of RDX at finite temperature and calculation of the harmonic phonon properties such as phonon mode frequencies, group velocities, and modewise specific heat which are essential ingredients for estimating the amount of vibrational energy stored in the phonon modes and the rate of transmission of vibrational energy between phonon wave packets. We also present a harmonic-oscillator based model for calculating the contribution of the phonon modes to the stretching and rotation of the bonds and bond angles in RDX.

Phonon lifetimes indicate the strength of anharmonic interaction between the phonon modes and are an essential ingredient for assessing the nature of thermal transport (diffusive vs. ballistic) in the material. In Chapter 4, we present two different techniques for calculating the anharmonic phonon-phonon scattering rates and lifetimes: 1) A quantum mechanical theory called Fermi's Golden Rule (FGR), and 2) A lattice dynamics based Normal Mode Decomposition (NMD) method. Fermi's Golden Rule is a fully quantum mechanical theory that provides an estimate for the
probability of transition from an initial quantum state i to a final quantum state f. This transition probability is used to calculate the 3-phonon scattering rates and phonon lifetimes. In contrast, the NMD technique models the fluctuations in phonon population, the ingredients for which are obtained from a classical Molecular Dynamics (MD) simulation. Although, only the first order anharmonic term of the Hamiltonian is used in the FGR technique and the MD captures all higher order crystal anharmonicities, however, the FGR technique enables the calculation of energy transfer between individual modes in the system via quantum mechanical transitions such as emission and absorption processes and therefore can provide a more detailed picture of the vibrational energy transfer between the phonon modes.

To develop an understanding of hotspot formation and its growth, it is crucial to understand how much heat is stored and dissipated out of the hotspot regions due to thermal conductivity. In Chapter 5, we evaluate three thermal conductivity models, namely the Phonon Gas Model (PGM), Cahill Watson and Pohl (CWP) model, and Allen and Feldman (AF) model. We assess the accuracy of these models in estimating the thermal conductivity of RDX by comparing them with values obtained from Green-Kubo molecular dynamics (GK-MD) [94]. Analysis of the phonon linewidths and lifetimes indicate that RDX is a highly anharmonic crystal which results in a breakdown of the PGM due to a breakdown of the Peierls picture for thermal transport [77]. Allen-Feldman harmonic theory provides the most accurate thermal conductivity estimate (within 6.4% of the GK-MD estimate) indicating that the diffusive mechanism of heat transport is dominant in RDX.

The overarching problem statement of this work is to understand the pathways for vibrational energy transfer in energetics via which the shock energy gets transferred from the long wavelength external vibrations (acoustic waves and molecular translations) to the short wavelength intramolecular vibrations which may result in the fission of bonds and initiate the thermal decomposition of the material. In Chapter 6, we break down the 3-phonon scattering rate terms obtained from FGR to calculate mode-to-mode scattering rates. The mode-to-mode scattering rates are investigated to identify the modes that are responsible for the majority of energy transfer into or out of any particular mode of interest. This investigation provides a detailed picture of the possible pathways for vibrational energy up-pumping from the low frequency lattice vibrations to the critical N-N stretching modes. Based on the results, an indirect mechanism of vibrational energy up-pumping is proposed where the energy from the low frequency modes must get transferred to the mid-frequency doorway modes which then further up-pump the energy to the high frequency intramolecular vibrations.

The harmonic properties such as phonon mode specific heat and group velocities, and anharmonic properties such as scattering rates and mode-to-mode scattering rates can provide a detailed picture of how vibrational energy is carried and gets transferred between different modes in energetic materials. This information can be exploited to understand how changing certain phonon properties such as phonon occupation may affect the physical properties like thermal diffusivity, conductivity, etc., and therefore can provide insights into controlling the behavior of energetics. In Chapter 7, we perform a numerical experiment to investigate how stimulating certain IR active modes can affect the heat transport properties in RDX. The stimulation of vibrational modes is performed one mode at a time and the corresponding change in 3phonon scattering rates is estimated using the perturbation theory (also known as Fermi's Golden Rule) under Single Mode Relaxation Time Approximation. Subsequently, modewise thermal diffusivity and conductivity are calculated using the Phonon Gas Model. The stimulation of each IR active mode is performed using six different optical energy inputs (3 high intensity: few eV, and 3 low intensity: tens of meV). The effect of mode stimulation is measured by calculating average values of percent change in modewise properties. Finally, we identify three best cases when stimulating an IR active mode in RDX can result in the largest increase/decrease in thermal diffusivity and conductivity which can potentially result in a substantial decrease/increase in the sensitivity of the energetic material.

Chapter 2: Background

In this Chapter, we discuss the theory of crystal structure and phonons, and computational details for calculating harmonic phonon properties that are essential ingredients for understanding the nature of heat transport in energetics.

For electrical insulators (majority of energetic materials) and semiconductors (Si, Ge, etc.), the thermal energy is conducted through the material primarily via coupled vibrations of atoms and molecules, and the contribution of electrons to the thermal conductivity can be neglected. In particular, in crystalline materials, the collective vibrations of atoms and molecules result in lattice waves, called phonons, propagating through the material and are the primary thermal carriers.

On a continuum level, Fourier's Law provides an accurate description of the heat flux in the material which assumes that thermal transport in the system is diffusive in nature, i.e., the mean free of the thermal carriers (phonons) is smaller than the material length scale (often orders of magnitude smaller). However, such descriptions break down on length scales comparable to the size of the molecules (few Angstroms), crystal unitcell size (~1 nm), or mean free path of phonons (up to hundreds of nanometers), where heat transport is primarily ballistic i.e., mean free path of the thermal carriers is larger than the material dimension. Therefore, accurate modeling of phonons is required to describe the transport of thermal energy at such small length scales.

2.1 Crystal Structure

A perfectly crystalline solid consists of an infinitely periodic repetition of an identical group of atoms. The group of atoms is called the basis. The points in the threedimensional (3D) space to which the basis is attached are called the lattice points. Due to the periodic nature of the arrangement of basis in a crystal, the lattice in 3D may be defined by three translation vectors denoted by a_1 , a_2 , a_3 such that the arrangement of atoms in the crystals is indistinguishable when viewed from a point r as when viewed from a point r' translated by an integer multiple of the translation vectors.

$$r' = r + u_1 a_1 + u_2 a_2 + u_3 a_3 \tag{1}$$

Here u_1 , u_2 and u_3 are arbitrary integers. The choice of the smallest vectors a_1 , a_2 , a_3 for which the arrangement of atoms in the crystal looks the same when viewed from r and r' are called primitive translation vectors, or lattice vectors. The angles between the lattice vectors are represented by α , β , and γ . The parallelopiped defined by the primitive translation vectors is called a primitive cell or a unitcell. The volume of the unitcell (*V*) is given by

$$V = |\boldsymbol{a_1} \cdot \boldsymbol{a_2} \times \boldsymbol{a_2}| \tag{2}$$

2.2 Fourier Analysis

The periodicity of atoms in a crystal means that any local physical property of the crystal, such as charge concentration, electron number density, magnetic moment density etc. is invariant under any translation of the form $\mathbf{T} = u_1 a_1 + u_2 a_2 + u_3 a_3$. For any physical property $n(\mathbf{r})$, this can be represented by

$$n(\mathbf{r}) = n(\mathbf{r} + \mathbf{T}) \tag{3}$$

This periodicity of the lattice makes it ideal for Fourier analysis. For simplicity, in one dimension, the Fourier expansion of any arbitrary function n(x) for a lattice with a translation vector $|a_1| = a$ can be written as

$$n(\mathbf{x}) = n_0 + \sum \left[C_p \cos\left(\frac{2\pi px}{a} + 2\pi p\right) + S_p \sin\left(\frac{2\pi px}{a} + 2\pi p\right) \right]$$
(4)

Where *p* are positive integers, and C_p and S_p are Fourier coefficients. $\frac{2\pi p}{a}$ is referred to as a point in the Fourier space or reciprocal space of the crystal. In 3D, Eq. (4) can be written as

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i(\mathbf{G} \cdot \mathbf{r})}$$
(5)

where **G** is a set of vectors such that $n(\mathbf{r})$ is invariant under all crystal translations **T**. For a crystal with lattice vectors $\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3}, \mathbf{G}$ is given by

$$\boldsymbol{G} = v_1 \boldsymbol{b_1} + v_2 \boldsymbol{b_2} + v_3 \boldsymbol{b_3} \tag{6}$$

where v_1 , v_2 , v_3 are integers and b_1 , b_2 , b_3 are primitive vectors of the reciprocal space and are defined as

$$b_1 = 2\pi \frac{a_2 \times a_3}{V}$$
, $b_2 = 2\pi \frac{a_3 \times a_1}{V}$, $b_3 = 2\pi \frac{a_1 \times a_2}{V}$ (7)

where $V = |\mathbf{a_1} \cdot \mathbf{a_2} \times \mathbf{a_3}|$ is the unitcell volume. The reciprocal lattice of the primitive cell is also called the Brillouin Zone. For an orthorhombic crystal where the lattice vectors can be defined as $\mathbf{a_1} = a_1 \,\hat{\mathbf{x}}$, $\mathbf{a_2} = a_2 \,\hat{\mathbf{y}}$ and $\mathbf{a_3} = a_3 \,\hat{\mathbf{z}}$, and $\alpha = \beta = \gamma = 90^o$, the reciprocal lattice vectors are $\mathbf{b_1} = \frac{2\pi}{a_1} \,\hat{\mathbf{x}}$, $\mathbf{b_2} = \frac{2\pi}{a_2} \,\hat{\mathbf{y}}$ and $\mathbf{b_3} = \frac{2\pi}{a_3} \,\hat{\mathbf{z}}$ which form an orthorhombic reciprocal lattice [78].

2.3 Crystal Vibrations

To analyze the motion or vibration of atoms in a crystal, we begin with a simple one-dimensional (1D) linear chain of equally spaced identical atoms, with one atom in every unitcell. The boundary of the unitcell is denoted by the dashed lines as shown in Figure 2.1. Assuming that all atoms behave as a harmonic oscillator where the elastic response of the crystal is a linear function of forces, the total force on any atom *s* can be calculated as

$$F_{s} = K(u_{s+1} - u_{s}) + K(u_{s-1} - u_{s})$$
(8)

where *K* is the spring constant (also referred to as the second order force constant) and u_s represents the displacement of the s^{th} atom. The equation of motion for s^{th} atom can be written as

$$M\frac{d^{2}\boldsymbol{u}_{s}}{dt^{2}} = K(\boldsymbol{u}_{s+1} + \boldsymbol{u}_{s-1} - 2\boldsymbol{u}_{s})$$
(9)

where *M* is the mass of the atom. This is a differential equation of the form $\frac{d^2 u_s}{dt^2} = -\omega^2 u_s$, where ω is the harmonic oscillation frequency. This differential equation has a traveling wave solutions of the form [78]

$$\boldsymbol{u}_{s+1} = \boldsymbol{u} \, e^{iska} \, e^{\pm ika} \tag{10}$$

where **u** is the atomic displacement having time dependence $e^{-i\omega t}$, *a* is the inter-atomic spacing and **k** is the wavevector. Substituting Eq. (10) into Eq. (9), we obtain the dispersion relation $\omega(\mathbf{k})$

$$\omega^{2} = \frac{2K}{M} (1 - \cos \mathbf{k}a) = \frac{4K}{M} \sin^{2} \frac{1}{2} \mathbf{k}a$$
(11)

For simplicity, assuming K = M = a = 1, the plot of dispersion relation is shown in Figure 2.2.



Figure 2.1 Schematic of a one-dimensional linear chain of equally spaced identical atoms behaving as harmonic oscillators. The stiffness of the spring represents the second derivative of the interatomic interaction energy (force constant K) that determines the oscillation frequency. The dashed line represents the boundary of unitcell boundary.



Figure 2.2 Dispersion relation for a linear chain of equally spaced identical atoms shown in Figure 2.1, assuming unit mass (M), force constant (K) and interatomic spacing (a).

2.3.1 Group Velocity

The transmission velocity of a wave packet is called the group velocity (v_g) which is obtained from the dispersion relation as

$$\boldsymbol{v}_{\boldsymbol{g}} = \frac{d\omega}{d\boldsymbol{k}} \tag{12}$$

This represents the velocity at which the vibrational energy of the wave packet travels in the material. For the 1D chain of equally spaced identical atoms, the group velocity is

$$\boldsymbol{\nu}_{\boldsymbol{g}} = \left(\frac{Ka^2}{M}\right)^{0.5} \cos\frac{1}{2}\boldsymbol{k}a \tag{13}$$

The group velocity is zero at $\mathbf{k} = \frac{\pi}{a}$, i.e., we have a standing wave at the edge of the Brillouin zone and the only mechanism for the transmission of vibrational energy is via interaction of these lattice waves with other lattice waves (scattering of lattice waves or phonons is discussed in detail in Chapter 4).

2.4 Phonons

The energy of the lattice vibrations contained in wave packets is quantized and the quantum of energy is called a phonon. The energy of a vibrational mode with frequency ω is given by

$$E_{\omega} = \left(n_{\omega} + \frac{1}{2}\right)\hbar\omega \tag{14}$$

where \hbar is the reduced Planck's constant, $\hbar\omega$ is the energy of a single phonon, n_{ω} is the number of phonons that occupy the energy level $\hbar\omega$, and $\frac{1}{2}\hbar\omega$ is the zero point

energy which is the lowest possible energy that a quantum mechanical system may have. A crystalline material consisting of N atoms has a total of 3N degrees of freedom which result in a total of 3N vibrational modes or phonon modes. In real materials, N is a very large number ($\sim 10^{23}$) and the calculation of physical properties such as thermal conductivity requires integrating the material properties over the entire real space $(0 \rightarrow \infty)$. For the purpose of computation, instead of calculating the physical properties in the real space, the properties can be calculated in the reciprocal space by simulating only a single unitcell with a large number of wavevectors sampled throughout the Brillouin zone. The advantage of using the reciprocal space for calculations is that it reduces the limit over which the integral is calculated, for instance, the same integral from zero to infinity in real space can be transformed into an integral from zero to $\frac{\pi}{a_1}$ in the reciprocal space. If the unitcell contains n atoms, it results in a total of 3n phonon branches, and the total number of phonon modes is equal to $3n \times n_k$ where n_k is the number of wavevectors. Thus, every phonon mode in the system can be identified uniquely with a phonon branch number (1 to 3n) and a wavevector (1 to n_k). In this work, we use the symbol ϕ to index the phonon modes, where $\phi \in (n_k, 3n)$.

2.4.1 Phonon Specific Heat

In this Section, we discuss the computational details for the contribution of the phonon modes to the lattice specific heat. The heat capacity at constant volume is defined as $C = \left(\frac{\partial U}{\partial T}\right)_V$ where the U is the total internal energy defined as $U = U_{static} + U_{phonon}$ and T is the temperature. U_{static} accounts for the energy due to two-body, three-body, four-body, etc. interactions defined as $U_{static} = \sum_{i=1}^{N} U_i + U_{static}$

 $\frac{1}{2}\sum_{i=1}^{N}\sum_{i=1}^{N}U_{i,j} + \sum_{i=1}^{N}\sum_{i=1}^{N}\sum_{i=1}^{N}U_{i,j,k} + \cdots$, and is independent of temperature. The contribution of the phonons to the internal energy can be obtained by summing the energy of all phonons in the crystal which is given by

$$U_{phonon} = \sum_{\phi} E_{\phi} = \sum_{\phi} n_{\phi} \hbar \omega_{\phi}$$
(15)

where n_{ϕ} is the equilibrium occupancy of the phonon mode ϕ , and ω_{ϕ} is the phonon mode frequency. To derive the expression for n_{ϕ} , we consider a set of identical harmonic oscillators in thermal equilibrium where the ratio of the number of oscillators in the $(n + 1)^{\text{th}}$ state to the n^{th} state is given by $\frac{N_{n+1}}{N_n} = e^{-\frac{\hbar\omega}{K_bT}}$, where K_b is the Boltzmann constant, and N_n is the number of oscillators in the n^{th} quantum state. The fraction of oscillators in the n^{th} state can be calculated as

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{e^{-\frac{n\hbar\omega}{K_bT}}}{\sum_{s=0}^{\infty} e^{-\frac{s\hbar\omega}{K_bT}}}$$
(16)

Using Eq. (16), the average/expected number of oscillators at energy level $\hbar\omega$ can be calculated as

$$\langle n_{\hbar\omega} \rangle = \frac{\sum_{s} s \, e^{-\frac{s\hbar\omega}{K_b T}}}{\sum_{s} e^{-\frac{s\hbar\omega}{K_b T}}} \tag{17}$$

The expression in Eq. (17) is of the form $\frac{\sum_{s} s x^{s}}{\sum_{s} x^{s}} = \frac{\frac{x}{(1-x)^{2}}}{\frac{1}{(1-x)}}$ and can be rewritten to obtain

the phonon occupation of mode ϕ with energy $\hbar \omega_{\phi}$ as

$$\langle n_{\hbar\omega_{\phi}} \rangle = n_{\phi} = \frac{1}{e^{\frac{\hbar\omega_{\phi}}{K_bT}} - 1}$$
(18)

The phonon occupation calculated in Eq. (18) is also called Bose-Einstein (BE) statistics or BE distribution or Planck's distribution. A plot of phonon mode occupation with respect to phonon mode frequency at T = 300 K is shown in Figure 2.3. Substituting Eq. (18) into Eq. (15)

$$U_{phonon} = \sum_{\phi} \hbar \omega_{\phi} \frac{1}{e^{\frac{\hbar \omega_{\phi}}{K_b T}} - 1}$$
(19)

In real materials, on continuum scale, with over 10^{23} atoms and therefore an almost infinite number of phonon modes, the summation in Eq. (19) can be written as an integral. If the system has $D(\omega_{\phi}) d\omega$ modes in the frequency range ω_{ϕ} to $\omega_{\phi} + d\omega$, the phonon energy can be written as

$$U_{phonon} = \int_{\phi} D(\omega_{\phi}) \frac{\hbar \omega_{\phi}}{e^{\frac{\hbar \omega_{\phi}}{K_b T}} - 1} d\omega$$
(20)

where the integral is over all phonon modes throughout the Brillouin zone. The function $D(\omega_{\phi})$ is called the density of modes or density of states (DOS). Differentiating Eq. (20) with respect to temperature, the phonon specific heat $C_V = \frac{c}{V}$ is given by

$$C_V = \frac{K_b}{V} \int_{\phi} D(\omega_{\phi}) \frac{x^2 e^x}{(e^x - 1)^2} d\omega$$
(21)

where $x = \frac{\hbar \omega_{\phi}}{K_b T}$, and *V* is the material volume. For the purpose of computer simulation where the length scales are small and the wavevectors can be represented as discrete points, the phonon specific heat is calculated as a sum over all modes

$$C_V = \frac{K_b}{V} \sum_{\phi} \frac{x^2 e^x}{(e^x - 1)^2}$$
(22)

The contribution of any mode ϕ to the lattice specific heat can be calculated as

$$C_{V\phi} = \frac{K_b}{V} \left(\frac{\hbar\omega_{\phi}}{K_b T}\right)^2 \frac{e^{\frac{\hbar\omega_{\phi}}{K_b T}}}{\left[e^{\frac{\hbar\omega_{\phi}}{K_b T}} - 1\right]^2}$$
(23)



Figure 2.3 Phonon mode occupation vs frequency calculated using Bose-Einstein statistics at T = 300 K. The phonon occupation decreases exponentially as the phonon mode frequency increases. A small phonon occupation is one of the factors for the relatively small contribution of the high frequency modes to the phonon specific heat, scattering rates and lattice thermal conductivity as discussed in the later chapters.

2.4.2 Crystal Anharmonicity

The theory of lattice vibrations discussed so far considers only up to the harmonic term of the crystal Hamiltonian. The harmonic theory is limited to the terms quadratic in the interatomic displacements and is unable to explain phenomena such as thermal expansion, interaction between lattice waves, finite lattice thermal conductivity, etc. [78]. The higher order terms in the Hamiltonian, also called the anharmonic terms, must be considered to accurately depict the interatomic interactions and explain the above phenomena [79].

Due to the crystal anharmonicity and anharmonic interaction between the phonon modes in the system, the crystal has a finite thermal conductivity. From the kinetic theory of gases [80], the scalar thermal conductivity of the material (κ) is calculated as [79, 77, 81, 82]

$$\kappa = \frac{1}{3} C_V \, \nu \, \Lambda \tag{24}$$

where v is the average particle velocity, Λ is the mean free path of the particle between collisions, and the scalar thermal conductivity is defined as $\kappa = \frac{\kappa_{xx} + \kappa_{yy} + \kappa_{zz}}{3}$, where κ_{xx} , κ_{yy} and κ_{zz} represent thermal conductivity along three crystallographic directions. Similarly, the contribution of phonons to the lattice thermal conductivity tensor can be written as [77, 79, 83]

$$\boldsymbol{\kappa} = \sum_{\boldsymbol{\phi}} C_{V\boldsymbol{\phi}} \, \boldsymbol{\nu}_{\boldsymbol{g}\boldsymbol{\phi}} \, \boldsymbol{\Lambda}_{\boldsymbol{\phi}} \tag{25}$$

where $C_{V\phi}$ is the phonon mode specific heat, $v_{g\phi}$ is the phonon mode group velocity and Λ_{ϕ} is the mean free path of a phonon ϕ between collisions. The expression in Eq. (25) is also called the Phonon Gas Model (PGM) and is one of the prevalent models for estimating lattice thermal conductivity in simple crystals like Si, Ge etc. [84, 85, 86, 87, 88, 89, 83]. The phonon mean free path is determined by scattering of the phonon with other phonons, crystal boundaries, isotopes, electrons etc. The details of phononphonon scattering is discussed in Chapter 4.

2.5 RDX Crystal Structure

Cyclotrimethylenetrinitramine ($C_3H_6N_6O_6$, also commonly known as RDX) is an organic compound which has high energy density and low sensitivity to external stimuli, making it suitable for use in various military and industrial applications as a secondary explosive (SE). A single RDX molecule contains 21 atoms (3 Carbon atoms, and 6 atoms of Hydrogen, Nitrogen and Oxygen each) shown in Figure 2.4, and under ambient conditions, RDX exists in a crystalline α phase [90]. The α phase RDX exhibits an orthorhombic *Pbca* crystal structure (lattice parameters $a_1 \neq a_2 \neq a_3$, $\alpha =$ $\beta = \gamma = 90^\circ$) and a single unitcell contains 8 RDX molecules resulting in a total of $21 \times 8 = 168$ atoms in the unitcell [91] shown in Figure 2.5. This results in a total of $3 \times 168 = 504$ phonon branches, which is one to two orders of magnitude larger than most simple crystals [92, 87, 93, 94, 95, 96, 97, 98, 99].

At zero Kelvin, the total energy of a group of atoms or molecules comprises of two-body, three-body, etc. interactions between the atoms (U_{static}) as shown in Eq. (26). In real materials, the atoms and molecules arrange themselves such that the total energy of the system is minimized. This is referred to as the equilibrium structure of the material. The zero Kelvin equilibrium structure of RDX is obtained by minimizing the internal energy using a quantum-chemistry based flexible molecule force field developed by Smith et al. [100, 90, 101]. The estimated equilibrium lattice parameters and components of energy in RDX after energy minimization using a uniform $8 \times 8 \times 8$ k-points mesh are shown in Table 2.1 and Table 2.2. The fractional atomic coordinates (fraction of the lattice parameters) of the atoms in the first molecule of

RDX unitcell are shown in Table 2.3. The calculation details of the minimum free energy structure of RDX at finite chapter are discussed in Chapter 3.



Figure 2.4 A single molecule of RDX containing 3 Carbon atoms and 6 atoms of Hydrogen, Nitrogen and Oxygen each (C₃H₆N₆O₆).



Figure 2.5 α RDX unitcell (orthorhombic, $a_1 \neq a_2 \neq a_3$, $\alpha = \beta = \gamma = 90^{\circ}$) containing 8 RDX molecules and therefore 168 atoms in the unitcell. This results in a total of 3 × 168 = 504 phonon branches.

a ₁ (Ang)	a ₂ (Ang)	a ₃ (Ang)	α (deg)	β (deg)	γ (deg)	Volume (Ang ³)
13.010441	11.423369	10.569626	90	90	90	1570.890390

Table 2.1 Estimated lattice parameters of RDX unitcell at 0 K after minimizing internal energy using a quantum chemistry based flexible molecule force field [100].

Interatomic potential	3-body	4-body	Monopole-	Total lattice
	potential	potentials	Monopole	energy
-4.18064574	24.04555906	4.09723264	77.96051924	101.92266520

Table 2.2 Components of energy after internal energy minimization of RDX unitcell at 0 K using a uniform $8 \times 8 \times 8$ k-points mesh (units of eV).

Atom No.		Atom Type	Fractional Atomic Coordinates			
			х	у	Z	
	1	С	0.183902	0.357802	0.440004	
	2	С	0.059865	0.226658	0.329309	
	3	С	0.155945	0.370542	0.206586	
	4	Ν	0.179568	0.430357	0.325849	
	5	Ν	0.093932	0.281029	0.447739	

6	Ν	0.059001	0.307043	0.221144
7	Ν	0.242148	0.530872	0.321648
8	Ν	0.017448	0.308799	0.53719
9	Ν	0.971619	0.379902	0.215169
10	0	0.253285	0.579796	0.218516
11	0	0.279624	0.565224	0.422152
12	0	0.935925	0.254066	0.532099
13	0	0.03896	0.379523	0.621304
14	0	0.892706	0.346637	0.268831
15	0	0.977736	0.46939	0.150427
16	Н	0.251075	0.300406	0.433688
17	Н	0.192807	0.411553	0.525067
18	Н	0.986859	0.179579	0.339157
19	Н	0.117085	0.160237	0.307561
20	Н	0.216611	0.306396	0.187648
21	Н	0.152888	0.430016	0.125177

Table 2.3 Fractional atomic coordinates (fraction of lattice parameter) of atoms in the first molecule of RDX unitcell obtained after internal energy minimization using uniform $8 \times 8 \times 8$ k-points mesh.

Chapter 3: Harmonic Phonon Properties and Bond Distortion Behaviors in RDX²

The harmonic properties of phonon modes such as frequencies or eigenvalues (ω_{ϕ}) , eigenvectors (e_{ϕ}) , group velocities $(v_{g\phi})$, occupation (n_{ϕ}) , specific heat $(C_{V\phi})$ are essential ingredients for determining the vibrational energy stored in the modes, the rate of transmission of vibrational energy, contribution of the modes to the stretching and rotation of bonds etc. The computational details and estimates of harmonic phonon properties in RDX are discussed in this chapter.

3.1 Minimum Energy Structure

At finite temperature, in addition to U_{static} as shown in Eq. (26), the total energy of the system also comprises of the energy due to vibrations of the atoms and molecules (U_{vib}) as shown in Eq. (27). In this section, we discuss the computational details for calculating the minimum energy structure for RDX.

Using the minimum energy equilibrium structure of RDX calculated at zero Kelvin in Section 2.5 as the initial configuration, the crystal structure of RDX at finite temperature is then calculated using the open source package GULP [102] which minimizes the Helmholtz free energy $A = U_{static} + U_{vib} - TS_{vib}$ under the quasi-

² Portions of this Chapter appear in G. Kumar, F. G. VanGessel, P. W. Chung, "Bond Strain and Rotation Behaviors of Anharmonic Thermal Carriers in α -RDX", *Propellants, Explosives, Pyrotechnics*, vol. 45, 2019, p. 169-176. [74]

harmonic approximation (Quasi-Harmonic Lattice Dynamics or QHLD), which assumes that the vibrational frequencies can be determined as if the atoms are vibrating harmonically while the lattice parameters are adjusted to minimize the free energy [103]. Here U_{static} is the static internal energy that would be calculated in a conventional energy minimization, U_{vib} is the vibrational energy, *T* is the temperature and, S_{vib} is the vibrational entropy defined as follows:

$$U_{static} = \sum_{i=1}^{N} U_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{i=1}^{N} U_{i,j} + \sum_{i=1}^{N} \sum_{i=1}^{N} \sum_{i=1}^{N} U_{i,j,k} + \cdots$$
(26)

$$U_{vib} = \sum_{\phi} \left(n_{\phi} + \frac{1}{2} \right) \hbar \omega_{\phi} \tag{27}$$

$$S_{vib} = R \ln Z_{vib} + RT \left(\frac{\partial \ln Z_{vib}}{\partial T}\right)$$
(28)

$$Z_{vib} = \sum_{\phi} \left(1 - e^{-\frac{\hbar\omega_{\phi}}{K_b T}} \right)^{-1}$$
(29)

Here Z_{vib} is the vibrational partition function, $R = 8.314 J \cdot mol^{-1} \cdot K^{-1}$ is the universal gas constant. The first term in Eq. (26) represents the self-energies of the atoms, the second term represents the pairwise interactions and so on.

The free energy minimization calculation is performed for a single RDX unitcell and a uniform $6 \times 6 \times 6 = 216$ k-points mesh (wavevectors) resulting in a total of $504 \times 216 = 32,256$ phonon modes. The temperature dependence of the lattice parameters is shown in Figure 3.1. The lattice parameters calculated in this work are in good agreement with the experimental values reported in [104, 105]. For instance, the estimated lattice parameters are within 0.3% of the experimental values

reported by Sun et al. [104]. The finite temperature phonon mode frequencies (ω_{ϕ}) and eigenvectors (e_{ϕ}) are also determined using GULP. The temperature dependence of

the RMS value of phonon mode frequencies calculated as $\omega^{RMS} = \sqrt{\frac{\sum_{\phi} \omega_{\phi}^2}{no.of \ modes}}$ is shown in Figure 3.2 indicating phonon softening (decrease in phonon frequencies due to a decrease in harmonic force constants) as the temperature increases. The phonon density of states for the modes in RDX at 300 K is shown in Figure 3.3. The phonon dispersion for all 504 branches in RDX from wavevector $\Gamma(0, 0, 0)$ to X(0.5, 0, 0) is shown in Figure 3.4 and the phonon dispersion surface $\omega(\mathbf{k}_x, \mathbf{k}_y)$ for first three phonon branches (acoustic branches) are shown in Figure 3.5, Figure 3.6. and Figure 3.7 respectively. A large density of states is observed in the dispersion curve at low frequencies indicating a large number of thermal carriers and possibly a substantial contribution of these low frequency modes to the thermal transport in RDX. The density of states is also important to consider while investigating the anharmonic interaction between the phonon modes as discussed in Chapter 4. The six elastic constants in RDX at 300 K are shown in Table 3.1. The results are in good agreement with the experimental values [106, 107] indicating the accuracy of the force field [100] to capture the harmonic interactions in RDX.

The *x*, *y*, *z* components of the phonon mode group velocities $\left(v_{g\phi} = \frac{d\omega_{\phi}}{dk}\right)$ are calculated using the following central differencing scheme:

$$\boldsymbol{v}_{g\phi,x} = \frac{d\omega_{\phi}}{d\boldsymbol{k}_{x}} = \frac{\omega_{\phi}(\boldsymbol{k}_{x} + \Delta \boldsymbol{k}, \boldsymbol{k}_{y}, \boldsymbol{k}_{z}) - \omega_{\phi}(\boldsymbol{k}_{x} - \Delta \boldsymbol{k}, \boldsymbol{k}_{y}, \boldsymbol{k}_{z})}{2\Delta \boldsymbol{k}}$$
(30)

$$\boldsymbol{v}_{g\phi,y} = \frac{d\omega_{\phi}}{d\boldsymbol{k}_{y}} = \frac{\omega_{\phi}(\boldsymbol{k}_{x}, \boldsymbol{k}_{y} + \Delta \boldsymbol{k}, \boldsymbol{k}_{z}) - \omega_{\phi}(\boldsymbol{k}_{x}, \boldsymbol{k}_{y} - \Delta \boldsymbol{k}, \boldsymbol{k}_{z})}{2\Delta \boldsymbol{k}}$$
(31)

$$\boldsymbol{v}_{g\phi,z} = \frac{d\omega_{\phi}}{d\boldsymbol{k}_{z}} = \frac{\omega_{\phi}(\boldsymbol{k}_{x}, \boldsymbol{k}_{y}, \boldsymbol{k}_{z} + \Delta \boldsymbol{k}) - \omega_{\phi}(\boldsymbol{k}_{x}, \boldsymbol{k}_{y}, \boldsymbol{k}_{z} - \Delta \boldsymbol{k})}{2\Delta \boldsymbol{k}}$$
(32)

where k_x , k_y and k_z are x, y and z components respectively of the wavevector k and Δk is a small perturbation. In terms of the fraction of the reciprocal lattice vector, $\Delta k = 10^{-3}$ is used in this work to calculate the group velocities (k = (0.5, 0.5, 0.5) refers to the edge of the Brillouin zone i.e. $(\frac{\pi}{a_1}, \frac{\pi}{a_2}, \frac{\pi}{a_3})$).



Figure 3.1. Temperature dependent lattice parameters in RDX calculated via Helmholtz free energy minimization in GULP. The results are in good agreement with the experimental values reported by Sun et al. [104] and Bolotina et al. [105]. For instance, the lattice parameters a_1 , a_2 , a_3 at 300 K calculated in this work are within 0.31%, 0.14% and 0.30% respectively, of the values reported by Sun et al. at 303 K.



Figure 3.2 Temperature dependence of phonon mode frequencies (ω^{RMS}) in RDX calculated using QHLD. As temperature increases, the second order force constants become smaller resulting in lower phonon mode frequencies (phonon softening).



Figure 3.3 Phonon density of states in RDX at 300 K. The low and mid-frequency modes below $\sim 600 \text{ cm}^{-1}$ have very high density of states which serves to provide a large number of phonon-phonon scattering channels as discussed in later chapters. Large

gaps in DOS indicates the gaps in phonon dispersion spectrum which limits the anharmonic interaction between the phonons in these bands.



Figure 3.4. Phonon Dispersion in RDX for up to 90 THz from wavevector Γ (0, 0, 0) to *X*(0.5, 0, 0). Different colors represent different phonon branches. A large density of modes is observed at lower frequencies and large gaps are present between different phonon branches, especially at higher frequencies.



Figure 3.5. Phonon dispersion surface $\omega(\mathbf{k}_x, \mathbf{k}_y)$ for the first acoustic branch in RDX.



Figure 3.6. Phonon dispersion surface $\omega(k_x, k_y)$ for the second acoustic branch in RDX.



Figure 3.7. Phonon dispersion surface $\omega(\mathbf{k}_x, \mathbf{k}_y)$ for the third acoustic branch in RDX.

Elastic Constant	This Work	Schwarz et al.	Haussühl
	(QHLD)	[106]	[107]
C11	26.1772	25.6	25.02
C22	19.2293	21.3	19.6
C33	15.0926	19	17.93
C12	9.2284	8.67	8.21
C13	4.8718	5.72	5.81
C23	4.9028	6.4	5.9
C44	3.5585	5.38	5.17
C55	4.4851	4.27	4.07
C66	7.6271	7.27	6.91

Table 3.1 Comparison of elastic constants calculated using QHLD at 300 K with experimental values reported in [106, 107] (units of GPa).

3.2 Bond Strain and Rotation

As experimental and computational studies have shown that the fission of NN bonds is the primary initial step in the thermal decomposition of RDX [21, 28, 29, 35], in this Chapter, we use a harmonic oscillator-based model to investigate how different phonon modes in the system can result in stretching and rotation of all bonds and angles in RDX. The goal of this investigation is to identify the phonon modes that are responsible for the largest stretching of critical bonds such as NN, CN, etc. It should be noted that this model considers only the harmonic part of the crystal Hamiltonian and therefore is insufficient to describe the anharmonic phonon interactions and transfer of vibrational energy between the modes.

3.2.1 Calculation of Atomic Displacements and Bond Distortions

Within the harmonic approximation, atoms can be considered to oscillate about their equilibrium positions and the amplitude of their oscillations can be written as a sum of contributions from all phonon modes. We use the phonon mode energy, which is the sum of kinetic and potential energy contributions from individual oscillating atoms [108], mode shapes, and eigenvectors to determine the contribution of each mode to the strain and rotation of bonds, and change in bond angles in α -RDX. A schematic of bond stretching and rotation and change in bond angles is shown in Figure 3.8 and Figure 3.9.

The displacement of the b^{th} atom in the unit cell can be written as

$$\boldsymbol{u}_b(t) = \boldsymbol{U}_b \ \exp(-i\omega t) \tag{33}$$

where the amplitude of oscillation U_b can be calculated by summing the contribution from individual modes as

$$\boldsymbol{U}_{\boldsymbol{b}} = \sum_{\boldsymbol{\phi}} a_{\boldsymbol{\phi}, \boldsymbol{b}} \ \boldsymbol{e}_{\boldsymbol{\phi}, \boldsymbol{b}} \tag{34}$$

Here e_{ϕ} is the normalised eigenvector and $a_{\phi,b}$ is a scaling coefficient denoting the contribution of mode ϕ to the amplitude of oscillation and can be determined from the phonon mode energy as [108]

$$a_{\phi,b} = \sqrt{E_{\phi}/m_b \omega_{\phi}^2} \tag{35}$$

where m_b is the mass of the b^{th} atom and the energy of the mode is calculated as $E_{\phi} = n_{\phi} \hbar \omega_{\phi}$ where n_{ϕ} is the phonon mode occupation given by BE statistics. The displaced position of atoms can therefore be written as

$$\boldsymbol{r}_{b} = \boldsymbol{r}_{b}^{\boldsymbol{o}} + \sum_{\phi} \boldsymbol{U}_{\phi,b} \exp(-i\omega t)$$
(36)

where r_b^o is the equilibrium position of atom b and $U_{\phi,b} = a_{\phi,b} e_{\phi,b}$ is the amplitude of oscillation of atom b due to the excitation of phonon mode ϕ . The new position of atom b due to the vibrational mode φ can be written as $r_{b\phi} = r_b^o + U_{\phi,b} e^{-i\omega t}$. The distance between any two atoms b_1 and b_2 is $(r_{b_2} - r_{b_1})$. For each mode, the deformation of each bonded pair can be expressed as a combination of pure strain and pure rotation. We use percent strain, ϵ_p , to quantify the amount of bond strain, defined as

$$\epsilon_{p,\phi,b_2,b_1} = 100 \; \frac{|\boldsymbol{r}_{b_2\phi} - \boldsymbol{r}_{b_1\phi}|}{|\boldsymbol{r}_{b_2}^o - \boldsymbol{r}_{b_1}^o|} \tag{37}$$

The expression in Eq. (37) represents the contribution of phonon mode ϕ to the percent strain of the bond between the atoms b_1 and b_2 . The bond rotation is quantified by angle β between the final bond vector and equilibrium bond vector calculated as

$$\beta_{\phi, b_2, b_1} = \cos^{-1} \frac{\left(r_{b_2 \phi} - r_{b_1 \phi} \right) \cdot \left(r_{b_2}^o - r_{b_1}^o \right)}{\left| r_{b_2 \phi} - r_{b_1 \phi} \right| \left| r_{b_2}^o - r_{b_1}^o \right|}$$
(38)

The contribution of the mode ϕ to the change in bond angle between atoms b_1 , b_2 and b_3 ($\Delta \alpha_{\phi,b_1,b_2,b_3}$) is calculated as

$$\Delta \alpha_{\phi,b_{1},b_{2},b_{3}} = \cos^{-1} \frac{(r_{b_{3}\phi} - r_{b_{2}\phi}) \cdot (r_{b_{1}\phi} - r_{b_{2}\phi})}{|r_{b_{3}\phi} - r_{b_{2}\phi}| |r_{b_{1}\phi} - r_{b_{2}\phi}|} - \cos^{-1} \frac{(r_{b_{3}}^{o} - r_{b_{2}}^{o}) \cdot (r_{b_{1}}^{o} - r_{b_{2}}^{o})}{|r_{b_{3}}^{o} - r_{b_{2}}^{o}| |r_{b_{1}}^{o} - r_{b_{2}}^{o}|}$$
(39)

The percent change in bond angle is defined as $\Delta \alpha_{p,\phi,b_1,b_2,b_3} = 100 \times \frac{\Delta \alpha_{\phi,b_1,b_2,b_3}}{\alpha_{\phi,b_1,b_2,b_3}^0}$. The

change in dihedral angle between the planes formed by atoms b_1, b_2, b_3 and atoms b_2, b_3, b_4 ($\Delta \Phi_{\phi, b_1, b_2, b_3, b_4}$) is calculated as

$$\Delta \Phi_{\phi,b_1,b_2,b_3,b_4} = \cos^{-1} \frac{(r_{b_1\phi} - r_{b_2\phi}) \times (r_{b_3\phi} - r_{b_2\phi}) \cdot (r_{b_2\phi} - r_{b_3\phi}) \times (r_{b_4\phi} - r_{b_3\phi})}{|r_{b_1\phi} - r_{b_2\phi}| |r_{b_3\phi} - r_{b_2\phi}| |r_{b_2\phi} - r_{b_3\phi}| |r_{b_4\phi} - r_{b_3\phi}|}$$
(40)
$$- \cos^{-1} \frac{(r_{b_1}^o - r_{b_2}^o) \times (r_{b_3}^o - r_{b_2}^o) \cdot (r_{b_2}^o - r_{b_3}^o) \times (r_{b_4}^o - r_{b_3}^o)}{|r_{b_1}^o - r_{b_2}^o| |r_{b_3}^o - r_{b_2}^o| |r_{b_2}^o - r_{b_3}^o| |r_{b_4}^o - r_{b_3}^o|}$$

The percent change in dihedral angle is defined as $\Delta \Phi_{p,\phi,b_1,b_2,b_3,b_4} = 100 \times \frac{\Delta \Phi_{\phi,b_1,b_2,b_3,b_4}}{\Phi_{\phi,b_1,b_2,b_3,b_4}^0}$. The change in improper angle between the planes formed by atoms

 b_1, b_2, b_3 and atoms b_2, b_3, b_4 ($\Delta \Phi_{im,\phi,b_1,b_2,b_3,b_4}$) is calculated in the same way as Eq. (40), however the indexing/position of atoms is different as shown in Figure 3.9.

There are 168 bonded pairs, 288 bond angles, 528 dihedral angles, 48 imporper angles in a RDX unitcell. The relative importance of phonon modes to the stretching and rotation of bonds and bond angles is estimated by calculating the root mean square values as

$$\epsilon_{p,\phi,rms} = \sqrt{\frac{\sum_{i=1}^{168} \epsilon_{p,\phi,i}^2}{168}}$$
(41)

$$\beta_{\phi,rms} = \sqrt{\frac{\sum_{i=1}^{168} \beta_{\phi,i}^2}{168}}$$
(42)

$$\Delta \alpha_{p,\phi,rms} = \sqrt{\frac{\sum_{i=1}^{288} \Delta \alpha_{p,\phi,i}^2}{288}}$$
(43)

$$\Delta \Phi_{p,\phi,rms} = \sqrt{\frac{\sum_{i=1}^{528} \Delta \Phi_{p,\phi,i}^2}{528}}$$
(44)

$$\Delta \Phi_{p,im,\phi,rms} = \sqrt{\frac{\sum_{i=1}^{48} \Delta \Phi_{p,im,\phi,i}}{48}}$$
(45)

To build an intuition for the way in which different modes distort the crystal, the normalized atomic displacements (largest atomic displacement = 1, represented by the color red and the smallest atomic displacement in the unitcell is represented by the color blue) for a few modes are shown in Figure 3.10. For ease in discussing the results, the spectrum is divided into twenty frequency bands, as shown in Table 3.2. The frequency ranges of the bands are defined roughly based on groupings of modes in contiguous ranges of the spectrum according to the way in which those modes distort the crystal as reported in experimental literature [61, 109, 110, 111, 112, 113, 114]. It should be noted that as a result of this approach to parsing the frequency bands, the number of phonon modes in different bands are unequal, depending on the density of states and the frequency range of individual bands.



Figure 3.8. Schematic of bond stretch, bond rotation and change in bond angle. The spheres represent the atoms and sticks represent the bonds. Translucent spheres and sticks represent the displaced position of atoms and bonds.



Figure 3.9. Schematic of change in dihedral angle and change in improper angle. The surfaces represent the planes formed by three atoms and the dihedral/improper angle is measured as the angle between two planes.



Figure 3.10. Normalized displacement of atoms in a single molecule of RDX at (left to right, top to bottom) 17.91 cm⁻¹, 98.24 cm⁻¹, 381.96 cm⁻¹, 592.61 cm⁻¹, 656.11 cm⁻¹, 731.0964 cm⁻¹, 1537.61 cm⁻¹, 2482.92 cm⁻¹ (largest atomic displacement = 1, represented by the color red and the smallest atomic displacement in the unitcell is represented by the color blue).

Bands	Frequency range (cm ⁻¹)	Mode assignment	Reference
1	0 to 50	Translation	-
2	50 to 77	w(all)NO2	[109]
3	77 to 102	ro(all)NO ₂	[109]
4	102 to 192	$ro(all)NO_2 + {}^{b}Molecular + {}^{u(eq)}N-NC_2$	[109]

5	217 to 324	ro(all)NO ₂ + $ro+t$ Ring	[109]
6	370 to 373	^{u(ax)} N-NC ₂	[109]
7	401 to 424	^{b(fo)} Ring	[61, 109, 110]
8	457 to 462	st(ax)N-N + ^{b(fo)} Ring	[61, 109, 110]
9	500 to 618	^{b+t+rc} Ring	[61, 109, 110]
10	786 to 791	${}^{st}C-N + {}^{sc(eq)}NO_2$	[109]
11	821 to 842	$^{st}N-N + ^{sc(ax)}NO_2$	[61, 109]
12	859 to 865	$^{st(ax)}$ N-N + st C-N	[61, 109, 110]
13	881 to 887	$^{st}N-N + ^{st}C-N + ^{rc}CH_2$	[61, 109]
14	912 to 925	$^{st(eq)}N-N + \ ^{rc}CH_2$	[61, 109, 110]
15	1121 to 1244	t+rcCH2	[109, 110, 111]
16	1298 to 1331	$st(eq, ax)$ N-N + tCH_2	[109, 110]
17	1475 to 1490	^b CH ₂	[110, 112]
18	1400 to 1554	st(as)NO ₂	[110, 112, 113, 111,
10	1490 to 1334		114]
19	1736 to 2103	-	
20	2824 to 2910	st(as)CH2	[110, 112, 113, 111]

Table 3.2 Frequency range of twenty phonon bands, and corresponding mode assignments. Superscripts: w= wag, ro= rotation, b= bending, u= umbrella, st= stretching, t= twist, sc= scissoring, rc= rocking, ax=axial, eq= equatorial, fo=folding, as=asymmetric.³

³ This table appears in the preprint: G. Kumar, F. G. VanGessel, L. B. Munday, P. W. Chung, "3-phonon scattering pathways for vibrational energy transfer in crystalline RDX", *J. Phys. Chem. A*, 2021 [76]

3.2.2 Modewise Bond Distortions

The modewise $\epsilon_{p,\phi,rms}$, $\beta_{\phi,rms}$, $\Delta \alpha_{p,\phi,rms}$, $\Delta \Phi_{p,\phi,rms}$ and $\Delta \Phi_{p,im,\phi,rms}$ are plotted in Figure 3.11, Figure 3.12, Figure 3.13, Figure 3.14, and Figure 3.15 respectively. The low frequency modes (< 133 cm⁻¹ or 4 THz) exhibit the largest contribution to the stretching and rotation of bonds and change in bond angles in RDX. The contribution of the mid-frequency and high frequency modes to the distortion of bonds and bond angles is one to three orders of magnitude lower, except the midfrequency modes ~500 cm⁻¹, which correspond to the bending, twisting and rocking of the ring, contribute significantly to the percent change in improper angles. In the distortion of every bond, $\sim 90\%$ of the bond strain and $\sim 60\%$ of the bond rotation is due to the low frequency modes up to ~4 THz. The largest bond strain is experienced by the N-N bonds and the smallest by the C-N bonds. In general, the largest to smallest strains (ϵ_p) are N - N > N - 0 > C - H > C - N. An identical trend is observed for the magnitude of bond rotation (β) as well. On averaging over all modes, bond strains in N-N are ~40% more than N-O, 65% more than C-N, ~400% more than C-H bonds. The largest N - N and N - O bond strains as well as rotations occur at frequencies of 0.63 THz (21 cm⁻¹) and 0.48 THz (16 cm⁻¹) respectively. The large strain and rotation of both N - N and N - O bonds result from a relatively larger displacement of the nitrogen atom in the nitro group $(-NO_2)$. The percent change in bond angle is the largest for the N-N-C bond angle followed by O-N-N, H-C-H, O-N-O, N-C-N and C-N-C bond angles. On averaging over all modes, bond angle distortion in NNC is 25% more than ONN, 66% more than HCH, 84% more than ONO, 120% more than NCN, 230% more than CNC bond angles. The largest N-N-C and O-N-N bond angle

deformation are observed at 0.63 THz and 0.48 THz respectively. Similarly, the dihedral angles corresponding to the torsion of the N-N bonds, on average, exhibited the largest percent change, ~122% more than the dihedral angle corresponding to the torsion of the C-N bond. The largest change in dihedral angle corresponding to the torsion of both N-N and C-N bonds occur at 0.48 THz. The percent change in improper angle is also observed to be the largest for the N-N-O-O atoms, which on average is observed to be ~200% more than the improper angle formed by N-N-C-C atoms. The largest distortion of N-N-O-O and N-N-C-C improper angles occur at 17.2 THz (573.7 cm⁻¹) and 0.67 THz (22.3 cm⁻¹) respectively.

3.2.3 Contribution of the Low Frequency Modes

Averaged over all bonded pairs in RDX unitcell, the low frequency modes up to 4 THz are estimated to contribute 67 to 98% to the bond strain (94% when averaged over all bonded pairs). On average, these low frequency modes contribute 97% to N-N, 95% to N-O, 87% to C-N and 99% to C-H bond strain. The same low frequency modes are estimated to contribute 30 to 98% to bond angle deformation (70% when averaged over all bond angles in RDX unitcell). On average, these low frequency modes contribute 60 % to ONO, 70% to ONN, 83% to NNC, 60% to NCN, 71% to NCH, 72% to HCH, and 62% to CNC bond angle deformation. These low frequency modes contribute 35 to 99% to the distortion of dihedral angles and 30 to 98% to the distortion of improper angles in RDX. On average, these low frequency modes contribute 97% to the N-N torsion, 65% to the C-N torsion, 80% to the distortion of N-N-C-C improper and 72% to the distortion of N-N-O-O improper angles.

The significance of the low frequency modes and their contributions to the distortion of bonds and bond angles will be discussed in further detail in Chapter 5 where we discuss the contribution of all modes to heat transport in RDX.



Figure 3.11. RMS value of percent bond strain ($\epsilon_{p,\phi,rms}$) vs frequency for all 504 phonon branches in RDX. The lowest frequency modes are estimated to contribute the most to the stretching of bonds in RDX.


Figure 3.12. RMS value of bond rotation angle $(\beta_{\phi,rms})$ vs frequency for all 504 phonon branches in RDX. The lowest frequency modes are estimated to contribute the most to the rotation of bonds in RDX.



Figure 3.13. RMS value of percent change in bond angle $(\Delta \alpha_{p,\phi,rms})$ vs frequency for all 504 phonon branches in RDX. The lowest frequency modes are estimated to contribute the most to the change in bond angles in RDX.



Figure 3.14. RMS value of percent change in dihedral angle $(\Delta \Phi_{p,\phi,rms})$ vs frequency for all 504 phonon branches in RDX. The lowest frequency modes are estimated to contribute the most to the change in dihedral angles (torsion) in RDX.



Figure 3.15. RMS value of percent change in improper angle $(\Delta \Phi_{p,im,\phi,rms})$ vs frequency for all 504 phonon branches in RDX. The lowest frequency modes are estimated to contribute the most to the change in improper angles in RDX.

Chapter 4: Phonon Scattering Rates and Lifetimes⁴

The nature of thermal transport in simple crystalline materials is well understood using the Phonon Gas Model (PGM) [79, 82, 83, 81] which treats phonons as quasi-particles carrying energy $\hbar\omega$ and their transport is modeled in a manner similar to gases [80]. In addition to the harmonic properties, the calculation of thermal conductivity requires knowledge of anharmonic phonon properties (phonon scattering rates and lifetimes) over the entire Brillouin zone. Theoretical calculations of phonon lifetimes date back to the work by Callaway [115], Holland [116], Klemens [117], and Slack [118] who postulated analytical models for phonon dispersion and lifetimes. These models contain parameters that are often obtained by fitting the Boltzmann Transport Equation (BTE) solution to experimental thermal conductivity values and therefore lack a predictive capability. Computational techniques which can capture the anharmonic interaction between the phonon modes and provide an accurate estimate of phonon-phonon scattering rates and lifetimes are, therefore, needed. In this Chapter, we investigate two different techniques for calculating the anharmonic phonon-phonon scattering rates and lifetimes: 1) A quantum mechanical model based on the perturbation theory, also known as Fermi's Golden Rule (FGR), and 2) A lattice

⁴ Portions of this Chapter appear in F. G. VanGessel, G. Kumar, D. C. Elton and P. W. Chung, "A Phonon Boltzmann Study of Microscale Thermal Transport in α-RDX Cook-Off,", *Proceedings of 16th International Detonation Symposium*, 2018. AND

G. Kumar, F. G. VanGessel, L. B. Munday and P. W. Chung, "3-phonon scattering pathways for vibrational energy transfer in crystalline RDX", *J. Phys. Chem. A*, 2021.

dynamics based Normal Mode Decomposition (NMD) method. Fermi's Golden Rule is a fully quantum mechanical theory that provides an estimate for the probability of transition from an initial quantum state i to a final quantum state f. This transition probability is used to calculate the 3-phonon scattering rates and phonon lifetimes. In contrast, the NMD technique models the fluctuations in phonon population, the ingredients for which are obtained from a classical Molecular Dynamics (MD) simulation. Although, only the first order anharmonic term of the Hamiltonian is used in the FGR technique and the MD captures all higher order crystal anharmonicities, however, the FGR technique can provide a lot more detailed picture of the vibrational energy transfer between the phonon modes. The results of this study were published in [75, 73, 74] and some of the results are currently under review for publication [76].

4.1 Fermi's Golden Rule

The crystal Hamiltonian can be written as

$$H = H_0 + H_3 + H_4 \dots (46)$$

where H_0 is the harmonic term, H_3 and H_4 are anharmonic terms also referred to as first and second order perturbation terms, respectively. If the Hamiltonian was purely harmonic i.e., all the anharmonic terms such as H_3 , H_4 etc. were zero, then the lattice waves or phonons in the material would never interact with one another. However, due to the presence of anharmonicity, the phonons interact with each other and during these processes referred to as phonon-phonon scattering, existing phonons can be annihilated, and new phonons get created. A schematic of 3-phonon scattering (a scattering process involving 3 phonon modes, say modes ϕ_1, ϕ_2 and ϕ_3) is shown in Figure 4.1. The probability of creation and annihilation of phonons during scattering can be calculated using a quantum mechanical theory called the perturbation theory. In this work, we only consider up to the first order perturbation term of the Hamiltonian. The first order perturbation term H_3 is defined as [119, 120]

$$H_3 = H_{\phi_1,\phi_2,\phi_3}^{(3)} (a_{-\phi_1}^{\dagger} + a_{\phi_1}) (a_{-\phi_2}^{\dagger} + a_{\phi_2}) (a_{-\phi_3}^{\dagger} + a_{\phi_3})$$
(47)

where ϕ is the phonon mode index (ϕ_1, ϕ_2, ϕ_3 are mode indices of the three phonons involved in scattering, $-\phi$ refers to a mode corresponding to a negative wavevector), $H^{(3)}_{\phi_1,\phi_2,\phi_3}$ are Fourier transforms of the third order Inter-atomic Force Constants (IFCs), a_{ϕ}^{\dagger} and a_{ϕ} are creation and annihilation operators respectively with $a_{\phi}^{\dagger} | n_{\phi} \rangle =$ $\sqrt{n_{\phi}+1} | n_{\phi}+1 \rangle$ and $a_{\phi} | n_{\phi} \rangle = \sqrt{n_{\phi}} | n_{\phi}-1 \rangle$, and n_{ϕ} is the phonon mode population. The creation operator increases the number of particles in a given energy state by one (adding a quantum of energy to the quantum mechanical oscillator) and the annihilation operator decreases the number of particles by one (removing a quantum of energy). These operators are a way of representing different 3-phonon scattering events which result in the creation and/or annihilation of phonons. With the above expression for the anharmonic Hamiltonian Eq. (47), Maradudin et al. formulated a method to calculate the intrinsic phonon scattering rates using the perturbation theory (Fermi's Golden Rule or FGR) [119, 120]. Since this technique captures the anharmonic interaction between the vibrational modes in the crystal, it is also referred to as Anharmonic Lattice Dynamics (ALD) technique. This method was first implemented to calculate the scattering rates in simple crystals with a small number of atoms in the unitcell such as Silicon and Germanium [121, 94] and has been used extensively since then [122, 123, 124, 125, 87]. Recently, the FGR technique was extended by Feng et al. to consider fourth order anharmonic terms and thereby four phonon processes in Argon, Diamond, Silicon and Germanium [126].

The mathematical expression of FGR is obtained by solving the Time Dependent Schrodinger Equation (TDSE) and is shown in Chapter 7. Based on FGR, the probability of transition from an initial state $|i\rangle$ to a final state $|f\rangle$ for the 3-phonon emission process $\phi_1 \rightarrow \phi_2 + \phi_3$ (annihilation of a phonon ϕ_1 and creation of two new phonons ϕ_2 and ϕ_3) is given by

$$\frac{2\pi}{\hbar} |\langle f|H_3|i\rangle|^2 \delta(E_i - E_f) \sim n_{\phi_1} (1 + n_{\phi_2}) (1 + n_{\phi_3}) \left| H_{\phi_1, \phi_2, \phi_3}^{(3)} \right|^2$$
(48)

Similarly, the transition probability for the process $\phi_1 \leftarrow \phi_2 + \phi_3$ (annihilation of two phonons ϕ_2 and ϕ_3 and creation of a new phonons ϕ_1) is given by

$$\frac{2\pi}{\hbar} |\langle i|H_3|f\rangle|^2 \delta(E_i - E_f) \sim (1 + n_{\phi_1}) n_{\phi_2} n_{\phi_3} \left| H_{\phi_1,\phi_2,\phi_3}^{(3)} \right|^2 \tag{49}$$

where E_i and E_f are energy of the initial and the final state respectively. The transition probabilities for the absorption processes $\phi_1 + \phi_2 \rightarrow \phi_3$ (annihilation of two phonons ϕ_1 and ϕ_2 and creation of a new phonons ϕ_3) and $\phi_1 + \phi_2 \leftarrow \phi_3$ (annihilation of a phonon ϕ_3 and creation of two new phonons ϕ_1 and ϕ_2) can be expressed in a similar manner. The coefficients $H^{(3)}_{\phi_1,\phi_2,\phi_3}$ are related to the analogous coefficients $V^{(3)}_{\phi_1,\phi_2,\phi_3}$ defined by Born and Huang [127]. They are related by

$$H_{\phi_1,\phi_2,\phi_3}^{(3)} = \frac{\hbar^{\frac{3}{2}}}{2^{\frac{3}{2}} \times 6N^{\frac{1}{2}}} \, \varDelta_{k_1+k_2+k_3} \frac{V_{\phi_1,\phi_2,\phi_3}^{(3)}}{\sqrt{\omega_{\phi_1}\omega_{\phi_2}\omega_{\phi_3}}} \tag{50}$$

where *N* is the total number of k points, ω_{ϕ} is the angular frequency of the phonon mode, Kronecker delta $\Delta_{k_1+k_2+k_3}$ enforces momentum conservation, and $V_{\phi_1,\phi_2,\phi_3}^{(3)}$ is the cubic anharmonic matrix of third order IFCs defined as

$$V_{\phi_{1},\phi_{2},\phi_{3}}^{(3)} = \sum_{0b_{1},l_{2}b_{2},l_{3}b_{3}} \sum_{\alpha_{1},\alpha_{2},\alpha_{3}} \Phi_{0b_{1},l_{2}b_{2},l_{3}b_{3}}^{\alpha_{1}\alpha_{2}\alpha_{3}} \frac{e_{\alpha_{1}b_{1}}^{\phi_{1}}e_{\alpha_{2}b_{2}}^{\phi_{2}}e_{\alpha_{3}b_{3}}^{\phi_{3}}}{\sqrt{m_{b_{1}}m_{b_{2}}m_{b_{3}}}} e^{ik_{2} \cdot r_{l_{2}}}e^{ik_{3} \cdot r_{l_{3}}}$$
(51)

where *b* is the index of atoms in the unitcell, *l* is the index of cells in a supercell, α represents the three Cartesian directions, m_b is the mass of the b^{th} atom, $\Phi_{0b_1,l_2b_2,l_3b_3}^{\alpha_1\alpha_2\alpha_3}$ are the third order force constants, $\boldsymbol{e}_{\alpha_1b_1}^{\phi_1}$ are the phonon mode eigenvectors, and \boldsymbol{k} represents the wavevector.

The rate of change of occupation of the mode ϕ_1 can be calculated based on the transition probabilities for the 3-phonon processes as

$$\frac{\partial n_{\phi_1}}{\partial t} = -\sum_{\phi_2,\phi_3} \left\{ \frac{1}{2} \left[n_{\phi_1} (1+n_{\phi_2}) (1+n_{\phi_3}) - (1+n_{\phi_1}) n_{\phi_2} n_{\phi_3} \right] L_{-} + \left[(1+n_{\phi_3}) n_{\phi_1} n_{\phi_2} - n_{\phi_3} (1+n_{\phi_1}) (1+n_{\phi_2}) \right] L_{+} \right\}$$
(52)

The first two terms of the summation in Eq. (52) account for the emission process (the difference between $\phi_1 \rightarrow \phi_2 + \phi_3$ and $\phi_1 \leftarrow \phi_2 + \phi_3$) and the last two terms account for the absorption process (the difference between $\phi_1 + \phi_2 \rightarrow \phi_3$ and $\phi_1 + \phi_2 \leftarrow \phi_3$). Using FGR under Single Mode Relaxation Time Approximation (SMRTA) where each mode ϕ_1 is perturbed in turn and the resulting change to the population of ϕ_1 can be determined due to the exchange of energy via scattering with all other modes. That is, $n_{\phi_1} = n_{\phi_1}^0 + n_{\phi_1}'$ and $n_{\phi_2} = n_{\phi_2}^0$, $n_{\phi_3} = n_{\phi_3}^0$, where n_{ϕ_1}' is the perturbation in

population of the mode ϕ_1 , n_{ϕ}^0 is the equilibrium phonon population of the mode ϕ given by Bose-Einstein (BE) statistics. Using SMRTA and equilibrium conditions, that is $n_{\phi_1}^0 (1 + n_{\phi_2}^0) (1 + n_{\phi_3}^0) = (1 + n_{\phi_1}^0) n_{\phi_2}^0 n_{\phi_3}^0$, and $(1 + n_{\phi_3}^0) n_{\phi_1}^0 n_{\phi_2}^0 = n_{\phi_3}^0 (1 + n_{\phi_1}^0) (1 + n_{\phi_2}^0)$, Eq. (52) leads to

$$\frac{\partial n_{\phi_1}}{\partial t} = -n'_{\phi_1} \sum_{\phi_2,\phi_3} \left\{ \frac{1}{2} \left(1 + n^0_{\phi_2} + n^0_{\phi_3} \right) L_- + \left(n^0_{\phi_2} - n^0_{\phi_3} \right) L_+ \right\}$$
(53)

and the summation on the right side is the intrinsic 3-phonon scattering rate (Γ_{ϕ_1}) ,

$$\Gamma_{\phi_1} = \sum_{\phi_2,\phi_3} \left\{ \frac{1}{2} \left(1 + n_{\phi_2}^0 + n_{\phi_3}^0 \right) L_- + \left(n_{\phi_2}^0 - n_{\phi_3}^0 \right) L_+ \right\}$$
(54)

where $L_{\pm} = \frac{\pi \hbar}{4N} \left| V_{\pm}^{(3)} \right|^2 \Delta_{\pm} \frac{\delta(\omega_{\phi_1} \pm \omega_{\phi_2} - \omega_{\phi_3})}{\omega_{\phi_1} \omega_{\phi_2} \omega_{\phi_3}}$ account for the conservation of crystal momentum and energy and the probability of transition from an initial state to a final state for emission (–) and absorption (+) processes. $V_{\pm}^{(3)}$ is cubic anharmonic matrix of the third order IFCs

$$V_{\pm}^{(3)} = \sum_{0b_1, l_2b_2, l_3b_3} \sum_{\alpha_1, \alpha_2, \alpha_3} \Phi_{0b_1, l_2b_2, l_3b_3}^{\alpha_1 \alpha_2 \alpha_3} \frac{e_{\alpha_1 b_1}^{\phi_1} e_{\alpha_2 b_2}^{\pm \phi_2} e_{\alpha_3 b_3}^{-\phi_3}}{\sqrt{m_b m_{b1} m_{b2}}} e^{\pm i k_2 \cdot r_{l_2}} e^{-i k_3 \cdot r_{l_3}}$$
(55)

The scattering rate (Γ_{ϕ_1}) can be considered to be a product of two terms, $|V_{\pm}^{(3)}|^2$ which indicates the anharmonicity of the modes and a 3-phonon phase space volume P_{3,ϕ_1} calculated as

$$P_{3,\phi_{1}} = \sum_{\phi_{2},\phi_{3}} \left\{ \frac{1}{2} \left(1 + n_{\phi_{2}}^{0} + n_{\phi_{3}}^{0} \right) \Delta_{-} \frac{\delta \left(\omega_{\phi_{1}} - \omega_{\phi_{2}} - \omega_{\phi_{3}} \right)}{\omega_{\phi_{1}} \omega_{\phi_{2}} \omega_{\phi_{3}}} + \left(n_{\phi_{2}}^{0} - n_{\phi_{3}}^{0} \right) \Delta_{+} \frac{\delta \left(\omega_{\phi_{1}} + \omega_{\phi_{2}} - \omega_{\phi_{3}} \right)}{\omega_{\phi_{1}} \omega_{\phi_{2}} \omega_{\phi_{3}}} \right\}$$
(56)

which indicates the number of allowed 3-phonon scattering events permitted by conservation of crystal momentum and energy. Finally, the phonon lifetime (τ_{ϕ_1}) is defined as the inverse of the scattering rate,

$$\tau_{\phi_1} = \frac{1}{\Gamma_{\phi_1}} \tag{57}$$

The relationship between energy transfer rate and scattering rate of a given perturbed mode ϕ_1 can be shown as follows. The energy transfer rate can be expressed as

$$\frac{\partial E_{\phi_1}}{\partial t} = \hbar \omega_{\phi_1} \frac{\partial n_{\phi_1}}{\partial t}$$
(58)

where the partial derivative on the right side can be obtained by solving the Boltzmann Transport Equation (BTE) which, in the absence of an external force such as mechanical load or shock, is expressed as [79]

$$\frac{\partial n_{\phi_1}}{\partial t} + \boldsymbol{\nu}_{g,\phi_1} \cdot \nabla n_{\phi_1} = \left(\frac{dn_{\phi_1}}{dt}\right)_{scattering}$$
(59)

where v_{g,ϕ_1} is the phonon mode group velocity and the term on the right is the rate of change in phonon population due to scattering as calculated in Eq. (52). Under the approximation of small perturbation i.e., $\Delta n_{\phi_1} \rightarrow 0$, Eq. (59) reduces to $\frac{\partial n_{\phi_1}}{\partial t} = \left(\frac{dn_{\phi_1}}{dt}\right)_{scattering}$. Using this result and substituting Eq. (52) into Eq. (58), the energy transfer rate for ϕ_1 is calculated as

$$\frac{\partial E_{\phi_1}}{\partial t} = -n'_{\phi_1} \hbar \omega_{\phi_1} \Gamma_{\phi_1} \tag{60}$$



Figure 4.1. Schematic of 3-phonon scattering processes ((left) emission and (right) absorption). Energy and momentum conservation rules must be satisfied for a non-zero probability of 3-phonon scattering, i.e., transition from any initial quantum state i to another final quantum state f.

4.1.1 Interpretation of 3-phonon Scattering Rates

Equations (52) and (53) may be interpreted in the following way. At equilibrium, the phonon occupation levels of all modes are governed by Bose-Einstein statistics and the rate of energy transfer to/from ϕ_1 must have a net change of zero. However, when ϕ_1 is perturbed i.e., the number of oscillators at energy level $\hbar \omega_{\phi}$ is higher than n_{ϕ} , the surplus energy is transferred to all other modes in the system via scattering. 3-phonon scattering can transfer energy from or to ϕ_1 in two possible ways. The first is indicated in the first set of square brackets in Eq. (52) where an emission process splits ϕ_1 into two new phonons ϕ_2 and ϕ_3 ($\phi_1 \rightarrow \phi_2 + \phi_3$), or when two phonons from modes ϕ_2 and ϕ_3 combine to create ϕ_1 ($\phi_1 \leftarrow \phi_2 + \phi_3$). The modes that can participate in these reactions must follow energy conservation, $\omega_{\phi_1} = \omega_{\phi_2} + \omega_{\phi_3}$. However, the combination reaction is necessarily slower when the occupation of ϕ_1 is above equilibrium. This is because the occupation of a mode must be a positive value which makes the coefficient of L_- in Eq. (53) strictly positive. In the second route, indicated by the second set of square brackets in Eq. (52), ϕ_1 can combine with ϕ_2 to create ϕ_3 at higher energy ($\phi_1 + \phi_2 \rightarrow \phi_3$), or ϕ_3 can split to create ϕ_1 and ϕ_2 ($\phi_1 + \phi_2 \leftarrow \phi_3$) following the same energy conservation requirement that restricts the possible modes that can participate in the reactions. The second route models absorption, and here, the splitting reaction is slower when ϕ_1 is perturbed since the coefficient of L_+ in Eq. (53), that is $(n_{\phi_2}^0 - n_{\phi_3}^0)$, must be strictly positive since $n_{\phi_2}^0 > n_{\phi_3}^0$ when $\omega_{\phi_2} < \omega_{\phi_3}$. This means that absorption must also have a cooling effect on the perturbed mode. Thus, the terms for emission and absorption both act to counteract the perturbation of ϕ_1 , which means the scattering is related linearly to the rate of energy transfer as shown in Eq. (60).

4.1.2 Computational Details

The minimum free energy structure of RDX at 300 K is calculated using the open source package GULP [102] which minimizes the Helmholtz free energy $A = U_{static} + U_{vib} - TS_{vib}$ [103]. The phonon mode frequencies and eigenvectors are also determined using GULP for a uniform $6 \times 6 \times 6$ grid of k-points. This results in a total of (504 branches) × (216 k-points) = 108864 phonon modes. The details of energy minimization and the calculation of harmonic properties can be found in Chapter 3.

The open source packages LAMMPS [128] and ShengBTE [129] are used to calculate the third order interatomic force constants (IFCs) and the 3-phonon scattering rates and mode-to-mode scattering rates. LAMMPS determines the single point energies which are then provided to ShengBTE to perform the finite differences needed to calculate the third derivatives of energy for the IFCs. The IFCs are determined over a symmetry-reduced crystal. Finally, using the phonon frequencies, eigenvectors and IFCs, the scattering rates are calculated for all modes. The convergence of the harmonic and anharmonic phonon properties with respect to the number of k-points is shown in Appendix 1.

4.1.3 FGR Scattering Rate Results

Experimentally, the phonon lifetimes can be obtained from Raman spectra whose width depend on the anharmonic coupling between the probed mode and other vibrational modes in the system [130, 131, 132, 133]. The calculated 3-phonon scattering rates and phonon lifetimes along with experimental lifetime values obtained from Raman linewidths as reported in [110, 134] are shown in Figure 4.2 and Figure 4.3 respectively. The calculated lifetimes are in good agreement with the experimental values indicating that the 3-phonon scattering model can provide an accurate description of the anharmonic coupling and energy transfer between the modes in RDX under ambient conditions. The calculated phonon lifetimes (or relaxation time) indicate a sub-picosecond relaxation of the nitro group wagging and rotation modes (bands 2 and 3) which was also suggested by Aubuchon et al. [51]. Aubuchon et al. also observed a relaxation time of 6.2 ± 0.4 ps for the asymmetric stretching of the nitro group (band 18) as compared to the 2.19 ps relaxation time estimated in this work. The number of

modes, the average scattering rate and relaxation time for each band, the highest and lowest relaxation time within each band, and normalized standard deviation in relaxation time within each band defined as $\sigma_{\tau_{band}}^{norm} =$

$$\sqrt{\frac{\sum_{\phi_1 \in band} |\tau_{\phi_1, band} - \tau_{band avg}|^2}{no.of modes in band}} / \tau_{band avg}$$
 are shown in Table 4.1. The low frequency

modes in bands 1, 2 and 3 have an average scattering rate of 263.46 ps⁻¹, 195.08 ps⁻¹ and 135.95 ps⁻¹ respectively, and an average relaxation time of ~0.01 ps. Similar subpicosecond relaxation times for the low frequency modes in PETN, HMX, and TATB at 295 K were reported by McGrane et al. [135]. Such low relaxation times (~0.01 ps) are uncharacteristic of pristine solid crystals and seem unrealistic prima facie. However, similar values have precedents in disordered solids such as amorphous silicon [136, 137], SiGe alloys [138], lead halide perovskites [139], etc. This is ultimately indicative of the diffusive nature of the thermal carriers in complex molecular crystals like RDX as shown by Kumar et al. [74, 73]. The high scattering rates of these low frequency modes can be understood by investigating the type of scattering processes (absorption vs emission) as shown in Figure 4.4, the strength of anharmonic coupling between the modes indicated by the Gruneisen parameter values and the number of 3-phonon scattering events indicated by the 3-phonon phase space volume as shown in Figure 4.5 and Figure 4.6 respectively. For the low frequency modes (ω_{ϕ_1}) in bands 1, 2 and 3, the majority of the scattering occurs via absorption processes involving two other low frequency modes ω_{ϕ_2} and ω_{ϕ_3} . These low frequency modes have a high occupancy (n_{ϕ}) , are highly anharmonic (large Gruneisen parameter magnitude), and have a large number of 3-phonon scattering channels

available (large 3-phonon phase space volume). All these factors combined result in high scattering rates for these low frequency modes.

The normalized standard deviation in relaxation time calculated across all modes is ~5.02 indicating that an average harmonic approximation may result in relatively large inaccuracies in the analysis, however, $\sigma_{\tau_{band}}^{norm}$ is relatively low (less than 0.5) for bands 5-8 and 10-18 indicating that an average anharmonic approximation applied within these bands individually may provide a reasonable estimate of the relaxation times.

The scattering rate of individual modes (Γ_{ϕ_1}) indicates the time scale for relaxation of the phonon population of that mode. However, mode-to-mode scattering rates are needed to identify the modes that are responsible for the majority of energy transfer into or out of any particular mode of interest. The mode-to-mode scattering rate calculations and results are presented in Chapter 5.

The calculations and results presented in this section are predicated on several approximations including SMRTA, only 3-phonon scattering events, a limited number of Brillouin Zone sampling points ($6 \times 6 \times 6$), and use of a quantum chemistry based force field to model the interactions between atoms and molecules instead of first principles electronic structure calculations. Although, a good agreement between the calculated results and experimentally reported values indicate a sufficient level of accuracy of the FGR based model under these approximations, however, the accuracy of the model can be improved at the cost of computational resources by including higher order anharmonic terms in the Hamiltonian (4-phonon scattering or higher) which become increasingly important at higher temperatures [126]. Further

improvement can be achieved by sampling the entire Brillouin zone using a larger number of kpoints, and by lifting the single mode relaxation time approximation to accurately model the change in phonon population and the anharmonic coupling between the modes. In addition, use of more accurate quantum mechanical models like Density Functional Theory to model the interaction between the atoms and molecules can provide greater insights into the physical and chemical processes that may lead to critical vibrational energy transfer mechanisms in energetics.



Figure 4.2 FGR based 3-phonon scattering rate (Γ_{ϕ_1} , ps⁻¹) in RDX at 300 K. The lowest frequency modes have the highest scattering rates indicating strong anharmonicity (large third order force constants) and large number of 3-phonon scattering channels (large 3-phonon phase space volume) for these modes. In contrast, the majority of high frequency optical modes have lower scattering rates possibly due to lower

anharmonicity and large band gaps in the phonon spectra resulting in smaller 3-phonon phase space volume for these modes.



Figure 4.3 FGR based phonon lifetime (τ_{ϕ_1} , ps) for all modes in RDX (504 branches for a uniform 6 × 6 × 6 kpoints mesh). The lifetimes estimated in this work are in good agreement with the experimental values obtained from Raman linewidth data reported in [110, 134]. Low frequency modes up to ~102 cm⁻¹ have the highest scattering rates and therefore the shortest phonon lifetimes.



Figure 4.4 FGR based 3-phonon scattering rates for all modes in RDX via absorption and emission processes. For the low frequency modes, majority of the contribution to the scattering rates comes from the absorption process involving two other low frequency modes. Since the occupation of the low frequency modes is relatively larger than the high frequency modes, and the scattering rates are directly proportion to the phonon mode occupation, therefore the low frequency modes have very high scattering rates.



Figure 4.5 Magnitude of modewise Gruneisen parameter values for all modes in RDX. The lowest frequency modes are highly anharmonic and exhibit the largest values for Gruneisen parameter magnitude thereby contributing to the high scattering rates of these modes. In contrast, the highest frequency modes are less anharmonic and therefore have relatively lower scattering rates.



Figure 4.6 3-phonon phase space volume for all modes in RDX. High scattering rates of the low frequency modes up to $\sim 102 \text{ cm}^{-1}$ in Figure 4.3 are due to the strong anharmonic coupling indicated by the large Gruneisen parameter values, and due to a large number of 3-phonon scattering events indicated by the large phase space volumes.

	No. of	Average	Average	Highest	Lowest	norm
Bands	modes	scattering rate	relaxation	relaxation	relaxation	$\sigma_{\tau_{band}}^{norm}$
		(ps ⁻¹)	time (ps)	time (ps)	time (ps)	
1	1481	263.46	0.01	0.16	0.00	1.15
2	1279	195.08	0.01	0.06	0.00	0.71
3	1136	135.95	0.01	0.09	0.00	0.71
4	2760	73.13	0.03	0.37	0.00	1.03
5	2048	3.45	0.38	1.54	0.03	0.50
6	512	4.39	0.26	0.68	0.06	0.37
7	1124	2.67	0.47	1.80	0.08	0.46
8	512	2.35	0.50	1.79	0.18	0.46
9	4608	7.30	0.25	2.90	0.02	1.04
10	512	1.05	1.14	4.44	0.27	0.45
11	1024	2.34	0.48	1.44	0.07	0.38
12	512	3.47	0.33	1.07	0.03	0.39
13	512	2.53	0.42	1.13	0.18	0.28
14	512	2.87	0.38	1.03	0.13	0.32
15	3072	0.56	2.00	5.64	0.51	0.33
16	1536	0.95	1.23	5.21	0.20	0.43
17	897	1.35	0.79	1.74	0.35	0.25
18	2175	1.27	0.89	2.19	0.30	0.35
19	3072	0.03	172.55	2272.90	2.46	1.55
20	3072	0.17	25.38	101.42	0.41	0.77

Table 4.1 Number of modes, average scattering rate and relaxation time for each band,

highest and lowest relaxation time, and normalized standard deviation in relaxation time within each band.

4.2 Normal Mode Decomposition

In this Section, we present the use of a frequency-domain normal mode decomposition (NMD) technique to estimate the phonon lifetimes for all branches in RDX. This technique was first applied to simple crystals like silicon and diamond by Wang et al. [140] and further extended by Koker [141] and McGaughey and co-workers [142, 99, 143, 125]. The calculation of phonon lifetimes using NMD requires calculation of Spectral Energy Density (SED, $\Phi(\mathbf{k}, \omega)$) which is the power spectrum of the mode velocity and reflects the kinetic energy density of each mode at different frequencies.

The expression for SED can be derived from the theory of lattice dynamics [82, 83, 81] where we begin with writing the crystal Hamiltonian as

$$H = \frac{1}{2} \sum_{\phi} \left[q_{\phi}^{\prime*}(t) \, q_{\phi}^{\prime}(t) + \omega_{\phi}^{2} q_{\phi}^{*}(t) q_{\phi}(t) \right]$$

$$= \sum_{\phi} \left[T_{\phi}(t) + V_{\phi}(t) \right]$$
(61)

where t is time, ω_{ϕ} is phonon mode frequency, $q_{\phi}(t)$ is phonon normal mode coordinate and $q'_{\phi}(t)$ represents time derivative of the phonon normal mode coordinate, and $q'^{*}_{\phi}(t)$ and $q^{*}_{\phi}(t)$ represent complex conjugates of $q'_{\phi}(t)$ and $q_{\phi}(t)$ respectively. The Hamiltonian can also be written as the sum of modewise kinetic and potential energies summed over all modes. The phonon normal mode coordinate $q_{\phi}(t)$ and its time derivative $q'_{\phi}(t)$ can be expressed as

$$q_{\phi}(t) = \sum_{\alpha,b,l}^{3,n,N} \sqrt{\frac{m_b}{N}} u_{\alpha,b,l}(t) \, \boldsymbol{e}^*_{\phi,\alpha,b} \, e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{o,l}} \tag{62}$$

$$q'_{\phi}(t) = \sum_{\alpha,b,l}^{3,n,N} \sqrt{\frac{m_b}{N}} u'_{\alpha,b,l}(t) \, \boldsymbol{e}^*_{\phi,\alpha,b} \, e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{o,l}} \tag{63}$$

where α is the index for three cartesian directions, m_b represents the mass of b^{th} atom in the unit cell, $r_{o,l}$ is the equilibrium position vector of l^{th} unit cell, $u_{\alpha,b,l}(t)$ represents the α component of displacement of b^{th} atom from its equilibrium position and $u'_{\alpha,b,l}(t)$ represents its velocity. The time response of phonon normal mode coordinate can be modelled as a sum of a steady state term $(q_{\phi,S}(t))$ and a transient term $(q_{\phi,T}(t))$ which takes into account the time-dependent fluctuations in the phonon occupation of the mode [83, 82]. The steady state and transient terms of the phonon normal mode coordinate and their time derivatives can be written as

$$q_{\phi,S}(t) = C_{1\phi}e^{i\omega_{\phi}t} + C_{2\phi}e^{-i\omega_{\phi}t}$$
(64)

$$q_{\phi,T}(t) = e^{-\Gamma_{\phi}t} \left(C_{3\phi} e^{i\omega_{\phi}t} - C_{4\phi} e^{-i\omega_{\phi}t} \right)$$
(65)

$$q'_{\phi,S}(t) = i\omega_{\phi} \left(C_{1\phi} e^{i\omega_{\phi}t} - C_{2\phi} e^{-i\omega_{\phi}t} \right)$$
(66)

$$q_{\phi,T}'(t) = e^{-\Gamma_{\phi}t} \left(C_{3\phi} \left(i\omega_{\phi} - \Gamma_{\phi} \right) e^{i\omega_{\phi}t} - C_{4\phi} \left(i\omega_{\phi} + \Gamma_{\phi} \right) e^{-i\omega_{\phi}t} \right)$$
(67)

Here *C*s are constants, ω_{ϕ} is the normal mode frequency and Γ_{ϕ} represents the rate of decay in phonon population of the mode ϕ .

The potential energy $(V_{\phi}(t))$ and kinetic energy $(T_{\phi}(t))$ of the normal mode represented by index ϕ are expressed as

$$V_{\phi}(t) = \frac{1}{2} \,\omega_{\phi}^2 q_{\phi}^*(t) q_{\phi}(t) \tag{68}$$

$$T_{\phi}(t) = \frac{1}{2} q_{\phi}^{\prime*}(t) q_{\phi}^{\prime}(t)$$
(69)

The expected value of the normal mode kinetic energy in the time domain is calculated as

$$\langle T_{\phi}(t) \rangle = \lim_{\tau_o \to \infty} \frac{1}{\tau_o} \int_0^{\tau_o} \frac{1}{2} q_{\phi}^{\prime *}(t) \times q_{\phi}^{\prime}(t) dt$$
(70)

The expression in Eq. (70) can be transformed from the time domain to the frequency domain using Parseval's theorem [144] as

$$T_{\phi}(\omega) = \lim_{\tau_o \to \infty} \frac{1}{2\tau_o} \left| \frac{1}{\sqrt{2\pi}} \int_0^{\tau_o} q'_{\phi}(t) \exp(-i\omega t) dt \right|^2$$
(71)

Substituting Eq. (67) into Eq. (71) and integrating the expression,

$$T_{\phi}(\omega) = \frac{1}{16\pi\tau_{o}} \left| \sum_{j} e^{-i\omega t_{j}} \left(A_{\phi,j} \frac{\omega_{\phi} + i\Gamma_{\phi}}{\omega_{\phi} - \omega + i\Gamma_{\phi}} + B_{\phi,j} \frac{\omega_{\phi} - i\Gamma_{\phi}}{\omega_{\phi} + \omega - i\Gamma_{\phi}} \right) \right|^{2}$$

$$(72)$$

where A_s and B_s are constants related to the growth and decay of phonons in the system. Since we are interested in values of ω close to ω_{ϕ} to calculate the linewidth Γ_{ϕ} , when $\omega \approx \omega_{\phi}$, the $A_{\phi,j}$ term becomes large and $B_{\phi,j}$ term can be neglected. Thus, the expression in Eq. (72) can be reduced to the following form

$$T_{\phi}(\omega) = \frac{1}{16\pi\tau_o} \sum_j \sum_{j'} \cos\left(\omega(t_{j'} - t_j)\right) A_{\phi,j} A_{\phi,j'} \frac{\omega_{o\phi}^2 + \Gamma_{\phi}^2}{\Gamma_{\phi}} \frac{\Gamma_{\phi}}{\left(\omega_{o\phi} - \omega\right)^2 + \Gamma_{\phi}^2}$$
(73)

The expression in Eq. (73) can be written as

$$T_{\phi}(\omega) = \frac{1}{2} \sum_{\phi} C_{o\phi} \frac{\frac{\Gamma_{\phi}}{\pi}}{\left(\omega_{o\phi} - \omega\right)^2 + \Gamma_{\phi}^2}$$
(74)

Here $C_{o\phi} = \sum_{j} \sum_{j'} [cos(\omega(t_j - t_{j'}) A_{j\phi} A_{j'\phi} \frac{\omega_{o\phi}^2 + \Gamma_{\phi}^2}{\beta \tau \Gamma_{\phi}})]$

Finally. the expression for modewise Spectral Energy Density can be written as

$$\Phi_{\phi}(\omega) = 2 \times T_{\phi}(\omega) = C_{o\phi} \frac{\frac{I_{\phi}}{\pi}}{\left(\omega_{o\phi} - \omega\right)^2 + \Gamma_{\phi}^2}$$
(75)

The factor of two in Eq. (75) comes from equipartition of potential and kinetic energy for a harmonic classical system. The SED of each mode is an approximate Lorentzian function whose linewidth (half width at half-max Γ_{ϕ}) can be calculated by fitting the SED to a Lorentzian function. Finally, the phonon mode lifetime can be calculated as inverse of full width at half-max

$$\tau_{\phi} = \frac{1}{2\Gamma_{\phi}} \tag{76}$$

4.2.1 Computational Details

The harmonic ingredients for SED such as phonon mode frequencies and eigenvectors are calculated using the open source package GULP [102] as shown in Chapter 3. In order to calculate $q_{\phi}(t)$ and $q'_{\phi}(t)$ as shown in Eq. (62) and (63), a molecular dynamics simulation of a supercell size $N = 2 \times 2 \times 2 = 8$ cells at 300 K

is performed using the open-source package LAMMPS [128] to obtain the time dependent displacement of atoms from their equilibrium position and their velocities. A 1.0 fs timestep is chosen for integrating the equations of motion (less than $\frac{1}{10}th$ of the smallest time period of atomic vibration in RDX) and the system is equilibrated for 10 ns under NPT conditions followed by data collection for another 2 ns under NVE conditions. During equilibration under NPT conditions, the temperature and pressure are controlled using the Nose-Hoover thermostat and barostat respectively with a time constant of 100 fs for both. At every MD time-step, using the phonon normal mode coordinates and their time-derivatives, the total kinetic energy of the system can be calculated as shown in Eq. (61). The time domain kinetic energies are then transformed into frequency domain via Fourier transform as shown in Eq. (71). The SED for each mode is then obtained from the frequency domain kinetic energies as shown in Eq. (75). Finally, a Lorentzian function is fitted to the SED to obtain the linewidth Γ_{ϕ} [75]

$$\Phi_{\phi}(\omega) = \sqrt{P_3} \frac{\left[P_1 \frac{P_2^2 + P_3}{4\pi}\right]}{\left[(P_2 - \omega)^2 + P_3\right]}$$
(77)

Here P_1 is a parameter representing the largest value of the SED for mode ϕ , P_2 is a parameter representing $\omega_{o\phi}$, and P_3 represents Γ_{ϕ}^2 . The Lorentzian fitting is performed by minimizing the least square error. The following metrics are used to quantify the error in the Lorentzian fitting of all modes

$$error_{\phi} = \sqrt{\frac{\sum_{l=1}^{n_d} \left(SED_{\phi l} - SED_{fit,\phi l}\right)^2}{n_d}}$$
(78)

% error =
$$100 \sqrt{\frac{\sum_{\phi} error_{\phi}^2}{3n}} / \sqrt{\frac{\sum_{\phi} \sum_{1}^{n_d} (SED_{\phi})^2}{3n \times n_d}}$$
 (79)

where n_d is the number of data points in the SED of each mode, and 3n is the number of sampled phonon modes. Further, the standard deviation of $error_{\phi}$ is calculated as

$$\sigma_{fit} = 100 \sqrt{\frac{\sum_{\phi}^{3n} \left(error_{\phi} - \frac{\sum_{\phi}^{3n} error_{\phi}}{3n}\right)^{2}}{3n}} / \frac{\sum_{\phi}^{3n} error_{\phi}}{3n} \qquad (80)$$

4.2.2 Phonon Lifetime Results

Among the phonon modes that were studied, over 90 % of the modes exhibit an SED curve with a clear single peak. Occasionally, smaller peaks with heights less than 10 % of the main peak value were observed for some modes. The small peaks were caused by non-negligible $B_{\phi,j}$ term, at frequencies well above or below ω_{ϕ} and therefore do not affect the Lorentzian fitting centred at ω_{ϕ} . For our choices of MD simulation parameter values, some noise was observed in the SED data that was most likely related to the randomness of thermal fluctuations and could be reduced by much longer thermalization and equilibration stages. However, we found that the noise was insensitive to reasonable deviations in the parameter values and did not affect the SED of a randomly chosen mode is shown in Figure 4.7. Using the error metric defined in Eq. (79), a % *error* = 2.61% in SED fitting is observed and the standard deviation of fitting across all modes σ_{fit} as shown in Eq. (80) is found to be 0.59% indicating a consistently good Lorentzian fit of the SED for all modes.

A plot of phonon lifetimes vs frequency for all modes in RDX is shown in Figure 4.8. We observed that the phonon lifetimes decrease with increasing frequency up to $\sim 100 \text{ cm}^{-1}$, followed by flattening and subsequent increase for some higher frequency modes (above $\sim 300 \text{ cm}^{-1}$) [73]. This is in contrast to the trend observed in simple atomic crystals like silicon [142], and carbon nanotubes [123] in which phonon lifetimes monotonically decrease with frequency. The non-monotonic nature of lifetimes in RDX can be attributed to the large frequency gaps that exist in the band structure that result in the higher frequency optical modes (above 1500 cm⁻¹) participating in relatively fewer third-order phonon scattering events and thereby having longer lifetimes [97]. A decrease in the number of allowed phonon-phonon interactions due to an increase in the acoustic-optical bandgap is similarly observed in III-V materials [97]. A histogram of the number of phonon modes vs phonon lifetime is shown in Figure 4.9. It should be noted that the magnitude of the phonon lifetime for the majority of modes is quite low, on the order of 10 picoseconds, closer to lifetimes in amorphous solids than atomic crystals that have phonon lifetimes on the order of nanoseconds [142]. Lifetime values calculated in this study are in good agreement with vibron lifetimes in RDX which have been reported to fall in the range of 2.5 ps to 11 ps [56]. The short lifetimes indicate that RDX is a strongly anharmonic crystal.



Figure 4.7 Spectral Energy Density fitted to a Lorentzian for 375^{th} phonon branch in RDX at 300 K. Using the error metric defined in Eq. (79), a % *error* = 2.61% in SED fitting is observed and the standard deviation of fitting across all modes σ_{fit} as shown in Eq. (80) is found to be 0.59% indicating a consistently good Lorentzian fit of the SED for all modes.



Figure 4.8 Phonon Lifetimes for all branches in RDX at 300 K using NMD technique. The linewidths are obtained by fitting a Lorentzian to the modewise Spectral Energy Density function. The phonon lifetimes are on the order of few picoseconds to tens of picoseconds. Such small lifetimes indicate a strong anharmonic coupling between the phonon modes in RDX.



Figure 4.9 Histogram of number of phonon modes vs phonon lifetime in RDX. The majority of phonons are estimated to have small lifetimes, on the order of a few picoseconds.

Chapter 5: Thermal Conductivity in RDX⁵

In molecular crystals, commonly used in energetics, phonons facilitate the formation of the microscale reaction zones, i.e. hotspots, wherein the flow of energy into key vibrational modes initiates the chemical decomposition process [50, 54, 48]. The growth of hotspots depends on the balance of the amount of energy generated due to the exothermic fission of bonds and the amount of energy dissipated due to thermal conductivity. For instance, if the energy generation exceeds the energy dissipated, then the thermal decomposition of the material continues, and the hotspots can grow in size. However, open questions remain as to the exact mechanism through which intermodal and spatial thermal energy transfer occurs in molecular crystals. Dlott et al. postulated a multiphonon up-pumping mechanism to explain the intermodal energy transfer phenomenon, while other works speculated that the energy transfer process occurs through a direct route [52, 48]. Furthermore, there exists a relative lack of knowledge regarding how thermal energy is conducted in van der Waals bonded organic molecular crystals in relation to "simple" atomic crystalline materials such as Si or Ge. Highlighting the possible shortcomings of the existing kinetic theory for thermal transport in molecular crystals is the extremely low thermal conductivity of α -RDX, TATB, and β -HMX, ≤ 1 W/m·K [145, 146]. Such values are more akin to

⁵ Portions of this Chapter appear in G. Kumar, F. G. VanGessel, D. C. Elton and P. W. Chung,

[&]quot;Phonon Lifetimes and Thermal Conductivity of the Molecular Crystal α-RDX," *MRS Advances*, pp. 1-9, 2019. AND

G. Kumar, F. G. VanGessel and P. W. Chung, "Bond Strain and Rotation Behaviors of Anharmonic Thermal Carriers in a-RDX," *Propellants, Explosives, Pyrotechnics,* vol. 45, no. 2, 2019.

conductivities observed in amorphous or glassy materials than in atomic crystalline systems. A similar phenomenon of ultralow thermal conductivity has been observed in certain inorganic perovskite and selenide compound crystals [147, 148]. Theoretical and experimental studies of both of these systems have shown a breakdown of Peierls-Boltzmann theory [148, 149, 77], which is based on a partial Hamiltonian and breaks down when the full crystal Hamiltonian is sufficiently anharmonic [150]. Peierls-Boltzmann is a popular approach for the calculation of bulk thermal conductivity in crystalline solids, often calculated through the so-called phonon gas model (PGM) [79, 83, 85, 86, 87, 84, 88]. The breakdown of the PGM in the perovskite and selenide compounds has been linked to the strong anharmonicity present in those systems. Molecular crystals, notably RDX, possess similarly large unit cells that generally have a highly anharmonic Hamiltonian. Therefore, the PGM, as well as alternative thermal conductivity models, must be evaluated for their accuracy in modelling phonon mechanisms in molecular crystals. Only then will it be possible to elucidate the manner in which phonons store, transport, and transfer energy in complex molecular crystalline systems.

In this Chapter, we evaluate the strength of anharmonic coupling in the molecular crystal RDX via the phonon lifetimes. Subsequently, using harmonic and anharmonic phonon properties, we evaluate three thermal conductivity models, namely the PGM [79], Cahill Watson and Pohl (CWP) model [151], and Allen and Feldman (AF) model [152]. We assess the accuracy of these models in estimating the thermal conductivity of RDX by comparing them with values obtained from Green-Kubo molecular dynamics (GK-MD) [145]. The PGM has been shown to give excellent

predictions of bulk thermal conductivity in a wide range of simple atomic crystalline systems [85, 86, 87, 98, 84, 88, 153]. In contrast, the CWP model was initially developed for application to weakly disordered (i.e., mixed species such as in alloys) crystals [151], but has been shown to provide better predictions than the PGM model for certain Se-based compounds [148]. Finally, the theory of Allen and Feldman [152] was initially developed for disordered phases in which heat transfer is diffusive in nature. However, it has been shown that significant heat currents may be carried by diffusive modes in certain "complex" crystalline materials [149].

In the following sections, we present the calculation details for estimating the thermal conductivity using the PGM, CWP, and AF models respectively.

5.1 Phonon Gas Model

The nature of thermal transport in simple crystalline materials is well understood using the Phonon Gas Model (PGM) [79, 82, 83, 81] which treats phonons as quasi-particles carrying energy $\hbar\omega$ and their transport is modeled in a manner similar to gases [80]. The calculation of thermal conductivity requires knowledge of harmonic (phonon mode specific heat, frequencies and group velocities) and anharmonic (phonon scattering rates and lifetimes) phonon properties over the entire Brillouin zone. The thermal conductivity tensor based on PGM is obtained from a sum over the contributions of all phonon carriers [79, 83]

$$\boldsymbol{\kappa}_{PGM} = \sum_{\phi} C_{\phi} \boldsymbol{\nu}_{g,\phi} \boldsymbol{\Lambda}_{\phi}$$
(81)

where C_{ϕ} is the phonon mode specific heat, $v_{g,\phi}$ is the phonon mode group velocity and Λ_{ϕ} is the phonon mode mean free path. For an accurate calculation of the thermal conductivity, we use a uniform sampling of $15 \times 15 \times 15$ wavevectors within the first Brillouin zone for calculation of the harmonic properties. Due to the relatively larger computational cost of calculating phonon lifetimes on a $15 \times 15 \times 15$ size RDX supercell, we took only the Γ point (0,0,0) lifetime values calculated using the NMD technique. This simplification was justified in part through more refined calculations, where we saw that the average Γ point phonon lifetimes were within ~7% of the value at the BZ edge. Table 5.1 shows the predicted κ_{PGM} of α -RDX along 3 crystallographic directions using PGM, along with the GK-MD value [145]. As GK-MD considers all phonon modes and all higher order anharmonic interactions, we consider it a good source for the reference thermal conductivity to compare against alternative calculation approaches based on the same molecular potential.

PGM clearly under-predicts the thermal conductivity of α -RDX by an order of magnitude. To understand the cause of this discrepancy we appeal to the underlying assumptions of the PGM, which assumes that a phonon wavepacket interacts only weakly with other phonons and therefore propagates a large distance before experiencing a scattering event. Quantitatively, this corresponds to the requirement that the phonon MFP be much larger than the lattice constant, i.e., the phonon wave packet must "sample" the periodicity of the lattice [154]. In Figure 5.1, we plot the phonon MFP with respect to frequency and compare this value to the average lattice constant in RDX. Except for a relatively small fraction (< 1%) of low frequency phonon modes, the vast majority of carriers have a MFP smaller than the lattice constant, i.e., these

carriers fall within the Ioffe-Regel regime [155]. Thus, for these *diffusive* carriers the PGM is *not* a valid descriptor for how they transport thermal energy and therefore under-predicts their contribution to thermal conductivity. We note that in [75] analysis of propagating and diffusive carrier contributions to thermal conductivity were calculated within the PGM framework. However, in that study the phonon lifetime was treated as a fitting parameter in order to match the GK-MD values of κ . It is clear that an accurate thermal conductivity model for molecular crystals should account for the highly anharmonic, diffusive thermal carriers present in these systems.

Model	a_1	<i>a</i> ₂	<i>a</i> ₃
κ _{PGM}	0.014	0.011	0.023
κ_{GK-MD}	0.387	0.353	0.394

Table 5.1 Thermal conductivity estimate in RDX along three principal crystallographic directions using PGM and GK-MD (units of W/mK).



Figure 5.1 Comparison of phonon MFP to average lattice spacing in RDX. Majority of the carriers have a mean free path smaller than the lattice constant indicating a strong anharmonicity and a dominant diffusive heat transfer mechanism.

5.2 Cahill-Watson-Pohl Model

The CWP formula [151] was initially developed to describe the low thermal conductivity observed in crystalline alloys where the lattice structure remains intact but there is randomness in regards to the species lying at each lattice site. It can account for the dispersive nature of the acoustic mode carriers. Recently, the CWP model has been successful in predicting a qualitatively accurate thermal conductivity versus temperature trend in a Se-based compound with zero disorder. The improvement over PGM was due to the treatment of carriers that fall below the Ioffe-Regel limit with the CWP model, while propagating carrier contributions were still calculated using the PGM. The CWP model for thermal conductivity is [151]

$$\kappa_{CWP} = \left(\frac{\pi}{6}\right)^{\frac{1}{3}} K_B n^{\frac{2}{3}} \sum_{\lambda} c_{\lambda} \left(\frac{T}{\theta_{\lambda}}\right)^2 \int_0^{\frac{\theta_{\lambda}}{T}} \frac{x^3 e^x}{(e^x - 1)^2} dx \tag{82}$$

where the sum is restricted to the 3 acoustic phonon branches, indexed by λ , c_{λ} is speed of sound, n is the number density of atoms, and $\theta_{\lambda} = v_{\lambda} \left(\frac{\hbar}{k_B}\right) (6\pi^2 n)^{\frac{1}{3}}$. Applying the CWP formula to RDX yields a conductivity estimate of 0.167 W/m-K. This is still 50% of the averaged κ predicted using GK-MD which is ~ 0.378 W/m-K [145]. Although CWP performs markedly better than PGM, the disagreement with GK-MD is still relatively large. The cause is that the CWP model only accounts for the dispersion contributions in the three acoustic branches. However, due to the large number of optical modes, and small interband spacing, a significant fraction of heat is carried by the optical branches through coherence or non-diagonal effects [149, 150, 154]. This leads us to apply the AF model in order to account for such contributions to thermal transport in α -RDX.

5.3 Allen-Feldman Model

Due to the majority of α -RDX carriers falling in the Ioffe-Regel regime, the phonons likely carry thermal energy in a manner more akin to amorphous solids than atomic crystals. To test this, we applied the theory of Allen and Feldman (AF) which was originally developed for disordered systems such as amorphous solids, alloys, etc. [152]. In this model, heat is assumed to move by coherences, i.e. interband effects and the scalar thermal conductivity κ is calculated as [152]

$$\kappa_{AF} = \frac{1}{V} \sum_{\phi} C_{\phi} D_{\phi} \tag{83}$$

Here D_{ϕ} is mode diffusivity defined as

$$D_{\phi} = \frac{V^2}{3\hbar^2 \omega_{\phi}^2} \sum_{\phi'}^{\phi' \neq \phi} \left| S_{\phi\phi'} \right|^2 \delta(\omega_{\phi} - \omega_{\phi'})$$
(84)

where $S_{\phi\phi'}$ is the off-diagonal term of the heat current operator [150] and δ is the Dirac delta function that enforces energy conservation. The diffusivity is an intrinsic property of the normal modes and requires no assumption about the propagating nature of the phonons, such as in the PGM. We calculate the phonon mode diffusivity using a $3 \times 3 \times 3$ supercell in GULP [102]. Thermal conductivity from the AF approach is 0.354 W/m-K which is within 6% of the GK-MD estimate [145], see Table 5.2 below. The marked improvement of the AF prediction of κ relative to PGM and CWP indicates strongly that diffusive like carriers contribute to the majority of thermal transport in α -RDX.

Within the AF theory, we can break down the contributions to κ_{AF} by individual carrier's accumulation and by each carrier separately. The modewise thermal conductivity contributions and diffusivity values are shown in Figure 5.2 and Figure 5.3 respectively. The cumulative thermal conductivity with respect to frequency is shown in Figure 5.4. We observe that the majority of heat is carried by low frequency phonon modes and the contribution from high frequency modes is negligible. According to Figure 5.4, 11% of the low frequency modes account for 90% of the total κ . We also found that ~70% of κ contribution can be attributed to optical mode phonons, primarily low frequency optical phonons which are neglected in the CWP model. This is a consequence of the fact that high frequency optical phonons have very small specific heat ($C_{\phi} \rightarrow 0$ when $\hbar \omega_{\phi} \gg k_B T$) which combined with their relatively
small diffusivity results in very small contribution to κ . It is also interesting to note that the AF theory considers heat transport due to the off-diagonal terms of heat current operator, which are non-propagating, while PGM considers heat transport via propagating phonon carriers (i.e., diagonal component) [149]. Within the unified approach [149], the propagating and non-propagating contributions are additive (termed the Peierls and coherence contributions respectively in that work). Thus, if we combine contributions from both κ_{AF} and κ_{PGM} , we obtain a thermal conductivity of 0.371 W/m·K which is within 2% the GK-MD prediction. Note that this comparison may suffer from insufficient BZ sampling as a 3 × 3 × 3 supercell was used for AF approach while using 15 × 15 × 15 grid of wavevectors was used for calculation of the propagating contribution. However, it is evident that both propagating and diffusive carriers contribute substantially to thermal transport in α -RDX, where the diffusive component is dominant, contributing 95% to the total thermal conductivity.

κ_{GK-MD}	κ_{AF}	κ_{CWP}	κ_{PGM}	$\kappa_{AF} + \kappa_{PGM}$
0.378	0.354	0.167	0.017	0.371

Table 5.2 Comparison of κ predicted by different thermal conductivity models (units of W/mK).



Figure 5.2 Modewise thermal conductivity estimate using the AF model. The lowest frequency modes, which includes a large number of optical branches, contribute the most to the thermal conductivity.



Figure 5.3 Modewise diffusivity values (calculated using the AF theory) with respect to frequency in RDX. The lowest frequency modes are estimated to have the highest diffusivity which explains a large contribution of these modes to the lattice thermal conductivity.



Figure 5.4 Cumulative thermal conductivity with respect to frequency estimated using AF model in RDX. Low frequency modes below 4 THz are estimated to contribute over 90% to the total thermal conductivity. A significant contribution to the thermal conductivity comes from the optical phonons (~70%).

In this Chapter, we have presented our findings on the nature of thermal transport in the complex molecular crystal RDX. Analysis of the phonon linewidths and lifetimes indicate that RDX is a highly anharmonic crystal. The inability of the PGM to accurately estimate thermal conductivity indicates that the strong anharmonicity leads to a breakdown of the Peierls picture for thermal transport. For RDX, Allen-Feldman harmonic theory performs the best. This result is intuitive as AF theory involves fewer assumptions than PGM or CWP. We observed that low frequency optical phonons play a significant role in carrying heat in RDX. It is notable that these results suggest that diffusive carriers are the primary mechanism of heat transport in RDX, where propagating phonon modes contribute less than 5%. Similar

phenomena involving a partitioning of thermal transport between diffusive and propagating modes have been previously observed in inorganic crystalline materials [148, 149]. However, the relative contribution of diffusive carriers in RDX is significantly larger than previously observed in other crystalline systems. We suspect these observations regarding the nature of heat transfer in α -RDX will extend to other organic molecular crystals, particularly those with applications to energetics technology. In such systems, accurate description of thermal transport requires accounting for both acoustic and optical phonon bands, as well as both propagating and diffusive phonon modes.

5.4 Thermal Conductivity and Bond Distortions

In this section, we show the contributions of different crystal distorting modes to heat conduction in RDX by comparing the contributions of individual phonon modes to bond strain and rotation as calculated in Chapter 3 to the modewise thermal conductivity estimates obtained from the AF theory. To further illustrate the relative importance of different phonon modes in distorting the crystal, the modewise contributions to bond strain and rotation weighted by thermal conductivity are calculated as

$$\epsilon_{p,\phi,rms}^{weighted} = \frac{\kappa_{\phi,AF} \epsilon_{p,\phi,rms}}{\sum_{\phi} \kappa_{\phi,AF}}$$
(85)

$$\beta_{\phi,rms}^{weighted} = \frac{\kappa_{\phi,AF}\beta_{\phi,rms}}{\sum_{\phi}\kappa_{\phi,AF}}$$
(86)

$$\Delta \alpha_{p,\phi,rms}^{weighted} = \frac{\kappa_{\phi,AF} \Delta \alpha_{p,\phi,rms}}{\sum_{\phi} \kappa_{\phi,AF}}$$
(87)

$$\Delta \Phi_{p,\phi,rms}^{weighted} = \frac{\kappa_{\phi,AF} \Delta \Phi_{p,\phi,rms}}{\sum_{\phi} \kappa_{\phi,AF}}$$
(88)

$$\Delta \Phi_{p,im,\phi,rms}^{weighted} = \frac{\kappa_{\phi,AF} \Delta \Phi_{p,im,\phi,rms}}{\sum_{\phi} \kappa_{\phi,AF}}$$
(89)

The modewise contributions to crystal distortion ($\epsilon_{p,\phi,rms}$, $\beta_{\phi,rms}$, $\Delta \alpha_{p,\phi,rms}$, $\Delta \Phi_{p,\phi,rms}$, $\Delta \Phi_{p,im,\phi,rms}$) vs $\kappa_{\phi,AF}$ are shown in Figure 5.5, Figure 5.6, Figure 5.7, Figure 5.8 and Figure 5.9. The $\kappa_{\phi,AF}$ weighted modewise contributions to crystal distortions vs phonon mode frequency are shown in Figure 5.10, Figure 5.11, Figure 5.12, Figure 5.13 and Figure 5.14. We find that the modes corresponding to large bond strain and bond rotation contribute significantly more to thermal conductivity. In fact, just as low frequency modes (up to ~4 THz) contribute ~90 % to total bond strain, we also observe that the same low frequency modes (up to ~4 THz) contribute ~90 % to the total thermal conductivity. Since the low frequency modes are often characterized by large strain and rotation of N - N and N - O bonds, we believe that large deformations of the nitro groups occuring throughout the crystal are responsible for carrying significant amounts of heat in α -RDX.

Fried et al. [53] and Ye et al. [56] studied energy transfer rates in various secondary explosives (SEs) such as α -RDX, HMX, PETN etc and observed a correlation between energy transfer rate and impact sensitivity of SEs. Namely, SEs

with higher total energy transfer rate over all frequencies are also more sensitive to impact. They also observed that low frequency vibrational modes correspond to high energy transfer rates and therefore will be critical in determining the sensitivity of SEs. Based on the relatively large strain of the N - N and N - O bonds and the trends observed in Figure 3.11 and Figure 5.5, the N - N and N - O bonds are likely to play a proportional role in mechanisms associated with heat conduction, heat storage, and cook-off.



Figure 5.5 RMS values of percent bond strain vs modewise AF thermal conductivity for all branches in RDX at Γ point.



Figure 5.6 RMS values of bond rotation angle vs modewise AF thermal conductivity for all branches in RDX at Γ point.



Figure 5.7 RMS values of percent change in bond angle vs modewise AF thermal conductivity for all branches in RDX at Γ point.



Figure 5.8 RMS values of percent change in dihedral angle vs modewise AF thermal conductivity for all branches in RDX at Γ point.



Figure 5.9 RMS values of percent change in improper angle vs modewise AF thermal conductivity for all branches in RDX at Γ point.



Figure 5.10 Weighted RMS value of percent bond strain vs phonon mode frequency for all branches in RDX at Γ point.



Figure 5.11 Weighted RMS value of bond rotation angle vs phonon mode frequency for all branches in RDX at Γ point.



Figure 5.12 Weighted RMS value of percent change in bond angle vs phonon mode frequency for all branches in RDX at Γ point.



Figure 5.13 Weighted RMS value of percent change in dihedral angle vs phonon mode frequency for all branches in RDX at Γ point.



Figure 5.14 Weighted RMS value of percent change in improper angle vs phonon mode frequency for all branches in RDX at Γ point.

Chapter 6: 3-phonon Scattering Pathways for Vibrational Energy Transfer in RDX⁶

Considerable efforts have studied the initial decomposition and initiation mechanisms in EMs where mechanical energy input creates conditions in the material that make it more susceptible to bond rupture and possible self-sustaining chemical reactions. Early efforts to study the thermal decomposition route by Robertson suggested that the primary reaction step involved the transfer of an oxygen atom from the nitro group to a neighboring carbon atom followed by the elimination of CH₂O and N₂O [20]. Based on the rapid initial production of NO₂, Rauch et al. suggested that the first step in the gas phase decomposition of RDX is the homolytic fission of the N-N bond [21]. Other works have also suggested N-N cleavage and HONO elimination to be more likely than other reaction routes such as C-N β -scission, oxygen insertion, nitro-nitrite isomerization, etc. [22, 23, 24, 25, 26, 27, 28, 29, 30]. Based on electronic structure calculations, barriers to N-N fission and HONO elimination are estimated to be significantly lower than other mechanisms [31, 32, 33]. Between N-N fission and HONO elimination, fission proceeds via a so called loose transition structure and is entropically favored [34]. In a recent study by Schweigert who performed a unimolecular dynamics simulation of RDX for a sampling temperature of 2000 K, N-N fission was found to be the dominant reaction mechanism, especially above ~ 1250 K [35]. Bowden and Yoffe [36, 37, 38] showed that the bulk heating of the material in

⁶ Portions of this Chapter appear in the preprint: G. Kumar, F. G. VanGessel, L. B. Munday and P. W. Chung, "3-phonon scattering pathways for vibrational energy transfer in crystalline RDX", *J. Phys. Chem. A*, 2021.

shocked energetic crystals is insufficient to describe the initiation processes. As a result, the concept of localization of energy into highly concentrated regions, called hotspots, was developed [37, 39, 40, 41]. Subsequently, to explain the localization of energy, a mechanism of energy transfer via multi-phonon up-pumping was postulated [42, 43, 44, 45]. This model assumed that mechanical energy from the shock excites the low frequency phonons which results in a rapid increase in their population. The energy from these low frequency modes is then scattered into the mid-frequency modes, referred to as doorway modes, via phonon-phonon scattering. The energy from the doorway modes is, in turn, transferred into the high frequency intramolecular vibrations which is believed to increase the population and energy of internal molecular vibrations beyond bond dissociation limits. This picture of energy transfer meant that the mid frequency doorway modes are critical for phenomena leading to initiation in energetics. The model was further extended by Dlott and co-workers who studied terahertz excitation in molecular solids, measured by ps timescale vibrational spectroscopy, and included a description of localization of energy at crystal defects [46, 47, 48, 49]. Dlott et al. concluded that the rate of up-pumping of energy depends on the number of doorway modes and the Gruneisen parameter values which are indicative of the strength of anharmonic coupling between the modes [50].

For the up-pumping model for initiation to work, strong scattering must occur among a) modes at the low frequencies close to the frequencies associated with mechanical shock, b) the frequencies of the modes believed to serve as the doorway modes, and c) the modes associated with the largest distortions of the bonds, so-called vibrons, likely to possess dissociation energies which, when released, can sustain exothermic reactions. Aubuchon et al. [51], in their work on modes that result in asymmetric stretching of the nitro functional group (NO_2) in TNAZ, RDX, HMX, and CL-20, suggested that the relaxation of the intra-molecular vibrons occurs through a pathway involving a combination of high frequency (> 400 cm⁻¹) modes. Other works have also posited that the energy transfer process may occur through a direct route simply due to the NN activity found in low frequency eigenmodes without intermediate energy transfer or the involvement of doorway modes [52]. A definitive understanding of multi-phonon mechanisms in energetic materials therefore is needed. It requires a detailed determination of vibrational energy transfer of not only the relaxation behavior of individual modes but a complete picture of mode-to-mode scattering that may drive energy through the intrinsic scattering network.

Much progress has occurred toward this goal motivated by early interest in the relationship between vibrational energy transfer and sensitivity. To calculate the total energy transfer rate into vibron bands, Fried and Ruggiero [53] derived a simple formula in terms of the density of vibrational states and the vibron-phonon coupling, which were calculated using existing inelastic neutron scattering data. They studied TATB, γ and β -HMX, RDX, Pb-styphnate, Styphnic acid, and Picric acid, and observed that the estimated energy transfer rates in pure unreacted material are several times greater in sensitive explosives than in insensitive explosives. Following Fried and Ruggiero's formula, Koshi and co-workers investigated a broad range of EMs including PETN, HMX, RDX, Tetryl, TNT, FOX-7, ANTA, PN, NQ, and DMN, and observed a good correlation of the energy transfer rates with the impact sensitivity [54, 55, 56]. Similar observations were made by Bernstein [57], Joshi et al. [58], and

McNesby et al. [59] who investigated the rate of energy transfer from the low frequency phonons to the higher frequency vibrons. Aubuchon et al. used IR pump-probe spectroscopy to show rapid relaxation (2 to 6 ps time scale) of the asymmetric stretching mode of the nitro functional group (NO_2) of several molecules used in TNAZ, RDX, HMX, and CL-20 [51]. Ostrander et al. also used IR pump-probe spectroscopy to study the asymmetric stretching of the nitrate ester groups in PETN thin films and observed a 3.7 ps decay, attributing this decay to rapid energy transfer due to intermolecular vibrational coupling [60]. Numerous other works have explored the role of various crystal distorting modes in the transfer of energy in EMs [52, 61, 62, 63, 64, 65, 66, 67]. These works provide useful insights into the phonon modes which can be critical in phenomena leading to initiation and have motivated investigation of the critical bond stretching and bending modes.

A significant challenge in the development of a complete phonon picture of uppumping has been the lack of a quasiparticle model that accurately accounts for third (and higher) order terms in the Hamiltonian vis-à-vis Fermi's Golden Rule [68] across a larger range of the Brillouin zone. But with the perpetual development of advanced computational architectures, efforts have been made to calculate the anharmonic phonon properties more accurately to model the energy transfer between the vibrational modes. Early efforts were based on approximations to the anharmonic terms that made it possible to overcome the computational costs at the expense of making it difficult to generalize the consideration of distinct phonon modes. Hooper developed a parametric expression for transition probabilities for nitromethane, RDX, and HMX that require assumptions including the Single Mode Relaxation Time Approximation (SMRTA),

the applicability of Debye's model for the pDOS, the occupation numbers being independent of frequency, and that only modes of equal frequency can scatter [69]. Long and Chen calculated phonon-phonon scattering rates in TATB by developing a stress-frequency relationship as a means of representing anharmonic effects without the high computational cost of a 3-phonon scattering Hamiltonian [70]. Michalchuk et al. studied the sensitivity of a wide range of EMs using a 3-phonon scattering model derived from Fermi's Golden Rule (FGR) [71]. This work was built on the so-called average anharmonic approximation [72], which reduces the computational cost by assuming that all elements of the cubic anharmonic matrix $V^{(3)}$ are equal. Recently, however, estimates of thermal properties based on quasiparticle models have shown that a more complete representation of carriers in the Brillouin zone may be necessary for the accurate modeling of phonon mechanisms. Kumar and coworkers showed that the thermal conductivity of energetic crystals like RDX can be dominated by nonacoustic carriers, which constitute the majority of the phonon modes [73], and that modes outside of the acoustic bands can contribute substantially to NN and other intramolecular bond distortions [74, 75]. These observations suggest that the use of approximations that otherwise reduce the complexity of the rich set of optical modes in these materials may omit important contributions from a large number of modes to the transfer of vibrational energy.

In this work, the perturbation theory is used to calculate the 3-phonon scattering rates and the mode-to-mode scattering rate matrix for all modes in the energetic material RDX under ambient conditions. The role of all phonon modes in the transfer of vibrational energy is investigated with full consideration of the statistical nature of scattering and the probabilistic mode-to-mode transfer of energy.

6.1 Mode-to-Mode Phonon Scattering Rates

Due to the present consideration of the discrete phonon modes, each term in the sum of the phonon mode scattering rate in Eq. (54) can be evaluated and examined. Namely, we can breakdown the sum $\Gamma_{\phi_1} = \sum_{\phi_3} \Gamma_{\phi_1,\phi_3}$ to understand the mediating role of all other modes on the relaxation of a given mode ϕ_1 . Thus, the mode-to-mode scattering rate (contribution of ϕ_3 to the relaxation of the ϕ_1) is the part of Eq. (54) involving the sum over all ϕ_2 , namely

$$\Gamma_{\phi_1,\phi_3} = \sum_{\phi_2} \left\{ \frac{1}{2} \left(1 + n_{\phi_2}^0 + n_{\phi_3}^0 \right) L_- + \left(n_{\phi_2}^0 - n_{\phi_3}^0 \right) L_+ \right\}$$
(90)

Since, during both the absorption and emission processes ϕ_1 is annihilated and ϕ_3 is created, this definition of Γ_{ϕ_1,ϕ_3} provides the rate of energy transfer from ϕ_1 to ϕ_3 , as mediated by *all* allowable 3-phonon scattering events involving ϕ_2 . Thus, the contribution of any ϕ_3 to energy transfer rate of ϕ_1 is calculated as

$$\frac{\partial E_{\phi_1,\phi_3}}{\partial t} = -n'_{\phi_1}\hbar\omega_{\phi_1}\Gamma_{\phi_1,\phi_3} \tag{91}$$

For a given ϕ_1 , we see that $\frac{\partial E_{\phi_1,\phi_3}}{\partial t}$ is directly proportional to Γ_{ϕ_1,ϕ_3} through a linear relationship. Furthermore, due to the mediating role of ϕ_2 and the conservation rules, the scattering rates are not necessarily symmetric with respect to ϕ_1 and ϕ_3 ; namely the effect of scattering involving ϕ_3 on the occupation of ϕ_1 is unequal to the scattering involving ϕ_1 on the occupation of ϕ_3 .

It is noteworthy that relationships analogous to Eqs. (90) and (91) cannot be developed for the scattering and flow between ϕ_1 and ϕ_2 . This is because of two reasons. Firstly, notice that the while the emission term is symmetric with respect to ϕ_2 and ϕ_3 , the absorption is not symmetric. Thus, a directionality is implied in the use of FGR. This is because ω_{ϕ_3} must always be greater than ω_{ϕ_2} to ensure energy is conserved during absorption. As a result, ϕ_2 must be cooled if ϕ_3 is heated. Thus, in every phonon triplet in this model, ϕ_1 is the originating mode, ϕ_2 is the mediating mode, and ϕ_3 is the target mode. Secondly, while emission can create ϕ_2 , the absorption process will also annihilate ϕ_2 and therefore a mode-to-mode scattering rate defined between ϕ_1 and ϕ_2 , Γ_{ϕ_1,ϕ_2} , cannot be directly related to the net rate of transfer of energy from ϕ_1 to ϕ_2 ; the scattering rate counts event probabilities but does not determine the net change to the energy unless all terms in the energy rate are of the same sign, as is the case for the relationship between ϕ_1 to ϕ_3 .

Finally, to facilitate the study of scattering involving large numbers of modes, the bands defined in Table 3.2 are used to define scattering in a band-averaged sense. We extend the use of SMRTA by imagining all modes in a band are perturbed one at a time and their subsequent scattering behaviors are analyzed using averages. The target modes ϕ_3 can also be grouped in bands. In this way, *band1* corresponds to ϕ_1 while *band3* corresponds to ϕ_3 . The average percent contribution of any *band3* to the scattering rate of any *band1* is then determined from the individual modes using

$\Gamma_{band1,band3}$

$$=\frac{1}{no.\,of\,\,modes\,\,in\,\,band1}\sum_{\phi_1\in band1}100\frac{\sum_{\phi_3\in band3}\Gamma_{\phi_1,\phi_3}}{\Gamma_{\phi_1}} \tag{92}$$

To account for the unequal number of modes in the bands, band-to-band scattering rates weighted by the number of modes in band 3 are also used

$$\Gamma_{band1,band3}^{weighted} = \frac{\Gamma_{band1,band3}}{no. of modes in band3}$$
(93)

6.1.1 Mode-to-Mode Energy Transfer Results

Mode-to-mode scattering rates are needed to identify the modes that are responsible for the majority of energy transfer into or out of any particular mode of interest. The mode-to-mode scattering rates (Γ_{ϕ_1,ϕ_3}) are shown in Figure 6.1 and the band-to-band scattering rate contributions ($\Gamma_{band_1,band_3}$) are shown in Figure 6.2.

The results indicate a sub-picosecond relaxation of the nitro group wagging and rotation modes (bands 2 and 3) which was also suggested by Aubuchon et al. [51]. Aubuchon et al. also observed a relaxation time of 6.2 ± 0.4 ps for the asymmetric stretching of the nitro group (band 18) as compared to the 2.19 ps relaxation time estimated in this work. Ostrander et al. observed cross- peak dynamics of ~2 ps and anisotropy decay of ~400 fs while probing the nitro group asymmetric stretching mode in PETN and attributed the ps decay to the rapid intramolecular vibrational energy transfer [60]. This is consistent with our observations in RDX where the high frequency intramolecular modes in bands 15-18 contribute ~40% to the scattering of band 18 (shown in) with relaxation times up to 2.19 ps (shown in). Our results indicate that the sub-picosecond anisotropy decay could be due to scattering of the nitro group modes with the low frequency phonon modes up to 192 cm⁻¹ which exhibit relaxation times up to 370 fs and account for over 57% of the scattering of band 18 modes as shown in.

spectroscopy to probe a narrow band at 1533 cm⁻¹ in thin film RDX [156]. Following the excitation, instantaneous vibrational energy transfer (within 200 fs) to all modes was observed, indicating a strong anharmonic coupling of the mode at 1533 cm⁻¹ with all other modes in RDX. This instantaneous energy transfer could be due to the high mode-to-mode scattering rate between the low frequency modes (0 to ~ 192 cm⁻¹) and the nitro stretching mode in band 18 (band 18 being ϕ_1) as shown in Figure 6.1 as well as, indirectly, due to scattering of other modes by these low frequency modes. Ramasesha et al. also observed energy transfer dynamics up to 10 ps for modes in the 800 to 900 cm⁻¹ and 1200 to 1600 cm⁻¹ regions, and over 100 ps dynamics for NO₂ stretching, NN stretching and CN stretching modes [156]. Such large relaxation times can be explained by the mode-to-mode scattering rates on the order of 10^{-1} to 10^{-5} ps⁻¹ between band 18 and bands 11-17 as shown in. The large relaxation times could be due to the relatively weaker anharmonic coupling and lower number of 3-phonon scattering events for these modes as shown in Figure 4.5 and Figure 4.6. The band-to-band scattering rate contributions $\Gamma_{band1,band3}$ and $\Gamma_{band1,band3}^{weighted}$ are shown in Figure 6.2 and Figure 6.3 respectively. These results indicate that the low frequency modes in bands 1-3, which constitute ~12% of the total number of modes in RDX, are responsible for the majority of scattering of all the modes, accounting for 67.3% of the mode-to-mode scattering rates (Γ_{ϕ_1,ϕ_3}) averaged over all modes ϕ_1 , calculated as $\frac{1}{total no.of modes} \sum_{\phi_1} 100 \frac{\sum_{\phi_3 \in band \ 1,2,3} \Gamma_{\phi_1,\phi_3}}{\Gamma_{\phi_1}}$. In contrast, the mid frequency bands 4-16, which constitute ~60% of the total number of modes, account for 24.3% of the modeto-mode scattering and the high frequency bands 17-20, which constitute $\sim 28\%$ of the total number of bands, account for 8.4% of the mode-to-mode scattering averaged over all modes ϕ_1 . The trivial contribution of the high frequency modes to vibrational energy transfer is due to their weak anharmonic coupling and lack of participation in 3-phonon scattering as shown in . indicates that perturbing the low frequency modes up to 102 cm⁻¹ results in over 99% of the vibrational energy transfer to other low frequency modes up to 102 cm⁻¹. Further, perturbing the modes up to 424 cm⁻¹ results in less than 0.5% vibrational energy transfer to the NN bands. Perturbing the modes in band 8 (457 to 462 cm⁻¹) results in 5.16% energy transfer to the NN bands. However, the majority of energy transfer to the NN bands occurs when phonons in bands 12, 13, 14, 16 and 20 are perturbed resulting in 34.5%, 30.3%, 56.3%, 20.6% and 12.8% energy transfer to the NN bands, respectively. This indicates that perturbing the very low frequency lattice modes results in transfer of energy to other low frequency modes only and that the mid-frequency modes must be excited in order to transfer the vibrational energy to the NN stretching modes. These results strongly indicate that the modes in these bands are the likely doorway modes in RDX.

Based on the results in Table 4.1 and Table 6.1, the following up-pumping pathway is suggested: Low frequency modes up to 50 cm⁻¹ transfer ~4.8% of the vibrational energy to the modes between 50 and 102 cm⁻¹. The energy transfer from these low frequency modes lasts for less than 0.16 ps which is the highest relaxation time of phonons in the frequency range 0 to 102 cm⁻¹. Next, the mid frequency modes from 102 to 1331 cm⁻¹, which include the ring, nitro, and nitramine distortion modes, further up-pump the vibrational energy until it reaches the NN bands. Among the mid frequency modes, the NN stretching and CH₂ rocking contained in band 14 transfer the largest amount of energy to the NN bands (56.3%). This is followed by band 12

(34.5%) and band 13 (30.3%) which correspond to NN and CN stretching. Although the relaxation time of the mid frequency modes can be as small as 5.6 ps, the energy transfer process may occur over hundreds of ps due to smaller average mode-to-mode scattering rates. Finally, the high frequency modes from 1475 to 2910 cm⁻¹ scatter and redistribute a small fraction of the vibrational energy to all other modes. The energy transfer from these high frequency modes is slow with relaxation times over 2000 ps.

Figure also indicates that when all of the modes in the NN bands 8, 11, 12, 13, 14 and 16 are perturbed one band at a time, the low frequency modes in bands 1-3 combined contribute to the scattering ~54%, ~84%, ~57%, ~65%, ~38%, and 65%, respectively, resulting in a rapid flow of energy out of the NN bands and vibrational cooling of the NN stretching modes. Likewise, the contribution of the mid frequency bands 4-16 combined are ~46%, ~16%, ~43%, ~35%, ~62%, and ~35%, respectively. The highest frequency bands 17-20 appear to neither heat nor cool the NN bands.

A large number of 3-phonon scattering channels is available to the low frequency modes up to 102 cm⁻¹. These modes are highly anharmonic and therefore scatter quickly and redistribute the majority of any nonequilibrium energy to other low frequency modes within 160 fs. Similar fast energy transfer dynamics were also observed by Cole-Filipiak et al. [64] who reported vibrational energy transfer to all the modes in PETN within 200 fs following excitation of the nitro group asymmetric stretching mode at 1660 cm⁻¹. This could have resulted from the rapid vibrational energy transfer to the highly anharmonic low frequency modes. In addition, the transient spectra of the modes in PETN presented in [64] show strong absorption within 1 ps timescale. Such fast energy transfer dynamics, which are commensurate with the

sub-picosecond relaxation times of the low frequency molecular translation modes, indicate the primary role played by these modes in vibrational cooling of the NO₂ and NN stretching modes. Although the quantitative contribution of the low frequency modes in energy transfer is not well-studied, our results indicate that among the low frequency modes, band 1 modes contribute more to the vibrational cooling of other modes than band 2 or 3. Averaged over all first phonon modes (ϕ_1), the contribution of band 1 to the mode-to-mode scattering rate is 4.55 times larger than the contribution of band 2 and 14.65 times larger than the contribution of band 3. That is, modes in band 1 have the tendency to be the target of much of the energy from scattering events that cool other modes.

The vibrational energy transfer pathways via 3-phonon scattering identified in this work suggest that a unit of energy imparted to the lowest frequency modes under equilibrium would result in an instantaneous transfer of energy directly to all other low frequency vibrational modes up to 102 cm⁻¹. A negligible amount of energy is transferred directly from the lowest frequency modes to the NN stretching modes. The transfer of energy from the low frequency modes to the NN stretching modes likely travels through mid-frequency doorway modes. Although the current use of equilibrium conditions does not accurately imitate the material behavior under shock, qualitative conclusions can still be drawn regarding the strength of phonon-phonon scattering and the likely pathways of energy transfer in molecular crystalline solids. The accuracy of the model can also be improved at the cost of computational resources by including higher order anharmonic terms in the Hamiltonian (4-phonon scattering or higher) which become increasingly important at higher temperatures. Further improvement can be achieved by sampling the entire Brillouin zone using a larger number of kpoints, and by lifting the single mode relaxation time approximation to accurately model the change in phonon population and the anharmonic coupling between the modes. In addition, use of more accurate quantum mechanical models like Density Functional Theory to model the interaction between the atoms and molecules can provide greater insights into the physical and chemical processes that may lead to critical vibrational energy transfer mechanisms in energetics.



Figure 6.1 3-phonon mode-to-mode scattering rates (Γ_{ϕ_1,ϕ_3} , ps-1) for all modes in RDX. Low frequency modes up to 102 cm⁻¹ have the highest mode-to-mode scattering rates averaged over all modes ϕ_1 . The figure represents a total of ~12 billion pathways for vibrational energy transfer between the phonon modes in RDX and the colors represent the energy transfer rate (scattering rate) for all possible pathways.

		Band 3																			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	1	94.51	3.61	1.17	0.54	0.02	0.01	0.01	0.00	0.03	0.00	0.01	0.00	0.00	0.00	0.02	0.01	0.01	0.01	0.02	0.02
	2	93.27	5.93	0.57	0.22	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3	69.43	26.79	3.65	0.11	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4	50.85	11.49	12.25	25.38	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5	42.62	10.10	9.60	24.39	13.18	0.00	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
	6	51.44	16.49	4.41	3.51	24.09	0.00	0.02	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	7	39.00	8.77	6.39	13.43	7.13	19.75	4.99	0.51	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	8	20.51	17.69	15.42	5.39	0.79	7.53	27.52	5.07	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	9	63.81	4.83	1.28	1.18	0.27	0.14	1.11	1.49	25.89	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ι	10	55.40	35.64	0.92	1.77	2.04	0.34	0.45	0.00	3.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Band	11	63.99	10.96	8.56	0.00	0.50	0.00	1.00	0.22	0.50	10.92	3.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Η	12	45.88	10.82	0.00	0.00	0.53	0.00	5.43	5.43	0.55	2.29	29.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	13	57.87	7.16	0.31	0.00	1.98	0.00	0.16	0.04	1.95	0.31	18.51	11.72	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	14	18.98	8.63	10.63	0.15	2.11	0.65	0.07	18.54	2.33	0.15	11.93	7.36	18.23	0.25	0.00	0.00	0.00	0.00	0.00	0.00
	15	44.23	14.32	3.50	2.27	1.94	0.07	1.13	0.00	10.74	0.17	1.10	0.01	0.04	1.19	19.29	0.00	0.00	0.00	0.00	0.00
	16	57.38	7.00	0.76	2.17	1.80	0.00	0.39	2.44	0.66	0.02	3.09	0.00	0.38	0.00	9.16	14.72	0.00	0.02	0.00	0.00
	17	78.00	13.18	0.00	0.71	0.17	0.00	0.00	0.00	1.93	0.00	0.00	0.32	0.00	1.61	0.17	0.71	3.17	0.00	0.00	0.00
	18	51.72	5.81	0.00	0.10	2.01	0.18	0.54	0.00	0.28	0.00	0.00	0.00	0.03	0.24	1.24	1.61	19.49	16.75	0.00	0.00
	19	52.05	0.01	0.01	0.12	0.05	0.00	0.25	0.00	15.38	0.29	0.38	0.65	0.52	0.38	5.37	0.54	1.08	9.27	13.63	0.02
	20	8.30	33.62	1.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.04	12.81	0.00	12.81	6.04	18.55

Table 6.1. 3-phonon band-to-band scattering rate contributions ($\Gamma_{band1,band3}$,%). Rows represent *band1* and columns represent *band3*. Each column represents the percent contribution of that band to the scattering rate of the phonons in the corresponding rows.



Figure 6.2. Colors represent Band-to-Band scattering rate contributions $\Gamma_{band1,band3}$. The majority of energy leaving the low frequency bands gets deposited into other low frequency bands, and the energy must reach the mid-frequency bands which then redistribute a substantial amount of the energy to the NN active bands.



Figure 6.3. Colors represent Band-to-band scattering rate contributions weighted by the number of modes in band 3, $\Gamma_{band1,band3}^{weighted}$.

6.1.2 Conclusion

An FGR-based 3-phonon scattering model is used to calculate the mode-tomode scattering rates in crystalline RDX. The low frequency modes up to 102 cm⁻¹ scatter quickly and transfer over 99% of its nonequilibrium vibrational energy to other low frequency modes up to 102 cm⁻¹ within 0.16 ps. These low frequency molecular vibration modes have a low scattering probability with NN stretching modes. The mid frequency modes between 457 and 462 cm⁻¹, and between 831 and 1331 cm⁻¹ are responsible for the majority of energy transfer to the NN stretching modes, within 5.6 ps, and are therefore the likely doorway modes. Furthermore, the low frequency modes up to 102 cm⁻¹ dominate vibrational cooling, receiving 38% to 65% of the nonequilibrium energy scattered out of the NN stretching bands. The mid-frequency modes from 102 to 1331 cm⁻¹ also contribute substantially, though to a lesser degree, to the vibrational cooling of the NN bands. The highest frequency modes have the lowest contribution to vibrational cooling due to their trivial participation in 3-phonon scattering. The timescales associated with these modes is over 2000 ps. Based on these observations, the mid-frequency modes are the most critical for vibrational heating of the NN stretching modes and phenomena leading to initiation in energetics and, in contrast, the low frequency modes up to 102 cm⁻¹ dominate vibrational cooling of the NN stretching modes.

Chapter 7: Mode-selective Stimulation of Phonons: A Numerical Experiment

The 3-phonon scattering rates and mode-to-mode scattering rates calculated in Chapters 4 and 6 provide a detailed picture of anharmonic interactions and vibrational energy transfer between phonon modes in RDX and how these properties can affect physical properties such as thermal conductivity as discussed in Chapter 4. For instance, the lowest frequency modes have high modewise specific heat values and are also the dominant carriers of heat in RDX, however, it is the mid-frequency doorway modes that must be excited for the up-pumping of vibrational energy to the intramolecular vibrations. In this chapter, we perform a numerical experiment to investigate the effects of stimulating different Infrared (IR) active vibrational modes in RDX (stimulating one mode at a time) on the vibrational energy transfer rates between the modes. This may result in an enhancement or frustration of physical properties such as thermal conductivity and diffusivity and, therefore, may have an influence over the sensitivity of the energetic material.

7.1 Introduction

The desire to control material properties and discover new materials with exotic properties such as high temperature superconductivity, a high figure of merit for thermoelectrics, etc. has motivated a considerable effort to study the nature of interaction between photons and phonons in perovskites, cuprates [157, 158, 159, 160, 100]

161], manganates [162, 163, 164, 165, 166, 167], piezoelectrics [168], optical [169, 170, 171], semi-conductor materials, etc. [172, 93, 173]. The use of strong optical pulses in far-infrared to mid-infrared frequency range (0.1 to 100 THz) with optical power ranging from milli-Watts to several Watts has emerged as a powerful tool to control material properties in solid state and condensed matter systems [174, 175, 176, 177, 172, 93, 178, 179]. The excitation of material leads to a highly non-equilibrium distribution of electrons or phonons (depending on the photon-matter interaction) which relaxes via anharmonic scattering processes such as electron-electron, electronphonon, phonon-phonon scattering, etc. [95, 180, 96, 181, 182, 92, 183, 179, 178, 184]. In complex highly anharmonic systems, there exists a delicate balance between different degrees of freedom such that small perturbations may result in significant changes in material properties, or even phase transitions [184, 185]. As a result, optical stimulation can be highly effective in tuning the material behavior, such as insulatorto-metal transition, excitation of coherent orbital waves, crystal structure modification, etc. [186, 187, 188, 189, 190, 191].

Recent advances in ultrafast infrared spectroscopy have enabled the investigation of vibrational energy transfer dynamics in complex molecular crystals such as energetics where crucial physical and chemical processes may occur on subpicosecond timescales [64, 65, 192, 156, 193, 194, 195, 196, 197]. The majority of these studies have focused on shock-induced chemistry [195, 196, 197], or investigation of vibrational energy transfer dynamics via probing certain vibrational modes [64, 65, 156, 192, 193, 194] to form a more complete understanding of the shock-to-initiation process in energetics. However, investigating every phonon mode in the system experimentally can be extremely expensive and time consuming, and therefore a more thorough investigation can be performed using computational techniques to provide useful insights into the relative importance of stimulating certain phonon modes in controlling the physical properties of energetics.

7.2 Infrared-Phonon Interaction

In this Section, we discuss the theory of interaction between electromagnetic radiation and lattice vibrations which can be used to stimulate the desired vibrational modes and measure the effects of stimulation such as the amount of optical energy absorbed, increase in phonon population, etc. The interaction between light (electromagnetic radiation or EMR) and lattice vibrations can be understood through a simple schematic shown in Figure 7.1, where the dipole moment of a molecule interacts with the electric field of light resulting in stretching/ shrinking of bonds. The probability of electromagnetic radiation interacting with molecules resulting in a transition from an initial vibrational state to a final state can be described by solving the Time Dependent Schrödinger Equation (TDSE). For EMR, the electric and magnetic fields can be written as

$$\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}_{\boldsymbol{o}}\cos(\boldsymbol{k}.\boldsymbol{r}-\omega t) \tag{94}$$

$$\boldsymbol{B}(\boldsymbol{r},t) = \boldsymbol{B}_{\boldsymbol{o}}\cos(\boldsymbol{k}.\boldsymbol{r}-\omega t) \tag{95}$$

where wavevector $|\mathbf{k}| = 2\pi/\lambda$ where λ is the wavelength of the EMR, $\mathbf{E} \perp \mathbf{B}$, and $|\mathbf{E}_o| = c |\mathbf{B}_o|$, where $c = 2.99798 \times 10^8 \text{ m/s}$ is the speed of light in vaccum, and \mathbf{r} is a spatial vector. In case of IR radiation, the wavelength $\lambda \gg size$ of the molecule.

Due to the large difference between λ and size of the molecule, *k*. *r* terms in Eq. (94) and (95) become negligible, and the electric and magnetic fields experienced by the molecule can be assumed to be the same throughout the molecule. This is referred to as The Dipole Approximation and as a result, the electric and magnetic fields can be expressed using only the zeroth order terms as

$$\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}_{\boldsymbol{o}}\cos(\omega t) \tag{96}$$

$$\boldsymbol{B}(\boldsymbol{r},t) = \boldsymbol{B}_{\boldsymbol{o}}\cos(\omega t) \tag{97}$$

The electronic component of the time dependent Hamiltonian can be written as

$$H(t) = H^{(0)} + H^{(1)}(t)$$
(98)

where $H_E^{(0)}$ is the zeroth order term, $H^{(1)}(t) = -\boldsymbol{\mu} \cdot \boldsymbol{E}(t)$ represents the first order perturbation term, $\boldsymbol{\mu}$ is the dipole moment. Any initial quantum state $\Psi(t)$ can be written as a linear combination of the zero order eigenstates $\psi_n(t)$

$$\Psi(t) = \sum_{n} c_n(t)\psi_n(t)$$
(99)

where $c_n(t)$ are time dependent coefficients, n is an index for the eigenstates. Substituting Eq. (99) into TDSE, $i\hbar \frac{\partial \Psi(t)}{\partial t} = H \Psi$, we get

$$i\hbar \sum_{n} c_{n}(t) \psi_{n}(t) + c_{n}(t) \psi_{n}(t) = H \sum_{n} c_{n}(t) \psi_{n}(t)$$
 (100)

The second term on the left hand side in Eq. (100) is equal to $c_n(t) \frac{1}{i\hbar} H^{(0)} \psi_n(t)$ where $H^{(0)}$ is the unperturbed Hamiltonian. Substituting this into Eq. (100)

$$i\hbar \sum_{n} \left[c_{n}(t) \psi_{n}(t) - \frac{i}{\hbar} E_{n} c_{n}(t) \psi_{n}(t) \right]$$

$$= \sum_{n} c_{n}(t) \left(E_{n} + H^{(1)}(t) \right) \psi_{n}(t)$$
(101)

The second term inside the summation on the left side of Eq. (101) is the same as the first term inside the summation on the right side, and therefore they cancel each other and Eq. (101) can be simplified as

$$i\hbar \sum_{n} c_n(t) \psi_n(t) = \sum_{n} c_n(t) H^{(1)}(t) \psi_n(t)$$
 (102)

Multiplying both sides by $\psi_f^*(t)$ and integrating, where the subscript f denotes the final state, the right side of Eq. (102) can be written as

$$\sum_{n} c_{n}(t) \int \psi_{f}^{*}(t) H^{(1)}(t) \psi_{n}(t) dt \qquad (103)$$

Substituting $H^{(1)}(t) = V \cos \omega t = V \frac{1}{2} (e^{i\omega t} + e^{-i\omega t})$ where V is a square matrix representing the anharmonic coupling between the vibrational modes, and $\psi_f^*(t) = \psi_f^*(0) \frac{1}{2} e^{-i\omega_{nf}t}$, where $\omega_{nf} = \frac{E_n - E_f}{h}$, the expression in (103) can be written as $\sum_n c_n(t) \int \psi_f^*(0) \frac{1}{2} V (e^{-i(\omega_{nf}t - \omega t)} + e^{-i(\omega_{nf}t + \omega t)}) \psi_n(0) dt$ (104)

The above expression is a resonance integral which will be non-zero only when $\omega_{nf} = \pm \omega$. This is referred to as the Gross Selection Rule of Infrared spectroscopy, i.e. $E_{EMR} = E_{vibration}$. Therefore, when stimulating a phonon mode with energy $\hbar \omega_{\phi_s}$, the frequency of the optical pulse also must be ω_{ϕ_s} .

Assuming that the initial state is one of the eigenstates and using the above simplification, Eq. (101) can be re-written as

$$c_f(t) = \lim_{T \to \infty} \frac{V}{2i\hbar} \int_0^T \left[e^{-i(\omega_f t - \omega t)} + e^{-i(\omega_f t + \omega t)} \right] dt$$
(105)

The probability of transition from an initial state i to a final state f can be calculated as

$$P_{fi}(t) = |c_f(t)|^2$$

$$= \lim_{T \to \infty} \frac{V_{fi}^2}{4\hbar^2} \left| \int_0^T [e^{-i(\omega_f t - \omega t)} + e^{-i(\omega_f t + \omega t)}] dt \right|^2$$
(106)

Note that the expression in Eq. (106) defines a probability and therefore should always be less than or equal to 1, however, the integral on the right side is greater than and therefore a normalization must be done. However, we are interested in calculating the rate of transition from the initial state *i* to the final state $f(W_{fi})$ which can be calculated by taking the time derivative of Eq. (106)

$$W_{fi}(t) = \lim_{T \to \infty} \frac{V_{fi}^2}{4\hbar^2} \left[\delta \left(E_i - E_f - \omega \right) + \delta \left(E_i - E_f + \omega \right) \right]$$
(107)

The above expression provides the rate of transition from an initial quantum state i to a final state f and is referred to as the Fermi's Golden Rule. The first term inside the square brackets on the right hand side represents the emission process and the second term represents the absorption process.

Once the Gross selection rule is satisfied, the intensity of absorption line (intensity of EMR absorbed by the phonon mode) can be calculated as

$$\langle \mu \rangle = \int_{\tau=all \ space} \Psi_{\text{final}}^* \left(-\boldsymbol{\mu} \cdot \boldsymbol{E} \right) \Psi_{initial} \ d\tau \tag{108}$$

where E is the electric field, and the dipole moment μ can be expanded as (up to first order term)

$$\boldsymbol{\mu} = \boldsymbol{\mu}_{\boldsymbol{o}} + \frac{\partial \boldsymbol{\mu}}{\partial \boldsymbol{Q}} q \tag{109}$$

where μ_0 is responsible for causing rotational transition and $\frac{\partial \mu}{\partial Q}$ causes vibrational transition, and Q is the normal mode coordinate. The molecules in crystal will absorb an IR radation and exhibit a vibrational transition only if the integral in Eq. (108) is non-zero, which implies that $\frac{\partial \mu}{\partial Q} \neq 0$. This is the Second Selection Rule of IR spectroscopy. As a result of the Second Selection Rule, the symmetric molecular vibrational modes for which the change in dipole moment is zero are IR inactive and the asymmetric vibrational modes are usually IR active, and therefore only the asymmetric molecular vibrational modes can be stimulated using IR pulses. The rate of vibrational transition during IR absorption is described by the Fermi's Golden Rule (FGR) and the intensity of IR absorption depends on the change in a molecule's dipole moment due the electric field.

No external electric field



Figure 7.1 Schematic of interaction between electric field and molecule dipole.

7.3 Computational Details

In this Section, we discuss the experimental details that are required to perform our numerical experiment for mode stimulation. For instance, identifying the IR active modes in RDX, the specifications of laser sources that are available such as EMR frequency, pulse duration, pulse width, optical energy, and fluence, etc.

In experiments, high intensity optical pulses used to probe the molecular vibrations in mid and far-infrared regions can be generated using a Free-electron laser (FEL) or gas lasers such as CO₂-TEA laser (TEA stands for Transversely Excited Atmospheric). Alternatively, a continuous wave (CW) laser with a relatively smaller optical power can also be used to stimulate the vibrational modes. The use of a lower optical power comes with the benefit of avoiding laser ablation of the target material,
however, the pulsed lasers can improve the throughput. A schematic of the optical power of pulsed and CW lasers spaced in time (temporal profile) is shown in Figure 7.2. The available laser sources can be used to stimulate molecular vibrations in the frequency range of 0.1 to 100 THz (~ 3 to 3000 cm⁻¹). Besides the EMR frequency, other important details of the laser source include its temporal profile (Gaussian) i.e., pulse width/duration (ranging from ~30 fs to ~250 ns), pulse period/frequency (THz range), optical power (peak power of ~1 Watt to ~50 Watts, proportional to EMR frequency), fluence (typically 1 to 2.5 mJ/cm²), and the spectral profile [179, 162, 172, 163, 166, 184, 186, 93, 178]. The optical power of ~ 1 Watt for a pulse frequency of ~ 1 THz corresponds to optical energy of 10^{-12} J. Typically, the spectral profile is also a Gaussian with a linewidth of few cm⁻¹ (spectral). A schematic of the spectral profile of the optical pulse is shown in Figure 7.3. Next, the IR is focused on to the material using an optical lens leading to the interaction between the electric field and the vibrational modes.

In the subsequent sub-sections, we identify the IR active vibrational modes in RDX and discuss the computational details of our numerical experiment.



Figure 7.2 Schematic of the optical power of (top) a pulsed laser, and (bottom) a continuous wave laser spaced in time.



Figure 7.3 Schematic of spectral profile of an optical pulse.

7.3.1 IR Active Vibrational Modes in RDX

Numerous computational and experimental studies have investigated the absorption of electromagnetic radiation by the molecules in RDX using *ab-initio* calculations and Terahertz spectroscopy [112, 198, 199, 200, 201, 110, 202, 203, 114, 204]. Based on the EMR absorption spectra, the assignment of IR and Raman modes is performed by comparing the absorption lines with those of related chemical moieties such as nitro, amino, etc. However, the majority of phonon modes in the system are a combination of vibrational modes involving more than one type of motion.

In this Section, we identify the IR active modes in α phase RDX based on IR spectroscopy data in the literature. The fraction of radiation energy absorbed by different vibrational modes can be obtained from the IR spectroscopy absorption/transmission spectral lines. Some literature report absolute values of % absorption or transmission, whereas others report a normalized value by dividing the % absorption of all modes with the largest % absorption among all modes. Due to this normalization, the absolute %absorption of the modes can be unclear. For consistency between the data obtained from different literature, we compare the normalized absorption values to the absolute absorption values and scale the normalized values accordingly. The IR active modes and % transmission or absorption reported in different literature are shown in Appendix 4. Out of all IR active modes identified by the experimental literature, we selected 15 modes for stimulation in this work. The mode frequencies (ω_{ϕ_s}) , energies $(E_{\phi_s} = \hbar \omega_{\phi_s})$, equilibrium phonon population (n_{ϕ_s}) calculated using BE statistics, and % absorption of these 15 modes are shown in Table 7.1.

Mode Frequency	Mode Energy,	Equilibrium	% Absorption $_{\phi_s}$
$\omega_{\phi_s} (\mathrm{cm}^{-1})$	E_{ϕ_S} (meV)	Occupation n_{ϕ_s}	
22.74	2.82	57.1140	19.54
43.99	5.46	29.2848	4.21
71.25	8.83	17.8920	17.14
83.38	10.34	15.2178	33.08
190.87	23.67	6.3760	23.81
405.03	50.22	2.7603	28.32
503.51	62.43	2.1339	27.94
582.36	72.21	1.7866	64.80
786.90	97.57	1.2147	50.67
914.84	113.43	0.9898	30.18
1140.67	141.44	0.7202	51.33
1299.72	161.16	0.5893	36.99
1501.31	186.15	0.4661	20.69
1739.89	215.74	0.3605	70.97
2823.76	350.13	0.1310	23.51

Table 7.1 15 IR active modes in RDX selected for stimulation and corresponding % absorption obtained from literature [204, 205, 109, 200, 112, 206, 114, 207]. Subscript *s* denotes that these modes have been selected for stimulation.

7.3.2 Mode-Selective Stimulation Energy

In our numerical experiment, for the sake of simplicity, we assume a CW laser source and a constant spectral profile with a linewidth of 1 cm⁻¹. Although, the optical energy of the laser sources used in experiments is on the order of 10^{-12} J, in this work, we use a smaller optical energy input, few meV to few eV (~ 10^{-22} J to 10^{-19} J). For instance, an optical energy input of 1 eV for stimulating the mode at 22.74 cm⁻¹ means that 1 eV is incident on the material, and a portion of this energy will be absorbed by the molecular vibrations depending on the %absorption shown in Table 7.1. An example of the spectral profile of the laser source assumed in our numerical experiment is shown in Figure 7.4. For each mode shown in Table 7.1:

- The frequency of the laser source is assumed to be exactly the same as the frequency of the phonon mode to be stimulated i.e., $\omega_{\phi_s} = \omega_{EMR}$.
- To investigate the sensitivity of the physical properties with respect to the stimulation energy, six different energy values of the optical pulse (E_{in,ϕ_s}) are used for stimulating the modes, three at high intensity (few eV) and three at low intensity (tens of meV) (1 eV= 1.6021×10^{-19} Joules) as shown in Table 7.2 and Table 7.3 respectively.
- Since the optical power of the lasers is directly proportional to the frequency of the vibrational mode being stimulated, for each case in (b), the modewise input energies are calculated such that E_{in,ϕ_s} is linearly proportional to ω_{ϕ_s} . For instance, if the energy input to the mode at 22.74 cm⁻¹ is 1.0 eV then the energy input to a mode at 43.99 cm⁻¹ is $1 \times \frac{43.99}{22.74} = 1.935$ eV.

- The energy absorbed by any mode is calculated as E_{abs,φs} = E_{in,φs} × % Absorption_{φs} where modewise % Absorption_{φs} are shown in 2nd column of Table 7.1.
- The increase in phonon population of any mode ϕ_s after stimulation is calculated as $\Delta n_{\phi_s} = \frac{E_{abs,\phi_s}}{E_{\phi_s}}$, where $E_{\phi_s} = \hbar \omega_{\phi_s}$.
- For each mode, a constant spectral profile of the optical pulse is assumed with a linewidth of 1 cm⁻¹ centered at the phonon mode frequency as shown in Figure 7.4. This means that during the numerical stimulation of any mode at ω_{φs}, modes at ω_{φs} ± 0.5 cm⁻¹ will also be stimulated receiving the same input energy E_{in,φs}.

The stimulated phonon mode frequencies, modewise energy input, energy absorbed and increase in phonon population for all six cases are shown in Table 7.2. Finally, for every case i.e., 15 stimulated modes \times 6 cases each = total 90 cases, 3-phonon scattering rates and mode-to-mode scattering rates are calculated under the Single Mode Relaxation Time Approximation (SMRTA) as discussed in Chapter 4. Subsequently, properties such as phonon mean free path, modewise diffusivity and thermal conductivity (using the Phonon Gas Model) are calculated.

It should also be noted that as a result of stimulating the modes, the scattering rates for some of the modes become negative. This can be understood as follows: The calculation of scattering rates as shown in Eq. (54) describes the rate at which the phonon population of the perturbed mode (ϕ_1) reduces via 3-phonon scattering. However, when a particular mode is stimulated (ϕ_s) with a large amount of energy, this

results in a large deviation from the equilibrium of the system (much larger than small perturbation of mode ϕ_1). As a result of this large deviation from equilibrium, the mode with a small perturbation (ϕ_1) is likely to accept a lot more energy from the stimulated mode (ϕ_s) than it is releasing. Mathematically, this can be represented as $\Gamma^{eq} \cdot_{\phi_1} \ll \Gamma^{neq} \cdot_{\phi_s,\phi_1}$, where $\Gamma^{eq} \cdot_{\phi_1}$ represents the scattering rate of the mode ϕ_1 when mode stimulation is absent, and $\Gamma^{neq} \cdot_{\phi_s,\phi_1}$ represents mode-to-mode scattering rate of energy from the stimulated mode ϕ_s to mode ϕ_1 . A schematic diagram is shown in Figure 7.13 to illustrate the same. Since there is a larger influx of energy for the mode ϕ_1 than the energy leaving, the scattering rate of the mode ϕ_1 is represented by a negative number. It should also be noted that a negative scattering rate or a negative change in scattering rate can still mean an increase in the magnitude of the scattering rate and thereby a smaller mean free path of the phonons.

The effect of mode stimulation is measured by calculating average values of percent change in modewise properties. For instance, the average percent change in scattering rates (average over all modes) when mode ϕ_s is stimulated (% $\Delta\Gamma^{avg,\phi_s}$) is calculated as

$$\% \, \Delta \Gamma^{avg,\phi_s} = \frac{1}{no.\,of \, modes \, \phi} \sum_{\phi} 100 \frac{\Gamma_{\phi}^{\phi_s} - \Gamma_{\phi}}{\Gamma_{\phi}} \tag{110}$$

where $\Gamma_{\phi}^{\phi_s}$ is the scattering rate of mode ϕ when mode ϕ_s is stimulated and $100 \times \frac{\Gamma_{\phi}^{\phi_s} - \Gamma_{\phi}}{\Gamma_{\phi}}$ represents modewise percent change in scattering rate. Similarly, bandwise average percent change in scattering rates (average over frequency bands) is defined as

$$\% \, \Delta \Gamma^{band_{1,\phi_{s}}} = \frac{1}{no.\,of \, modes \, in \, band_{1}} \sum_{\phi \in band_{1}} 100 \frac{\Gamma_{\phi}^{\phi_{s}} - \Gamma_{\phi}}{\Gamma_{\phi}} \quad (111)$$

The average percent change in modewise diffusivity (D_{ϕ}) is calculated as

$$\% \Delta D^{avg,\phi_s} = \frac{1}{no.\,of\,modes\,\phi} \sum_{\phi} 100 \frac{D_{\phi}^{\phi_s} - D_{\phi}}{D_{\phi}}$$
(112)

and bandwise average percent change in diffusivity is defined as

$$\% \Delta D^{band_{1,\phi_{s}}} = \frac{1}{no.\,of\,modes\,in\,band_{1}} \sum_{\phi \in band_{1}} 100 \frac{D_{\phi}^{\phi_{s}} - D_{\phi}}{D_{\phi}} \quad (113)$$

The percent change in x, y and z components of the thermal conductivity tensor κ_{xx} , κ_{yy} and κ_{zz} are calculated as

$$\% \Delta \kappa_{xx}^{\phi_s} = 100 \frac{|\kappa_{xx}^{\phi_s} - \kappa_{xx}|}{|\kappa_{xx}|}, \qquad \% \Delta \kappa_{yy}^{\phi_s} = 100 \frac{|\kappa_{yy}^{\phi_s} - \kappa_{yy}|}{|\kappa_{yy}|},$$

$$(114)$$

$$\% \Delta \kappa_{zz}^{\phi_s} = 100 \frac{|\kappa_{zz}^{\phi_s} - \kappa_{zz}|}{|\kappa_{zz}|}$$

and the percent change in scalar thermal conductivity is calculated as

$$\% \Delta \kappa_s^{\phi_s} = 100 \ \frac{\kappa_s^{\phi_s} - \kappa_s}{\kappa_s} \tag{115}$$

where κ_s represents the scalar thermal conductivity calculated as $\kappa_s = \frac{|\kappa_{xx}| + |\kappa_{yy}| + |\kappa_{zz}|}{3}$.

Mode				High E	nergy Stir	nulation			
Frequency		Case 1			Case 2			Case 3	
$\omega_{\phi_s} (\mathrm{cm}^{-1})$	E_{in,ϕ_s}	E_{abs,ϕ_s}	Δn_{ϕ_s}	E_{in,ϕ_s}	E_{abs,ϕ_s}	Δn_{ϕ_s}	E_{in,ϕ_s}	E_{abs,ϕ_s}	Δn_{ϕ_s}
	(eV)	(eV)		(eV)	(eV)		(eV)	(eV)	
22.74	0.50	0.10	34.7	1.00	0.20	69.3	2.00	0.39	138.7
43.99	0.97	0.04	7.5	1.94	0.08	14.9	3.87	0.16	29.9
71.25	1.57	0.27	30.4	3.13	0.54	60.8	6.27	1.07	121.6
83.38	1.83	0.61	58.7	3.67	1.21	117.4	7.33	2.43	234.7
190.87	4.20	1.00	42.2	8.40	2.00	84.5	16.79	4.00	168.9
405.03	8.91	2.52	50.2	17.82	5.05	100.5	35.63	10.09	200.9
503.51	11.07	3.09	49.5	22.15	6.19	99.1	44.29	12.37	198.2
582.36	12.81	8.30	114.9	25.62	16.60	229.9	51.23	33.20	459.7
786.90	17.31	8.77	89.9	34.61	17.54	179.8	69.22	35.08	359.5
914.84	20.12	6.07	53.5	40.24	12.14	107.1	80.48	24.29	214.1
1140.67	25.09	12.88	91.1	50.17	25.76	182.1	100.34	51.51	364.2
1299.72	28.58	10.57	65.6	57.17	21.15	131.2	114.34	42.29	262.4
1501.31	33.02	6.83	36.7	66.03	13.66	73.4	132.07	27.33	146.8
1739.89	38.26	27.16	125.9	76.53	54.31	251.8	153.06	108.63	503.5
2823.76	62.10	14.60	41.7	124.20	29.20	83.4	248.41	58.39	166.8

Table 7.2 Optical energy input, energy absorbed and corresponding increase in phonon population of the selected 15 IR active modes for three high energy stimulation cases.

Mode				Low E	nergy Stin	nulation			
Frequency		Case 4			Case 5			Case 6	
$\omega_{\phi_s} (\mathrm{cm}^{-1})$	E_{in,ϕ_s}	E_{abs,ϕ_s}	Δn_{ϕ_s}	E_{in,ϕ_s}	E_{abs,ϕ_s}	Δn_{ϕ_s}	E_{in,ϕ_s}	E_{abs,ϕ_s}	Δn_{ϕ_s}
	(meV)	(meV)		(meV)	(meV)		(meV)	(meV)	
22.74	5.00	0.98	0.3	10.00	1.95	0.7	20.00	3.91	1.4
43.99	9.68	0.41	0.1	19.35	0.81	0.1	38.70	1.63	0.3
71.25	15.67	2.69	0.3	31.34	5.37	0.6	62.68	10.75	1.2
83.38	18.34	6.07	0.6	36.67	12.13	1.2	73.35	24.27	2.3
190.87	41.98	9.99	0.4	83.96	19.99	0.8	167.91	39.98	1.7
405.03	89.08	25.23	0.5	178.15	50.45	1.0	356.31	100.91	2.0
503.51	110.73	30.93	0.5	221.47	61.87	1.0	442.94	123.74	2.0
582.36	128.08	82.99	1.1	256.15	165.99	2.3	512.30	331.97	4.6
786.90	173.06	87.70	0.9	346.12	175.40	1.8	692.23	350.79	3.6
914.84	201.19	60.72	0.5	402.39	121.44	1.1	804.78	242.89	2.1
1140.67	250.86	128.78	0.9	501.72	257.55	1.8	1003.44	515.11	3.6
1299.72	285.84	105.73	0.7	571.68	211.47	1.3	1143.36	422.93	2.6
1501.31	330.17	68.32	0.4	660.35	136.64	0.7	1320.70	273.29	1.5
1739.89	382.65	271.56	1.3	765.29	543.13	2.5	1530.58	1086.25	5.0
2823.76	621.01	145.98	0.4	1242.03	291.95	0.8	2484.05	583.90	1.7

Table 7.3 Optical energy input, energy absorbed and corresponding increase in phonon population of the selected 15 IR active modes for three low energy stimulation cases.



Figure 7.4 Example of spectral profile of the optical pulse assumed in this work (linewidth of 1 cm^{-1}).

7.4 Mode-Selective Stimulation Results

The average percent change in scattering rates (% $\Delta\Gamma^{avg,\phi_s}$) for mode-selective phonon stimulation for high and low energy stimulation are shown in Figure 7.5 and Figure 7.6 respectively. Among all stimulation cases, a substantially large increase in scattering rates is observed while (1) Stimulating the mode at 22.74 cm⁻¹, 43.99 cm⁻¹ or 71.25 cm⁻¹ in Case 3 resulting in ~58% average percent increase in the scattering rates (% $\Delta\Gamma^{avg,\phi_s}$), and (2) Stimulating the mode at 1140.67 cm⁻¹, 1299.72 cm⁻¹ or 1501.31 cm⁻¹ in Case 3 resulting in over 300% average percent increase in the scattering rates (% $\Delta\Gamma^{avg,\phi_s}$). The large change in scattering rates upon stimulating the low frequency modes can be attributed to a combination of two factors (1) The low frequency modes dominate the mode-to-mode scattering (Γ_{ϕ_1,ϕ_3}) due to their strong anharmonic coupling with other modes (especially with other low frequency modes)

and a relatively larger phase space volume (including a large density of states) available for 3-phonon scattering as shown in Figure 4.5 and Figure 4.6 respectively, and (2) The majority of low frequency modes scatter via absorption processes $(\phi_1 + \phi_2 \rightarrow \phi_3)$ involving two other low frequency modes, and since the increase in the phonon population of these low frequency modes due to stimulation is few hundred percent, a proportionate ~58% increase is observed in the scattering rates (% $\Delta \Gamma^{avg,\phi_s}$). Thus, as the phonon population of the low frequency modes is driven out of equilibrium, an equally strong increase in 3-phonon scattering rates is observed since the scattering rate is directly proportional to the phonon population as shown in Eq. (54). It should also be noted that stimulating the low frequency modes has a negligible effect on the scattering rates (Γ_{ϕ_1}) of the majority of the mid and high frequency modes due to a lack of 3-phonon scattering involving these modes as shown in bandwise-average $(\% \Delta \Gamma^{band_{1},\phi_{s}})$ plots in Figure 7.7 through Figure 7.12. On the contrary, the mid frequency modes between 1140 and 1501 cm⁻¹ scatter primarily via emission processes $(\phi_1 \rightarrow \phi_2 + \phi_3)$ involving one more mid frequency mode. Since the increase in phonon population of the mid-frequency modes upon stimulation might be over 1000%, a similarly large increase in the scattering rates is observed. In addition, stimulating the mid-frequency modes has a small effect on the scattering rates (Γ_{ϕ_1}) of the low frequency modes but results in a large percent increase in scattering rates of other mid frequency modes from ~ 1150 cm⁻¹ to ~ 1250 cm⁻¹, from ~ 1510 cm⁻¹ to ~ 1514 cm⁻¹, and of some high frequency modes in bands 19 and 20. In contrast, stimulating the high frequency mode at 2823.76 cm⁻¹ has a substantial effect on the scattering rates of only a small number of other high frequency modes in band 20 (from ~2894 cm⁻¹ to

~2897 cm⁻¹) which explains the overall small percent increase when averaged over all modes.

A higher stimulation energy (E_{in,ϕ_s}) , in general, results in a larger average percent change in the scattering rates ($\% \Delta \Gamma^{avg,\phi_s}$). For instance, when the mode at 22.74 cm⁻¹ is stimulated, the average percent change in scattering rates (($\% \Delta \Gamma^{avg,\phi_s}$) is 14.57%, 29.14% and 58.28% for Case 1 ($E_{in} = 0.5 \text{ eV}$), Case 2 ($E_{in} = 1 \text{ eV}$) and Case 3 ($E_{in} = 2 \text{ eV}$) respectively. The larger change in scattering rates for higher stimulation energy can be attributed to a union of two facts: 1) A higher stimulation energy results in a larger increase in the phonon population of the stimulated mode, and 2) The scattering rate is directly proportional to the phonon population as shown in Eq. (54). However, the second point is an oversimplified explanation for how the scattering rates are affected. More rigorously, the scattering rate for any mode ϕ_1 as shown in Eq. (54) is a summation over all phonon modes in the system which includes the stimulated mode ϕ_s . Thus, the expression in Eq. (54) can be further broken down as

$$\Gamma_{\phi_{1}} = \sum_{\phi_{2} \in \phi_{s}, \phi_{3} \in \phi_{s}} \left\{ \frac{1}{2} \left(1 + n_{\phi_{2}}^{0} + n_{\phi_{3}}^{0} \right) L_{-} + \left(n_{\phi_{2}}^{0} - n_{\phi_{3}}^{0} \right) L_{+} \right\} \\
+ \sum_{\phi_{2} \notin \phi_{s}, \phi_{3} \in \phi_{s}} \left\{ \frac{1}{2} \left(1 + n_{\phi_{2}}^{0} + n_{\phi_{3}}^{0} \right) L_{-} + \left(n_{\phi_{2}}^{0} - n_{\phi_{3}}^{0} \right) L_{+} \right\} \\
+ \sum_{\phi_{2} \notin \phi_{s}, \phi_{3} \notin \phi_{s}} \left\{ \frac{1}{2} \left(1 + n_{\phi_{2}}^{0} + n_{\phi_{3}}^{0} \right) L_{-} + \left(n_{\phi_{2}}^{0} - n_{\phi_{3}}^{0} \right) L_{+} \right\} \\
+ \sum_{\phi_{2} \in \phi_{s}, \phi_{3} \notin \phi_{s}} \left\{ \frac{1}{2} \left(1 + n_{\phi_{2}}^{0} + n_{\phi_{3}}^{0} \right) L_{-} + \left(n_{\phi_{2}}^{0} - n_{\phi_{3}}^{0} \right) L_{+} \right\}$$
(116)

where ϕ_s represents the stimulated mode. Breaking down the terms in this way can help in identifying the terms for which stimulating a mode will result in a corresponding increase in the phonon population and thereby scattering rate. For instance, in the first summation, since both ϕ_2 and ϕ_3 belong to ϕ_s , an "X" % increase in population of ϕ_s also means an "X" % increase in the population n_{ϕ_2} and n_{ϕ_3} and therefore, there will be an "X" % increase in the contribution to the scattering rate Γ_{ϕ_1} by the terms in the first summation. In the third summation, neither ϕ_2 nor ϕ_3 belong to ϕ_s , and therefore any increase in population of ϕ_s will not affect the phonon populations n_{ϕ_2} or n_{ϕ_3} and therefore will result in no extra contribution to the scattering rate. For the second and fourth summation, an "X" % increase in the population of ϕ_s will result in an "X" % increase in the population of ϕ_s will result in an "X" % increase in the population of ϕ_s and n_{ϕ_2} respectively, and therefore their contribution towards increase in scattering rate will depend on the magnitude of the coefficients L_- and L_- .

Overall, the highest average percent increase in scattering rates ((% $\Delta\Gamma^{avg,\phi_s}$) is achieved by stimulating the mode at 1140.67 cm⁻¹, 1299.72 cm⁻¹ or 1501.39 cm⁻¹ in Case 3, resulting in an average 329.01 % increase. In contrast, a reduction in scattering rates can be achieved by stimulating the mode at 1501.31 cm⁻¹, 1739.89 cm⁻¹ or 2823.76 cm⁻¹ in Case 2, resulting in an average reduction by 0.35%.



Figure 7.5 Average percent change in scattering rates (% $\Delta\Gamma^{avg,\phi_s}$) for Cases 1, 2 and



Figure 7.6 Average percent change in scattering rates (% $\Delta\Gamma^{avg,\phi_s}$) for Cases 4, 5 and



Figure 7.7 Bandwise average percent change in scattering rates (% $\Delta \Gamma^{band_1,\phi_s}$) for Case 1.



Figure 7.8 Bandwise average percent change in scattering rates (% $\Delta \Gamma^{band_1,\phi_s}$) for Case 2.



Figure 7.9 Bandwise average percent change in scattering rates (% $\Delta \Gamma^{band_1,\phi_s}$) for Case 3.



Figure 7.10 Bandwise average percent change in scattering rates (% $\Delta \Gamma^{band_{1},\phi_{s}}$) for Case 4.



Figure 7.11 Bandwise average percent change in scattering rates (% $\Delta\Gamma^{band_{1},\phi_{s}}$) for

Case 5.



Figure 7.12 Bandwise average percent change in scattering rates (% $\Delta \Gamma^{band_{1},\phi_{s}}$) for Case 6.



Figure 7.13 Schematic of vibrational energy transfer between the modes during equilibrium, a small perturbation (as modeled under SMRTA), and during mode stimulation.

The average percent change in diffusivity (% $\Delta D^{avg,\phi_s}$, average over all modes) and bandwise average percent change in diffusivity (% $\Delta D^{band1,\phi_s}$) are shown in Figure 7.14 through Figure 7.21. Similar to the scattering rates, the largest average percent increase in diffusivity (% $\Delta D^{avg,\phi_s}$) is observed when the mode at 1140.67 cm⁻¹, 1299.72 cm⁻¹ or 1501.39 cm⁻¹ is stimulated under Case 3, resulting in an average percent increase in diffusivity by 33.13%. For Case 1, the largest average percent change in diffusivity is observed when the mode at 582.36 cm⁻¹, 786.90 cm⁻¹ or 914.84 cm⁻¹ is stimulated resulting in a 30.35% increase, and for Case 2, the largest average percent change in diffusivity is observed when the mode at 405.03 cm⁻¹ is stimulated resulting in a 20.27% increase. In general, the large increase in diffusivity is also consistent with a large increase in the scalar thermal conductivity (% $\Delta \kappa_s^{\phi_s}$) as shown in Figure 7.22 and Figure 7.23. For instance, the largest increase in scalar thermal conductivity (71.79%) is observed upon stimulating the mode at 1140.67 cm⁻¹, 1299.72 cm⁻¹ or 1501.31 cm⁻¹ under Case 3 which is consistent with the largest average percent increase in diffusivity (% $\Delta D^{avg,\phi_s}$). Stimulating the mode at 1140.67 cm⁻¹ or 1299.72 cm⁻¹ under Case 1 results in a substantial increase in diffusivity (25.71%) and scalar thermal conductivity (21.87%).

The primary reason for the large increase in diffusivity and thermal conductivity can be attributed to a large increase in the phonon mean free path of some of the modes which exhibit a reduction in scattering rates upon mode stimulation. For instance, stimulating the mode at 582.36 cm⁻¹ in Case 1 results in an average 30.00% reduction in the scattering rate of the phonons in band 9 (% $\Delta\Gamma^{band_{1},\phi_{s}}$) which translates into an average 403.24% increase in the mean free path and diffusivity of the phonons in band 9 (% $\Delta D^{band_{1,\phi_s}}$). Stimulating the 582.36 cm⁻¹ mode also results in an average 84.38% and 89.99% increase in scattering rate of band 13 and band 15 modes respectively, resulting in an average 41.46% and 22.12% decrease in mean free path and diffusivity of the modes in band 13 and band 15 respectively. However, due to the relatively larger increase in diffusivity of the band 9 modes, the percent change in modewise diffusivity is positive when averaged over all modes (% $\Delta D^{a\nu g,\phi_s}$). Thermal diffusivity controls the amount of heat that flows through the modes (since it is thermal conductivity per unit energy stored i.e., specific heat). An increase in diffusivity of a mode can mean that more heat is flowing out of the phonon mode and therefore there is a smaller possibility of any localization of vibrational energy in the mode. This might, in turn, indicate that the energetic material has been de-sensitized, or its sensitivity has reduced, since the localization of vibrational energy which leads to the formation of hotspots is one of the prominent mechanisms leading to initiation in energetics. Thus, stimulating the modes at 582.36 cm⁻¹ or 786.90 cm⁻¹ in Case 1 may result in a substantial reduction in the sensitivity of crystalline RDX. In contrast, stimulating the low frequency modes at 22.74 cm⁻¹ or 43.99 cm⁻¹ in Case 1 results in an average reduction in diffusivity by 24.39% or 10.64% respectively. This large reduction in diffusivity can be attributed to the large increase in scattering rates when the low frequency modes are stimulated which leads to a reduction in the average mean free path of the phonons. This suggests that stimulating the low frequency modes may lead to an increase in the sensitivity of energetic materials. In Table 7.4, we rank order the phonon modes based on their overall effect on diffusivity and thereby an ability to increase or decrease the sensitivity of RDX.

For thermal conductivity κ_{xx} , the largest increase (743.00%) can be achieved by stimulating the mode 914.84 cm⁻¹ or 1140.67 cm⁻¹ in Case 2, and the largest reduction (-36.54%) can be achieved by stimulating the mode at 22.74 cm⁻¹ or 43.99 cm⁻¹ in Case 3. For κ_{yy} , the largest increase (406.24%) can be achieved by stimulating the mode 1140.67 cm⁻¹, 1299.72 cm⁻¹ or 1501.31 cm⁻¹ in Case 3 and , similar to κ_{xx} , the largest reduction (-27.60%) can be achieved by stimulating the mode at 22.74 cm⁻¹ or 43.99 cm⁻¹ in Case 3. For κ_{zz} , the largest increase (122.25%) can be achieved by stimulating the mode 582.36 cm⁻¹ or 786.90 cm⁻¹ in Case 2 and , similar to κ_{xx} and κ_{yy} , the largest reduction (-22.91%) can be achieved by stimulating the mode at 22.74 cm⁻¹ or 43.99 cm⁻¹ in Case 3.

The results of our numerical experiment suggest that stimulating certain phonon modes in RDX using a narrow linewidth optical pulse may result in a substantial increase or decrease in the heat transport properties of the material, however, it should be noted that the current work is based on several approximations such as Single Mode Relaxation Time Approximation (SMRTA), only 3-phonon scattering processes have been considered, and modewise thermal diffusivities and conductivities have been calculated using the phonon gas model (PGM) which considers the contribution of propagating thermal carriers only. It is expected that a significant improvement in the accuracy of these results can be achieved by lifting or minimizing these approximations.



Figure 7.14 Average percent change in diffusivity (% $\Delta D^{a\nu g,\phi_s}$) for Cases 1, 2 and 3.



Figure 7.15 Average percent change in diffusivity (% $\Delta D^{a\nu g,\phi_s}$) for Cases 4, 5 and 6.



Figure 7.16 Bandwise average percent change in diffusivity (% $\Delta D^{band_1,\phi_s}$) for Case 1.



Figure 7.17 Bandwise average percent change in diffusivity (% $\Delta D^{band_1,\phi_s}$) for Case



Figure 7.18 Bandwise average percent change in diffusivity (% $\Delta D^{band_1,\phi_s}$) for Case



Figure 7.19 Bandwise average percent change in diffusivity (% $\Delta D^{band_1,\phi_s}$) for Case



Figure 7.20 Bandwise average percent change in diffusivity (% $\Delta D^{band_1,\phi_s}$) for Case



Stimulated Mode Frequency, $\omega_{\phi_s} \text{ cm}^{-1}$

Figure 7.21 Bandwise average percent change in diffusivity (% $\Delta D^{band_1,\phi_s}$) for Case



Figure 7.22 Percent change in scalar thermal conductivity for Cases 1, 2 and 3.



Figure 7.23 Percent change in scalar thermal conductivity for Cases 4, 5 and 6.

Ranking	Ability to Reduce Sensitivity	Ability to Increase Sensitivity			
1	1140.67 cm ⁻¹ , 1299.72 cm ⁻¹ or 1501.31 cm ⁻¹ in	22.74 cm^{-1} , 43.99 cm^{-1} or 71.25 cm^{-1}			
	Case 3 (33.13%)	in Case 3 (-22.07%)			
2	582.36 cm^{-1} , 786.90 cm ⁻¹ or 914.84 cm ⁻¹ in	22.74 cm ⁻¹ in Case 2			
	Case 1 (30.35%)	(-15.58%)			
3	1140.67 cm ^{$^{-1}$} or 1299.72 cm ^{$^{-1}$} in Case 1	22.74 cm ^{$^{-1}$} in Case 1			
	(25.71%)	(-9.97%)			

Table 7.4 Ranking of IR active modes in RDX based on their ability to result in an increase or decrease in diffusivity upon stimulation.

Ranking	Increase in Conductivity	Decrease in Conductivity
1	1140.67 cm^{-1} , 1299.72 cm ⁻¹ or 1501.31 cm ⁻¹	22.74 cm^{-1} , 43.99 cm^{-1} or 71.25 cm^{-1}
	¹ in Case 3 (71.79%)	in Case 3 (-17.21%)
2	83.38 cm^{-1} , 190.87 cm $^{-1}$ or 405.03 cm $^{-1}$ in	22.74 cm ⁻¹ in Case 2
	Case 3 (22.03%)	(-12.46%)
3	1140.67 cm ^{$^{-1}$} or 1299.72 cm ^{$^{-1}$} in Case 1	22.74 cm^{-1} in Case 1
	(21.87%)	(-8.22%)

Table 7.5 Ranking of IR active modes in RDX based on their ability to result in an increase or decrease in thermal conductivity.

7.5 Conclusion

In this work, a numerical experiment is performed to investigate the effects of stimulating different IR active vibrational modes in RDX on vibrational energy transfer rate between the modes and subsequent change in physical properties such as thermal diffusivity and conductivity that may have an influence over the sensitivity of the energetic material. The stimulation of vibrational modes is performed one mode at a time and the corresponding change in 3-phonon scattering rates is estimated using the perturbation theory (also known as Fermi's Golden Rule) under Single Mode Relaxation Time Approximation. Subsequently, modewise thermal diffusivity and conductivity are calculated using the Phonon Gas Model. The stimulation of each IR active mode is performed using six different optical energy inputs (3 high intensity: few eV, and 3 low intensity: tens of meV). Our results indicate that stimulating the mode at 1140.67 cm⁻¹, 1299.72 cm⁻¹ or 1501.31 cm⁻¹ in Case 3 results in an average percent change in scattering rates ($\% \Delta \Gamma^{avg, \phi_s}$) by over 300%. Stimulating these modes

also results in an average percent increase in thermal diffusivity (% $\Delta D^{avg,\phi_s}$) by ~33% indicating that these modes are likely to play a significant role in reducing the sensitivity of RDX. In contrast, stimulating the modes at 22.74 cm⁻¹, 43.99 cm⁻¹ or 71.25 cm⁻¹ in Case 3 results in an average percent decrease in thermal diffusivity (% $\Delta D^{avg,\phi_s}$) by ~22% indicating that these modes are likely to play a significant role in increasing the sensitivity of RDX.

Chapter 8: Conclusion

In this Chapter, we present a summary of contributions and several possibilities for future research that can be built upon the work done in this dissertation.

8.1 Summary of Contributions

The overarching problem statement of this dissertation is to understand the phonon-mediated mechanisms via which the energy from shock may get up-pumped from the long wavelength molecular translation modes to the short wavelength intramolecular vibrations which may result in phenomena such as thermal decomposition of the material leading to initiation in energetics. Based on this problem statement and the current understanding of phonons in energetics, we identified and investigated four research questions:

1) As experimental and computational studies have shown that fission of NN bonds and HONO elimination are the primary initial steps in the thermal decomposition of RDX, in Chapter 3, we use a harmonic oscillator based model to calculate the contribution of every phonon mode to the stretching and rotation of all bonds and angles in RDX. Our results indicate that among all bonds, NN bonds exhibit the largest strain which is consistent with experimental observations that NN fission is the initial step in the thermal decomposition of RDX. We also observed that the low frequency modes up to 133 cm⁻¹ are responsible for the majority of stretching and rotation of all bonds and angles

in RDX. In particular, the low frequency mode at 21 cm⁻¹ is responsible for the largest stretching of the NN bonds. However, it should be noted that these results take into account only the harmonic part of the crystal Hamiltonian and therefore can be improved by considering the anharmonic terms.

2) Since the growth of hotspots and subsequent initiation depend on a balance between the amount of energy generated due to exothermic fission of bonds and the amount of energy dissipated due to thermal conductivity, in Chapter 4 and 5, we evaluate the strength of anharmonic coupling between the modes in RDX and subsequently evaluate three thermal conductivity models, namely the Phonon Gas Model, Cahill Watson and Pohl model, and the Allen & Feldman model. We assess the accuracy of these models in estimating the thermal conductivity of RDX by comparing them with values obtained from Green-Kubo molecular dynamics. Our results indicate that the widely used Phonon Gas Model provides a thermal conductivity estimate which is an order of magnitude lower than the GK-MD value indicating a breakdown of this model for RDX. We showed that this breakdown happens because the thermal carriers in RDX are highly diffusive (the majority of phonons have a mean free path smaller than the unitcell size) and therefore the underlying assumptions of the PGM (phonons are weakly interacting and have a mean free path orders of magnitude larger than the unitcell size) are no longer valid. In contrast, the Allen-Feldman model which was originally developed for disordered materials provides the closest estimate for thermal conductivity, again indicating that the thermal carriers in RDX are highly diffusive in nature. The CWP estimate is only ~44% of the GK-MD value since the CWP model neglects the contributions of the optical phonons. We also observed that the low frequency modes up to ~133 cm⁻¹ are responsible for over 90% of the thermal conductivity in RDX and ~70% of the contribution comes from the optical phonons.

3) In Chapter 6, we use a quantum mechanical model called Fermi's Golden Rule to calculate the 3-phonon mode-to-mode scattering rates for 108,864 modes in RDX. This results in ~12 billion pathways for vibrational energy transfer in RDX. Our results indicate that although the low frequency modes up to ~102 cm⁻¹ are responsible for the largest amount of energy transfer between the modes, however over 99% of the energy leaving these low frequency modes gets deposited into other low frequency modes up to ~102 cm⁻¹ and therefore the vibrational energy does not directly reach the mid and high frequency phonon modes with significant NN activity. Our results indicate that the modes between 457 and 1331 cm⁻¹ are responsible for the majority of energy transfer to modes with NN activity. We identify these as the doorway modes and suggest an indirect mechanism of vibrational energy up-pumping where the energy must first reach these mid frequency modes which then redistribute a significant amount of the energy to the NN active modes.

It should be noted that this work considers only the first anharmonic term of the Hamiltonian and therefore is limited to 3-phonon scattering events. However, at a higher temperature, higher order processes such as 4-phonon scattering may become significant for an accurate modeling of vibrational energy transfer between the modes. In addition, the scattering rates are calculated under Single Mode Relaxation Time Approximation which may be inaccurate under highly non-equilibrium conditions such as in shocked materials.

4) The 3-phonon scattering rates, mode-to-mode scattering rates and modewise thermal diffusivities and conductivities provide a detailed picture of anharmonic interactions and vibrational energy transfer between the modes in RDX. Using this information, in Chapter 7, we perform a numerical experiment to investigate the effects of stimulating different Infrared (IR) active vibrational modes in RDX (stimulating one mode at a time) on vibrational energy transfer rate between the modes and subsequent effects on physical properties such as thermal diffusivity and conductivity. Our results indicate that stimulating the mid frequency mode at 1140.67 cm⁻¹, 1299.72 cm⁻¹ or 1501.31 cm⁻¹ may result in an average 33% increase in the modewise thermal diffusivities (averaged over all modes) and therefore these modes are likely to play a significant role in reducing the sensitivity of RDX. In contrast, stimulating the low frequency modes at 22.74 cm-1, 43.99 cm-1 or 71.25 cm-1 may result in an average 22% decrease in modewise thermal diffusivities indicating that these modes are likely to play a significant role in increasing the sensitivity of RDX.

The approximations inherent in scattering rate calculations such as SMRTA and 3-phonon scattering only are also present in this investigation. In addition, the thermal diffusivities and conductivities are calculated using the Phonon Gas Model and considers the contributions of propagating phonons only.

8.2 Future Work

In this section, we discuss several possibilities for future research that can be built upon the work done in this dissertation.

1) Improvement of Current Models

The modeling techniques used in this dissertation are based on several approximations which limit the accuracy, and in some cases limit the applicability of these models. For instance, the investigation of the contribution of phonon modes to the stretching and rotation of bonds in Chapter 3 is based on a harmonic oscillator model and therefore even though we identified several critical phonon modes adding energy to which may result in a significant increase in bond strains, however, it does not provide any information on how the added energy might get transferred to other phonon modes. For instance, the energy added to a specific phonon mode may get transferred to other modes almost instantaneously and the increase in bond strains may not be as large as predicted. Therefore, modeling the bond distortion behaviors using a fully anharmonic Hamiltonian is likely to provide a more accurate and elaborate description.

The calculation of phonon-phonon scattering rates and mode-to-mode scattering rates using Fermi's Golden Rule in Chapters 4 and 6 consider only the first anharmonic term of the Hamiltonian, however, higher order scattering processes such as 4-phonon scattering and so on are known to be significant at higher temperature [126]. Therefore, considering the higher order anharmonic terms of the Hamiltonian is

likely to improve the accuracy of our current models, especially at high temperature and for modeling hotspots, etc.

In addition, the 3-phonon scattering rates using FGR are calculated under the Single Mode Relaxation Time Approximation (SMRTA) which models the perturbation in phonon population of the modes one at a time. However, in real materials, under non-equilibrium conditions such as shock modeling, etc., a large number of phonon modes may be driven out of equilibrium and therefore the use of SMRTA may result in large inaccuracies. The use of SMRTA is also likely to cause inaccuracies in our numerical experiment of stimulating the phonon modes, where multiple phonon modes are driven out of non-equilibrium. Therefore, developing a model which considers perturbation/relaxation of multiple phonon modes simultaneously may enable more accurate modeling of vibrational energy transfer between the modes.

Further improvements in accuracy, at the cost of computational resources, may be achieved by choosing a larger number of Brillouin zone sampling points and first principles DFT calculations which may enable modeling critical chemistries in addition to the vibrational energy transfer dynamics.

2) Extension to Other Energetic Materials

In this work, we investigated the vibrational energy transfer dynamics in RDX. However, there is a large number of other widely used energetic materials such as Lead Azide, PETN, HMX, TNT, TATB, etc., with widely different sensitivity and degrees of crystal anharmonicity. Therefore, extending the methods used in this work to other energetics may provide a more general picture of vibrational energy transfer and thermal transport in energetic materials.

3) Time evolution of Vibrational Energy Transfer Dynamics

The investigations undertaken in this work provide a detailed picture of vibrational energy transfer between the phonon modes at a single point in time. However, as time progresses, the population of the phonon modes would change thereby affecting the 3phonon scattering rates and energy transfer rates. A more elaborate picture of energy transfer dynamics may be obtained via combining the techniques such as FGR with other techniques as Molecular Dynamics or Boltzmann Transport Equation (BTE) which can enable the investigation of mode energies as a function of time.

4) The breakdown of the widely used Phonon Gas Model (considers propagating carriers) and the success of the Allen-Feldman model (considers diffusive carriers) in estimating the thermal conductivity in RDX indicates that a more complete understanding of the nature of thermal carriers is needed for highly anharmonic materials like RDX. Recent works have explored the possibility of a unified theory of thermal transport that can be used for both simple crystals as well as high anharmonic crystals and amorphous materials [149]. Investigation of thermal transport in different energetic materials using a unified theory may provide a more detailed and complete picture of thermal transport in these complex molecular crystals.

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Appendix 1: Convergence of Phonon Properties⁷

To check for convergence of phonon properties with respect to the number of Brillouin zone sampling points, harmonic phonon properties (frequencies and group velocities) and anharmonic properties (Gruneisen parameter values, phase space volume, scattering rates and thermal conductivity) are calculated using uniform kpoint grids of size $1 \times 1 \times 1 = 1$, $2 \times 2 \times 2 = 8$, $3 \times 3 \times 3 = 27$, $4 \times 4 \times 4 = 64$, $5 \times 5 \times 5 = 100$ 125, $6 \times 6 \times 6 = 216$, $8 \times 8 \times 8 = 512$ and $10 \times 10 \times 10 = 1000$ kpoints. The convergence of all phonon properties are shown with respect to the number of Brillouin Zone (BZ) sampling points (kpoints) using the root mean square (RMS) values. In addition, all error values henceforth are calculated based on the reference property value determined from the $10 \times 10 \times 10$ grid. Scattering rate convergence is shown in Figure A1.1. The RMS value of scattering rates for 216 kpoints is within 0.17% of the RMS value for 1000 kpoints. This indicates that 216 kpoints are able to capture a majority of the 3-phonon scattering events and they should yield a reasonably accurate estimate of scattering rates. Similar convergence is observed for other anharmonic properties like the RMS value of modewise Gruneisen parameter and 3-phonon phase space volume as shown in Figure A1.2 and Figure A1.3, respectively. A scalar value for thermal conductivity is based on the trace of the thermal conductivity tensor given

⁷ Portions of this Chapter appear in the Supplementary Information for : G. Kumar, F. G. VanGessel, L. B. Munday and P. W. Chung, "3-phonon scattering pathways for vibrational energy transfer in crystalline RDX", *J. Phys. Chem. A*, 2021.

as $\kappa^{scalar} = \frac{\kappa^{xx} + \kappa^{yy} + \kappa^{zz}}{3}$ where $\kappa^{xx}, \kappa^{yy}, \kappa^{zz}$ are thermal conductivity values along *x*, *y* and *z* directions respectively calculated using the Phonon Gas Model (PGM). The convergence of scalar thermal conductivity is shown in Figure A1.4. κ^{scalar} for 216 kpoints is estimated to be within 5.3% of the κ^{scalar} value for 1000 kpoints. Similar convergence is observed for the RMS value of modewise wave packet speed as shown in Figure A1.5, where the wave packet speed for any mode ϕ_1 is calculated as

 $Speed_{\phi_1} = \sqrt{v_{gx,\phi_1}^2 + v_{gy,\phi_1}^2 + v_{gz,\phi_1}^2}$ where v_{g,ϕ_1} is the phonon mode group velocity.



Figure A1.1 Modewise scattering rates Γ_{ϕ_1} : (left) RMS values, (right) error.



Figure A1.2 Modewise Gruneisen parameter: (left) RMS values, (right) error.



Figure A1.3 Modewise 3-phonon phase space volume (left) RMS values, (right) error.



Figure A1.4 Scalar thermal conductivity κ^{scalar} (left) values, (right) error.



Figure A1.5 Modewise wave packet speed: (left) RMS values, (right) error.

Appendix 2: Computational Cost and Scalability



Figure A2.1 Computational cost for Molecular Dynamics simulation vs Equilibration Temperature, using LAMMPS. Simulation box size= 1x1x1 unitcell of RDX=168 atoms, timestep= 1fs, simulation time= 2.1 ns, No. of processors= 10. For each temperature, the starting configuration is obtained by minimizing the Helmholtz free energy at that temperature using GULP. The results indicate that the minimum free energy structure calculated using GULP is closer to the MD equilibrated structure at temperatures above 125 K.



Figure A2.2 Computational cost for Molecular Dynamics simulation of a single RDX unitcell vs No. of processors, using LAMMPS. MD timestep= 1fs, simulation time= 2.0 ps, T= 300 K. The starting configuration for MD is obtained by minimizing the Helmholtz free energy at 300 K using GULP. The best performance is achieved while using 32 to 40 processors. Although, a 13% speed up is observed when increasing the no. of processors from 32 to 80, use of 32 to 40 processors might be the most efficient use of compute power.



Figure A2.3 Computational cost for Molecular Dynamics simulation vs No. of RDX unitcells, using LAMMPS. MD timestep= 1fs, simulation time= 3.0 ns, No. of processors= 40, T= 300 K. The starting configuration for MD is obtained by minimizing the Helmholtz free energy at 300 K using GULP. The computational cost increases exponentially with increase in size of the simulation box (no. of atoms).



Figure A2.4 Computational cost for Spectral Energy Density Calculation vs No. of kpoints, using our FORTRAN code. No. of RDX unitcells= 1, T= 300 K, No. of processors= 32. The computational cost increases exponentially with increase in the no. of kpoints.



Figure A2.5 Computational cost for Quasi-Harmonic Lattice Dynamics (QHLD) calculation to obtain minimum Helmholtz free energy structure of RDX (including the calculation of eigenvalues and eigenvectors) vs Temperature, using GULP. Simulation box size= 1x1x1 unitcell of RDX=168 atoms, uniform 6x6x6 kpoints mesh. The 0 K equilibrium structure is used as the starting configuration of atoms in the unitcell for each temperature case. The computational cost increases substantially at higher temperatures, primarily due to a large difference between the equilibrium and finite temperature structures.



Figure A2.6 Computational cost for calculation of 3-phonon scattering rates in a single unitcell RDX for 1x1x1 kpoints, and considering up to third nearest neighbor for calculation of third order force constants (using ShengBTE) vs no. of processors used. The computational cost excludes the time taken to calculate the second and third order force constants. Based on the results, use of 40 processors is recommended.



Figure A2.7 Computational cost for calculation of 3-phonon scattering rates in a single unitcell RDX using 40 processors, and considering up to third nearest neighbor for calculation of third order force constants (using ShengBTE) vs no. of kpoints in the Brillouin Zone. The computational cost excludes the time taken to calculate the second and third order force constants.

Appendix 3: Spectral Energy Density and Lorentzian Fitting



Figure A3.1 Phonon Lifetimes calculated via fitting the modewise Spectral Energy Density to a Lorentzian vs a Gaussian function. Use of Lorentzian results in a slightly lower fitting error (norm error = 0.0402) against using a Gaussian (norm error = 0.0537).



Figure A3.2 Phonon Lifetimes calculated via fitting the modewise Spectral Energy Density to a Lorentzian (considering only the $A_{j\phi}$ terms) vs fitting to the complete form of SED (considering both the $A_{j\phi}$ and $B_{j\phi}$ terms). Use of the complete functional form of SED for fitting results in a slightly lower error (norm error = 0.0391) than fitting only Lorentzian to the SED (norm error = 0.0402). However, since the difference is negligible, use of Lorentzian for fitting to SED is encouraged due to its simplicity.



Figure A3.3 Phonon lifetimes calculated via fitting modewise SED to a Lorentzian function. The comparison is done between use of central differencing vs finite differencing schemes while minimizing the least square error between the Lorentzian and the SED. The difference in errors is negligible, norm error = 0.0402 while using a central difference scheme, and norm error = 0.0400 while using a forward differencing scheme.



Figure A3.4 Calculated Spectral Energy Density for branch no. 454 in RDX at 300 K. The comparison of SED obtained via 3 different MD simulation conditions is shown, (1) Timestep of 1 fs and equilibration time of 1 ns, (2) Timestep of 1 fs and equilibration time of 1 ns, and (3) Timestep of 0.1 fs and equilibration time of 1 ns. The results indicate that the resonant frequency and the overall SED obtained after 1 ns and 10 ns equilibration are similar (the difference in root mean square value of the SEDs is ~15%) and the resulting phonon lifetimes are also similar. This suggests that 1 ns equilibration should be sufficient for RDX to capture the energy transfer dynamics between the modes. The comparison of 1 fs vs 0.1 fs time-steps reveals that although the linewidths of the two SEDs are similar however a minor shift in the phonon mode frequency is observed (the difference in root mean square value of the SEDs is ~23%). This could be due to the anharmonic effects which are neglected during QHLD.



Figure A3.5 Comparison of phonon lifetimes obtained via SED fitting for three different MD simulation conditions (1) Timestep of 1 fs and equilibration time of 1 ns, (2) Timestep of 1 fs and equilibration time of 10 ns, and (3) Timestep of 0.1 fs and equilibration time of 1 ns. The difference between root mean square value of phonon lifetimes calculated via (1) and (2) is ~20%, and the difference between (1) and (3) is ~16%.



Figure A3.6 Spectral Energy Density for branch no. 100 in RDX at 300 K calculated using the original eigenvectors (obtained via QHLD) compared against perturbed eigenvectors (1%, 5% and 10% increase from the original eigenvectors). The results indicate that the SED is insensitive to small inaccuracies that might be present in the eigenvectors due to QHLD approximation. The difference in the root mean square value of the SED between original and perturbed eigenvectors is ~0.04% for 1% perturbation, ~0.14% for 5% perturbation, and 0.10% for 10% perturbation in eigenvectors respectively.

Appendix 4: IR Active Modes in RDX

Mode Frequency (cm ⁻¹)	Normalized Intensity
32.7	0.025
36.3	0.052
38.1	0.028
42.1	0.014
45.4	0.004
46.4	0.017
52	0.06
60.3	0.062
62	0.016
64.1	0.008
73.3	0.057
74.2	0.004
84.3	0.11
84.7	0.009
87	0.1
88.8	0.023
92.7	0.001
95.5	0.038

98.7	0.266
101.7	0.007
104.7	0.016
108.8	0.009
112.7	0.031
114.4	0.022
119.9	0.009
125.3	0.01

Table A4.1 Infrared active modes and relative intensities in RDX reported in [205].

Mode Frequency (cm ⁻¹)	Normalized Absorbance
774	0.284
853	0.185
904	0.331
947	0.763
1078.1	0.687
1242.18	0.517
1259	0.513
1323.7	1
1336.36	0.492
1370.67	0.409

1419	0.595
1441.78	0.402
1450	0.372
1482.29	0.508
1561.1	0.58
1613.32	0.712
1630.58	0.748

Table A4.2 Infrared active modes and normalized absorbance in RDX reported in [200].

Mode Frequency (cm ⁻¹)	Normalized Intensity
225.94	0.248
349	0.162
413.04	0.295
463.83	0.46
489.31	0.291
595.95	0.675
606	1
675.47	0.155

Table A4.3 Infrared active modes and normalized intensity in RDX reported in [109].

Mode Frequency (cm ⁻¹)	Reflectance-Absorbance
851.83	0.987
880.749	0.972
921.86	0.832
947.07	0.956
1017.63	0.952
1040.05	0.96
1217.397	0.986
1236.71	0.965
1276.85	0.8
1312.61	0.962
1349.966	0.978
1388.5	0.962
1435.77	0.895
1460.129	0.959
1535.35	0.846
1581.707	0.735
1594.25	0.814

Table A4.4 Infrared active modes and (Reflectance-Absorbance) in RDX reported in [114].

Mode Frequency (cm ⁻¹)	Absorbance (mm ⁻¹)	
26.90866	1.51	
49.23414	0.9287	
65.17852	1.6998	
97.76779	2.3189	
235.57	6.18099	

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Table A4.5 Infrared active modes and normalized absorbance in RDX reported in [204].

Mode Frequency (cm ⁻¹)	% Transmission
3608.42	55.64
1776.84	29.03
1505.26	0.8
1069.47	63.71
974.736	81.45
538.947	63.71

Table A4.6 Infrared active modes and % Transmission in RDX reported in [207].

Mode Frequency (cm ⁻¹)	% Transmission
3463.818	68.46
3400.37	8.05
3341.138	34.16
3231.508	60.72
2889.42	76.494
2059.239	8.976
1990.339	9.146
1875.999	8.029
1781.91	8.642
1681.1	9.258
1549.969	8.44
1291.16	8.82
1146.53	6.844
1075.957	7.159
1012.36	12.69
931.2666	4.023
891.256	10.704
689.24	3.821
481.151	10.273
414.207	16.093

Table A4.7 Infrared active modes and % Transmission in RDX reported in [206].

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