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Matter in Extreme Conditions: Probing Shock-Induced Reactions in Explosive Materials

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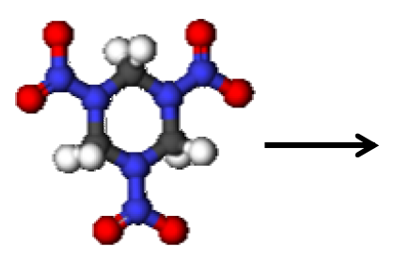
Motivation: Understanding Shock-Induced Reactions in Explosives


RDX

$\longrightarrow$ $H_2O + N_2 + CO + CO_2 + HCN + \ldots$

- **Why do we need to understand shock-induced reactions at the molecular level?**
- Explosive science is an unusual field: we have developed a variety of explosives for various applications and they work well, yet we understand little at the molecular level
- We do a good job of describing detonation at the macroscopic level
  - Detonation so fast that chemical details don't really matter
  - Thermodynamic + hydrodynamic treatment works fairly well
  - Knowing equation of state of reactants and products is sufficient to model many detonation scenarios

Problem is that we can only really model what happens during steady detonation of pristine materials at their time of manufacture and after extensive experimental characterization.

Lots of challenges predicting/understanding everything *besides* steady detonation:

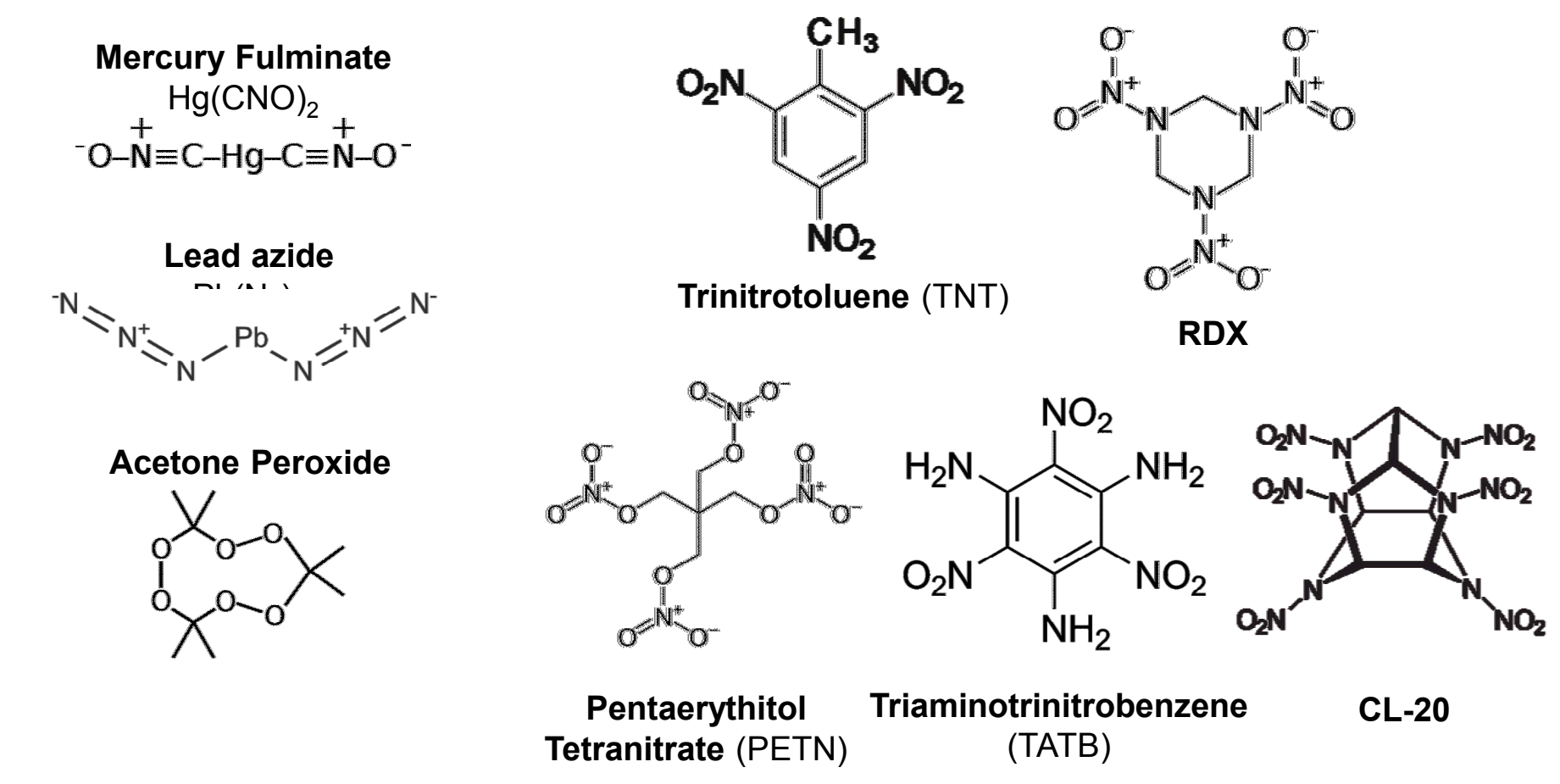
- Shock sensitivity
- Effects of material properties (microstructure, heterogeneity)
- Aging characteristics
- Rational design of new materials

Explosive science is underdeveloped in terms of molecular and quantum-level understanding

Types of Explosives

We are concerned with secondary explosives, which require significant energy input (shock wave) to initiate

Primary Explosives	**Secondary Explosives**
Very sensitive to heat, light, friction Detonates easily Unstable molecules	Not sensitive to heat, light, friction Requires shock wave to detonate Stable molecules



What Controls Shock Sensitivity of Materials?

Many correlations have been made between shock sensitivity and molecular properties (for groups of similar compounds)

P. Politzer and J. S. Murray, in *Advances in Quantum Chemistry* **69**, 1 (2014)

- Bond energies
- Bond lengths
- Bond polarities
- Band gaps
- Atomic charges
- NMR shifts
- Rates of vibrational energy transfer
- Oxygen balance
- Heat of fusion
- Heat of detonation

However, each of these correlations only apply within limited sets of similar compounds.

This means these properties "*reflect causation but do not directly reveal it*"; there is an underlying mechanism that we have not yet assembled.

Probing Reaction Mechanisms

How can we probe the quantum-mechanical mechanism(s)?

- **Understanding the molecular level involves understanding the underlying quantum mechanics.**
  - Potential energy surfaces (+ Distortion under shock)
  - Nuclear motion (Response of molecules and lattice to shock)
  - Energy transfer mechanisms
- **Experiments can only probe so much:**
  - Changes in electronic and vibrational structure of unreacted material
  - Identification of post-reaction product species
  - Quantum state distributions of post-reaction products
- **This leads to two types of experiments to probe reaction processes:**
  - Electronic and vibrational spectra to quantify dynamic processes *before reaction occurs*
  - Spectroscopic identification to identify reaction products *after reaction occurs*.
- **Both types of experiments are discussed here.**

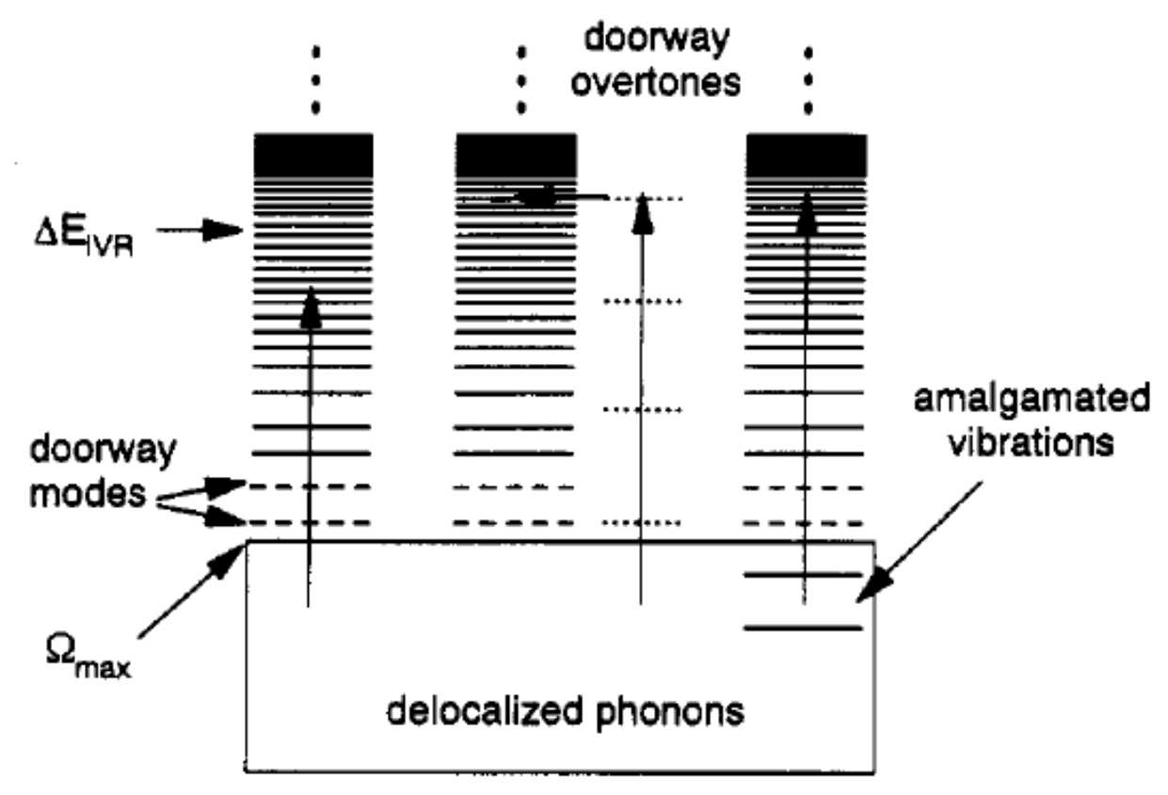
Shock-Induced Reaction Mechanisms

Shock-induced reactions span a broad range of phenomena, from elastic shocks to detonation. Mechanisms are expected to vary accordingly.

Two examples of QM reaction mechanisms are discussed here.

Weak shocks: Phonon up-pumping (Dlott, Fayer, Tokmakoff, *et al.*)

- Energy transferred from phonons to molecular vibrations
- Energy transfer depends on anharmonic couplings
- Thermal process



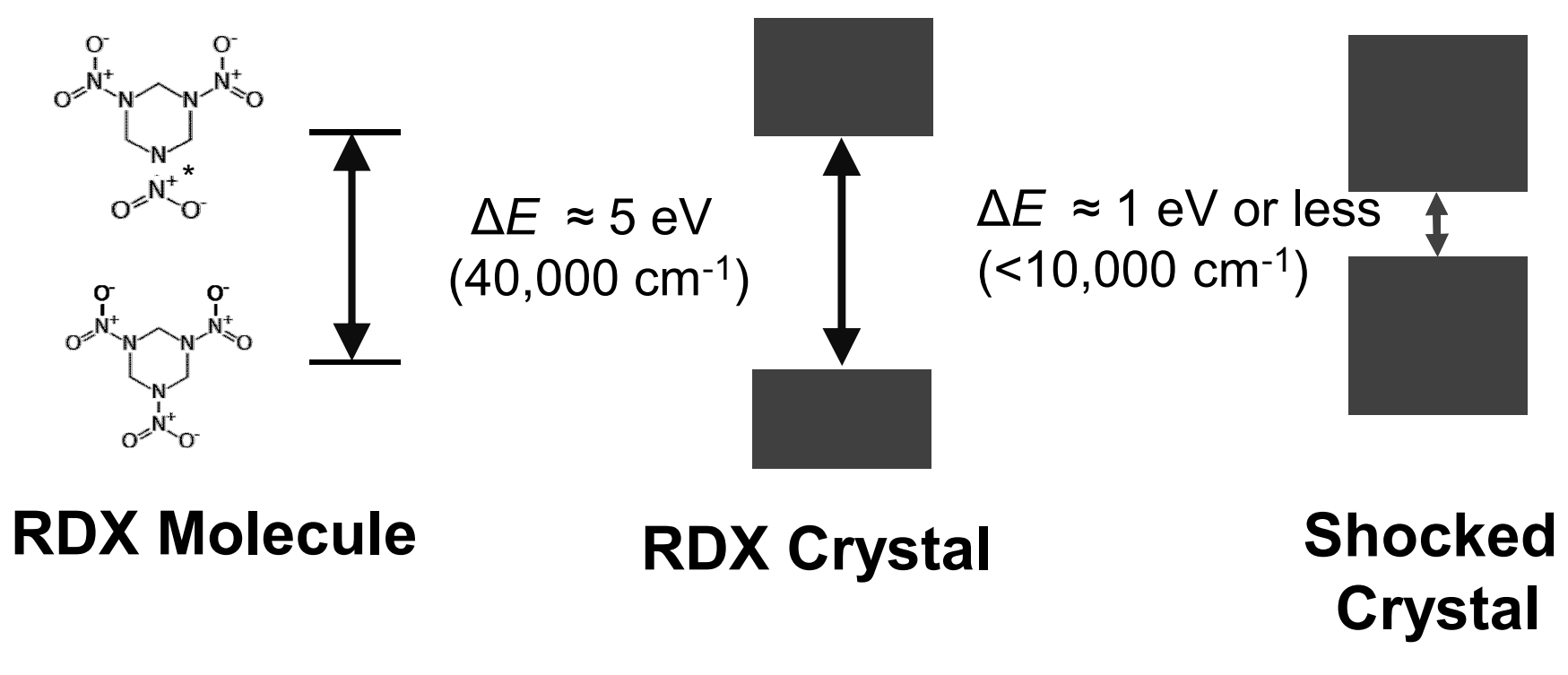
Tokmakoff, Fayer, and Dlott, *J. Phys. Chem.* **97**, 1901 (1993)

Several pathways allow for energy transfer between low-frequency phonons and high-frequency molecular vibrations. Low-frequency "doorway" modes are key. Anharmonic coupling couples the molecular vibrations with phonon modes of crystal:

$$V = \frac{1}{2!}\sum_{q} \left.\frac{\partial^2 V(\{q\})}{\partial^2 q}\right|_{\{q\}_0} q^2 + \frac{1}{3!}\sum_{q_1q_2q_3} \left.\frac{\partial^3 V(\{q\})}{\partial q_1 \partial q_2 \partial q_3}\right|_{\{q\}_0} q_1q_2q_3 + \ldots$$

Stronger shocks: Electronic band gap reduction (Kuklja, Kunz, Gilman, *et al.*)

- Compression reduces energy difference between ground and excited electronic states, thermally assisting reactions and potentially allowing spontaneous reactions to occur
- Thermally-assisted or non-thermal process
- Pressure and degree of compression are controlling variables

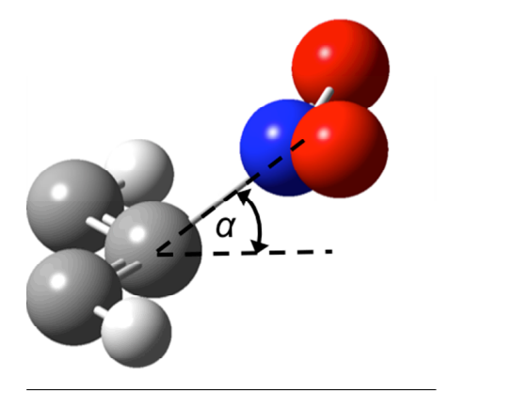


Compression is expected to reduce band gap of material, placing excited states within range of thermal excitation.

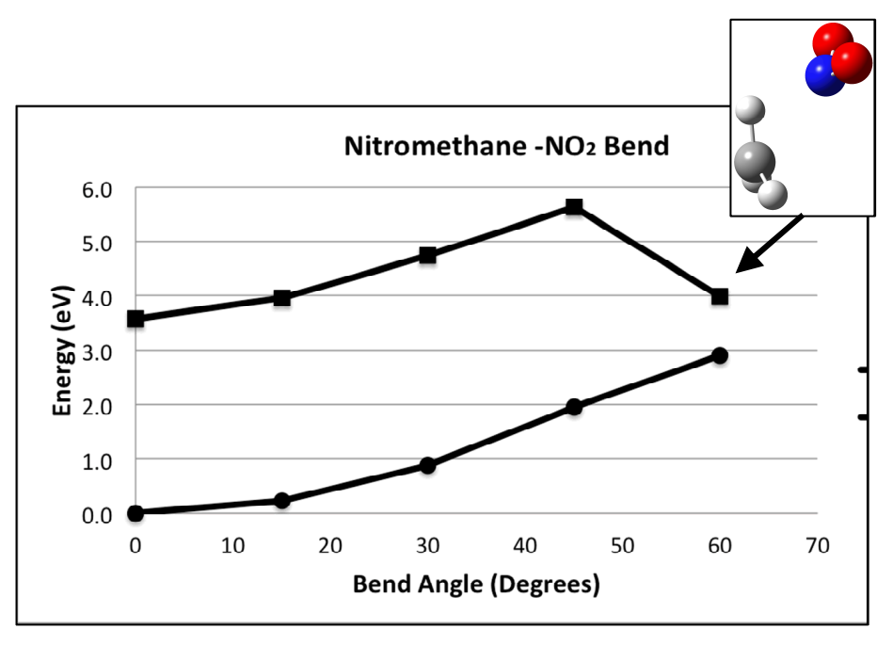
Pre-Reaction Dynamic Processes

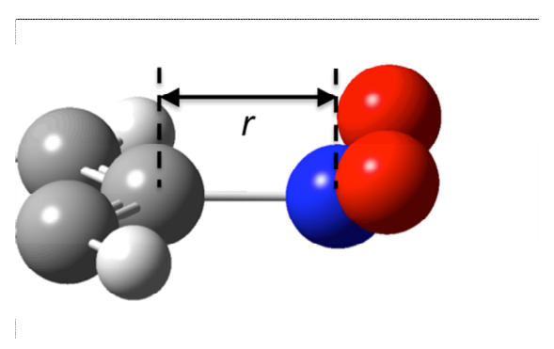
Modeling: Effects of Large-Amplitude Motion on Molecules

Compression of the crystal lattice can induce large-amplitude distortion in constituent molecules. We are computationally investigating how these distortions affect molecular properties.

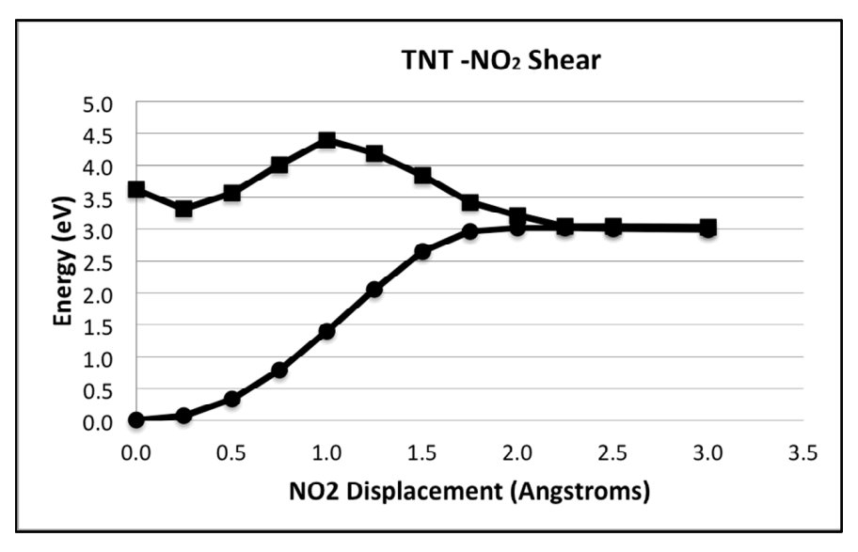


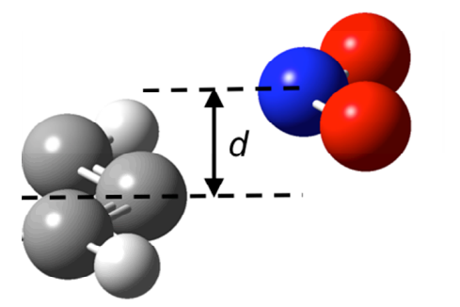
Large-amplitude bending strains the molecule but does not directly lead to bond breakage.



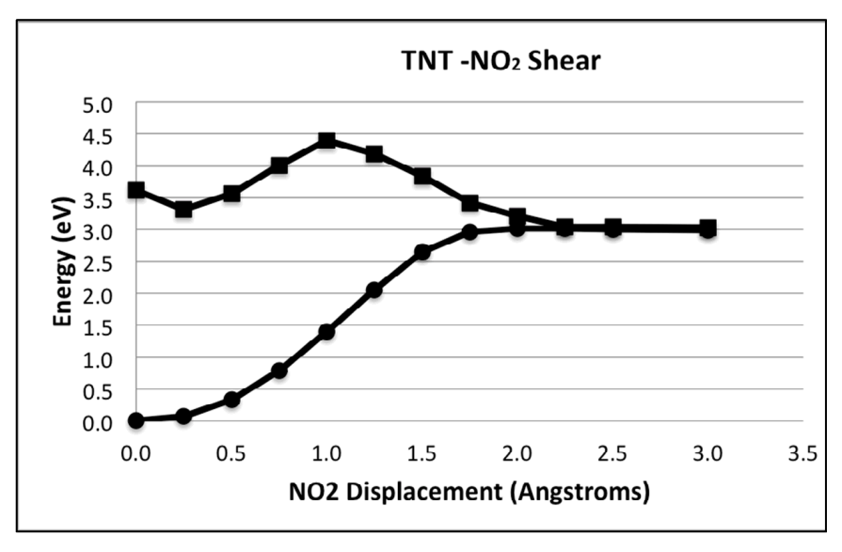


Large-amplitude stretching, as expected, leads to direct bond breakage.



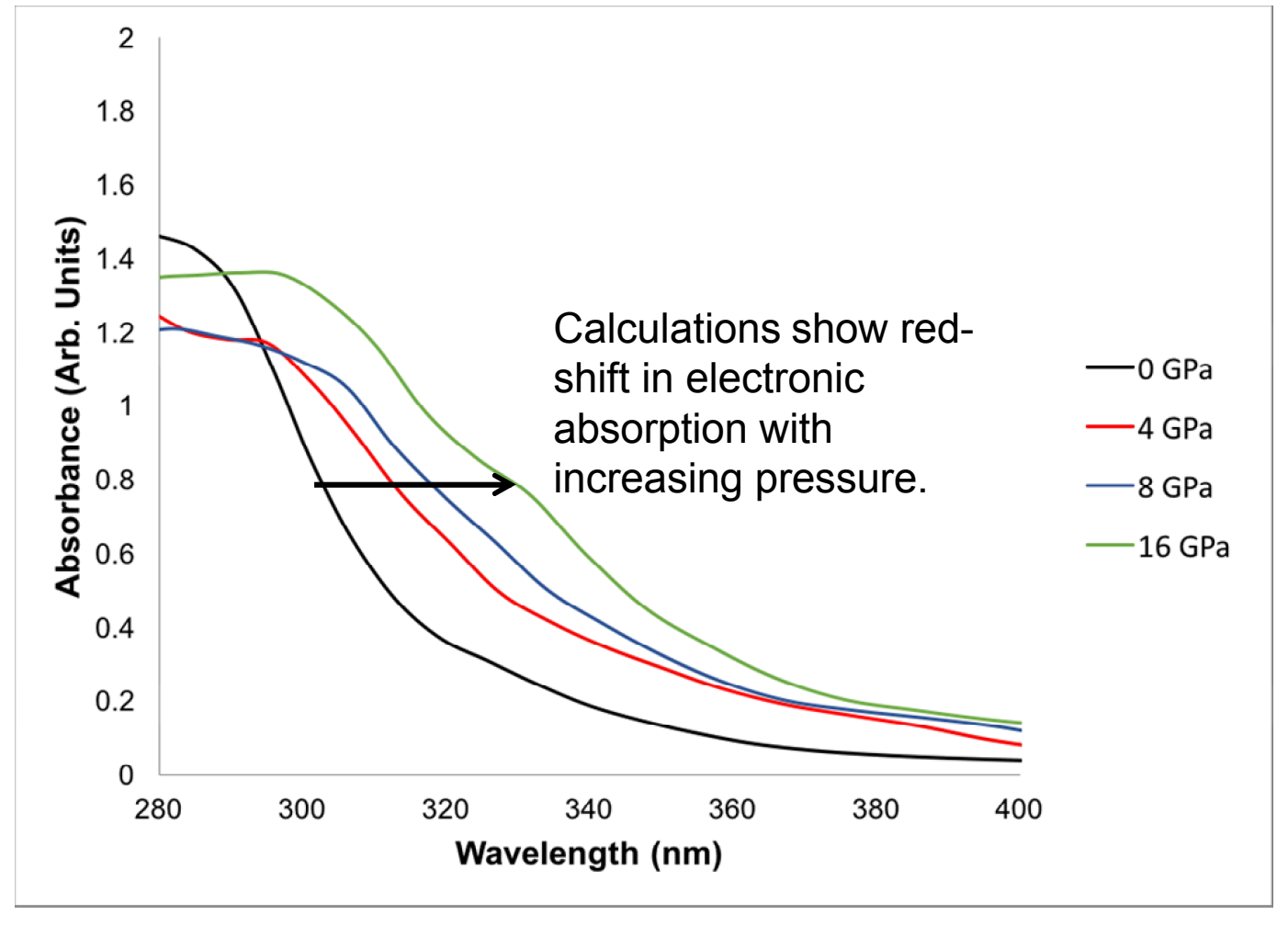


Shearing motions can lead to bond breakage, with the same energetic cost as large-amplitude stretching.



Modeling: Effects of Compression on Electronic Structure of Solid

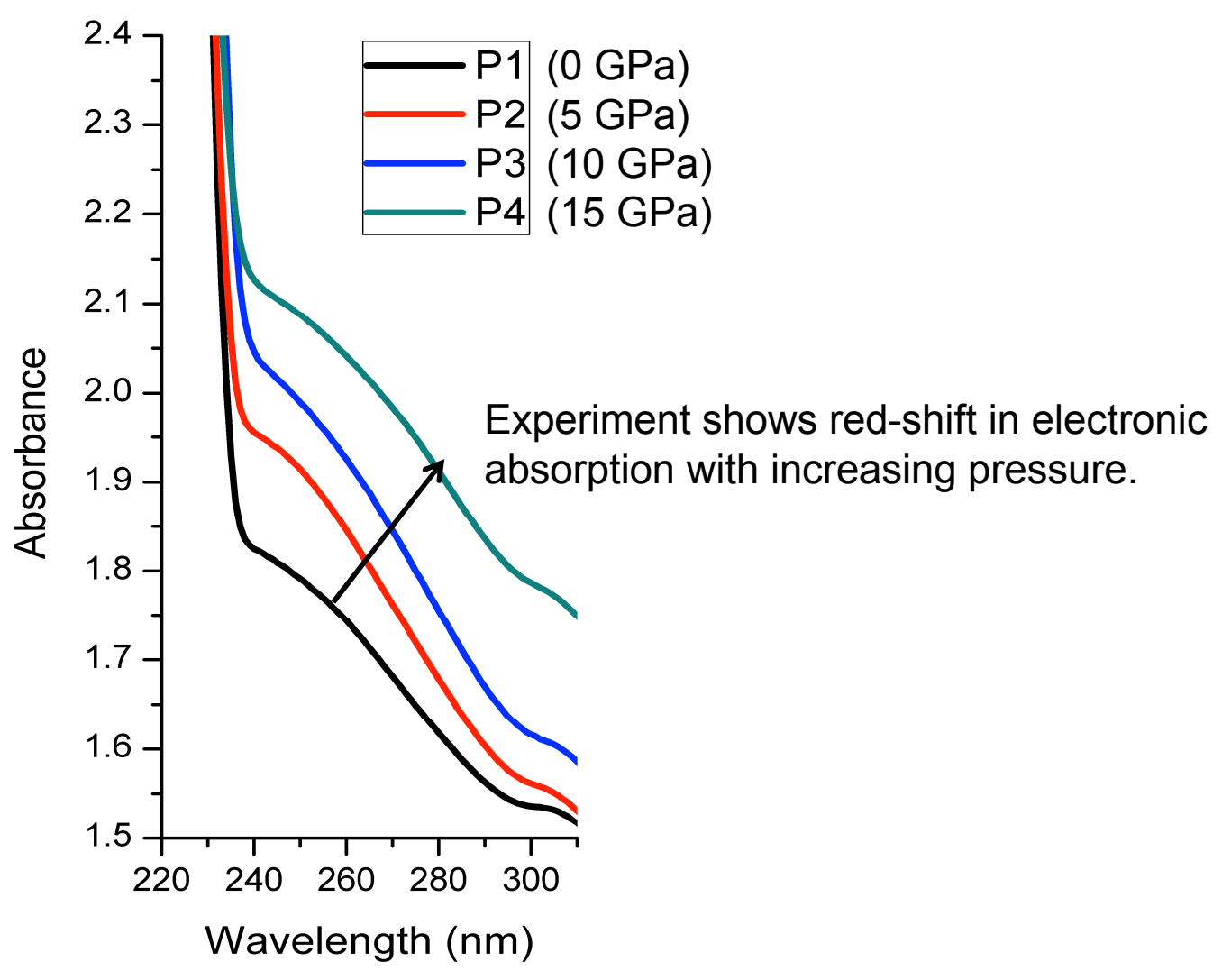
Compression can cause changes in electronic structure, which may activate reaction pathways. We are computationally investigating how compression affects electronic structure and how this may influence reactivity.



Calculations show red-shift in electronic absorption with increasing pressure.

Experiment: Electronic Structure of Compressed Solid

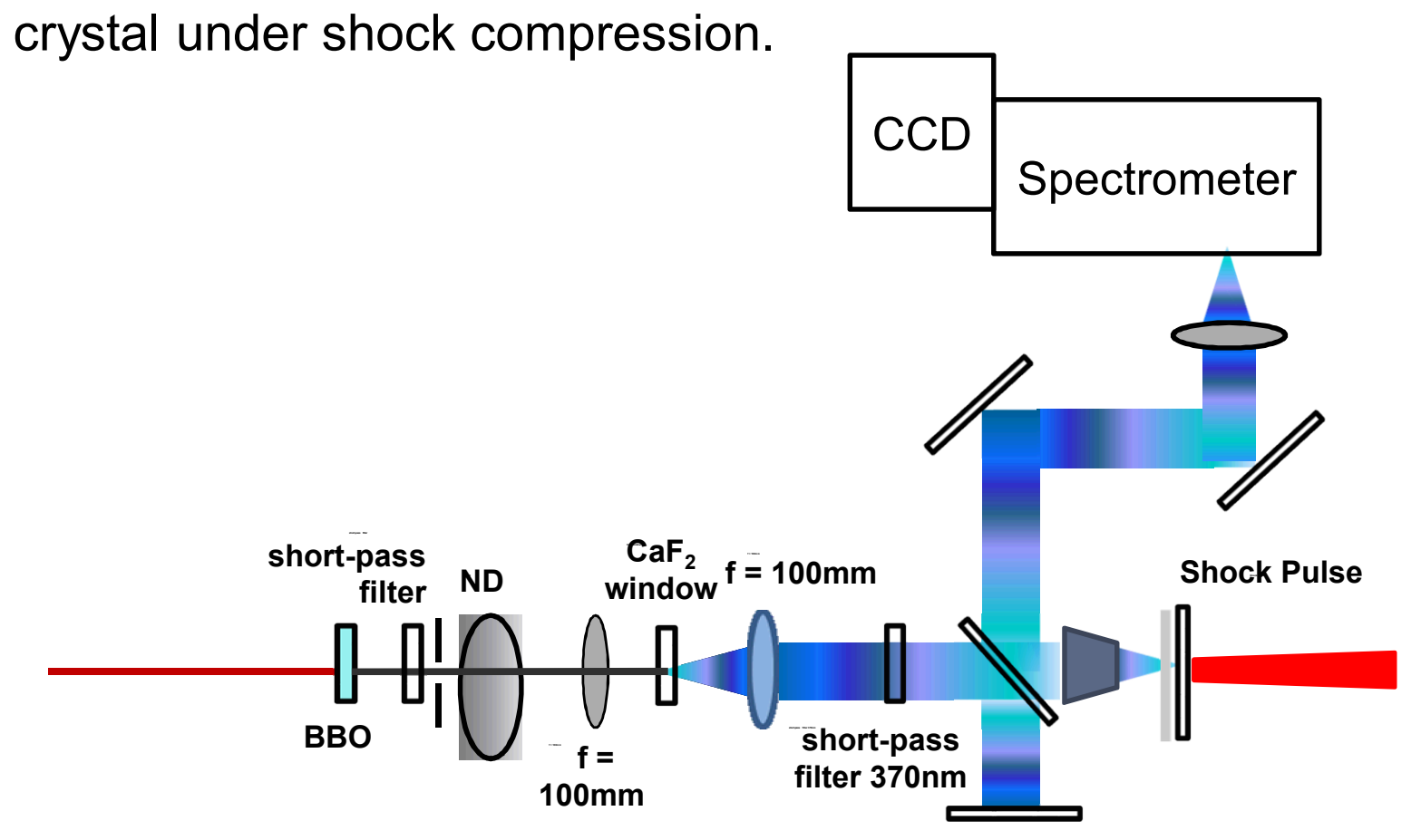
We are using diamond anvil cell spectroscopy to examine how static compression changes the properties of explosive materials. This experiment is designed to detect change in electronic structure of crystal under hydrostatic compression.



Experiment shows red-shift in electronic absorption with increasing pressure.

Experiment: Electronic Structure of Shocked Solid

We are using transient absorption to examine how dynamic compression changes the properties of molecular crystals. This experiment is designed to detect change in electronic structure of crystal under shock compression.

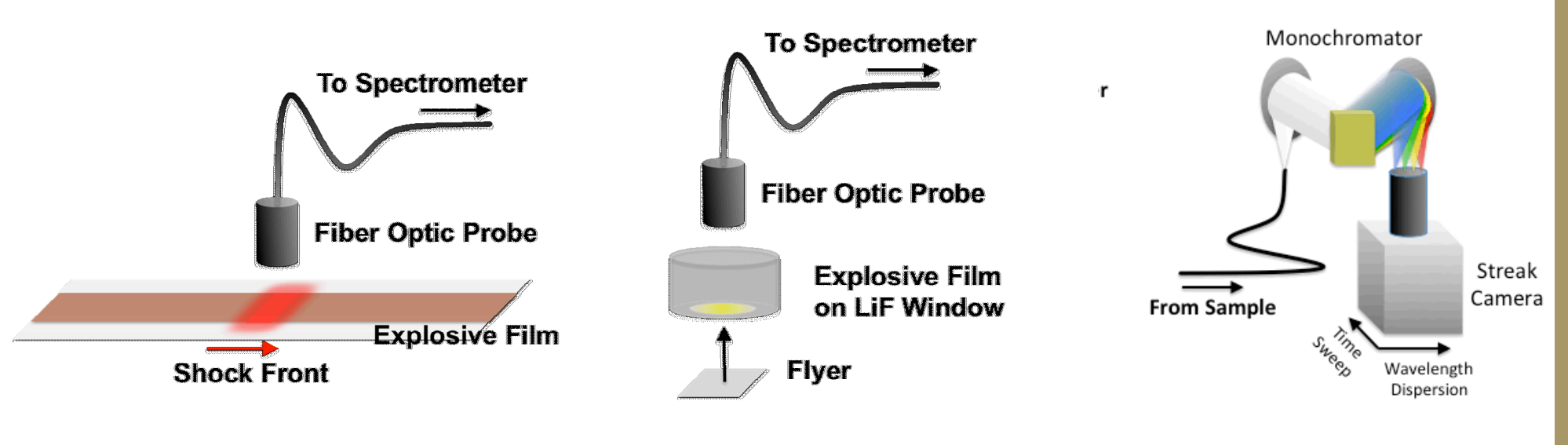


Schematic of transient absorption experiment. Broadband ultrafast pulse probes change in absorption spectrum during shock compression.

Post-Reaction Products and State Distributions

We use streaked optical spectroscopy to examine light emitted from shocked and detonating samples. This provides diagnostic information about species and product state distributions, which can be used to develop reaction mechanisms.

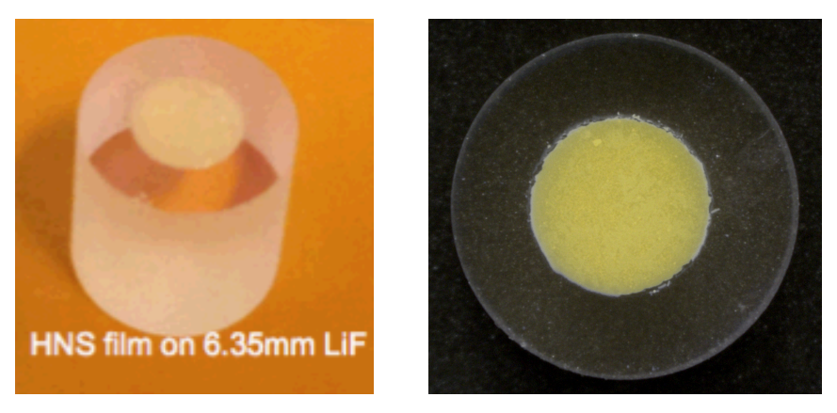
Sample and Probe Geometries



Explosive Samples

We use thin film explosive samples, which are optically thin and enable spectroscopic measurements.

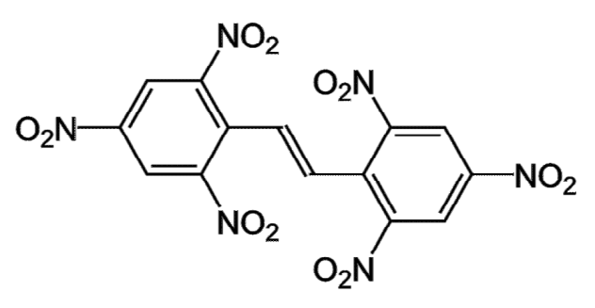
Thin film of HNAB deposited on a glass substrate



25 um (right) film of HNS deposited on LiF window

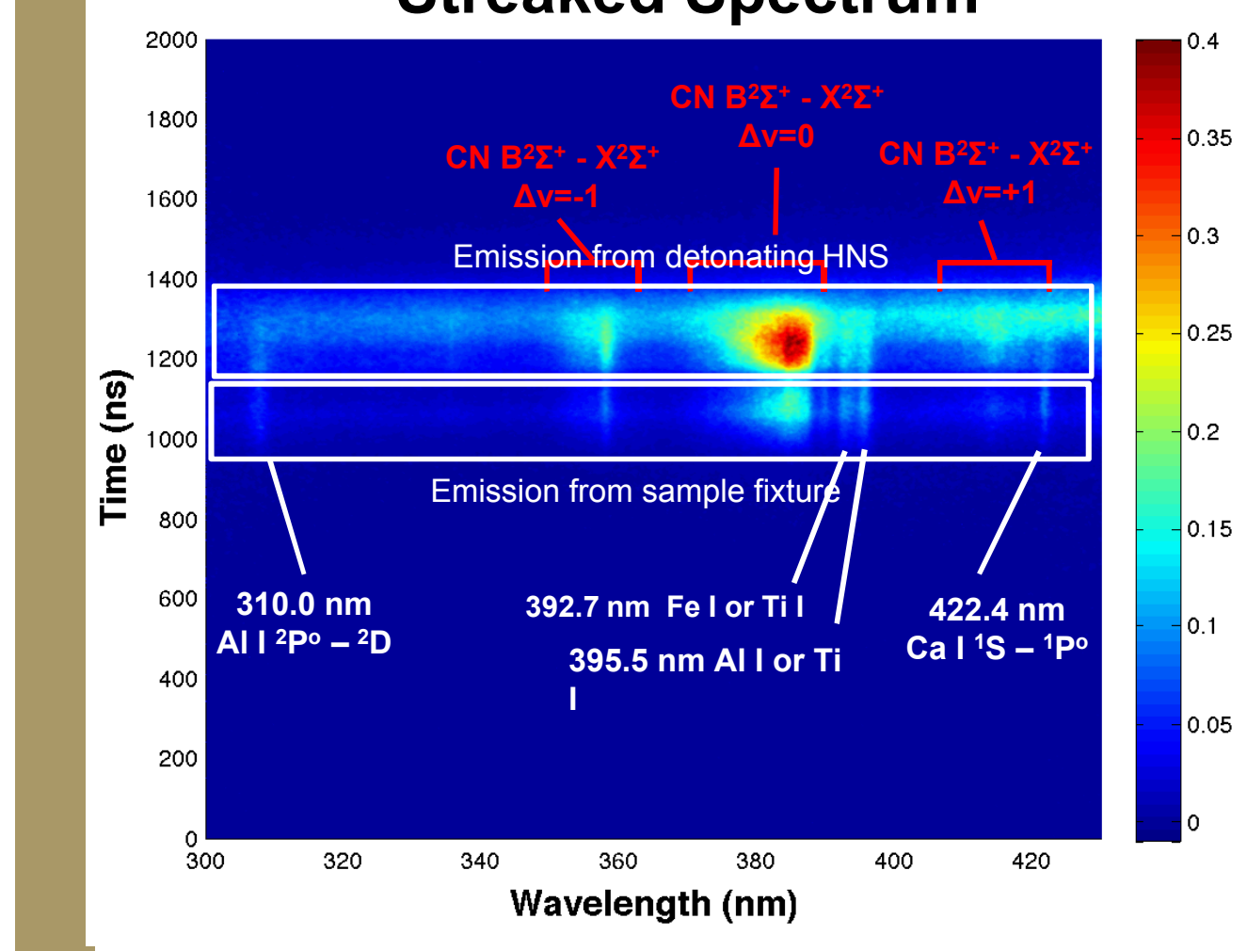
Detonation Measurements

This spectrum shows ultraviolet emission from detonating HNS, with distinct molecular emission features.



Hexanitrostilbene (HNS)

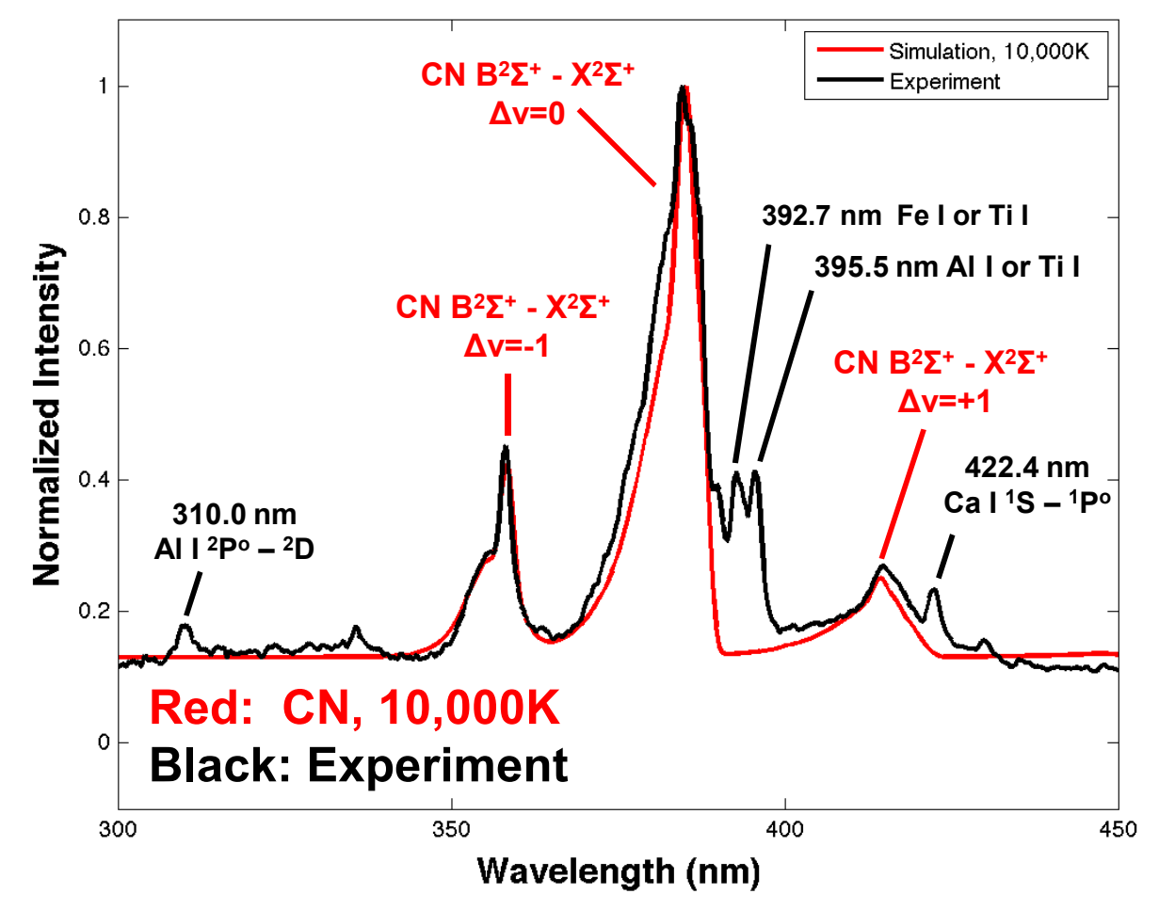
Streaked Spectrum



Spectrum consists of CN $B^2\Sigma^+ - X^2\Sigma^+$ and broadband emission.

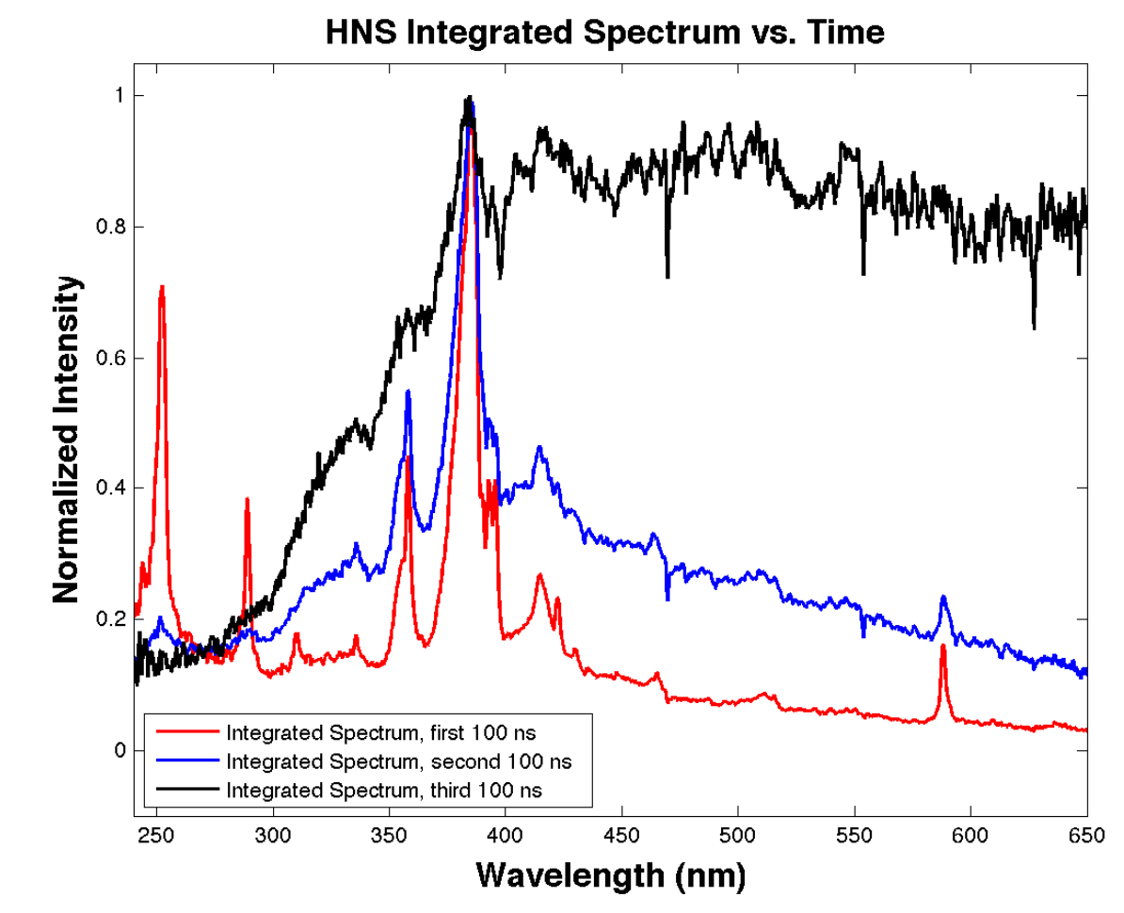
- Atomic emission from Si, Al, metal impurities in fused silica fixture (+detonation light from early time)
- Emission from detonating explosive (CN + broadband emission)

Time-Integrated Spectra



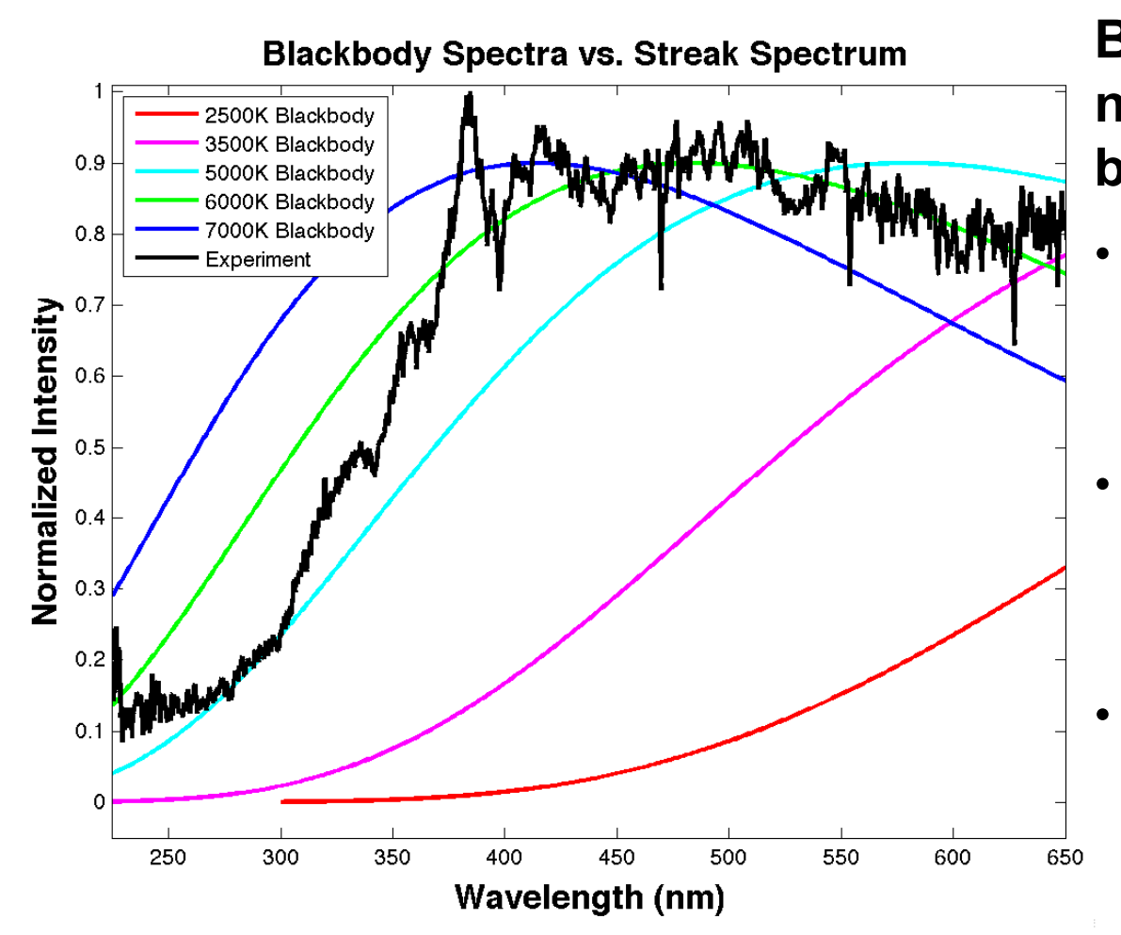
CN $B^2\Sigma^+ - X^2\Sigma^+$ emission is observed with high rotational and vibrational excitation.

- Simulation with T_{rot}, T_{vib} = 10,000K shown
- Detonation temperature of HNS ≈ 3,600 – 3,700K (A. Tappan, personal communication)



CN $B^2\Sigma^+ - X^2\Sigma^+$ emission is observed at early time, with broadband emission at later time

- Early emission is primarily CN $B^2\Sigma^+ - X^2\Sigma^+$, plus atomic impurities from sample fixture
- Later emission is broadband, 300nm to > 650nm, increase in visible emission at late time



Broadband emission does not appear to be thermal blackbody emission

- Detonation temperature of HNS ≈ 3,600 – 3,700K (A. Tappan, personal communication)
- Peak emission occurs ~450 nm; 450 nm peak emission corresponds to 6000K blackbody
- Emission corresponds to emission from polyatomic intermediates (possibly NO_2, others)

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