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Ultrafast Spectroscopic Studies of Vibrational Energy Transfer in Energetic Materials

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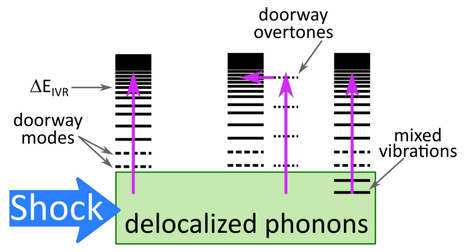
Introduction

Shock-induced detonation is a key property of EM that remains poorly understood. One mechanism is the "thermal" mechanism where shock excitation of lattice phonon modes is hypothesized to transfer energy to intramolecular vibrations, resulting in the breaking of chemical bonds and reaction.[1] However, this theory faces challenges based on energy differences (vibrations ≤ 3000 cm^{-1} *vs*. bond energies ≈ 30 000 cm^{-1}) and expected energy redistribution away from reactive coordinates.[2] Previous experiments have examined molecular vibrational energy transfer[3] and spectroscopy of EM following a shock on picosecond (ps) timescales (*e.g*. ref. 4), though none of these techniques have directly investigated resonantly pumped phonon up-conversion within bulk EM; information vital to establishing rigorous *bottom-up* understanding and theory.

Proposed Mechanisms[1]

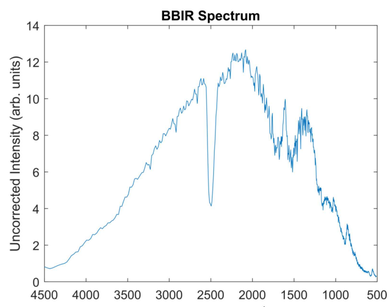


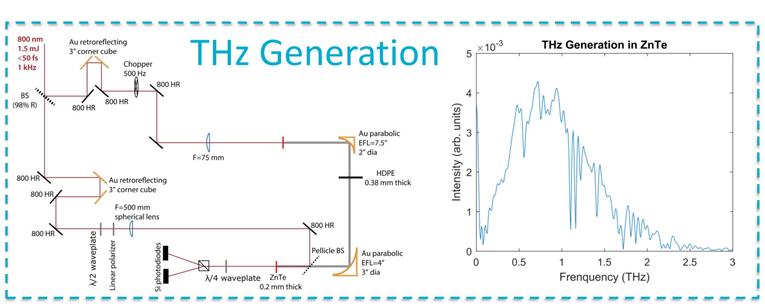
Experimental Methods

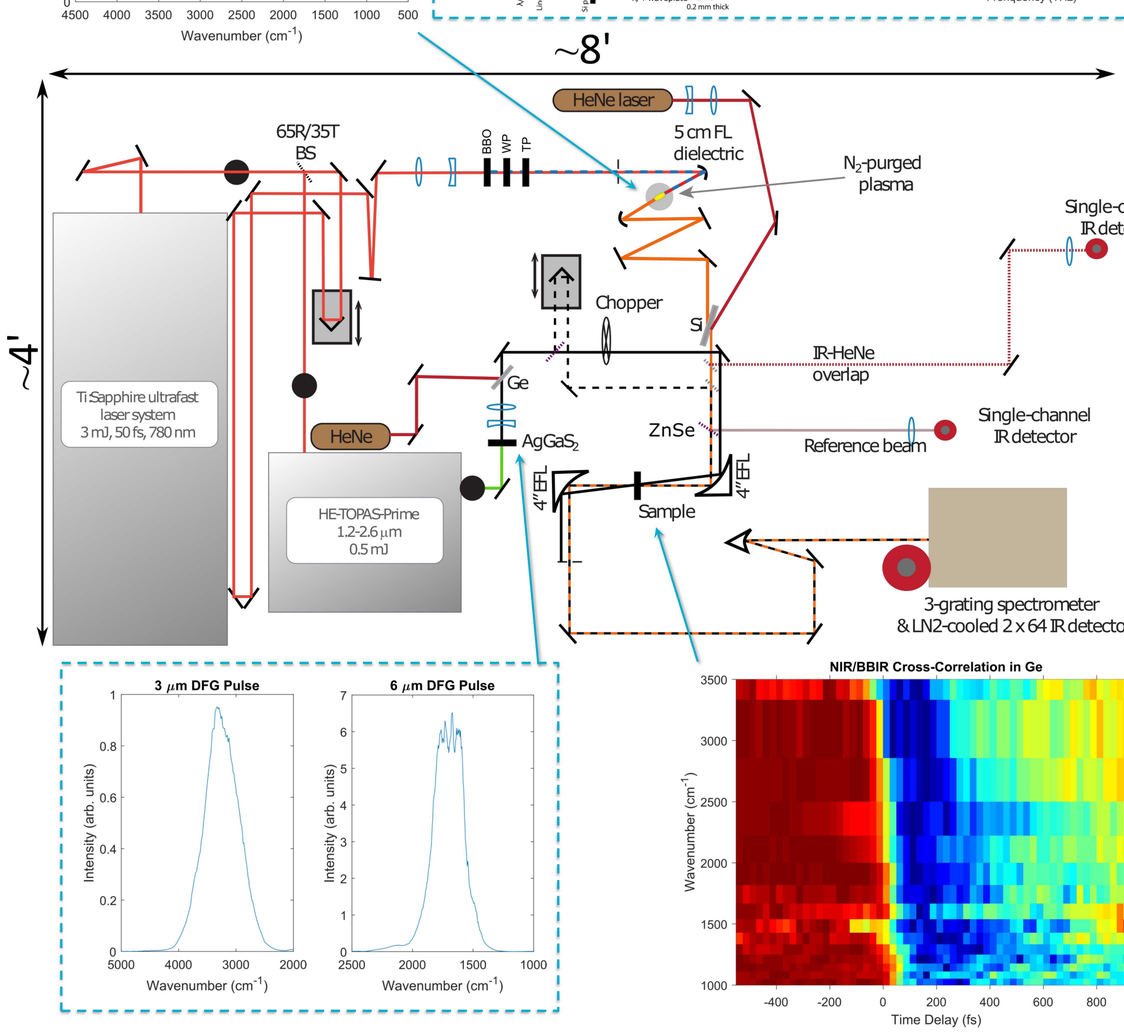
Through combinations of plasma-generated supercontinuum infrared (BBIR; 2–20 µm), tunable near infrared (1.2–2.6 µm), tunable mid-infrared (3–7 µm) and terahertz (100–1000 µm) pulses in pump-probe spectroscopy, we can explore energy transfer processes on a sub-ps time scale.

– NIR/BBIR temporal cross-correlation FWHM = 110 fs

– MIR/BBIR temporal cross-correlation FWHM = *ca*. 500 fs

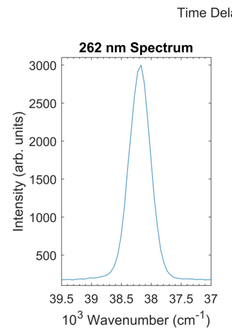






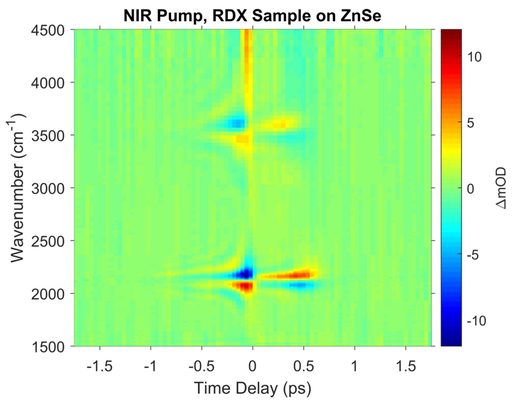
Additional Capabilities

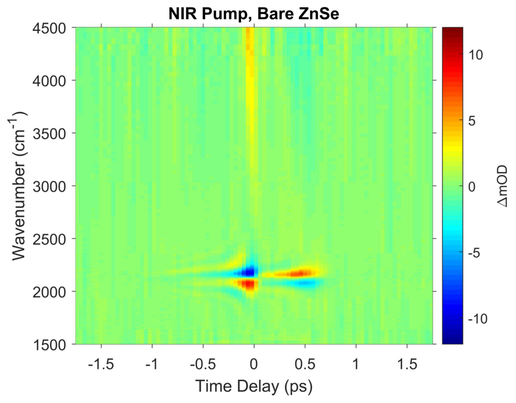
We can also produce ultrashort 262 nm and 195 nm ultraviolet pulses for exciting electronic transitions in materials or simulating irradiative aging. A small vacuum chamber may be placed at the sample position for studying gas-phase dynamics, such as the primary photolysis[5] of model EM systems (*e.g.* nitromethane.).



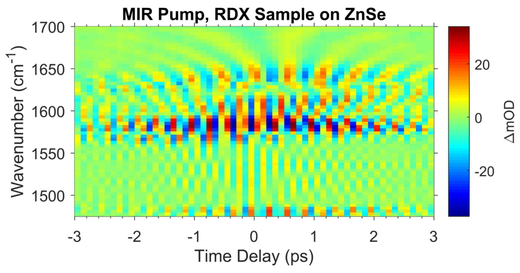
First Results: RDX

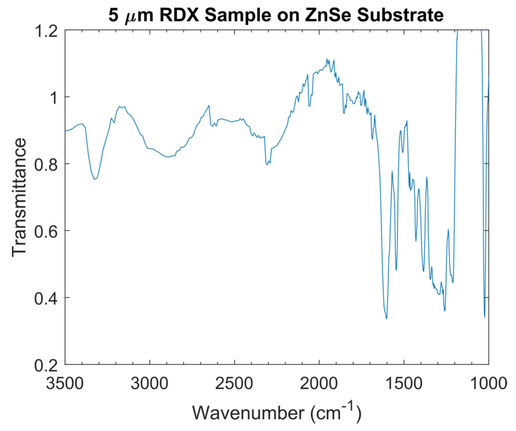
C–H overtone pumping (v = 2 ← v = 0) at 1.67 µm in a 5 µm thick RDX sample shows a clear feature at ~3 µm which is not present when probing the bare ZnSe substrate.





However, narrow band MIR pump-narrow band MIR probe in the 6 µm region (N–O stretch) reveals a time-dependent interference pattern due to inhomogeneous RDX sample.





Ongoing and Future Work

- Improve MIR time resolution (non-colinear DFG, reduce temporal chirp of pulses)
- Improve EM homogeneity (new RDX and PETN samples)
- Reduce atmospheric contamination of BBIR and THz spectra
- Explore vibrational dynamics of nitromethane model system (see Theory below)
- Generate intense THz pulses (tilted pulse front in $LiNbO_3$) for direct phonon pumping
- Directly pump "doorway" states with high-field THz pulses (NIR pumped organic crystal)

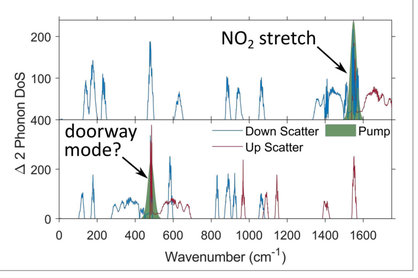
Theoretical Support

Theoretical work performed in parallel is using DFT and MD simulations to elucidate vibrational energy transfer pathways and lifetimes in EM; see talk S2.3 at 11 AM.

$$N_2^{(\mathrm{down})}(\mathbf{q},\omega) = \frac{1}{N}\sum_{\lambda'\lambda''} \Delta(-\mathbf{q}+\mathbf{q}'+\mathbf{q}'')(n_{\lambda'}-n_{\lambda''})[\delta(\omega+\omega_{\lambda'}-\omega_{\lambda''})-\delta(\omega-\omega_{\lambda'}+\omega_{\lambda''})]$$

$$N_2^{(\mathrm{up})}(\mathbf{q},\omega) = \frac{1}{N}\sum_{\lambda'\lambda''} \Delta(-\mathbf{q}+\mathbf{q}'+\mathbf{q}'')(n_{\lambda'}+n_{\lambda''}+1)\delta(\omega-\omega_{\lambda'}-\omega_{\lambda''})$$

Current capabilities include two phonon density of states for down-scattering and up-scattering events, "pumping" specific phonon modes, and incorporation of phonon-phonon scattering cross sections.



References

1. A. Tokmakoff *et al.,* J. Phys. Chem. **97**, 1901 (1993).
2. J. Hooper, J. Chem. Phys. **132**, 14507 (2010).
3. X. Hong *et al*., J. Phys. Chem. **99**, 9102 (1995).
4. C. M. Berg and D. D. Dlott, J. Phys. Conf. Ser. **500**, 142004 (2014).
5. T. Nelson *et al*., J. Phys. Chem. A **120**, 519 (2016).

Cheat Sheet

1 eV = 8065 cm^{-1}
1 kJ/mol = 83.6 cm^{-1}
6 µm = 1667 cm^{-1}
1 THz = 33 cm^{-1}

Acknowledgements

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