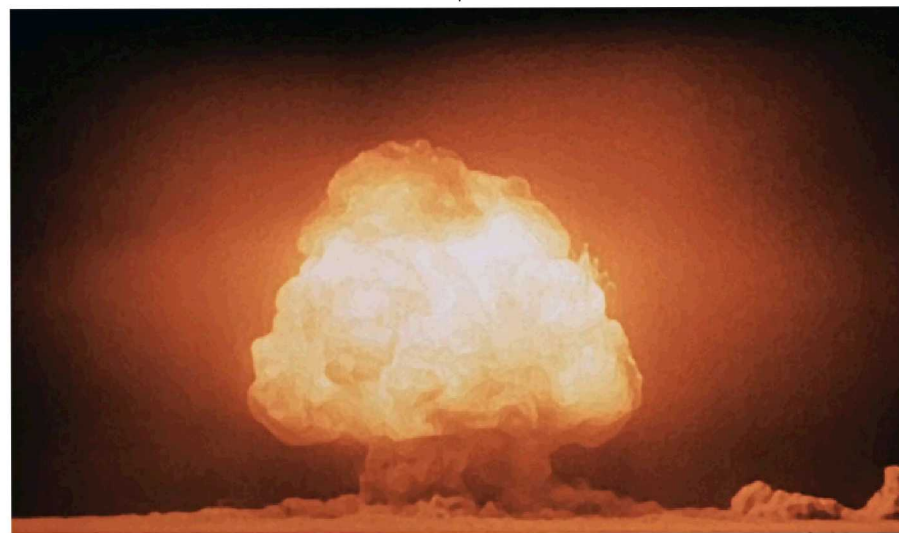
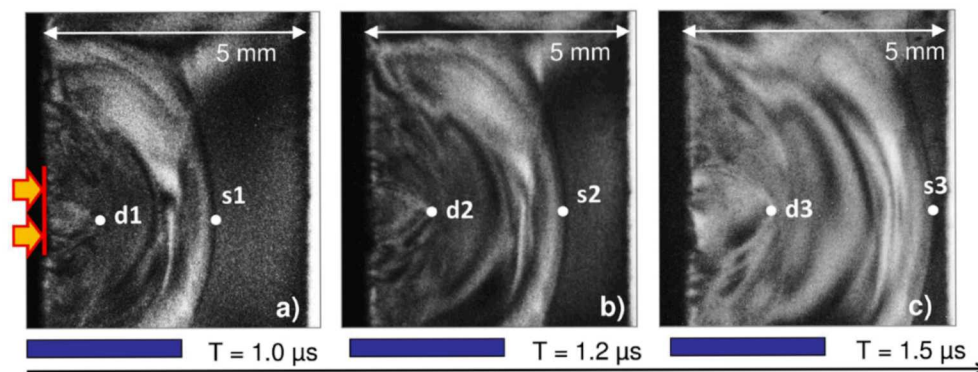
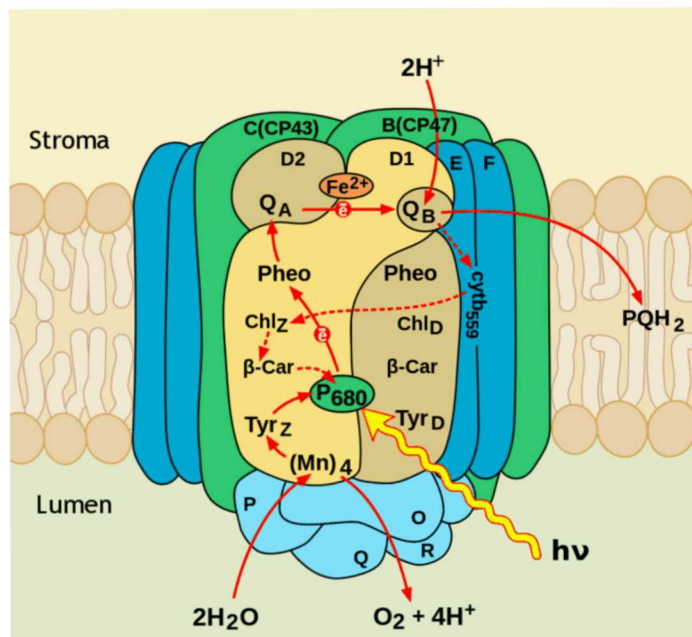


Sub-picosecond Vibrational Energy Transfer in Energetic Materials

Neil Cole-Filipiak
Ramasesha Lab, 8353

Energy Transfer Drives Chemistry



Energy Transfer Drives Chemistry

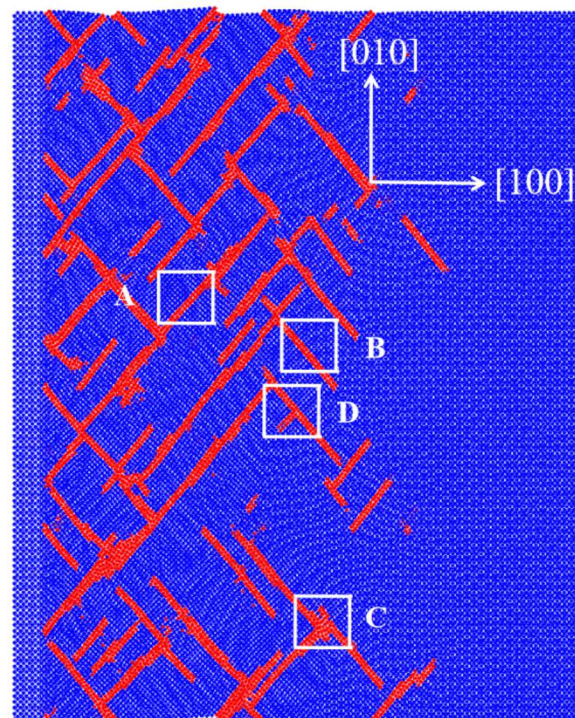
- What happens when you add energy to a system?
- Where is energy absorbed?
 - Electronic excitation
 - Vibrational excitation
- Where does the energy flow?
 - ground electronic state
 - vibrational modes of particular moieties
- What are the dynamics that get you there?
 - Coupled electron-nuclear motions
 - Anharmonic vibrational coupling
- How do these dynamics change with chemical structure?

Use lasers to study structural dynamics on the natural, ultrafast timescale of nuclear motion.

electronic excitation (UV) of combustion relevant chemicals
vibrational/phonon excitation (IR/THz) of energetic materials

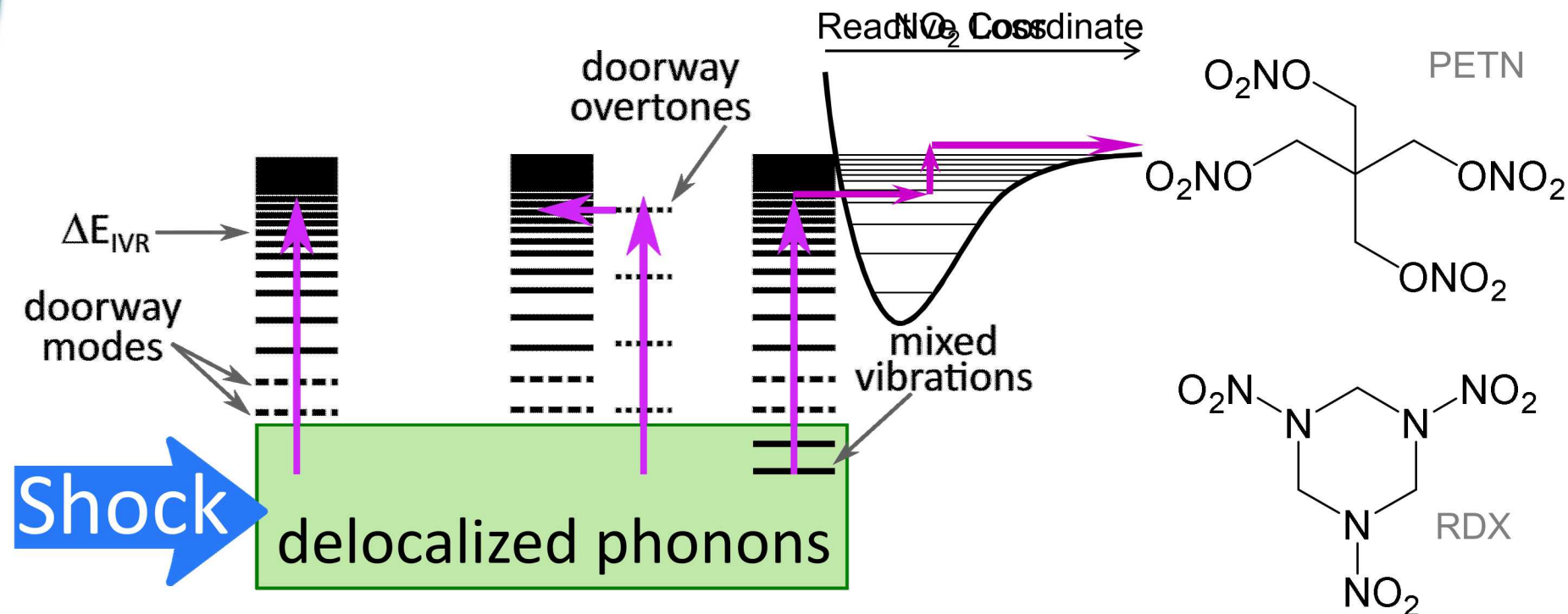
Energy Transfer in EM

- Use of solid, secondary EM as detonators for decades
 - Requires accurate timing of explosion
- Most understanding is empirical/heuristic
 - Very little chemical dynamics information, particularly for lifetime and aging processes
- Important to probe detailed chemical dynamics mechanisms
 - Improve performance/meet specific needs
- Ultimately, we need to understand existing, in use components
 - How can we (at Sandia) better understand detonation processes?
 - What tools do we need to develop?
 - What can we, as spectroscopists, bring to the table?



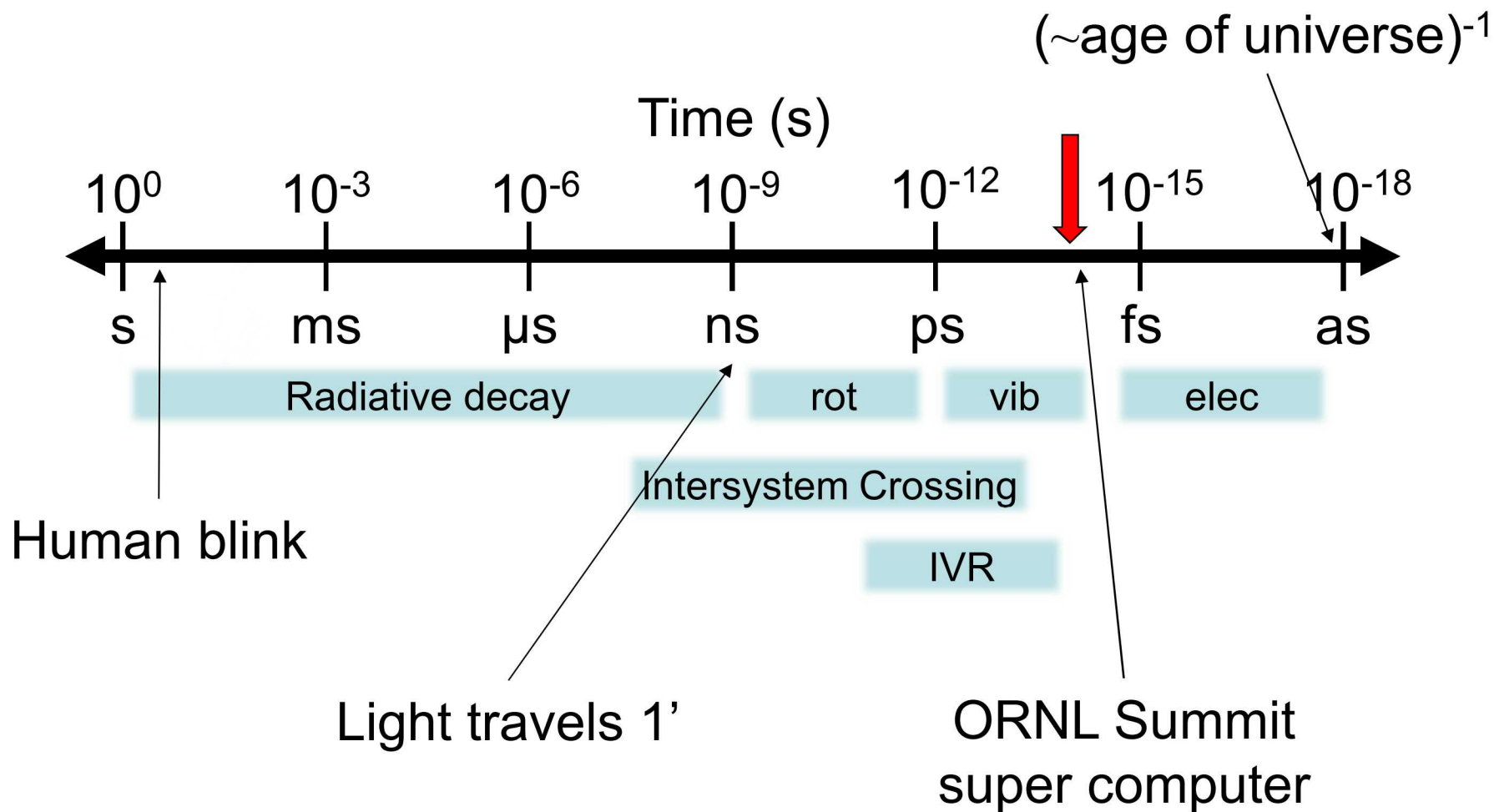
Energy Transfer in EM

- How do we go from a shockwave to chemical reaction (and detonation)?

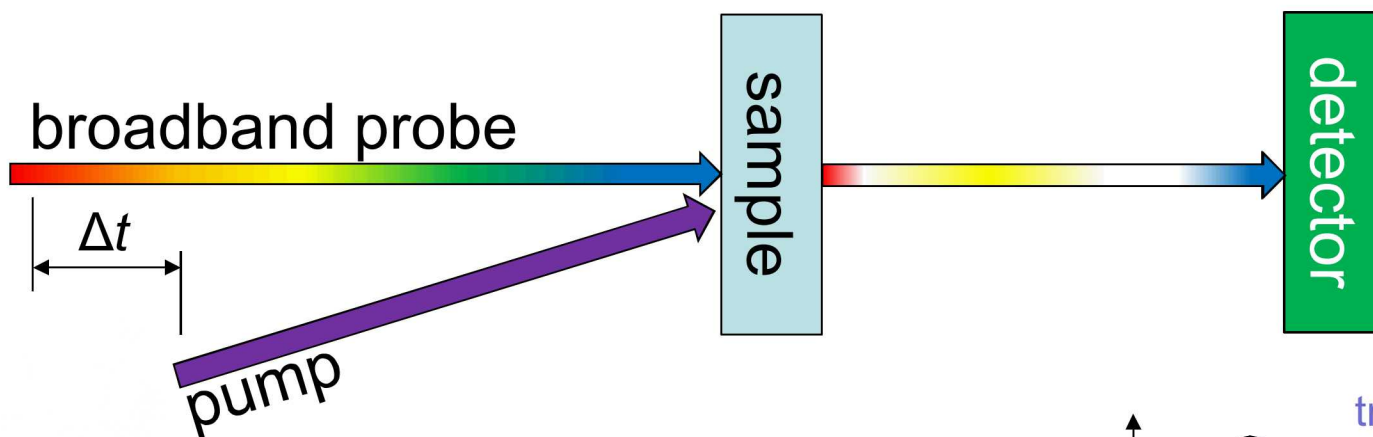


- Use IR to probe population changes following phonon excitation
- ... or following vibrational excitation (vibrational cooling)

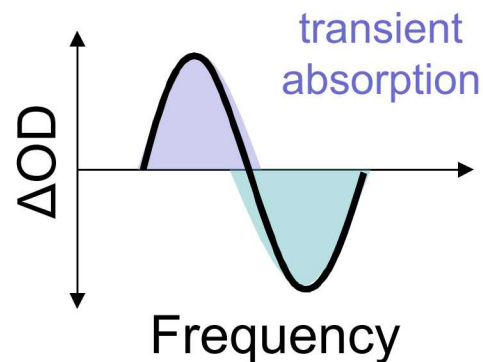
What is Ultrafast?



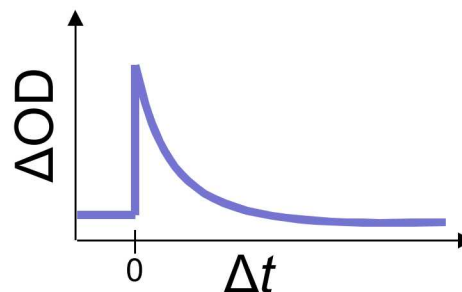
Ultrafast Transient Absorption Spectroscopy



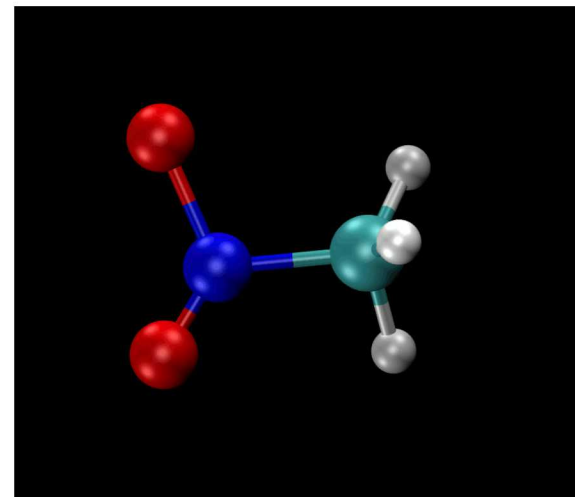
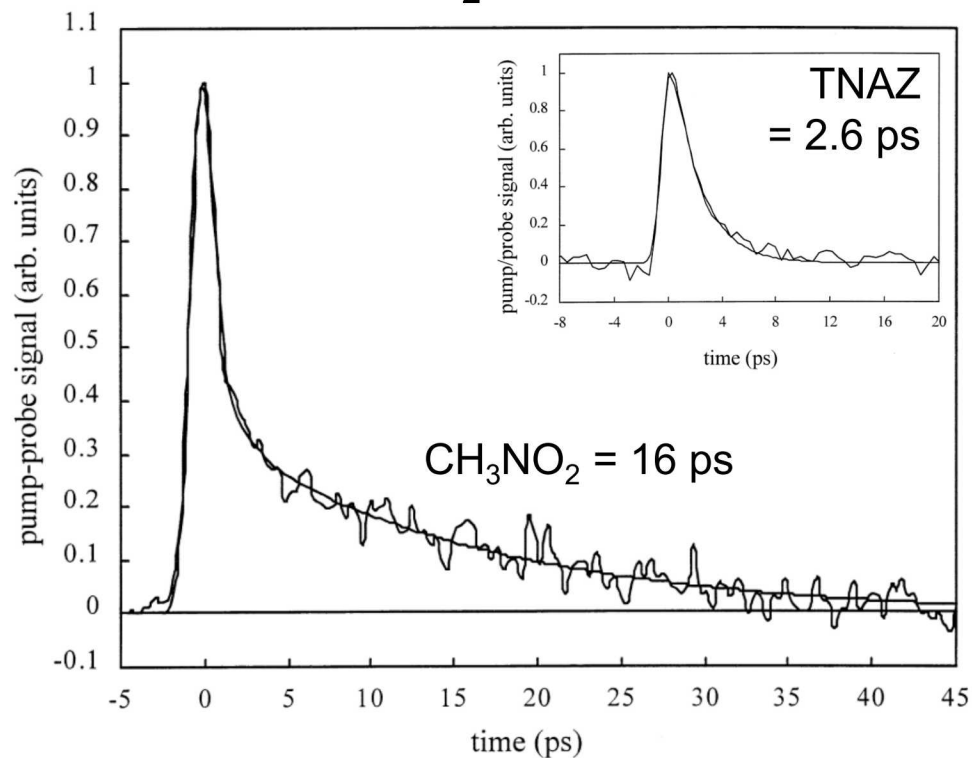
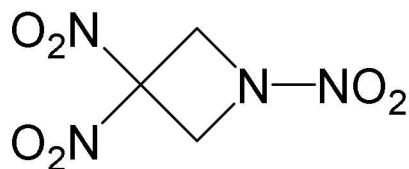
- For this talk, pump and probe will be mid-infrared (molecular vibrations)
- Energy units:
 - $E \text{ (cm}^{-1}\text{)} = 10^7 \div \lambda \text{ (nm)}$
 - $1 \text{ eV} = 8065 \text{ cm}^{-1}$
 - $1 \text{ kJ/mol} = 83.6 \text{ cm}^{-1}$
 - $1 \text{ THz} = 33 \text{ cm}^{-1}$
 - $6 \text{ }\mu\text{m} = 1667 \text{ cm}^{-1}$ (approx. C=O stretch vibration)
 - $35\,000 \text{ cm}^{-1} \approx$ covalent bond energy



stim. emission, ground state bleach



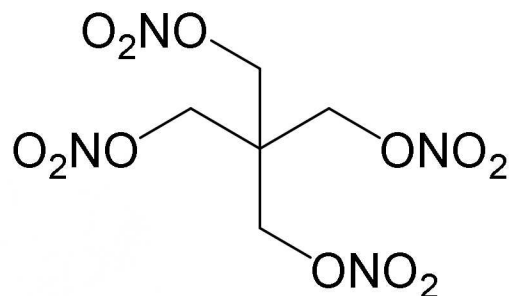
Vibrational Cooling in EM



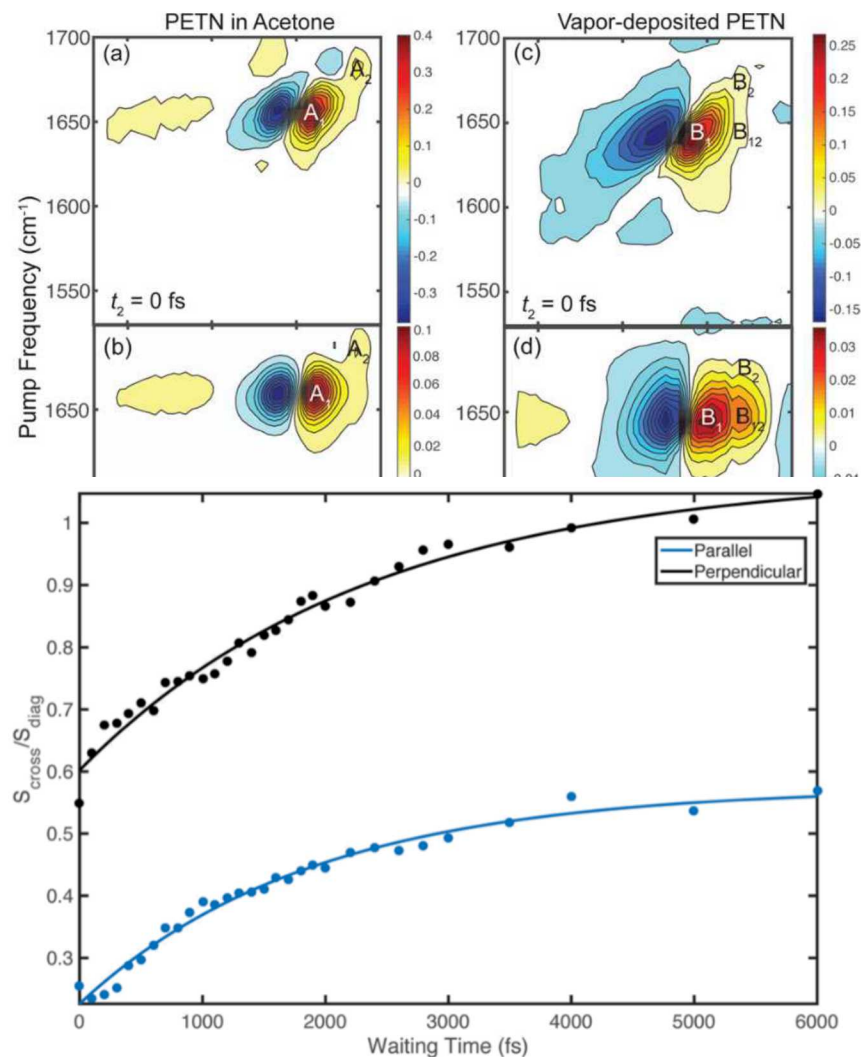
- Transient absorption to monitor NO_2 asymmetric stretch
- Lifetime independent of temperature and solvent
 - Intramolecular process
- VET is rapid in EM

Vibrational Cooling in EM

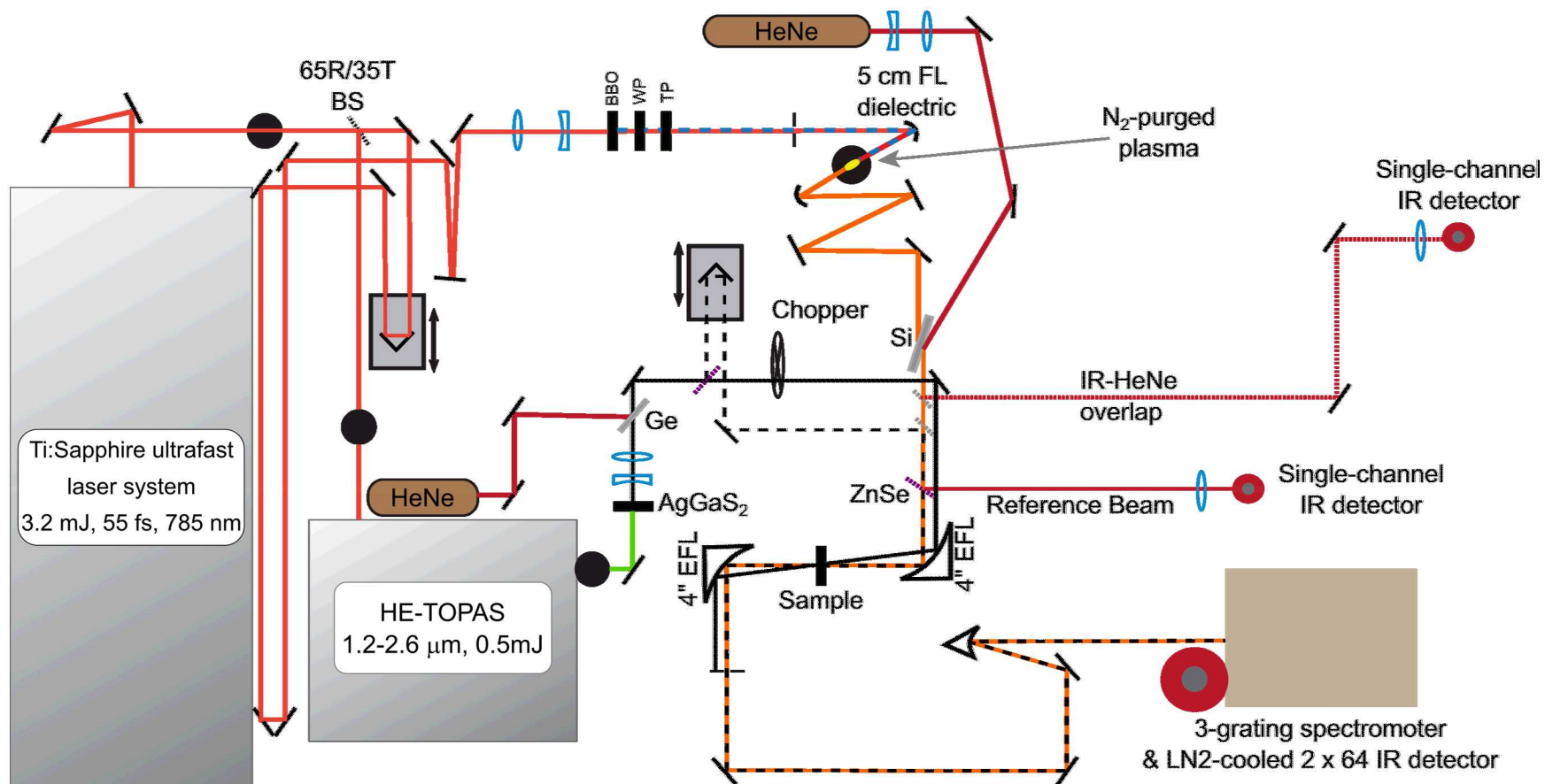
- Few ultrafast studies of *bulk* EM



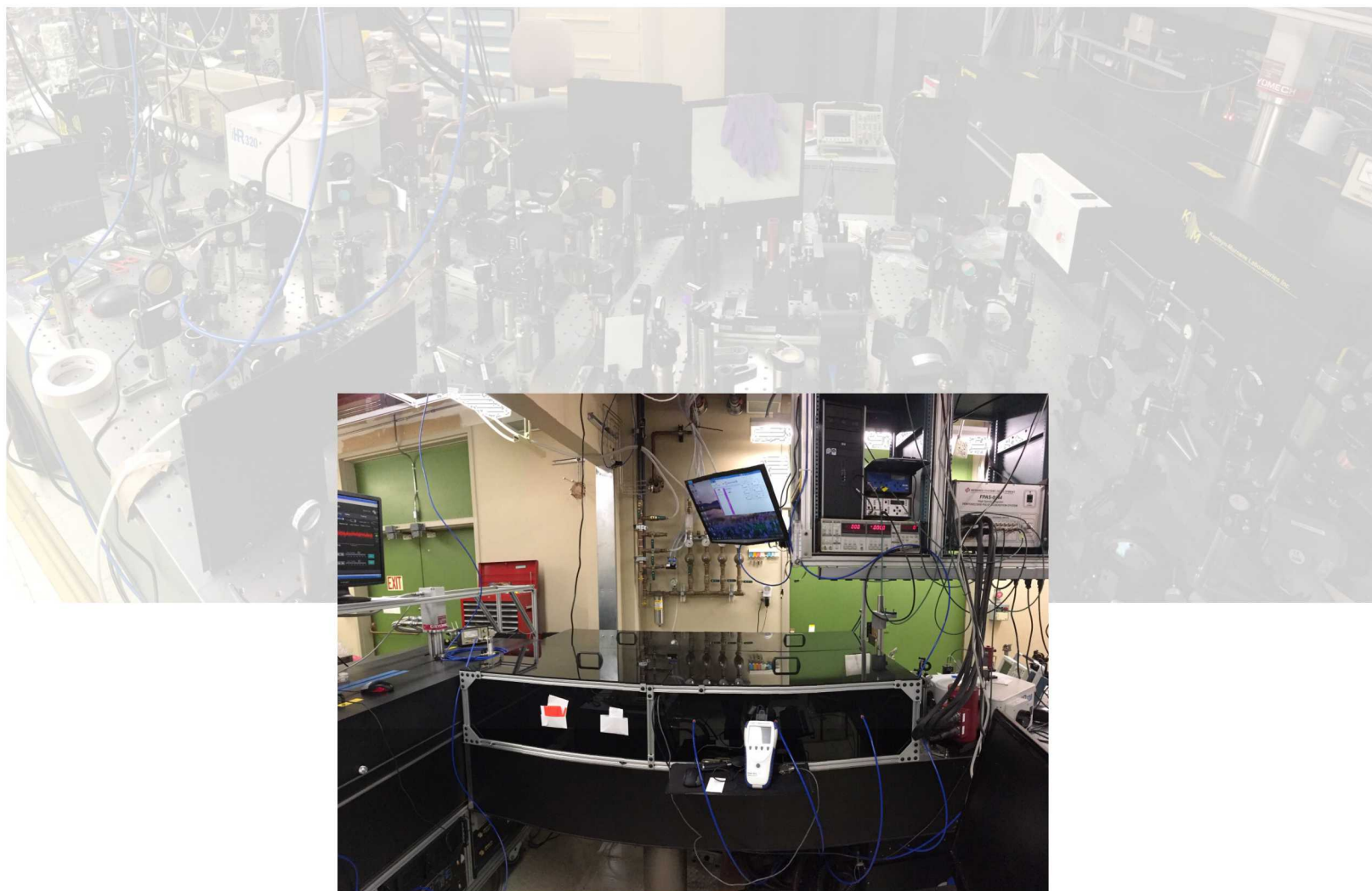
- Using time-resolved 2DIR to look at coupling between two specific NO₂ modes of PETN
- Can directly monitor cross peak growth to measure VET lifetime
- Only looking in a small spectroscopic and temporal window
 - What about all the other PETN modes?



Experimental Setup: Laser

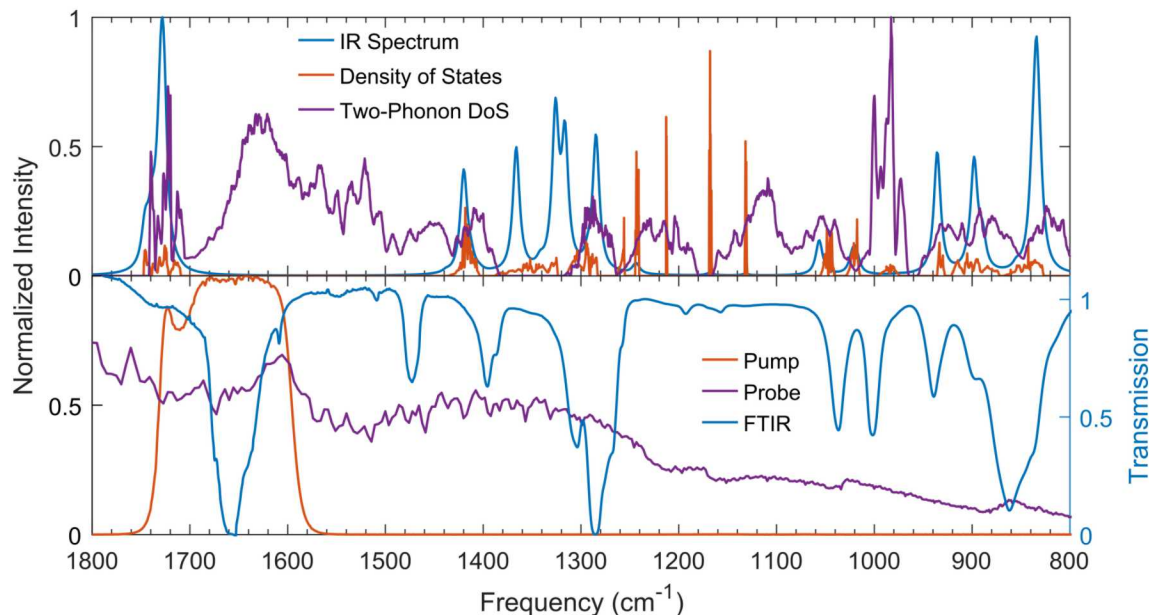


Experimental Setup: Laser



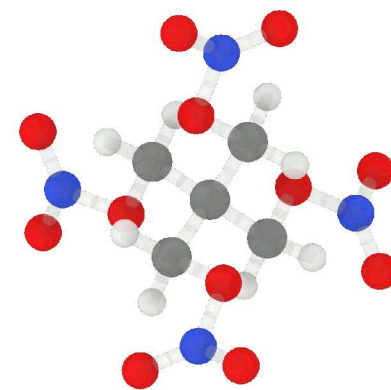
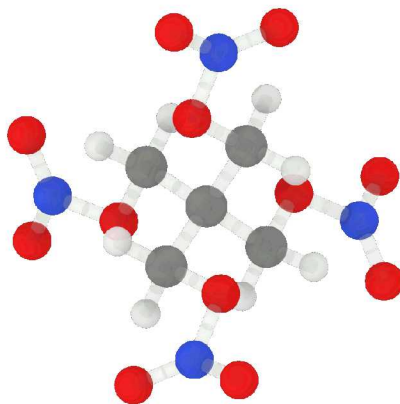
PETN: What To Expect?

- Theory collaboration with Mitch Wood (1444)
- Calculate PETN vibrational and phonon modes using DFT
- Calculate decay pathways from a “pumped” mode

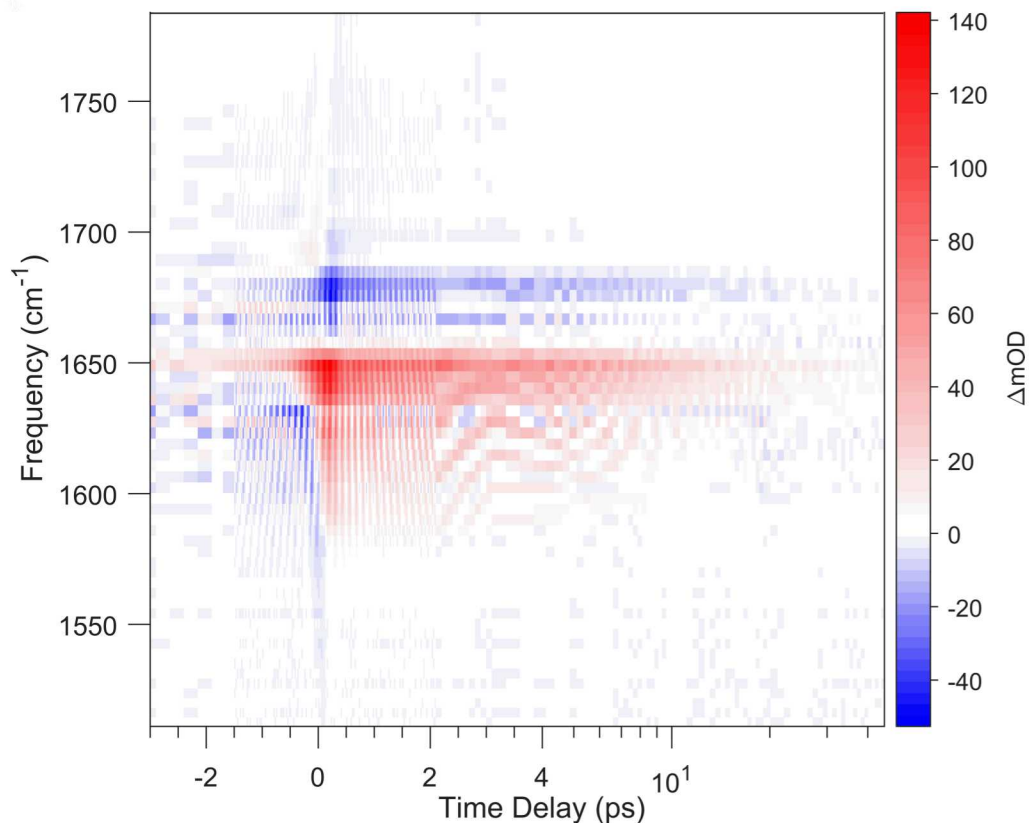


$$J^+(q, \omega) = \frac{1}{N} \sum_{\lambda' \lambda''} \Delta(-q + q' + q'') (n_{\lambda'} - n_{\lambda''}) [\delta(\omega + \omega_{\lambda'} - \omega_{\lambda''}) - \delta(\omega - \omega_{\lambda'} + \omega_{\lambda''})]$$

- NO₂ talks to every other PETN mode
- Every time we move energy, we pump a non-thermal phonon bath

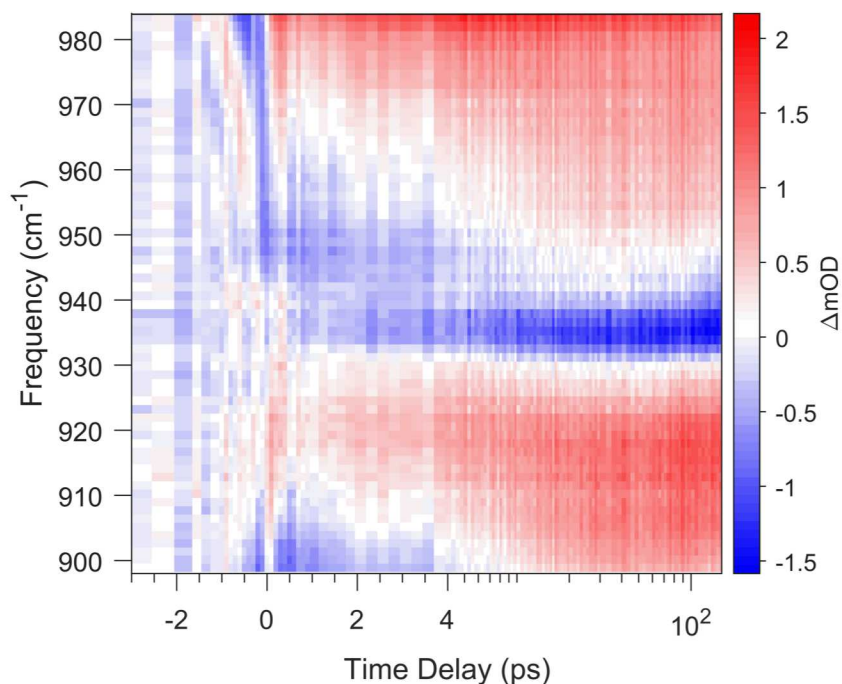
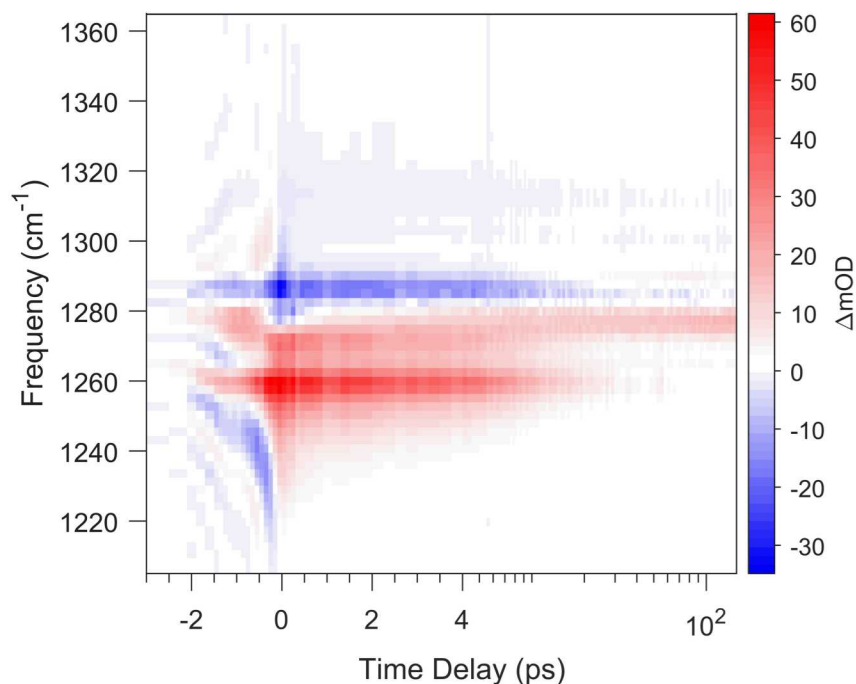


The Pumped Mode



- Similar to previous experiments, pump NO_2 asym. stretch and see what happens
- Loss of ground state signal
- Appearance of excited state absorption
- See expected, few ps decay
- Long lived offset is new, though resembles a thermal spectrum
- What about the other modes?

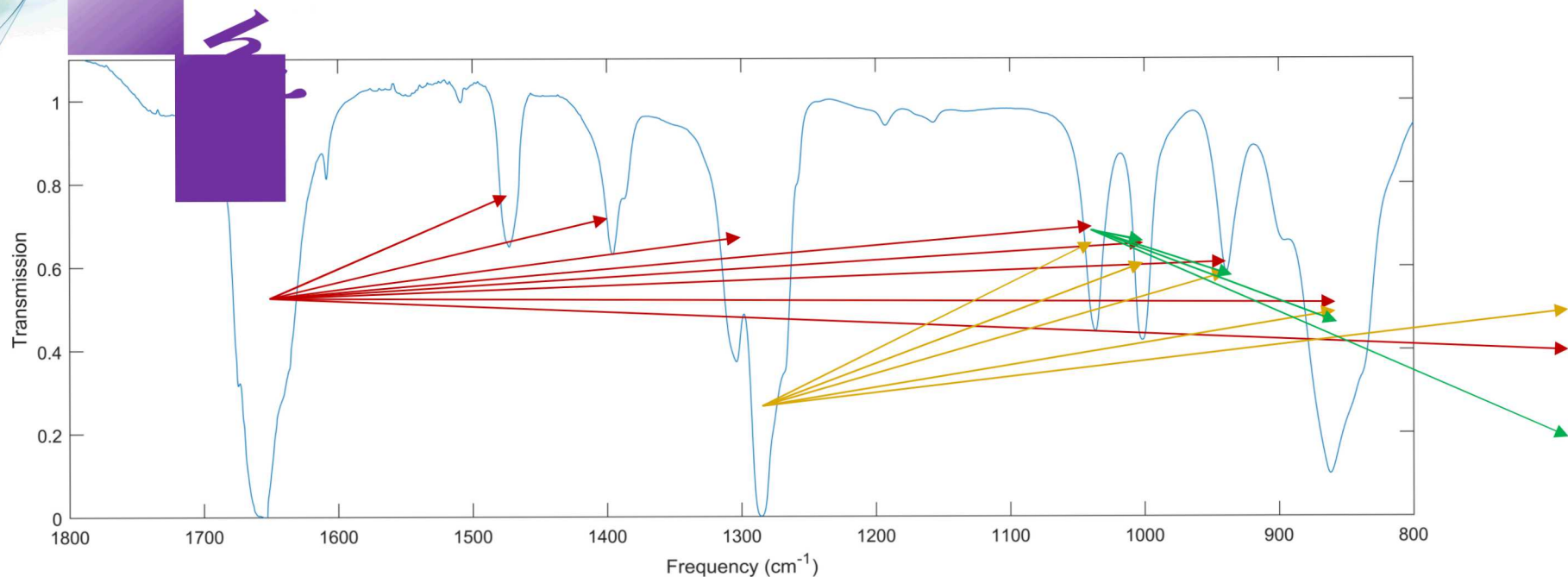
The Other Vibrational Modes



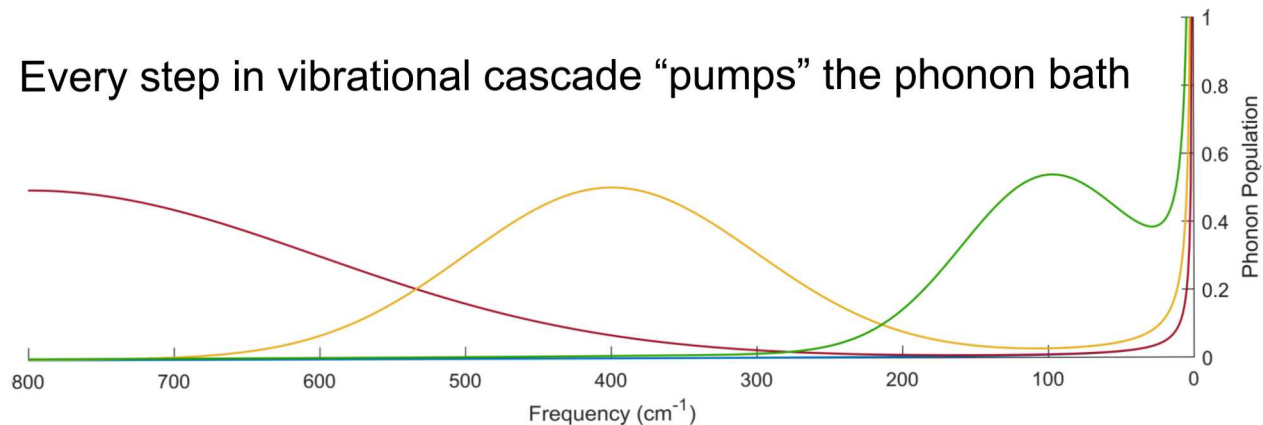
- < 200 fs response across the spectrum
- Some modes decay, others grow
 - Vibrational cascade

- Fits return 4 important lifetimes: 500 fs, o(1 ps), o(10 ps), and o(100 ps)
- By 150 ps, still haven't reached thermal equilibrium!

Vibrational Cascade

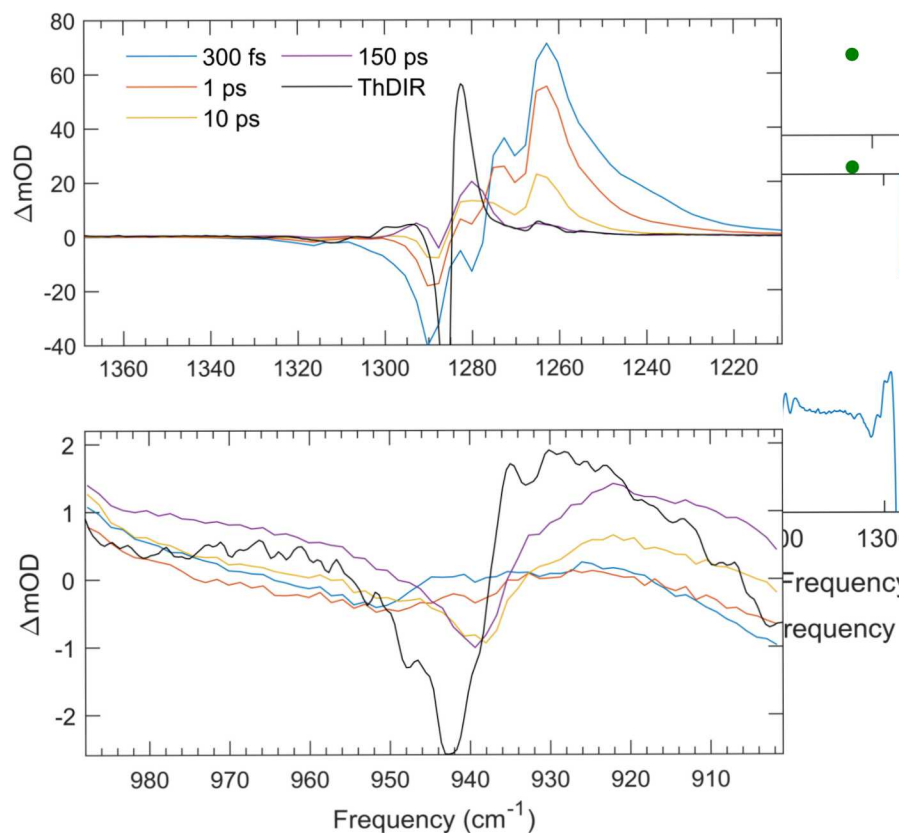


Every step in vibrational cascade “pumps” the phonon bath



Phonon Bath Perturbations

- Phonon pop. changes affect vibrational frequencies

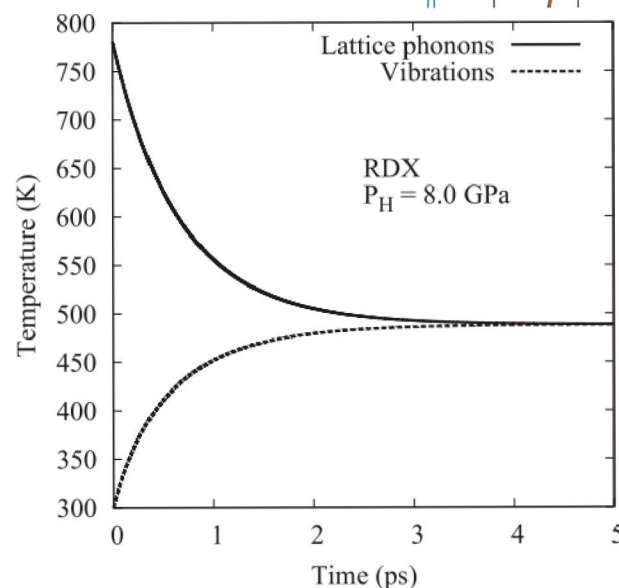


- Clear evolution towards thermal difference spectrum

— Doesn't quite reach by 150 ps

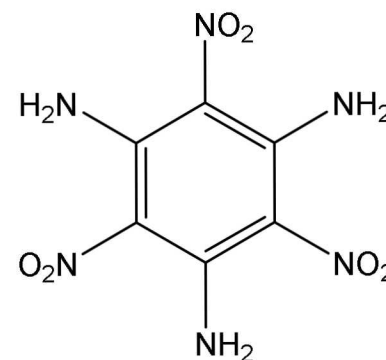
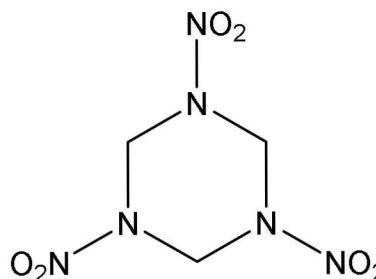
- Observed signal changes could be VET, phonon bath evolution, or both

- Challenges assumption of "instant" phonon thermalization in models



Conclusions and Future Work

- First, broadband study of VET in EM (and maybe molecular crystals)
- Ultrafast coupling of the initially pumped state to (apparently) every other PETN vibration
- Long time (100 ps) evolution of modes:
 - Could be long lived vibrational excitation
 - Could be long lived phonon bath excitation
- Both support up-pumping model
- Either way, we need to change EM theory, can't assume "instantaneous" thermalization
- Calculated IR spectra of PETN with non-thermal phonon bath
- Calculated VET dynamics
- Photoexcite other PETN modes
 - distinguish excited state absorption from perturbed ground state absorption
- Other systems: RDX, TATB

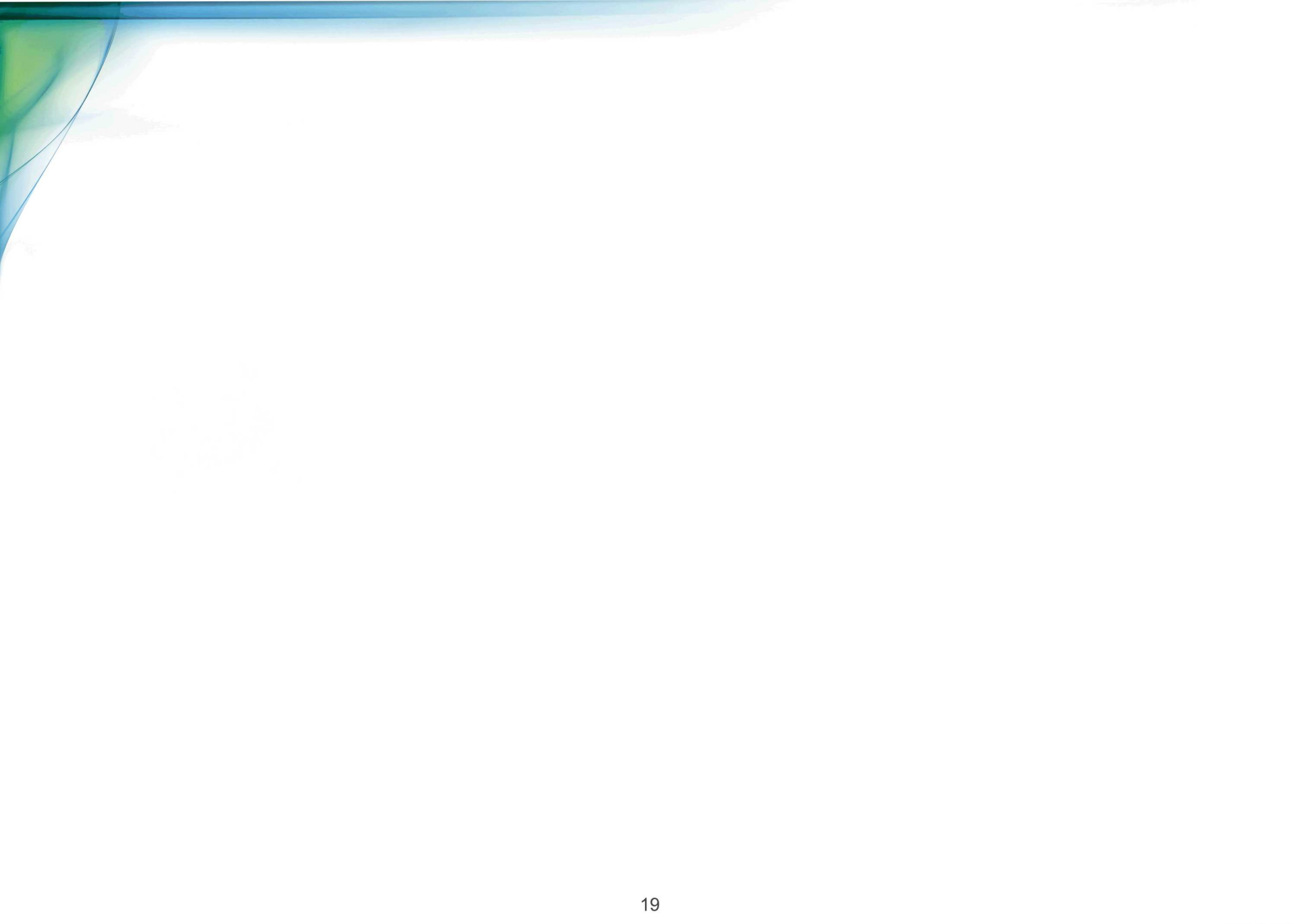


Acknowledgements

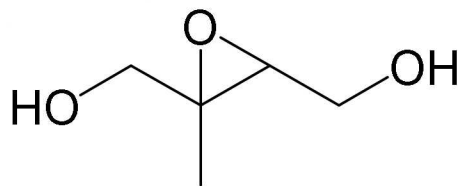
- LDRD funding
- Rob Knepper & team (2554)
- Deneille Wiese-Smith (2554)
- Mitch Wood (1444)
- 8353 colleagues
- Paul Schrader
- Krupa Ramasesha

This work is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This document describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the document do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

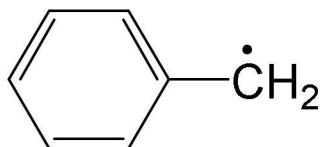
Questions?



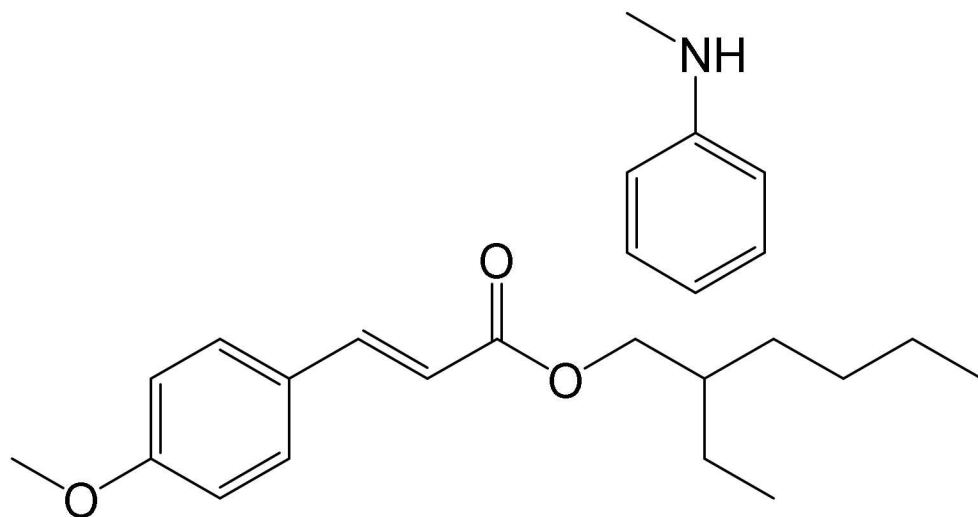
Who Am I?



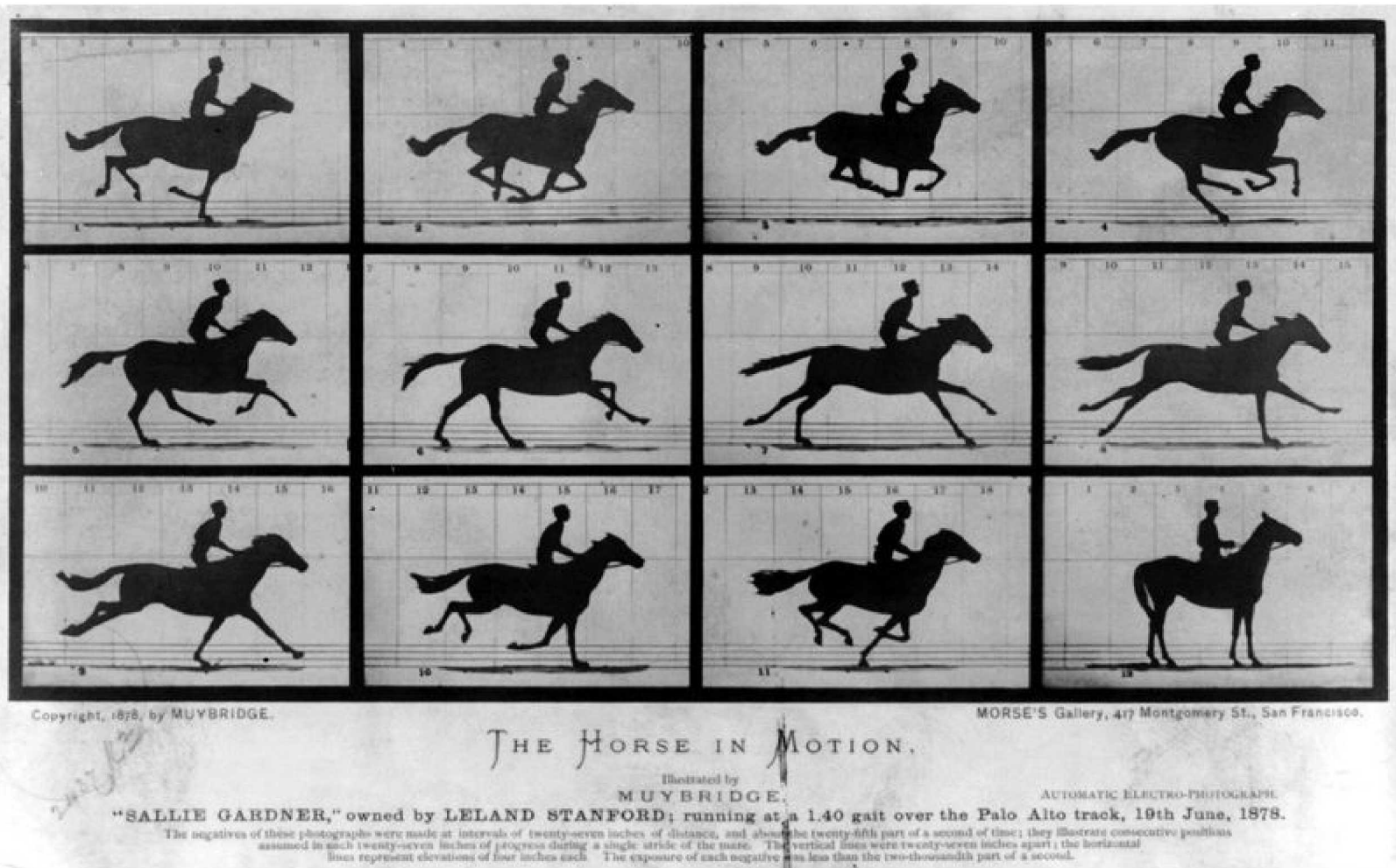
- First research projects were synthetic chemistry, including the synthesis and hydrolysis kinetics of isoprene hydroxyepoxides
- PhD at UC Berkeley studying primary gas-phase photochemistry of atmospherically relevant radicals, looking at product branching ratios



- Postdoc at Univ. Warwick (UK) doing ultrafast photodissociation on model biochromophores
 - Also looking at primary photodynamics of sunscreen chemical filters



Ultrafast Transient Absorption Spectroscopy



Energy Transfer in EM

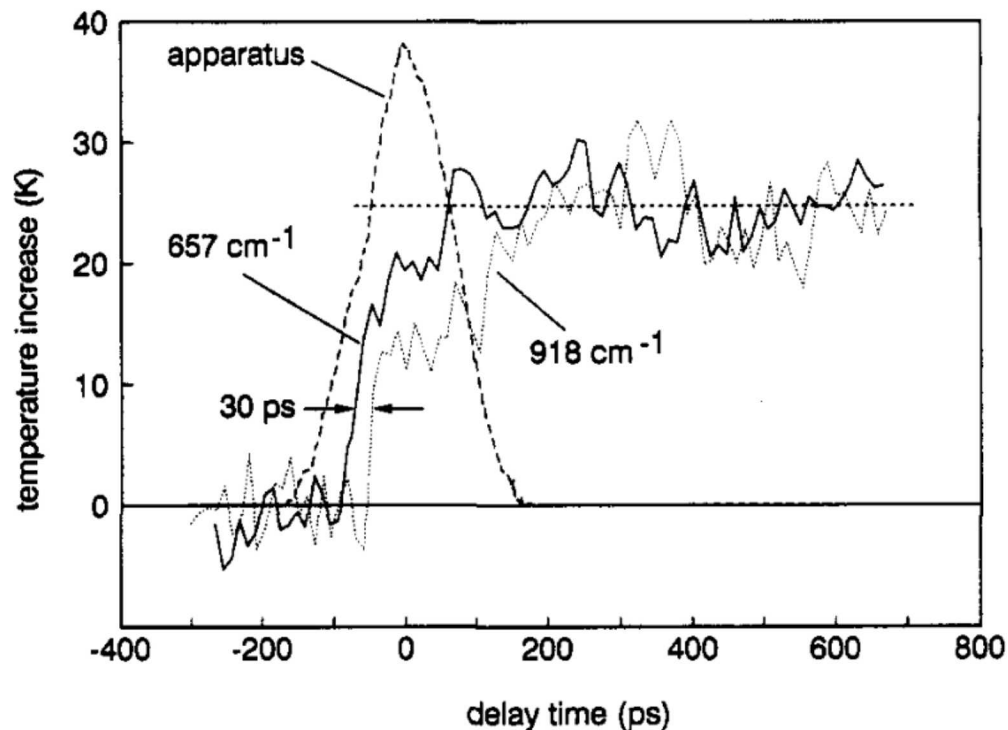
Looks good so far, but...

- Thermalization is expected to be fast
- Large energy difference between phonons (*ca.* 33 cm^{-1}) and bond energy (*ca.* $33\,000\text{ cm}^{-1}$)
- Most studies done in dilute solutions with few to hundreds of ps time resolution
 - Bulk studies done with narrow spectroscopic view
 - No investigations of direct coupling between phonon and intramolecular vibrations

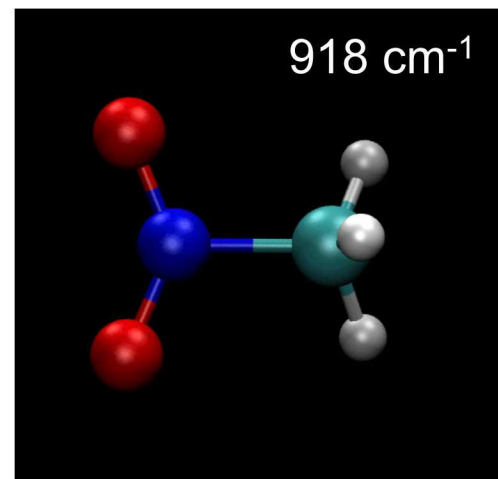
What happens in real-world, bulk EM samples?

- Vibrational cooling
 - Mid-IR pump, watch energy couple to lower lying modes
- Phonon up-pumping
 - THz pump, watch phonons “ladder climb” to higher energy modes

Vibrational Up-Pumping in EM



- Pump an IR dye in NM solution
 - Rapid, localized heating
- Used CARS to probe population changes following excitation
- Saw a delayed onset for higher energy vibrations
 - Sequential population of higher energy modes



The Pumped State?

