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Mode-Selective Vibrational Energy Transfer Dynamics in 1,3,5-Trinitroperhydro-1,3,5-Triazine (RDX) Thin Films

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ABSTRACT.

The coupling of inter- and intramolecular vibrations plays a critical role in initiating chemistry during the shock-to-detonation transition in energetic materials. Herein, we report on the sub-picosecond to sub-nanosecond vibrational energy transfer (VET) dynamics of the solid energetic material 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) using broadband, ultrafast infrared transient absorption spectroscopy. Experiments reveal VET occurring on three distinct timescales: sub-picosecond, 5 ps, and 200 ps. The ultrafast appearance of signal at all probed modes in the mid-infrared suggests strong anharmonic coupling of all vibrations in the solid whereas the long-lived evolution demonstrates that VET is incomplete, and thus thermal equilibrium is not attained, even on the hundred picosecond timescale. Density functional theory and classical molecular dynamics simulations provide valuable insights into the experimental observations, revealing compression-insensitive timescales for the initial VET dynamics of high frequency vibrations and drastically extended relaxation times for low frequency phonon modes under compression. Mode-selectivity of the longest dynamics suggests coupling of the N–N and axial NO₂ stretching modes with the long-lived, excited phonon bath.

TOC Graphic:

Keywords: ultrafast infrared spectroscopy; molecular crystals; energy transfer; energetic materials; RDX; HHTT; thin films; molecular dynamics; density functional theory; compression

1. INTRODUCTION

Vibrational energy transfer (VET) *via* coupled molecular and lattice vibrations in energetic materials (EMs) is thought to influence the earliest chemical processes that lead to chemical bond cleavage and, ultimately, a detonation following a mechanical shock. Long-range interactions—mediated by low-frequency phonon modes—between the molecular constituents in an energetic solid play a critical role in VET, resulting in a complex interplay between inter- and intramolecular vibrations that is unique to molecular crystals. To explain the first steps in the shock-to-detonation transition, the multiphonon up-pumping model^{1–3} posits that low frequency lattice modes (phonons) scatter into low-lying, molecular “doorway” states; thus multiple, successive scattering events partition more energy into successively higher energy vibrational modes until sufficient energy accumulates in vibrations associated with decomposition to begin the buildup to detonation. In an alternate and non-exclusive mechanism, the superposition of shock-excited lattice modes may directly couple to key reactive bonds with relatively few scattering events.⁴ Central to both models is whether or not the assumption of a rigid molecule^{5,6} holds true and the extent to which inter- and intramolecular vibrations are strongly coupled or may be treated separately, even when the lattice is compressed.

While there is rich literature investigating shockwave-induced processes in reactive and inert solids (see Refs. ^{7–10} for recent examples), little experimental work exists^{11–14} on vibrational dynamics in solid, neat EMs that shed light on VET through strongly coupled, delocalized vibrational modes. Much of the existing VET research is performed in EM mimics or solvated energetics (see Refs. ^{15–17} for examples), where the importance of phonon-mediated long range interactions that form the basis for a complete picture of VET in EMs is not captured, leading to observed dynamics that are not representative of the dynamics in solid EMs.^{11,12} Furthermore, the

molecular conformation of solvated energetics can be different from that in extended EM solids,¹² resulting in differences in the nature of intermolecular interactions and vibrational coupling. Therefore, understanding the role of phonon-mediated interactions in guiding vibrational energy flow requires direct studies of ultrafast VET in solid EMs.

Given the broad, far- to mid-infrared, frequency range of vibrations in molecular crystals, VET investigations require ultrafast infrared spectroscopy to be coupled with broadband infrared pulses to derive a global view of VET dynamics. A recent study by our team used ultrafast broadband infrared spectroscopy and density functional theory to investigate VET in a pentaerythritol tetranitrate (PETN-I) thin film, revealing dynamics ranging from sub-picosecond to hundreds of picosecond timescales, and suggesting that VET is incomplete even up to 150 ps,¹³ an unexpected finding given the typical timescales assumed for statistical energy partitioning.¹⁸ Unfortunately, due to the broad, overlapping vibrational transitions in PETN, we were unable to determine whether the long-lived VET process was due to persistent excitation of certain high-frequency vibrations or continued evolution of a non-thermal distribution of low frequency lattice modes that, in turn, perturbed⁶ the measured high-frequency vibrations. Regardless of the source of the long-time evolution, modes associated with the reactive nitrate ester (RO–NO₂) stretch coordinate revealed some of the most dramatic spectral changes on the longest time scale.

In order to test if these long-time dynamics are anomalous and isolated to PETN, herein we study another molecular crystal, the secondary explosive 1,3,5-trinitroperhydro-1,3,5-triazine (RDX, also known as HHTT or cyclotrimethylenetrinitramine)—see Fig. 1 for an isolated molecular structure. Crystalline RDX has several polymorphs with α -RDX as the most stable polymorph at room temperature and ambient pressure. In the α -polymorph, the RDX ring takes on a chair conformer with two of the NO₂ groups pointed axially and the third NO₂ group oriented

orthogonally along the equatorial direction^{19,20} (other polymorphs are characterized by different NO₂ group orientations) with the crystalline unit cell qualitatively described as a quartet of dimers linked through adjacent N···O interactions.^{21,22} Cleavage of an N–N bond and the production of various nitrogen-containing products (*e.g.* NO₂, HNO, HONO) have been observed from thermal-^{23–25} and shock-excited²⁶ samples and are thought to be one of the first chemical steps in RDX initiation. Recent theoretical treatments of bond excitation²⁷ and thermal conductivity²⁸ indicate that RDX is a highly anharmonic molecular crystal where excited lattice modes are able to directly couple into the N–N bond scission reaction coordinate; preliminary computational work by Chung and co-workers²⁹ reports timescales of 0.16 and 5.6 ps for direct coupling and multiphonon up-pumping to excite the N–N bond, respectively. Indeed, several experimental and theoretical studies (Refs. ^{30–32} for examples) have indicated anisotropic shock response in RDX, wherein it is hypothesized that select lattice distortions couple strongly to high frequency, “intramolecular” vibrations and also causes increased heating due to irreversible mechanical deformation on preferential slip planes.^{31,33,34}

To the best of our knowledge, there have been only two previous time-resolved, experimental studies of vibrational dynamics in solid RDX. The first study in single crystal RDX used anti-Stokes Raman spectroscopy to probe time-domain beating between different vibrational modes following broadband excitation below 1000 cm⁻¹.³⁵ From the measured beat frequencies and known Raman transitions, two ring breathing motions at 466 and 672 cm⁻¹ were postulated to play key roles in VET with decay timescales of ~1 ps. In the second study, Shi *et al.* employed ultrafast infrared pump-probe and two-dimensional infrared (2D IR) spectroscopy in the 1550 cm⁻¹ region corresponding to the axial and equatorial NO₂ asymmetric stretching vibrations of microcrystalline RDX suspended in paraffin oil.¹² Through measurements of vibrational relaxation

times and the time evolution of a cross-peak assigned to the coupling of two NO₂ stretching vibrations of α -RDX dimers, two timescales were extracted and related to vibrational energy transfer using a phenomenological model: a ~ 1.4 ps timescale was assigned to intermolecular energy transfer between two neighboring NO₂ stretching modes, whereas a 2–4.1 ps timescale was attributed to the vibrational relaxation of excited NO₂ stretching modes to vibrations outside the probed frequency region. Due to the narrowband infrared pulses used in these experiments, only the NO₂ stretching vibrations could be observed, and information regarding the role of other vibrations in VET could not be obtained.

In the current work, we present experimental and theoretical investigations of ultrafast, broadband VET dynamics in α -RDX to understand the influence of chemical moieties on phonon-mediated energy transfer. Work presented here uses a plasma-based source of broadband infrared pulses to probe vibrational dynamics in RDX from ~ 800 cm⁻¹ to 1700 cm⁻¹, and with < 300 fs instrument response time, following narrowband infrared excitation of modes near 1530 cm⁻¹ and 1260 cm⁻¹. Our experimental observations are compared to VET pathways derived from density functional theory (DFT), as well as to the mode- and excitation-specific dynamics revealed by non-equilibrium molecular dynamics (MD) simulations. Both simulation methods also shed light on the response of the infrared spectrum to compression along different orientations, allowing us to draw additional insight into the role of intermolecular coupling in the observed dynamics.

As a brief aside on terminology, the terms “vibration” and “phonon” have been used interchangeably by some publications (see Ref. ³⁶ for example) or with strict separation of molecular and lattice motions—intra- and intermolecular modes, respectively—in a molecular crystal (as in Ref. ¹⁸ for example). However, “intramolecular” modes may span a few tens of molecules¹¹ and a clear distinction between RDX molecular vibrations and phonons or lattice

vibrations appears to be inappropriate.²⁷ Herein, frequencies observed in the experimental probe window will be generally referred to as “intramolecular” or “vibrations” and low frequency modes lying outside of this window will be referred to as “intermolecular,” “phonon,” or “lattice” modes; we separate intra- and intermolecular vibrations to convey an overall picture while noting that this distinction, particularly in the case of RDX as noted above, is not rigorous. In discussions of computational results, there is similarly no concrete way to define inter- and intramolecular vibrations and we will therefore use the experimental naming convention for consistency.

2. METHODS

A. Experimental

The RDX thin film samples were vapor-deposited in a bespoke high-vacuum system onto 1 mm thick, 25 mm diameter substrates of both CaF₂ and BK-7 glass. Deposition was performed at a typical base pressure of 1×10^{-6} torr using an effusion cell thermal deposition source to a nominal thickness of ~ 3 μm . Immediately prior to deposition, both substrates were etched *in situ* using a Veeco Mark II Gridless End-Hall argon ion source to remove surface contaminants. Films on CaF₂ substrates were used for the experiments described below while those on BK-7 substrates were used for microstructure characterization. Though the morphology of the deposited film strongly depends upon the surface energy of the substrate,^{37–39} the surface energy of clean CaF₂ is similar to typical oxides^{40,41} and we expect the final morphologies to be comparable between substrates. Microstructure characterization was performed using scanning electron microscopy (SEM) to image the top surface and a fracture cross-section of films of each material. Samples were coated with ~ 5 nm of iridium prior to imaging to mitigate surface charging. Images, shown in Fig. S1 in the Supporting Information (SI), were collected using a Zeiss GeminiSEM 300 operating with a 1.1 kV accelerating voltage and using the secondary electron detector. For these

thin films, α -RDX is expected to be the dominant polymorph;^{19,42} the FTIR spectrum shown in Fig. 1 supports this conclusion.⁴³

The apparatus used for ultrafast broadband infrared spectroscopy has been previously described in detail.^{13,44} Briefly, the ~ 50 fs, 780 nm output from a commercial Ti:Sapphire laser is split into “pump” and “probe” arms, where the pump photoexcites the sample and the probe measures the pump-induced response. The pump arm of the laser output is first sent into a commercial optical parametric amplifier (OPA), whose signal and idler outputs are difference frequency mixed (DFM) and sent through a bandpass filter to generate tunable, narrowband mid-infrared pulses that excite specific infrared transitions in the material. Two pump frequencies were used in the present experiments: *i*) 1530 cm^{-1} at $\sim 1.8\text{ }\mu\text{J pulse}^{-1}$ with a full-width-at-half-maximum (FWHM) of 150 cm^{-1} and *ii*) 1260 cm^{-1} ($\sim 1.5\text{ }\mu\text{J pulse}^{-1}$, 100 cm^{-1} FWHM). A mechanical chopper wheel in the pump arm blocks alternating pump pulses to allow for shot-to-shot subtraction and measurement of pump-induced signal.

The probe arm of the laser output is used to generate a plasma which radiates light that spans visible to the terahertz frequencies;⁴⁵ we select the mid-infrared portion by passing the plasma emission through a 0.5 mm thick Si wafer. These weaker broadband infrared (BBIR) pulses serve as the probe to monitor all IR-active vibrations within the detected bandwidth of $800\text{--}4000\text{ cm}^{-1}$. The pump and probe pulses are delayed with respect to each other using a motorized optical delay line for ~ 330 ps of total time-delay (Δt), then focused and overlapped in the sample, and the transmitted probe pulse is sent into an infrared spectrometer and dispersed onto a 64-element, liquid nitrogen cooled HgCdTe array detector. Spectra were acquired with a 50 lines/mm grating for a spectral resolution of $\sim 15\text{ nm/pixel}$. Multiple grating positions were required to record transients over the probe region of interest; the static absorption features of RDX—as measured

by a commercial FTIR—were used to calibrate the reported frequencies at each spectrometer grating position. A 7.3 μm long-pass filter was placed in the beam path prior to the detector aperture to minimize artifacts from higher order diffraction in the spectrometer at probe frequencies $<1370\text{ cm}^{-1}$. Experiments involving narrowband IR pump and broadband IR probe were performed with parallel relative polarizations of the pump and probe and orientational dynamics may contribute to the observed dynamics.⁴⁶

The $1/e^2$ focal diameters of the pump and probe beams at the sample position are 290 μm (1530 cm^{-1} pump), 250 μm (1260 cm^{-1} pump), and 220 μm (probe). Pump power studies were conducted using a half-wave plate and polarizer in the pump beam path. By monitoring the transient signal from a pumped band at $\Delta t = 30\text{ ps}$, the power dependence was measured at 1450 cm^{-1} and 1258 cm^{-1} to be 1.1 ± 0.12 and 1.2 ± 0.16 for the 1530 and 1260 cm^{-1} pump pulses, respectively. The two pump spectra are shown in Fig. 1; the 1530 cm^{-1} pump excites both the axial and equatorially oriented NO_2 asymmetric stretching modes of α -RDX and the 1260 cm^{-1} pump will excite multiple modes with CH_2 bending, N–N and C–N–C stretching, and NO_2 bending/symmetric stretching character (see Fig. 1 and associated discussion).⁴⁷ While the 1260 cm^{-1} pump is expected to only directly pump the two vibrational modes within its bandwidth, the 1530 cm^{-1} pump may also excite both an overtone of the mode at 780 cm^{-1} (Ref. ⁴⁷) and possibly—*via* two-photon excitation—the high frequency C–H stretching modes⁴⁷ around 3060 cm^{-1} . Given the relatively low laser fluence used in the present work (*cf.* Refs. ^{11–13,17}) and that absorption cross-sections for both two-photon and overtone absorption are likely small, other photoexcitation pathways are unlikely and we will assume photoexcitation of only the RDX fundamental vibrations within the 1530 cm^{-1} pump bandwidth.

For transient infrared spectra where pump and probe frequencies are the same, the output from the OPA-DFM set-up is split into a 0.95/0.05 ratio, where the 95% arm serves as the pump and the 5% arm serves as the probe. In order to minimize scatter of the pump beam at the sample from reaching the detector, these degenerate pump-probe experiments are performed with the pump polarization perpendicular to the probe polarization; a wire-grid polarizer, oriented along the probe polarization axis, is placed before the detector to minimize the detected pump light.

The location of maximum pump-probe temporal overlap ($\Delta t = 0$) was found by placing a 0.5 mm thick sample of Ge (100) or InSb (100) at the sample position. The temporal instrument response function (IRF) is assumed to have a Gaussian profile centered at $\Delta t = 0$ with temporal FWHM given by the pump-probe cross-correlation in InSb. Cross-correlation widths with the 1530 cm^{-1} and 1260 cm^{-1} pump beams were approximately 200 and 300 fs, respectively, though we note that at least two photons of the 1260 cm^{-1} pump are required to excite the InSb bandgap. To minimize the effects of long-term drifts in laser power, time-delays between the pump and probe pulses were randomly sampled from a set list. Reported transient spectra are the average of repeated runs for a typical total of $\sim 10,000$ laser shots per difference spectrum.

Finally, linear infrared absorption spectra of RDX were taken at 24°C, 35°C, and 37°C using a commercial FTIR spectrophotometer. Temperatures were chosen based on an upper limit temperature rise of approximately 10 K assuming 2 μJ of pump light is absorbed into a 3 μm thick by 200 μm diameter cylinder of RDX with density 1.8 g/cm^3 and $C_p = 1.28 \text{ J g}^{-1} \text{ K}^{-1}$.⁴⁸

B. Computational

A combination of first-principles density functional theory (DFT) and classical molecular dynamics (MD) simulations were performed to complement the experimental VET work, each

providing detail on VET pathways and timescales, respectively. All DFT calculations were performed within the Vienna Ab-Initio Simulation Package^{49–51} (VASP) while all classical MD simulations were performed utilizing the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package.^{52,53} A set of DFT calculations were performed in order to aid vibrational mode assignments, with the starting point being an equilibrated α -RDX unit cell structure.¹⁹ We employ the generalized gradient approximation in the Perdew-Burke-Ernzerhof form,^{54,55} a plane wave cutoff of 1250 eV, $2 \times 3 \times 3$ Monkhorst Pack k-point mesh ($0.0386 \times 0.0298 \times 0.0317 \text{ \AA}^{-1}$), electronic smearing width of 0.2 eV,⁵⁶ and van der Waals corrections from Grimme.⁵⁷ Each calculation is converged to an energy difference of 10^{-8} eV. Normal modes of vibration are calculated utilizing the finite displacement method (FDM) that is available in Phonopy^{58,59} and infrared active modes are identified by projecting a polarizability tensor onto each normal mode.⁶⁰ Visualization of the mass-weighted, normal mode atomic displacements that accompanies each mode assignment utilized the OVITO software package.⁶¹ Anharmonic coupling between vibrations is calculated similarly through a finite displacement method only taking into account up to two-phonon scattering processes;⁶² more details are available in our previous work on PETN.¹³

Conversely, molecular dynamics simulations are used to study the time evolution of VET following a well-prescribed pump excitation. Vibrational density of states and IR spectra are calculated at any finite temperature *via* a Fourier-transform of atomic velocities⁶³ and the dipole autocorrelation function,⁶⁴ respectively. Each of these spectra are collected over tens of picoseconds of trajectories, either as one continuous run or the summation of shorter—but numerous—statistically equivalent simulations.⁶⁵ A velocity/dipole sampling interval of 5 fs yields a frequency resolution of 0.41 cm^{-1} . The non-reactive interatomic potential from Bedrov *et al.*⁶⁶

was employed after adjusting N–O and C–H bond strengths in order to make a better agreement to experimental IR spectra; see section S5 of the SI for further information.

It is important to stress that these MD simulations are classical in nature, meaning true light-matter interactions are not captured and thus we need alternate means to generate vibrational excitations in a controlled fashion. While the popular Langevin thermostat⁶⁷ has no preferential control over the temperature of individual vibrations (only the simulation as a whole *via* an external “thermostat” bath), the random and dissipative force terms that are used to control temperature can be modified to have a time dependent magnitude; this modification is known as the Generalized Langevin Equations (GLE).^{68,69} Since only a select few modes will resonate with these time-varying thermostat oscillations, the remaining vibrations of the material will interact with the thermal bath and only see random noise terms as the base Langevin equations prescribe. The net result is a few vibrations at higher temperature than the rest of the system, which is precisely what is needed to study VET from MD. Dettori *et al.*^{70,71} have demonstrated these methods for a pump-probe style simulation of hydrogen-bonded liquids and here we follow a similar protocol to selectively target vibrations of interest. Each of these GLE pumped vibrations emulate a Gaussian centered pump of width 33 cm^{-1} , which act on a $3 \times 3 \times 3$ super-cell of RDX for 10 ps to establish a non-equipartition of vibrational kinetic energy; the pump is subsequently removed and spectra are collected in the micro-canonical ensemble. During both the pump and measurement period, the average temperature (and total kinetic energy) is conserved and therefore, by comparing spectra at an equivalent temperature, excitations and depopulations of modes due to the pumped mode and subsequent VET may be identified. Spectra are collected for a total of 100 ps; the end of this sampling period is taken as the presumed equilibrium (thermalized) spectra to which the earlier mode populations are normalized. With these normalized spectra, the temporal behavior about a

small frequency window (10 cm^{-1}) is fit to a mono-exponential decay function to extract the single mode relaxation time (SMRT).

3. RESULTS AND ANALYSIS

A. Steady-State Results

Figure 1. a) Calculated IR spectrum and density of states for α -RDX using DFT. b) Experimental FTIR of the RDX thin film sample along with the pump and probe spectra. Representative crystalline α -RDX vibrations with arrows showing mass-weighted atomic displacements for calculated frequencies of c) 1594 cm^{-1} , d) 1432 cm^{-1} , e) 1240 cm^{-1} , and f) 1060 cm^{-1} . Carbon atoms are gray, hydrogens are white, nitrogen atoms are blue, and oxygen atoms are red; axial and equatorial NO_2 moieties are labeled A and E, respectively. See Table S1 for additional modes.

We begin the results section by first examining the DFT calculated and experimentally measured static IR spectrum shown in Fig. 1 a) and b), respectively. The vibrational spectrum has been previously assigned in detail⁴⁷ and the following is a brief summary of the main features with qualitative, “gas-phase”-like mode descriptions derived from our present calculations on crystalline α -RDX; we note that these descriptions simplify the true motions in the extended crystal. The two bands at ~ 1590 and 1540 cm^{-1} correspond to the asymmetric stretch (*as*) of the

two axial (ax) and one equatorial (eq) NO₂ moieties, respectively—see Fig. 1 c) for an example *as*-NO₂^(ax) vibration. Multiple peaks in the 1260–1480 cm⁻¹ range correspond to the CH₂ bending, twisting, and scissoring motions mixed with N–N stretching character; for some modes the NO₂ groups show bending and symmetric stretching (*ss*) motion, though the distinction between the two is less intuitive when accompanied by N–N stretch excitation. The band at ~1270 cm⁻¹ appears to be the N–N^(eq) stretching and CH₂ bending motion with a mix of NO₂ bending/*ss* character. The next three peaks at 1040, 1220, and 1230 cm⁻¹ are the ring N–C–N and C–N–C stretching modes which again contain N–N stretching, CH₂ twist or bend, and some NO₂ bend/*ss* character; see example in Fig. 1 f). The peak at 945 cm⁻¹ is composed of N–N stretching, CH₂ wag, NO₂ bending, and some ring breathing character while the large band centered at 930 cm⁻¹ may be described as ring distortion, CH₂ wag, and NO₂ bend. Finally, the lowest frequency peaks in our observation window at 840 and 880 cm⁻¹ are due to in- and out-of-plane ring deformations, respectively, mixed with C–N and N–N stretch, CH₂ wag, and NO₂ bending motions. Three IR-active, lower frequency modes outside of our probe spectral range have been previously assigned⁴⁷ as ring N–C–N stretching (780 cm⁻¹) and in-plane ring bending modes (600 and 590 cm⁻¹). The calculated IR spectrum is in good, qualitative agreement with the experimental IR features at high frequencies (>1200 cm⁻¹). At lower frequencies, the approximation of using a single unit cell for the FDM becomes more apparent as the predicted normal modes involve larger amplitude deformations (ring bending, intermolecular motions); peaks at <1050 cm⁻¹ are noticeably shifted by tens of wavenumber with some regions (*e.g.* ~925 cm⁻¹) in disagreement with experiment. These finite size effects are not easily overcome due to computational cost constraints: the unit cell of α -RDX already contains 168 atoms and two-phonon scattering predictions (anharmonic expansion of FDM, see below) require 51,642 unique DFT calculations.

Predictions of two-phonon density of states in RDX, shown in Fig. S2, count the number of possible two-phonon collisions (both promotion and decay) into each frequency. The plots show the change in scattering rates from a thermally occupied phonon population for a series of pumped modes each approximated as a Gaussian addition to the Bose-Einstein population at a prescribed frequency, henceforth called $\Delta 2\text{PhDoS}$. In general, the $\Delta 2\text{PhDoS}$ show dense spectra of possible collisions that do not strongly depend on the pumped mode, indicating that each pumped mode may potentially couple to a plethora of modes, including the low-frequency phonon bath. We note that the $\Delta 2\text{PhDoS}$ will predict scattering events into frequencies that are not native vibrations of the material, therefore the predicted IR spectrum is superimposed on these data.

B. Time-Dependent Results

Frequency-resolved transient absorption spectra for both pump frequencies are presented in Figures 2 and 3. Example transient spectra at select time-delays are shown in Fig. 4; additional transient spectra may be found in Figures S10 and S12. For the degenerate pump-probe experiments—Figures 2 a), 3 c), and 3 d)—significant oscillations due to pump-probe interference were present in the raw data (see Fig. S13). To minimize these oscillations, these data were filtered using an established method^{72,73} for removing time- and frequency-dependent oscillations due to perturbed free-induction decay (PFID);^{74,75} the resulting filtered transients are shown in Figs. 2 and 3. Briefly, the filtering procedure applies a damping function to the two-dimensional Fourier-transform of the transient signal to remove signal contributions that lie outside the time-bandwidth limit. Unfortunately, particularly for excitation at 1260 cm^{-1} , these oscillations were large in amplitude and varied too slowly for the filter to completely remove.

The transient behavior of RDX is qualitatively similar for both pump frequencies and, except where noted, the following descriptions will apply to all transient results. To avoid the

interpretation of coherent artifacts,^{74–76} we will limit our analysis to signal occurring for $\Delta t \geq 0.3$ ps. By 0.3 ps, the transient spectra show a negative change in absorbance due to stimulated emission or loss of ground state absorption (henceforth referred to as “bleach”) from all vibrational modes across the probed spectral range. Each bleach feature is paired with a positive transient absorption (TA) signal arising from the new, pump-induced vibrational transitions. Such prompt appearance of signal across the spectrum suggests strong anharmonic coupling between all vibrational modes of RDX. Following the sub-0.3 ps appearance, these bleach/TA couplets typically show an initial decay over the first ps, followed by a few-ps evolution until $\Delta t \approx 10$ ps where the spectra show hallmarks of vibrational relaxation (see below). Finally, the transient spectral features at select vibrational modes intensify over the next several hundred ps.

To help guide the discussion of spectral evolution and RDX dynamics, the Glotaran software package^{77,78} was used to extract the time-dependence of spectral features using global lifetime analysis with a sequential kinetic model. For both pump frequencies, the best fits were achieved with five time constants (5 τ model); fit parameters are summarized in Table 1, example fits in the 1560 cm⁻¹ spectral region are shown in Fig. 5, and fit residuals and evolution associated difference spectra may be found in the SI. The first time constant was fixed at 10 fs to account for remaining coherent artifacts near $\Delta t = 0$. Similarly, the final time constant was fixed at 10⁶ ps to account for the persistent signal extending beyond the temporal observation window. Due to uncertainties in the accurate location of $\Delta t = 0$ at every probed frequency and—particularly for the two regions where pump and probe frequencies are degenerate—residual pump interference, the ~0.5–0.9 ps behavior described by τ_2 in Table 1 will be referred to as “sub-ps.”

To help determine which modes contribute to the sub-ps time constant, fits were also performed omitting the first floating time constant (*i.e.* τ_2 in Table 1) and fixing the remaining four

at their optimized values (4τ model). The reduced fit quality from the 4τ model—compare the two fits in Fig. 5 for examples—highlights spectral regions which require the sub-ps time constant; we note that neither model appears to adequately describe the sub-ps *as*-NO₂^(eq) behavior following excitation at 1260 cm⁻¹. At both pump frequencies, the sub-ps time constant appears to be largely occurring at 1540 cm⁻¹ and, as shown in Fig. S19, around ~930 cm⁻¹. The sub-ps time constant also is needed near 1260 and 1040 cm⁻¹ following the 1530 cm⁻¹ pump, and near 1395 and 1460 cm⁻¹ following the 1260 cm⁻¹ pump; residual 1260 cm⁻¹ pump interference shown in Fig. 3 c) and d) makes it difficult to assess any sub-ps behavior in this spectral region. For these lower frequencies following the 1530 cm⁻¹ pump, the 4τ model fit appears to decay faster than the actual spectral response, possibly suggesting competing growth and decay dynamics. Conversely, following excitation at 1260 cm⁻¹ the 4τ model provides a reasonable fit around 1040 cm⁻¹ but does not appear to decay fast enough at lower frequencies. Indeed, the marked difference in initial spectral shape at ~930 cm⁻¹ for the two pump frequencies—compare Fig. 4 c) and f)—suggests a different pathway for the fastest VET steps. Finally, we note that our sub-ps fit time constants from the 5τ model are similar to both the coherence dephasing (0.48 ps) and intermolecular energy transfer (~1.4 ps) time constants reported by Shi *et al.*¹²

Following the sub-ps spectral evolution outlined above, a 5 ps time constant describes multiple line shape changes that reflect a broadening and shifting of all infrared peaks, akin to what is expected upon an increase in temperature (*e.g.* Refs. ^{36,79,80}). As can be seen in Figures 2, 3 and 4, the changes observed include loss of peak intensity, loss of TA peaks (*e.g.* 1380 cm⁻¹), shifts of peak frequencies (*e.g.* 900–960 cm⁻¹), and the appearance of positive signal at frequencies higher than the existing negative features (*e.g.* 1050 and ~1325 cm⁻¹). Our results reveal that this timescale reflects a global relaxation of all probed vibrations towards transient spectra that

qualitatively resemble the thermal difference infrared spectrum (ThDIR; *i.e.* the change in linear IR absorption between two different sample temperatures) shown in Fig. S14. The 5 ps time constant is in excellent agreement with the previous transient infrared spectroscopy studies in RDX microcrystals¹² (4.11 ps for the *as*-NO₂^(eq) stretch) and dilute solutions of RDX^{12,17} (~5–6 ps for the *as*-NO₂ stretching mode), which assigned this time constant to “vibrational relaxation” of the photoexcited NO₂ stretch.

Finally, the transient behavior of select IR transitions reveal a ~200 ps increase in signal intensity with minimal shifts to the frequencies, suggesting that VET is incomplete by the longest time-delay of $\Delta t = 300$ ps. These long-time changes are most obvious at ~1590 cm⁻¹ (*as*-NO₂^(ax) stretch), 1460 cm⁻¹ (CH₂ scissor, N–N stretch, NO₂ bend/ss), 1350 cm⁻¹ (CH₂ scissor and bend, N–N stretch), ~1270 cm⁻¹ (N–N^(eq) stretch, CH₂ bend, NO₂ bend/ss), 1220 cm⁻¹ (ring C–N–C stretch, CH₂ bend), 1040 cm⁻¹ (N–N^(eq) stretch, NO₂ bend/ss, ring C–N–C stretch, CH₂ twist and bend), and ~945 cm⁻¹ (N–N stretch, CH₂ wag, NO₂ bend, ring distortion) for both pump frequencies. Following excitation at 1260 cm⁻¹, the 200 ps evolution is also noticeable at 880 cm⁻¹ (out-of-plane ring distortion, CH₂ wag, N–N stretch, C–N stretch, NO₂ bend) and possibly 1320 cm⁻¹ (CH₂ scissor, CH₂ bend, N–N stretch), though the apparent pump-dependence is potentially attributable to the differences in signal-to-noise levels and the relative intensity of a neighboring positive feature at ~1330 cm⁻¹—compare Figs. S10 b) and S12 c)—respectively. To highlight these long-time changes, single-frequency transients of the above frequency set may be found in Figures 5, S19, S20, and S21. The remaining IR bands show little to no evolution after the 5 ps time constant; indeed, as shown in Fig. 5, there is a clear difference in the long-time evolution of the *as*-NO₂^(ax) and *as*-NO₂^(eq) stretching modes. The mode-selectivity of these long-time dynamics may indicate specific, vibrational modes that directly couple to the low frequency lattice motions.^{4,27}

Table 1. Time constants (ps) from the global lifetime analysis of the transient data. Reported bounds are the standard error of the fit.

Pump Freq.	τ_1	τ_2	τ_3	τ_4	τ_5
1530 cm^{-1}	0.01 (fixed)	0.93 ± 0.03	5.28 ± 0.07	190 ± 20	10^6 (fixed)
1260 cm^{-1}	0.01 (fixed)	0.46 ± 0.02	5.03 ± 0.07	260 ± 30	10^6 (fixed)
Reference in text	sub-0.3 ps	sub-ps	5 ps	~ 200 ps

Figure 2. Transient spectra following excitation at 1530 cm^{-1} at each spectrometer grating positions. Time-delays are linear up to 4 ps and logarithmic thereafter. The oscillations near $\Delta t = 0$ in a) are the residual pump-probe interference pattern that was not fully removed by filtering; see text for additional details. See Fig. S9 for an alternate colormap.

Figure 3. Transient spectra following excitation at 1260 cm^{-1} at each spectrometer grating positions. The oscillations near $\Delta t = 0$ in c) and d) are the residual pump-probe interference pattern that was not fully removed by filtering; see text for additional details. Time-delays are linear up to 4 ps and logarithmic thereafter. See Fig. S11 for an alternate colormap.

Figure 4. Example transient spectra at select time-delays following excitation at 1530 cm^{-1} (a–c) and 1260 cm^{-1} (d–f). Spectra in a) are from the filtered results shown in Fig. 2 a). The full set of spectra may be found in Figures S10 and S12.

Figure 5. Transient behavior of the axial and equatorial asymmetric NO₂ stretch modes following excitation at 1530 cm⁻¹ (a and b) and 1260 cm⁻¹ (c and d). Example fits from two different kinetic models are also shown to highlight the contribution of a sub-ps time constant; see text for further details of the fit models. Frequencies shown are 1582, 1523, 1588, and 1531 cm⁻¹ for parts a–d, respectively. Time-delays are linear up to 4 ps and logarithmic thereafter.

4. DISCUSSION

A. Early Time Behavior

We begin our discussion with the RDX dynamics associated with the initial excitation and sub-0.3 ps appearance of transient signal. As with our previous report on VET dynamics in PETN,¹³ the prompt appearance of a broad-spectrum signal suggests an ultrafast VET step which couples all vibrational modes in RDX. Prompt VET was also reported by Shi *et al.*¹² for RDX microcrystals, where 2D IR cross peaks were evident at dynamical times as early as 0.1 ps. Such rapid appearance of transient spectra, along with the reported 0.48 ps coherence dephasing time constant,¹² strongly suggests that the initial excitation of modes across the spectrum is due to a coherent VET process. Though these initial dynamics occur within the time resolution of our experiment, there are pump-dependent spectral differences which suggest particular VET pathways. For example, in the experimental transient absorption spectra, the earliest features around 930 cm⁻¹ show marked differences in shape and relative peak amplitudes between the two pump frequencies—compare Fig. 4 c) and f). Following photoexcitation with the 1530 cm⁻¹ pump, decay of the excited *as*-NO₂^(ax) mode at ~1590 cm⁻¹ could excite the ring distortion, CH₂ wag, and NO₂ bending modes around 930 cm⁻¹ and, by conservation of energy in a two-vibration scattering event, the in-plane ring breathing mode at ~670 cm⁻¹—this latter mode was previously identified as a key VET intermediate in RDX.³⁵ Similarly, the large initial transient response around 900–920 cm⁻¹ from the 1260 cm⁻¹ pump could be facilitated by coupling to the mode at 350 cm⁻¹ (Refs. 35,47).

Broad-spectrum VET is supported by the dense $\Delta 2\text{PhDoS}$ shown in Fig. S2, which reveal multiple possible pathways for pairs of vibrational modes to couple. The clearest example of mode-selectivity in the $\Delta 2\text{PhDoS}$ are the pumped (static Bose-Einstein population adjusted) modes at

frequencies $<1000\text{ cm}^{-1}$, which show very few available scattering pathways to higher lying vibrations while the inverse process shows a plethora of available scattering events. To evaluate the most probable VET pathways, we would normally turn to the DFT predicted single mode relaxation times (SMRTs) of the RDX crystal. These SMRTs are the product of the $\Delta 2\text{PhDoS}$ and the scattering cross-section for each collision;⁶² however, our predicted SMRTs are unrealistically low, ranging from 0.01–0.1 ps.³⁶ As the $\Delta 2\text{PhDoS}$ are strictly a count of allowable transitions,¹³ we are led to conclude that two-phonon collision cross-sections are the culprit for this poor prediction. While previous studies on metals and metal-oxides^{81,82} using the same computational method yield experimentally agreeable 1–10 ps SMRTs, these materials are starkly different from the molecular crystal studied here. Thus, without reliable two-phonon cross-sections, we cannot rigorously evaluate the most probable VET pathways and we limit our discussion to the above speculation. Further experimental work, such as a broadband 2D IR study (*e.g.* Ref. ⁸³), would provide considerable insight into these first VET steps.

After the prompt appearance of transient signal, multiple vibrational modes show evolution with sub-ps and 5 ps time constants from global fitting. The sub-ps time constant is similar to previously reported time constants in RDX microcrystals¹² as well as the lifetimes extracted from temperature-dependent Raman linewidths of β -octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine crystals (HMX, a related EM).³⁶ While it is tempting to separate and assign the two extracted time constants based solely on previous reports, we first consider our choice of kinetic model. For RDX microcrystals, Shi *et al.*¹² report mode-specific time constants of ~ 2 and 4.11 ps from simple exponential decay fits to single-frequency transients at the axial and equatorial *as*-NO₂ stretching modes. To directly compare our present results with the fits from Shi *et al.*, Fig. S22 shows lane integrated transients of the same spectral features following the 1530 cm^{-1} pump along with mono-

exponential decay function fits. While our mono-exponential fits return similar time constants of ~2 and 5 ps, our trends do not match the previously reported results;¹² the cause of this discrepancy remains unclear as, apart from a ~60 cm⁻¹ difference in central pump frequency and the use of microcrystals *versus* a thin film, the experiments appear to be comparable. Though the shorter, ~2 ps time constants could arise from simultaneous sub-ps and 5 ps decay dynamics, the extracted time-dependence of these features clearly depends on the kinetic model. While our assumption of a global sequential kinetic model is a useful description of correlated spectral changes across the probe window, it will not describe the multiple, parallel, and mode-specific VET pathways (and time constants) likely occurring following photoexcitation. Conversely, the independent fits to single frequencies by Shi *et al.*¹² will extract mode-specific time constants but may not accurately describe the time dependence of broadening or spectral shifts.

While neither kinetic model is entirely correct, we can still draw a few conclusions by comparing different models to the experimental data. For example, the spectral regions requiring a sub-ps time constant—see the 4τ model description in the previous section—may be interpreted as effectively modifying the 5 ps time constant to describe dynamics similar to those reported by Shi *et al.*¹² (*i.e.* mode-selective, mono-exponential decays). Alternatively, the noticeably flat or slightly rising transient behavior around 1040 and 920 cm⁻¹ following the 1530 cm⁻¹ pump—shown in Fig. S19—strongly indicates competing decay and growth dynamics (*i.e.* two separate time constants). Indeed, rising signal at ~920 cm⁻¹ could support our proposed VET pathway coupling the initially excited *as*-NO₂^(ax) mode at ~1590 cm⁻¹ to the modes at 930 and 670 cm⁻¹. However, as with the initial, sub-0.3 ps excitation of modes across the RDX spectrum, we are unable to firmly assign such pathways with the present results and again highlight the need for further experimental and computational work to decouple the numerous, competing VET pathways.

The appearance of a 5 ps time constant at both pump frequencies and for all the probed vibrational transitions strongly indicates that this time constant describes an aggregate VET behavior in RDX, though global fitting may miss mode-specific variations. Nonetheless, this 5 ps time constant corresponds to the clear evolution of all transient spectra to resemble the ThDIR spectrum shown in Fig. S14, with the caveat that direct quantitative comparisons between the transient spectra and ThDIR are inappropriate. As each VET process must necessarily couple to the low frequency vibrations to promote transitions, including the bath of long-range lattice motions, the strong similarity between the ThDIR and transient spectra for $\Delta t \geq 10$ ps suggests that the 5 ps time constant is the time required for the vibrationally excited, high frequency modes to decay and repopulate their ground vibrational state, as supported by the pump-probe style MD simulations (Figures S3 and S4; see discussion below for details). However, vibrational relaxation of the high frequency modes does not result in the repopulation of the pre-excitation ground state. Instead, a shifted ground state is populated since the VET-excited low frequency lattice modes will perturb the higher frequency vibrations,⁶ manifesting as shifting and broadening of the line shapes (see Fig. S14 and Refs. ^{13,36} for examples) and resulting in the reported transient spectra for $\Delta t \geq 10$ ps. Thus, because of these clear spectral changes, we may firmly assign the 5 ps time constant to de-excitation of the high frequency vibrational modes in RDX.

B. Long-Time Behavior

i. Signal Origin

The final, 200 ps time constant demonstrates that VET remains incomplete by $\Delta t = 300$ ps in α -RDX. Such long lived dynamics are not captured by standard theoretical treatments of VET^{84,85} and, to the best of our knowledge, have rarely been reported.^{13,14,86} In our previous investigation of VET in PETN,¹³ we speculated that a similar, $\sigma(100$ ps) time constant was due to evolution of

such an excited phonon distribution outside of the probe spectral window, though this conclusion remained tentative due to broad, overlapping spectral features. With the above assignment of the 5 ps time constant in RDX, the further 200 ps spectral evolution must be due to dynamics within the low frequency vibrations and lattice modes.

In RDX, the clear mode-selectivity of the 200 ps time constant thus suggests that select high frequency vibrations are more sensitive than previously thought to changes in the excited phonon bath. This enhanced sensitivity may imply strong coupling between low and high frequency vibrations, supporting a direct energy transfer^{4,27} model following a shockwave rather than a “doorway mode”-mediated multiphonon up-pumping scheme.^{1–3,87,88} To test that specific high frequency reporter vibrational modes are sensitive to long-lived phonon VET, we have recalculated the α -RDX IR spectrum (see Fig. 1) with a 10% static lattice compression to represent some characteristic of the experimental excited phonon bath. Figure 6 shows the ambient and compressed spectra for compression along the [010] crystal axis; similar compressions along the [100] and [001] axes each show unique peak shifting based on orientation of compression. Thus, these IR spectra of compressed RDX *i)* demonstrate that high frequency, “intramolecular” modes will be sensitive to lattice excitation (*i.e.* a breakdown of the rigid molecule approximation) and *ii)* suggest that the observed vibrational mode-selectivity arises from particular phonon excitations. However, without reliable two-phonon scattering cross-sections (see section 4.A) we cannot conclusively determine whether these reporter modes—which could potentially bypass a slow up-pumping process—are sensitive to VET in select phonon modes or to broad-spectrum phonon evolution.

Figure 6. (Top) DFT calculated infrared spectrum of α -RDX for both ambient and 10% compressed unit cells. Mild blue-shifting of all modes is observed, with *as*-NO₂ being an exception where a large, >50 cm⁻¹, shift is present. (Bottom) Calculated total vibrational density of states again highlights inhomogeneous frequency shifts given the [010] lattice compression.

ii. Low Frequency Vibrational Dynamics

Similar to the case of PETN,¹³ we next consider two possible, phonon-centric explanations for the observed 200 ps dynamics. First, we could assume that the 5 ps time constant describes the rapid and complete thermal equilibration¹⁸ of pump-induced excess energy within the laser-sample interaction volume (*i.e.* that VET is complete by $\Delta t \approx 10$ ps). The observed long-time spectral changes would thus be due to spatial conduction of the locally higher temperature phonon distribution out of the laser-sample interaction volume. However, on the 300 ps time scale of the present experiments, we would expect such cooling to only affect a small fraction of the total pumped volume.^{13,80} Furthermore, ThDIR spectra show decreasing signal intensity with decreasing temperature (Fig. S14 and Refs.^{13,80}) in contrast with the observed increase in transient signal (see Figures 5 and S19–S21) on a ~ 200 ps timescale. Thus, while thermal conduction of excited phonons out of the probe volume is certainly occurring, we believe this process alone does

not explain the present observations. We are thus left with the second possible explanation for the longest time constant: that VET is incomplete by $\Delta t = 300$ ps and we are observing continued evolution of a non-statistical, excited phonon distribution outside of the probe window—a conclusion again in marked contrast with previous theoretical treatments.^{18,89}

To explore the dynamics of low frequency phonon modes, and avoid the requisite and prohibitive cost of DFT, we conducted MD simulations of mid-IR pumped vibrations looking for signatures of long-lived, non-equilibrium dynamics. Figure 7 shows the MD predicted phonon mode SMRTs comparing ambient density and compressed α -RDX, where the vibrations at 1266 cm^{-1} (ambient pressure) and 1280 cm^{-1} (10% compression along the [010] axis) have been pumped. Additionally, a total and partial vibrational density of states is plotted that highlights axial or equatorial NO_2 contribution. Similar to Figures 2 and 3, the bottom panels of Fig. 7 show the evolving total vibrational density of states through time, where the color scale indicates if modes are in higher (red) or lower (blue) population relative to equipartition of energy. Importantly, these low frequency phonons are initially cold relative to the pumped vibrations, meaning that—while the pump is present—these vibrations act as a sink for the energy deposited into the system. In contrast with the DFT-derived SMRTs, here the SMRTs are derived from frequency-dependent, mono-exponential fits to the evolving mode populations; a single SMRT thus captures the most prominent dynamics occurring after the pump thermostat is removed. MD spectra in other probe frequency ranges, as well as additional simulations for different pumped modes, are available in section S2.3 of the SI.

The most striking result is a marked increase in the low frequency SMRTs when the RDX crystal is compressed, where again this compression is used to mimic some character of an excited phonon bath. In particular, phonons involving NO_2 motion (namely 180, 260, and 305 cm^{-1}) show

significant blue-shifting and broadening due to the compression. The longest lived of these excitations show SMRTs of 40–50ps, which are in stark contrast to the compression-insensitive SMRT of 1–5 ps near the pumped mode, as shown in Fig. S3. These elongated SMRTs cannot be attributed to irreversible peak shifts and broadening as both ambient and compressed samples were elevated by the pumped mode to very similar final temperatures (357 and 361 K, respectively). Though the initial, compression-insensitive VET dynamics of high frequency modes are somewhat surprising given large peak shifts shown in Fig. 6, a constant high frequency SMRT further supports the separation of timescales based on VET mechanism seen in experiments. Furthermore, the largest reliable SMRT of the compressed sample (~50 ps) challenges the assumption made that the spectra at 100 ps can be taken as fully thermalized. While the compressed SMRTs do not yet match the experimental time constant of 200 ps, the SMRTs assume independent decay dynamics for each mode and the difference in extracted time constants suggests some degree of sequential, phonon-centered VET dynamics. Thus, these MD results suggest that an excited phonon distribution produced by the initial VET steps will itself result in elongated relaxation dynamics for lower frequency vibrations—a key, novel insight into the energy redistribution mechanisms and timescales of EMs. Follow on MD work will need to focus on the relationship between mode-specific VET dynamics following a mechanical shock and the initial chemical reactions in RDX.

Figure 7. Pumped vibration is the N–N^(eq) stretch, CH₂ bend, and *ss*-NO₂ mode (1260 cm⁻¹, ambient pressure) in both sets of data, time origin is where the pump is removed from the probe volume. (a) Extracted exponential decay time constants as the uncompressed RDX crystal returns to an equipartition of energy among all vibrations. Total density of states (blue) and partial density of states (green, purple) highlight modes with axial *versus* equatorial NO₂ character. (b) Time constants per-mode for a compressed sample of RDX. Two-dimensional density of states normalized to an equipartition of energy (labeled as Mode Population) for (c) ambient and (d) compressed RDX; blue regions are under-populated and red over-populated with respect to the spectra at the same temperature. See Figures S3–S5 for additional MD results.

iii. Mode-Selectivity

With a firm grasp of the origin and nature of the long-time dynamics in RDX, we finally turn our attention to the observed mode-selectivity. As an $\sigma(100$ ps) time constant has now been observed in multiple EM thin films,^{13,14} the separation of VET timescales seems to be a material-independent feature and correlating the longest dynamics with likewise material-independent properties would be of significant interest. Since the specific vibrational modes are inherently material-dependent, we would like to understand the mode-selective VET through the chemically intuitive lenses of select bond excitation or of other chemical moieties. In our previous study of

PETN,¹³ the σ (100 ps) evolution was tentatively associated with modes involving the reactive nitrate ester stretch (RO–NO₂) coordinate. Though a direct correspondence between vibrational mode and chemical moiety is only an accurate description in the gas-phase, such an analysis has previously suggested facile energy partitioning into the N–N stretch of RDX.²⁷ With the above caveat in mind, we thus seek such a relationship between the longest, mode-selective dynamics and an intuitive chemical bond model.

From the list of the spectral regions which show a 200 ps evolution—see section 3.B—a possible unifying characteristic appears to be vibrational modes with N–N stretch character; for example, the mode associated with the strong time-dependent change at 1040 cm⁻¹ appears to include significant N–N^(eq) stretch character (see Fig. 1 f) and Table S1). However, this initial assessment is based on qualitative descriptions of mode character from the vector displacement diagrams of only one RDX molecule in the unit cell. To assess potential trends more rigorously, we have decomposed the DFT calculated IR spectrum along several likely dimensions. For all molecules within the α -RDX unit cell, each mass-weighted harmonic mode is characterized by: *i*) fractional displacement of each atom type, *ii*) projection onto the unit cell axes (as suggested by Fig. 6), *iii*) fractional change of each N–N bond length (from our initial assessment and Refs.^{27,29}), and *iv*) fractional change of each N–O bond length (from Fig. 7 b) and the observed dynamics around 1590 cm⁻¹). Of the 504 degrees of freedom in uncompressed α -RDX, 61 vibrations have a calculated IR intensity ≥ 0.1 e² amu⁻¹; 44 of these modes are within the experimental probe window. Based on the overlap of the calculated and experimental IR spectra in Fig. 1, and without considering our assigned mode character, each of these 44 modes was then assigned a “yes/no” value depending on whether the calculated frequency (CF) matches an experimental mode evolves with the 200 ps time constant. A third “neutral” value was assigned to modes whose CF could not

be unambiguously mapped to experimental frequencies; the resulting annotated list of 61 frequencies is given in Table S2. Two examples of these decomposed IR spectra, averaged over all molecules within the unit cell, are shown in Fig. 8 with the full set shown in Figures S6 and S7; red peaks highlight modes which evolve with the 200 ps time constant while peak intensity scales with fractional change in atomic displacement, projection onto a crystal axis, or relative N–X bond length.

In general, spectra reporting either atomic fractions of each mode or the projections onto the crystal axis (Fig. S6) do not show any obvious, global correlation with the 200 ps temporal behavior, though large N atom and O atom motions are present in the $as\text{-NO}_2^{(ax)}$ modes at $CF \approx 1610\text{ cm}^{-1}$. It is important to note that while compression along the principal crystal axes implied phonon-induced, mode-selective shifts to the high frequency vibrational spectra in general—see section 4.B.i—these particular projections do not correlate to the experimentally observed 200 ps behavior. In contrast, spectra detailing the average relative displacements of the N–N and N–O bonds, shown in Figures 8 and S7, begin to show some correspondence with the longest dynamics. For example, modes with the largest relative change in N–N^(eq) bond length tend to evolve with the 200 ps time constant while, excepting the $as\text{-NO}_2^{(ax)}$ modes, larger changes to the N–O^(ax) bonds appear to favor modes which do not evolve with the 200 ps time constant. Indeed, the correlation to N–N bond excitation appears strongest when plotting the maximum change in N–N bond length across all three N–N bonds, as shown in Fig. S7. Pairwise correlation plots comparing these spectral decompositions, as shown in Figures 8 c) and S8, reinforce the above conclusions: atomic displacement or crystal alignment typically results in no obvious pattern while displacements of the N–N vs. N–O bonds generally correlate evolution with the 200 ps time constant to excitation of the N–O^(ax) or N–N^(eq) bonds.

While these spectral decompositions generally support a connection between excitation of the N–N bond and long-time spectral evolution, even the strongest correlations—such as plotted in Fig. 8 c)—reveal multiple modes with minimal N–O^(ax) and N–N^(eq) bond excitation which nonetheless evolve with the 200 ps time constant and are as of yet unexplained. Given that the 200 ps time constant arises from long-range lattice motions, this bond-centric, intramolecular picture is undoubtedly insufficient and we would need to consider changes to the larger system (*i.e.* extended intermolecular interactions) to determine the underlying connection. As the approximation of using a single unit cell when employing the FDM is already evident for low frequencies within the probe window—see section 3.A—accurate correlations between intra- and intermolecular modes requires further computational effort beyond the scope of the present work. Nonetheless, these initial efforts reinforce the importance²⁷ of the reactive N–N bond in understanding the initial energy transfer dynamics in RDX.

Figure 8. Example decomposed spectra showing the fractional bond length change from equilibrium in (a) the $N-N^{(eq)}$ or (b) one of the four $N-O^{(ax)}$ bonds for each frequency. Bar height reports fraction while bar color highlights frequencies which experimentally demonstrate 200 ps evolution: red = “yes,” blue = “no,” and black = “neutral” (*i.e.* no unambiguous mapping to experiment). c) Example correlation plot comparing the relative fractional change in an $N-O^{(ax)}$ versus the $N-N^{(eq)}$ bond length for each frequency, highlighting large $N-N^{(eq)}$ and small $N-O^{(ax)}$ displacements as a reasonable predictor of long-time spectral evolution. Marker size scales with calculated IR intensity while marker color highlights frequencies which experimentally demonstrate 200 ps evolution. Additional decomposed spectra and correlation plots may be found in Figures S6–S8.

5. CONCLUSIONS

In the present work, we have employed a combination of experiment and theory to demonstrate incomplete VET in RDX on hundreds of picosecond timescales, challenging commonly utilized theories of shock initiation in these molecular crystals. If we assume that the VET timescales and pathways are reversible (phonon up-pumping *versus* vibrational relaxation), then the results herein of ~200 ps, phonon-mediated VET, point away from the “doorway mode” concept for shock initiation^{1,2} in favor of direct coupling to high frequency reporter modes^{4,27} which lie along commonly recognized reaction pathways.^{90,91} Indeed, our observations of σ (100 ps) dynamics in the three energetic materials we have presently or previously investigated—RDX, PETN,¹³ and TATB¹⁴—suggest that the direct coupling of phonons to reactive high frequency modes, and the breakdown of the rigid molecule approximation, may be a general feature of energetic molecular crystals. The observed mode-selectivity in these longest dynamics, coupled with DFT simulations showing compression orientation-dependent peak shifts, may provide key clues to the observed crystallographic orientation dependence on shock sensitivity.⁹² Finally, these MD results under static compression suggest that, following shock compression, excited phonon relaxation times will be substantially longer than have been previously assumed.¹⁸ Such a persistent, non-equilibrium phonon distribution would have more opportunity to excite higher frequency, chemically reactive coordinates through either the multiphonon up-pumping^{1,2} or direct coupling^{4,27} pathways. Further experimental work, such as transient infrared spectroscopy of a molecular crystal under static compression, would validate these calculations and add significant insights into the interplay between compression, phonon lifetime, and VET mechanisms.

Two outstanding experimental questions remain from our present work. First, what are the ultrafast pathways responsible for the sub-0.3 ps dynamics? Elucidating these first VET steps would help explain the pump-dependent differences in the earliest transient spectra—*cf.* Figures 4

c) and f). Second, what are the underlying chemical characteristics responsible for the mode-selective 200 ps dynamics? In both cases, broadband 2D IR studies would unveil key mechanistic pathways critical to understanding the *structure-dynamics-function* relationships of EM bulk properties. Further work utilizing IR pump-THz probe holds promise to directly test the timescales of VET within the low frequency phonon modes. Finally, as our samples are well-controlled thin films of material, more work is also needed to understand the phase, morphology, and temperature dependence of VET as well as whether the phonon-mediated, reporter modes are preserved. Extending the above suite of experiments to include static pressure loads would enable new EM polymorphs to be studied as well as explore the relationship between pressure and extended phonon lifetimes. VET studies of bulk polycrystalline EM samples could further contribute to understanding the interplay between the longest dynamics observed herein and the role of microstructure (*e.g.* grain boundaries^{93,94}) and hot-spot formation^{1,2,95,96} in the shock-to-detonation transition.

Though further work is needed to develop a fundamental understanding of shock sensitivity from VET timescales and pathways, such an explicit connection between VET and initial chemical reactivity would mark a critical step forward in our understanding of shock sensitivity. Indeed, currently used destructive methods for characterizing sensitivity—such as drop weight⁹⁷ or friction testing⁹⁸—could be augmented or replaced with non-destructive characterizations of VET. Recent work by McGrane and co-workers^{9,10} measuring the ultrafast behavior of shocked, thin film samples with broadband mid-IR sources highlights the converging applicability of these spectroscopic techniques. Such augmentation would be advantageous as both a safer way to screen newly synthesized compounds as well as a means to diagnose the state-of-health of energetic materials already in use.

Supporting Information. Characterization of the RDX thin film samples, additional theoretical results, additional experimental results, and details of the Zenodo data archive.

Author Information. The authors declare no competing financial interests.

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Data Accessibility. Experimental and computational data underpinning the present manuscript are freely available through the Zenodo data archive at DOI:10.5281/zenodo.4663415.

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Supporting Information

Mode-Selective Vibrational Energy Transfer Dynamics in 1,3,5-Trinitroperhydro-1,3,5-Triazine (RDX) Thin Films

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S1 RDX Sample Characterization

Figure S1: a) Fracture cross-section and b) surface morphology of RDX vapor deposited onto BK-7. The RDX films display a columnar morphology with columns oriented perpendicular to the surface. The surface itself reveals hillocks ($\leq 10 \mu\text{m}$ lateral size and approximately 100–200 nm tall) composed of smaller RDX grains (*ca.* 0.5 to 1 μm).

S2 Additional Theoretical Results

S2.1 Vibrational Modes of Crystalline RDX

Table S1: Vector displacement diagram of the major RDX modes, calculated and experimental frequencies, and mode assignments. Calculated frequencies in bold are shown as the example vector displacement diagram, values in parentheses represent a 10% compressed crystal along the [010] axis. The equatorial NO₂ group is labeled “E” in each unique view.

Example Vector Diagram	Calculated Frequency (cm ⁻¹)	Experimental Frequency (cm ⁻¹)	Assignment
1626, 1625, 1616, 1596, 1594 (1780, 1776, 1770, 1737, 1734)	~1590	NO ₂ ^(ax) asymmetric stretch
1562, 1552 (1648, 1643)	1540	NO ₂ ^(eq) asymmetric stretch
1432 , 1424, 1412 (1557, 1441, 1440)	1460, 1420	CH ₂ scissor, N–N stretch, NO ₂ bend/symmetric stretch

Example Vector Diagram	Calculated Frequencies (cm^{-1})	Experimental Frequency (cm^{-1})	Assignment
1398, 1395, 1388 , 1380, 1375 (1400, 1399, 1376, 1371)	1390	CH ₂ scissor, CH ₂ bend, N–N stretch
1344, 1342, 1336, 1331 , 1320, 1317, 1308 (1364, 1362, 1341, 1337, 1326, 1324, 1308)	1350, 1320	CH ₂ scissor, CH ₂ bend, N–N stretch
1286, 1270, 1268 , 1258, 1243, 1243 (1307, 1288, 1284, 1272, 1261)	~1270	N–N ^(eq) stretch, CH ₂ bend, NO ₂ bend/symmetric stretch
1240 , 1239, 1235 (1257, 1245, 1244)	1230, 1220	ring C–N–C stretch, CH ₂ bend
1064, 1060 (1101, 1091)	1040	N–N ^(eq) stretch, NO ₂ bend/symmetric stretch, ring C–N–C stretch, CH ₂ twist, CH ₂ bend

Example Vector Diagram	Calculated Frequencies (cm^{-1})	Experimental Frequency (cm^{-1})	Assignment
1000 (1014)	1010	N–N ^(ax) stretch, CH ₂ twist, CH ₂ wag
946, 944 (961, 960)	945	N–N stretch, CH ₂ wag, NO ₂ bend, ring breathing
910, 908, 893, 892 (928, 927, 906, 905)	930	ring distortion, CH ₂ wag, NO ₂ bend
882, 876 (893, 892)	880	out-of-plane ring distortion, CH ₂ wag, N–N stretch, C–N stretch, NO ₂ bend
846 (860)	840	in-plane ring distortion, NO ₂ bend, N–N stretch

S2.2 Two-Phonon Density of States

Part of our theory support for the experimentally observed VET comes from the analysis of the calculated two-phonon density of states where select mode populations have been modified to “pump” a vibration of interest ($\Delta 2\text{PhDoS}$). These data reveal which modes are coupled based on the selection rules of momentum conservation and allowable wavevectors within the Brillouin zone. Calculated $\Delta 2\text{PhDoS}$ between thermal occupation, *i.e.* $n_\lambda = \text{Bose-Einstein}$, and an additional Gaussian perturbed population at specific pump targeted modes are given in Fig. S2. Each of the $\Delta 2\text{PhDoS}$ spectra are summed over all sampled Brillouin zone points ($5 \times 5 \times 5$ mesh). These $\Delta 2\text{PhDoS}$ can be interpreted as the change in scattering intensity when the pump has been applied to the system: a non-zero value occurs when a mode is coupled to the pumped mode and any frequencies with $\Delta 2\text{PhDoS} = 0$ have no change relative to a system in equilibrium. In other words, any frequency plotted that exhibits a non-zero $\Delta 2\text{PhDoS}$ is coupled to the pumped mode given as the data series label. Given the infrared spectrum overlaid with this scattering intensity data, it is clear that there are numerous allowable two-phonon collisions that couple all native RDX modes together. Missing in these data—to complete the experimental to theory connection—are the cross-section (strength of mode-to-mode coupling) of each of the allowable transition, as discussed in the main text.

Contained in Fig. S2 are DFT predictions of the static IR spectrum (reproduced from Fig. 1) and $\Delta 2\text{PhDoS}$ for RDX; panels differ only in the two-phonon density of states with the pumped mode, see mode assignments in Table S1. An overlap of both data series is needed to identify vibrations which are both coupled to the pumped mode and experimentally observable. Further details regarding the calculation and interpretation of these $\Delta 2\text{PhDoS}$ have been detailed previously.¹

Figure S2: Two-phonon density of states prediction from VASP DFT calculations following an anharmonic (third-order) expansion of the potential energy surface of the ions. Plotted as the difference from a thermal equilibrium state (*i.e.* $\Delta 2\text{PhDoS}$), each calculation perturbs the occupation of specific modes to highlight coupling to this artificially pumped vibration. The Phonopy and Phono3py software packages are used to collect the finite displacement method calculations from VASP.

S2.3 MD Simulations

For these classical simulations in equilibrium, each vibration of the material will carry an equipartition of the kinetic energy ($\frac{1}{2}k_bT$), regardless of the mode frequency. All MD simulations are evolved through a finite timestep integration given some prescription of the thermodynamic ensemble. For example, coupling to an external thermal bath to maintain control of the temperature constitutes a simulation in the canonical ensemble, and these adjustments to the equations of motion are colloquially known as “thermostats.” Alternatively, an isolated system without a thermostat evolves in the micro-canonical ensemble, the ideal ensemble from which to sample vibrational spectra.

Additional SMRT fits and 2D spectra for frequency ranges containing the pumped mode, Figures S3 and S4, as well as low frequency modes that demonstrate elongated relaxation times in compressed RDX, Fig. S5. It is important to stress that the fitted SMRT are going to be most sensitive to the initial relaxation process as opposed to population redistribution toward the end of the simulation. While we do expect the evolving non-equilibrium phonon modes to perturb higher lying vibrations, as was observed in experiment, the effect will be subtle (<10% population changes) compared to the initial non-equilibrium state that pushes pumped (and coupled) modes up to twice an equipartition of energy. Future work will need to apply a similar fitting procedure as the experimental mid-IR data, allowing for multiple distinct timescales of relaxation to be extracted from the MD data.

Figure S3: Pumped vibration is the N–N^(eq) stretch, CH₂ bend, and NO₂ bend/symmetric stretch mode (1260 cm⁻¹, ambient pressure) in both sets of data, time origin is where the pump thermostat is removed from the probe volume. (a) Extracted exponential decay time constants as the uncompressed RDX crystal returns to an equipartition of energy among all vibrations. Total density of states (blue) and partial density of states (green, purple) highlight modes with axial *versus* equatorial NO₂ character. (b) Time constants per-mode for a 10% [010] compressed sample of RDX. Two-dimensional density of states normalized to an equipartition of energy (labeled as Mode Population) for (c) ambient and (d) compressed RDX; blue regions are under-populated and red over-populated with respect to the spectra at the same temperature. Frequency range shown highlights the pumped modes, and how there is no significant change in SMRT with compression. Fitted SMRT with high error are omitted from (a) and (b), while data is omitted from (c) and (d) at each minimum of the total density of states to avoid over-analyzing weak signal changes.

Figure S4: Pumped vibration is the combination of $\text{N}-\text{N}^{(\text{eq})}$ stretch, NO_2 bend/symmetric stretch, ring $\text{C}-\text{N}-\text{C}$ stretch, CH_2 twist, CH_2 bend in both sets of data, time origin is where the pump thermostat is removed from the probe volume. Pumped mode has weak NO_2 character, as seen in (a) and (b), and neither ambient nor compressed system shows significant evolution beyond the ~ 10 ps timescale. Shifting and broadening of peaks causes edge frequencies to central peaks to be spuriously fit with longer time dynamics than may be actually present.

Figure S5: Pumped vibration is the combination of N–N^(eq) stretch, NO₂ bend/symmetric stretch, ring C–N–C stretch, CH₂ twist, CH₂ bend in both sets of data, time origin is where the pump thermostat is removed from the probe volume. As with other pumped high frequency modes, the SMRT of these low frequency modes show much longer time evolution where the sample is compressed.

S2.4 Mode-Selectivity of the 200 ps Evolution

Table S2: Calculated harmonic modes of α -RDX with IR intensities $\geq 0.1 \text{ e}^2 \text{ amu}^{-1}$. Modes within the experimental probe window are then assigned a yes/no/neutral value for evolving with the 200 ps time constant; see main text for details.

Calc. Freq. (cm^{-1})	Calc. IR Intensity ($\text{e}^2 \text{ amu}^{-1}$)	Expt. 200 ps Evolution?
226	0.191	—
430	0.289	—
430	0.536	—
485	0.148	—
589	0.469	—
604	0.325	—
605	0.165	—
725	0.144	—
738	0.141	—
746	0.111	—
774	0.977	—
778	0.573	—
846	0.424	no
876	2.455	yes
882	0.507	yes
892	0.171	neutral
893	0.488	no
908	0.686	no
910	0.493	no
944	0.316	yes
946	0.793	yes
1000	1.137	neutral
1060	0.590	yes
1065	0.539	yes
1215	0.288	yes
1235	0.216	no
1239	0.229	no
1240	0.859	no
1243	0.233	no
1243	0.286	no
1258	1.724	yes
1268	1.185	yes
1270	1.188	yes

Calc. Freq.	IR Int.	200 ps?
1286	0.215	yes
1308	0.648	neutral
1317	0.155	yes
1321	0.285	yes
1331	0.685	neutral
1336	1.398	no
1342	1.168	no
1345	0.857	no
1375	0.691	neutral
1380	0.433	no
1388	1.121	no
1395	0.110	no
1398	0.138	no
1413	0.107	no
1424	1.531	no
1432	1.417	neutral
1552	2.630	no
1562	0.692	no
1594	1.984	yes
1597	0.110	yes
1616	1.913	yes
1625	1.695	yes
1626	0.210	yes
3025	0.364	—
3075	0.181	—
3075	0.739	—
3095	0.264	—
3107	0.354	—

Figure S6: Fraction of each harmonic mode associated with each atom type (top four plots) or projected onto each crystal axis (bottom three plots) averaged over all eight RDX molecules in the unit cell. Bar height reports fraction while bar color highlights frequencies which experimentally demonstrate 200 ps evolution: red = “yes,” blue = “no,” and black = “neutral.” Also plotted is the normalized, calculated IR spectrum from Fig. 1.

Figure S7: Fractional change of each N–X bond length for each frequency averaged over all eight RDX molecules in the unit cell. Bar height reports fraction while bar color highlights frequencies which experimentally demonstrate 200 ps evolution: red = “yes,” blue = “no,” and black = “neutral.” Also plotted is the normalized, calculated IR spectrum from Fig. 1.

Figure S8: Example correlation plots comparing the relative fractional changes in N–X bond lengths for each frequency. Marker size scales with calculated IR intensity while marker color highlights frequencies which experimentally demonstrate 200 ps evolution: red = “yes,” blue = “no,” and black = “neutral.”

S3 Additional Experimental Results

The full set of all transient spectra are shown as false-color surface plots in Figures 2, 3, S9 and S11. These plots visualize changes in the transient absorption signal as a function of time-delay (x axis) and frequency (y axis) by mapping spectral intensity to the color coordinate. For example, in Fig. 2 in the main manuscript, a value of 0 ΔmOD has been assigned to white; blue corresponds to negative, bleach features (due to stimulated emission or loss of ground state absorption); and positive, transient absorption (TA) features appear in red. Vibrational excitation of isolated frequencies at early time-delays results in bleach/TA pairs which appear as parallel features of different colors. Dynamics, such as decay of an excitation, appear as a change in color towards the baseline, 0 ΔmOD value. While the colormap used in Figures 2 and 3 is useful for highlighting sign changes, other features such as intensity changes may not be clear. To help visualize all of the transient features, Figures 2 and 3 have been reproduced in Figures S9 and S11 using an alternate colormap.

Two thermal difference infrared spectra are shown in Fig. S14, which may be calculated as follows:

$$-\log_{10} \left(\frac{\text{RDX transmission spectrum at } T_2}{\text{RDX transmission spectrum at } T_1} \right) \quad (\text{S1})$$

with temperatures $T_2 > T_1$. These thermal difference spectra highlight changes to the vibrational spectrum due to sample heating (*i.e.* exciting a higher energy phonon population distribution). The qualitative similarity of the positive/negative signal couplets in the thermal difference spectrum and transient spectra at $\Delta t \geq 10$ ps—shown in Figures 4, S10, and S12—suggests that dynamics within the excited phonon bath are responsible for the longest observed dynamics.

Figure S9: Reproduction of Fig. 2 (1530 cm^{-1} pump) using an alternate colormap; singularities are shown in white. Time-delays are shown in linear steps up to 4 ps and logarithmic thereafter.

Figure S10: Transient spectra (1530 cm^{-1} pump) taken at each spectrometer grating position and multiple time delays. Spectra shown in part a) are from the transient shown in Fig. 2 following the PFID filtering process as discussed in the main manuscript.

Figure S11: Reproduction of Fig. 3 (1260 cm⁻¹ pump) using an alternate colormap; singularities are shown in white. Time-delays are shown in linear steps up to 4 ps and logarithmic thereafter.

Figure S12: Transient spectra (1260 cm^{-1} pump) taken at each spectrometer grating position and multiple time delays. Spectra shown in parts c) and d) are from the transient shown in Fig. 3 following the PFID filtering process as discussed in the main manuscript.

Figure S13: Transient spectra from the degerate experiments at the a) 1530 cm^{-1} pump and b) 1260 cm^{-1} pump prior to the PFID filtering process as discussed in the main manuscript.

Figure S14: Thermal difference infrared spectra of RDX at 35°C and 37°C. The baseline drift for frequencies $\lesssim 900 \text{ cm}^{-1}$ is due to decreased transmission through the CaF_2 window.

S4 Kinetic Models and Fitting

S4.1 Fitting Transient Data

For the present work, all transient data were globally fit using the Glotaran software package.^{2,3} In the absence of a complete kinetic picture for RDX, a sequential decay mechanism (*e.g.* $A \rightarrow B \rightarrow C$) was assumed for all kinetic models. Fit time constants are given in Table 1 with the corresponding evolution associated difference spectra in Figs. S15 and S17; fit residuals are shown in Figs. S16 and S18.

Time delays were corrected to place $\Delta t = 0$ at the position determined by an IRF measurement in InSb or Ge. Fits to each spectral window assumed an IRF of 0.3 ps FWHM for both pump frequencies. Multiple ultrafast lifetimes were used to fit the transients near $\Delta t = 0$; the shortest, sub-0.3 ps lifetime may not exclusively represent pump-induced RDX

Figure S15: Evolution associated difference spectra (EADS) from global fits to the 1530 cm^{-1} pump transient absorption data. Time constants are given in Table 1 in the main text. EADS have been associated with τ_1 have been scaled for visual clarity.

vibrational dynamics. Glotaran does not model dynamics at $\Delta t < 0$; fits in this region will always be poor (see Figs. S16 and S18). For these data, global fitting assumes time-dependent vibrational state populations with time-independent absorption spectra.

Figure S16: Fit residuals from global fits to the 1530 cm^{-1} pump transient absorption data using the EADS from Fig. S15 and time constants from Table 1 in the main text.

Figure S17: Evolution associated difference spectra (EADS) from global fits to the 1260 cm⁻¹ pump transient absorption data. Time constants are given in Table 1 in the main text. EADS associated with τ_1 have been scaled for visual clarity.

Figure S18: Fit residuals from global fits to the 1260 cm^{-1} pump transient absorption data using the EADS from Fig. S17 and time constants from Table 1 in the main text.

Figure S19: Transient behavior of select frequencies following excitation at 1530 cm^{-1} (a and b) and 1260 cm^{-1} (c and d). Example fits from the 5 τ and 4 τ kinetic models are also shown to highlight the contribution of a sub-ps time constant; see main text for further details of the fit models. Time-delays are linear up to 4 ps and logarithmic thereafter.

Figure S20: Additional single-frequency transients highlighting the 200 ps temporal evolution following excitation at 1530 cm^{-1} (left column) and 1260 cm^{-1} (right column). Transients at other frequencies showing 200 ps behavior are shown in Figures 5, S19, and S21.

Figure S21: Additional single-frequency transients highlighting the 200 ps temporal evolution only observed following excitation at 1260 cm^{-1} . The transient at 886 cm^{-1} following the 1530 cm^{-1} pump is also shown for signal-to-noise comparison. Transients at other frequencies showing 200 ps behavior are shown in Figures 5, S19, and S20.

Figure S22: Transient behavior of select frequencies from the NO_2 stretch modes following excitation at 1530 cm^{-1} . For comparison to the results of Shi *et al.*,⁴ each frequency lane ($\sim 7\text{ cm}^{-1}$ wide) has been fit with a monoexponential decay function; time constants from these models are given in the figure legends. Example fits from the 5τ and 4τ kinetic models—as discussed in the main text—are also shown for comparison.

S5 Details of the Zenodo Archive

Data underpinning the present results are freely available through the Zenodo data repository at doi:10.5281/zenodo.4663415.

Experimental Data

All data are saved as a `.csv` file. Each transient `.csv` file is labeled according to molecule, pump wavelength, spectrometer grating position, file contents, pump laser power, polarization, and a date (*e.g.* `RDX8_9.5um_TA_1.4mW_para_15Sep2020.csv`). The first column contains frequencies (in cm^{-1}) while the first row indexes each time delay (in ps). Transient spectra at select time delays, *i.e.* spectra presented in Figures 4, S10, and S12, are similarly labeled (*e.g.* `RDX8_11.65um_spec_1.6mW_para_15Sep2020.csv`) with the same data organization within each file. Select transient spectra shown at the 1520 cm^{-1} (1530 cm^{-1} pump) or 1330 and 1240 cm^{-1} (1260 cm^{-1} pump) regions were taken from the $6.6\text{ }\mu\text{m}$, $7.5\text{ }\mu\text{m}$, and $8\text{ }\mu\text{m}$ “TA” datasets respectively. The static RDX FTIR and 35°C ThDIR spectra are given as two column `.csv` files: the first column is frequency (in cm^{-1}) while the second column is either transmission or ΔOD .

Theory Data

Included in the data repository are all of the necessary inputs to perform the vibrational analysis from FDM using the Phonopy software package.⁵ The minimized RDX crystal used in the finite displacement calculations is given as a `POSCAR` file format to be used in VASP, the enumeration of all displacements used in the first anharmonic expansion is given in `disp_fc3.yaml`. The collection of all individual VASP calculations into second- and third-order force constants are contained in the `.hdf5` files. The remaining files contain all of the details for the Phonopy calculations done herein, per-mode population adjustments in the JDOS are achieved by modifying the `phono3py/phonon3/triplets.py` source code file which is distributed with all versions of the code. Additionally, individual normal mode displacements are provided as `anime_*.xyz` files to be read in by most visualization packages, we have used OVITO.⁶ To produce the displacement vector diagrams shown throughout this work, an OVITO scene file (version 3.3+) `EigenModeVis_Solid_RDX.ovito` has been supplied.

For the MD simulations, the modified interatomic potential and an example LAMMPS input file for a GLE pump-probe simulation are supplied. The structure file of α -RDX has been relaxed at 1 atm of pressure and 300 K given the adjustments made to the N–O, C–H, O–N–O, and H–C–H bond strengths. These adjustments were made based on qualitative agreements between MD and VASP predicted IR spectra, and should not be considered as a general use potential for RDX without further validation.

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