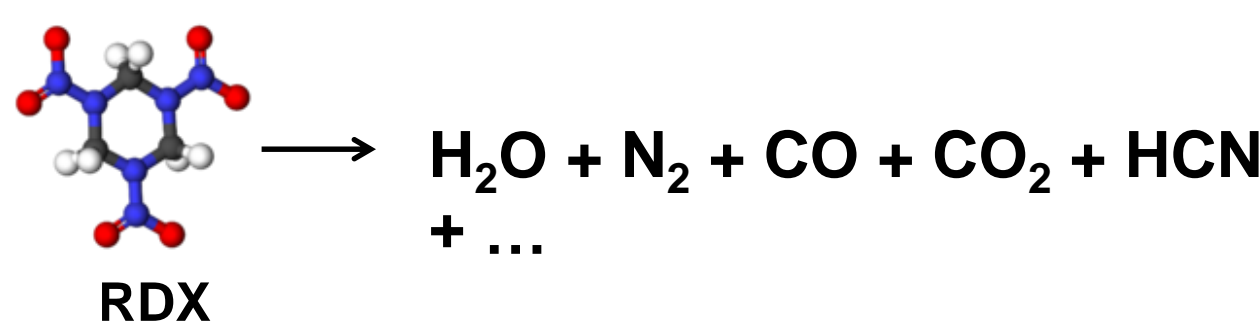


Probing Mechanisms of Shock-Induced Reactions in Explosive Materials

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Motivation: Understanding Shock-Induced Reactions in Explosives



- 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 detonation

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.

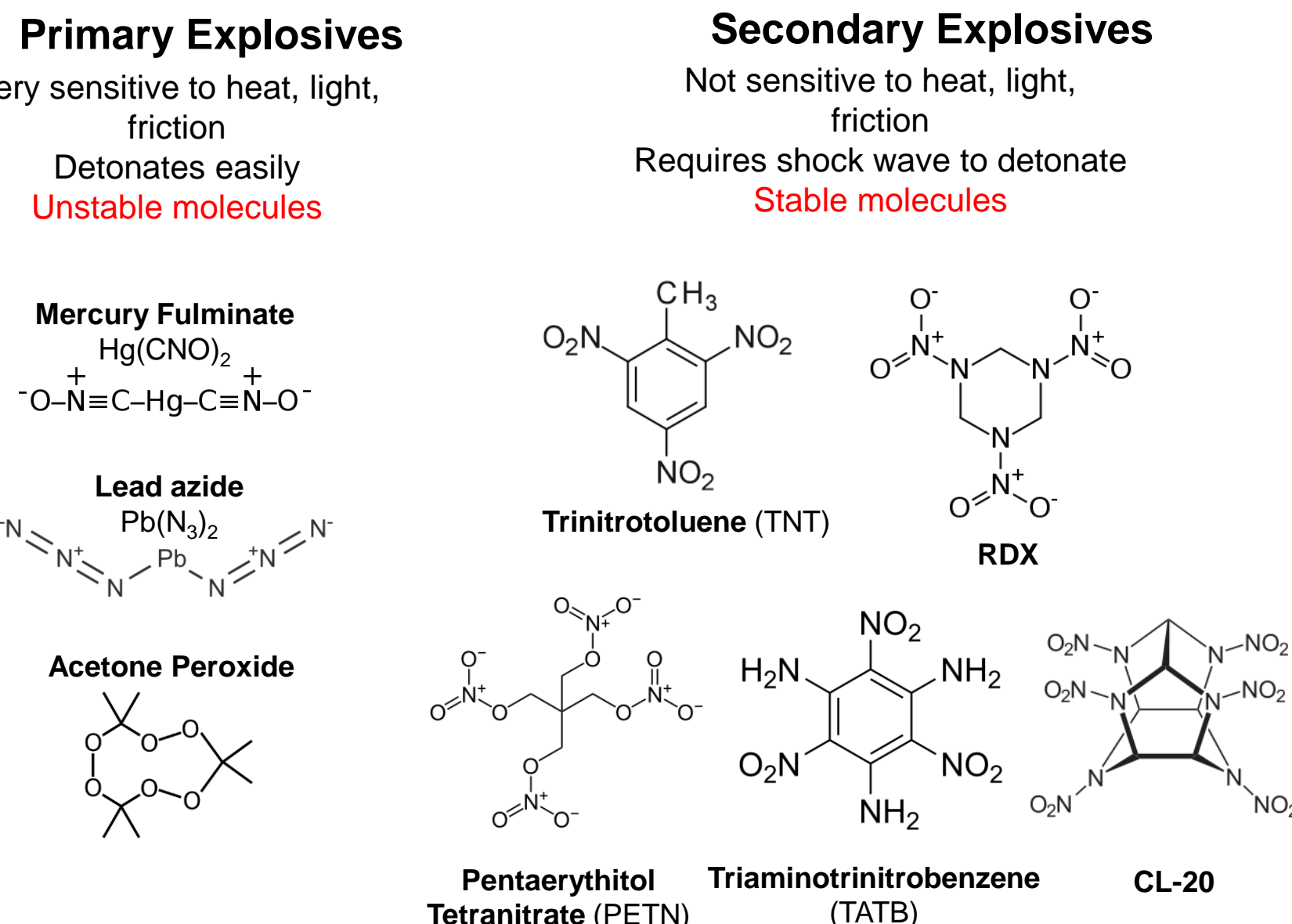
Lots of challenges predicting/understanding everything besides steady detonation:

- 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



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:
 - Identification of product species
 - Quantum state distributions
- One way to interrogate mechanism is to attempt to *infer* it from species and their quantum state distributions.
 - Typical approach used in chemical physics
 - e.g. Photochemistry – long history of success in using rotational, vibrational state distributions to infer mechanisms of bond breakage.
- This is done spectroscopically.

Shock-Induced Reaction Mechanisms

Two examples of QM reaction mechanisms:

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

- Energy transferred from phonons to molecular vibrations
- Thermal process
- Temperature is controlling variable
- Predicts thermal distribution of quantum states

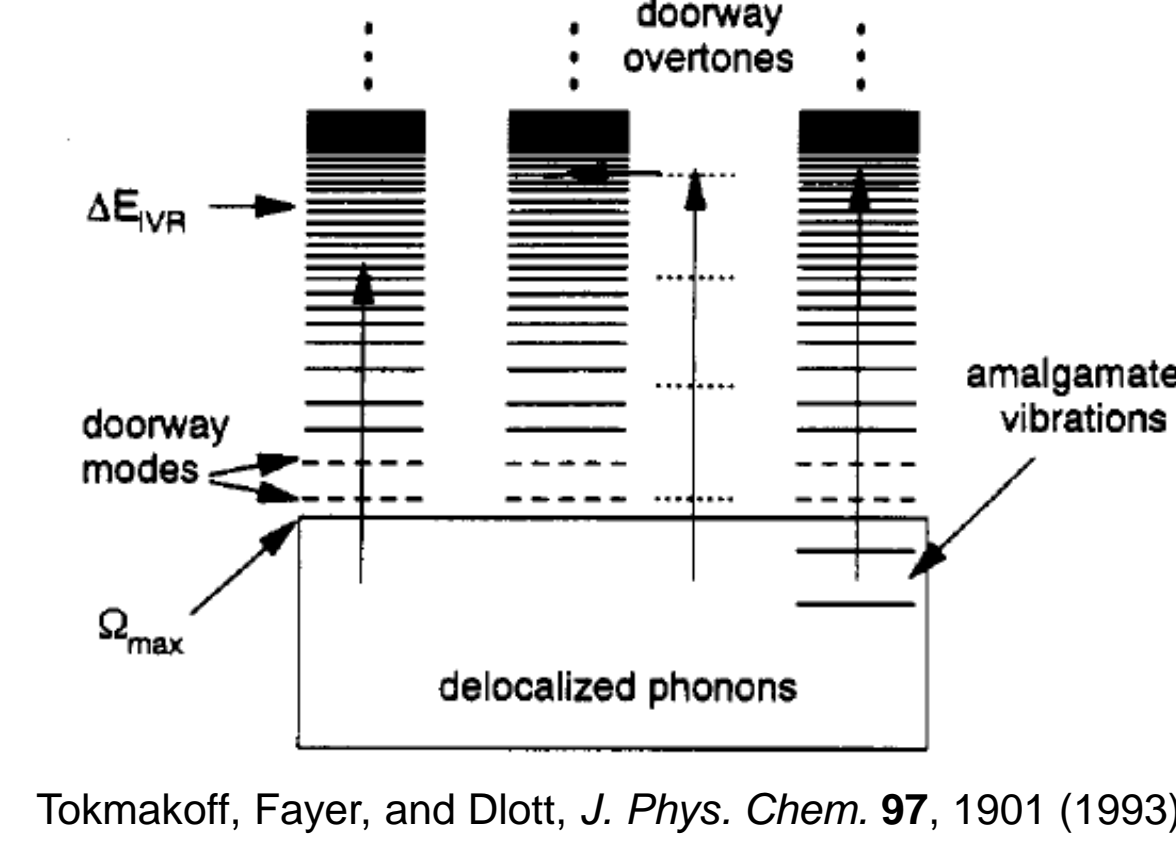
Athermal: Electronic band gap closure (Kuklja, Kunz, Gilman, *et al.*)

- Compression reduces energy difference between ground and excited electronic states, allowing spontaneous reactions to occur
- Non-thermal process
- Pressure is controlling variable
- Potentially athermal distribution with electronically excited products

These two theories allow different distributions of quantum states, appropriate under different physical conditions

Thermal Reactions

Energy transfer between lattice and molecular vibrations: Several pathways allow for energy transfer between low-frequency phonons and high-frequency molecular vibrations. Low-frequency "doorway" modes are key.



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

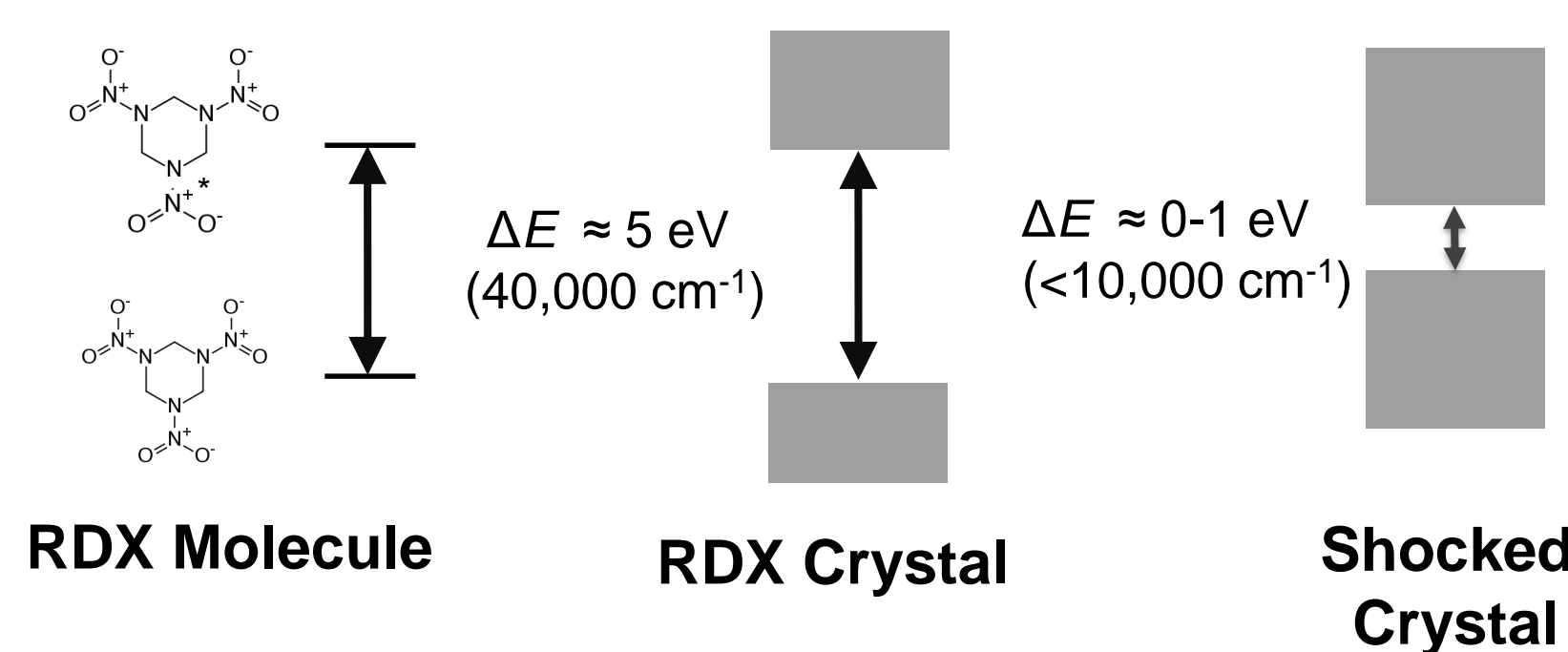
Anharmonic coupling couples the molecular vibrations with phonon modes of crystal

$$V = \frac{1}{2!} \hat{A} \frac{\partial^2 V(\{q\})}{\partial q^2} \bigg|_{\{q\}_0} q^2 + \frac{1}{3!} \hat{A} \frac{\partial^3 V(\{q\})}{\partial q_1 \partial q_2 \partial q_3} \bigg|_{\{q\}_0} q_1 q_2 q_3 + \dots$$

Athermal Reactions

Electronic changes and band gap closure:

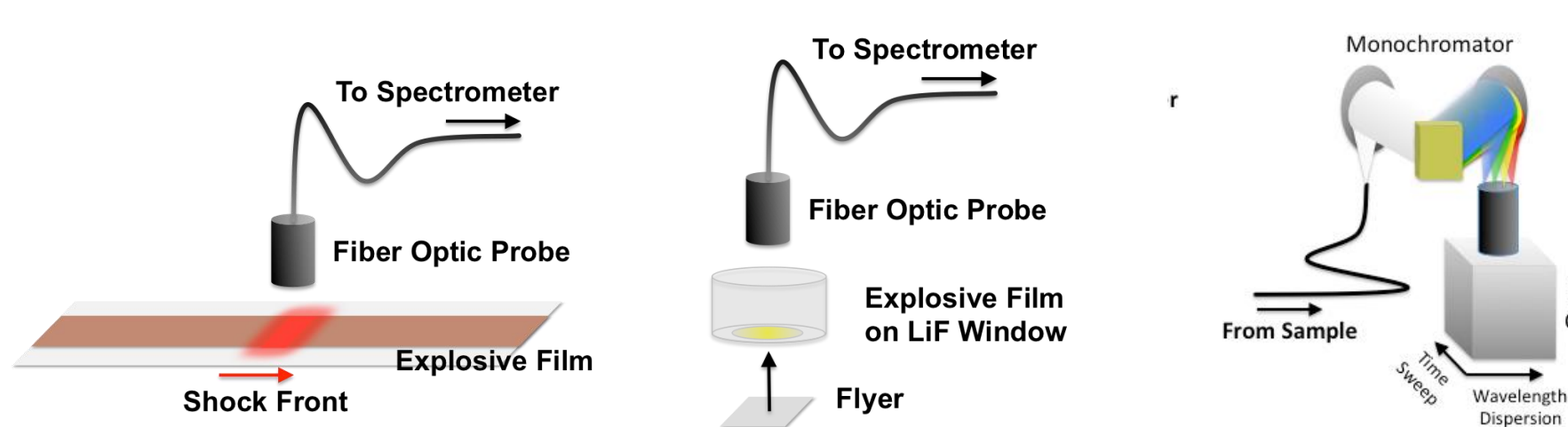
Compression is expected to reduce band gap of material, placing excited states within energetic reach.



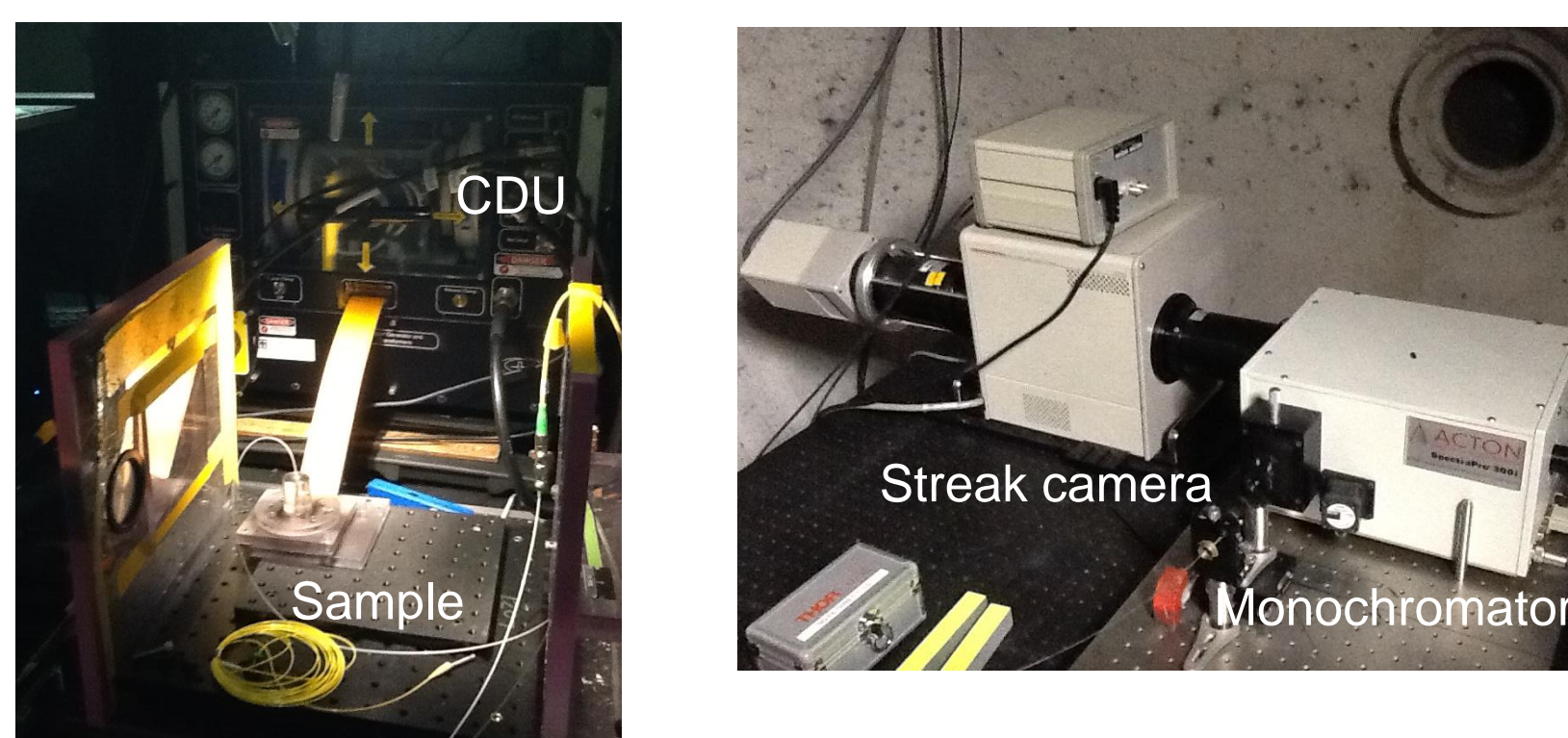
Time- and Frequency-Resolved Optical Emission

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

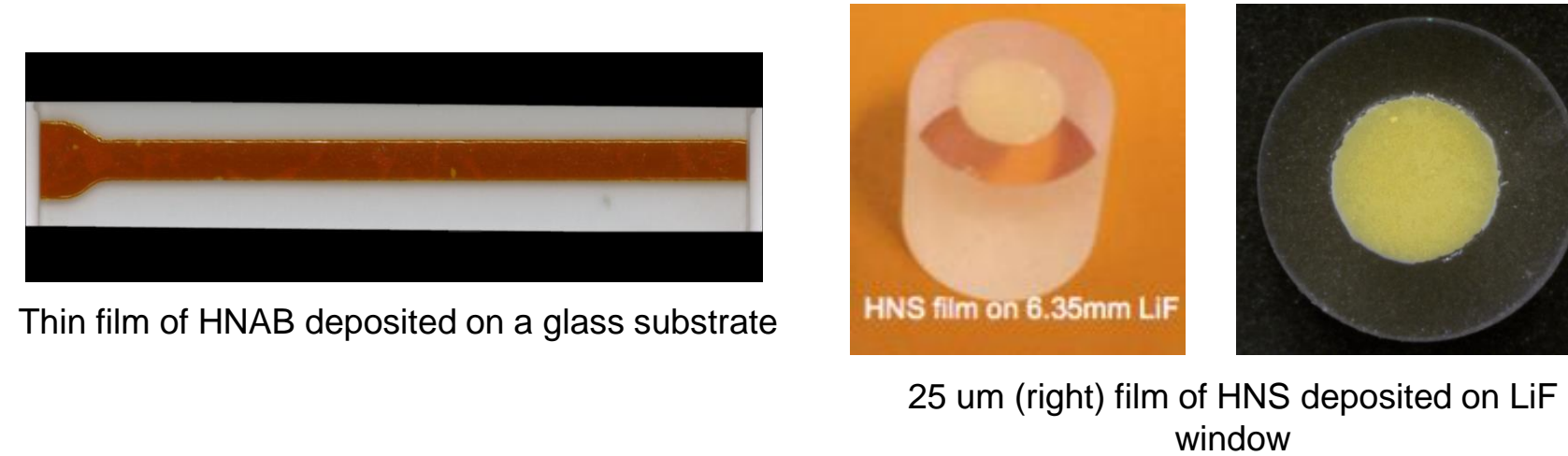


Experimental Apparatus



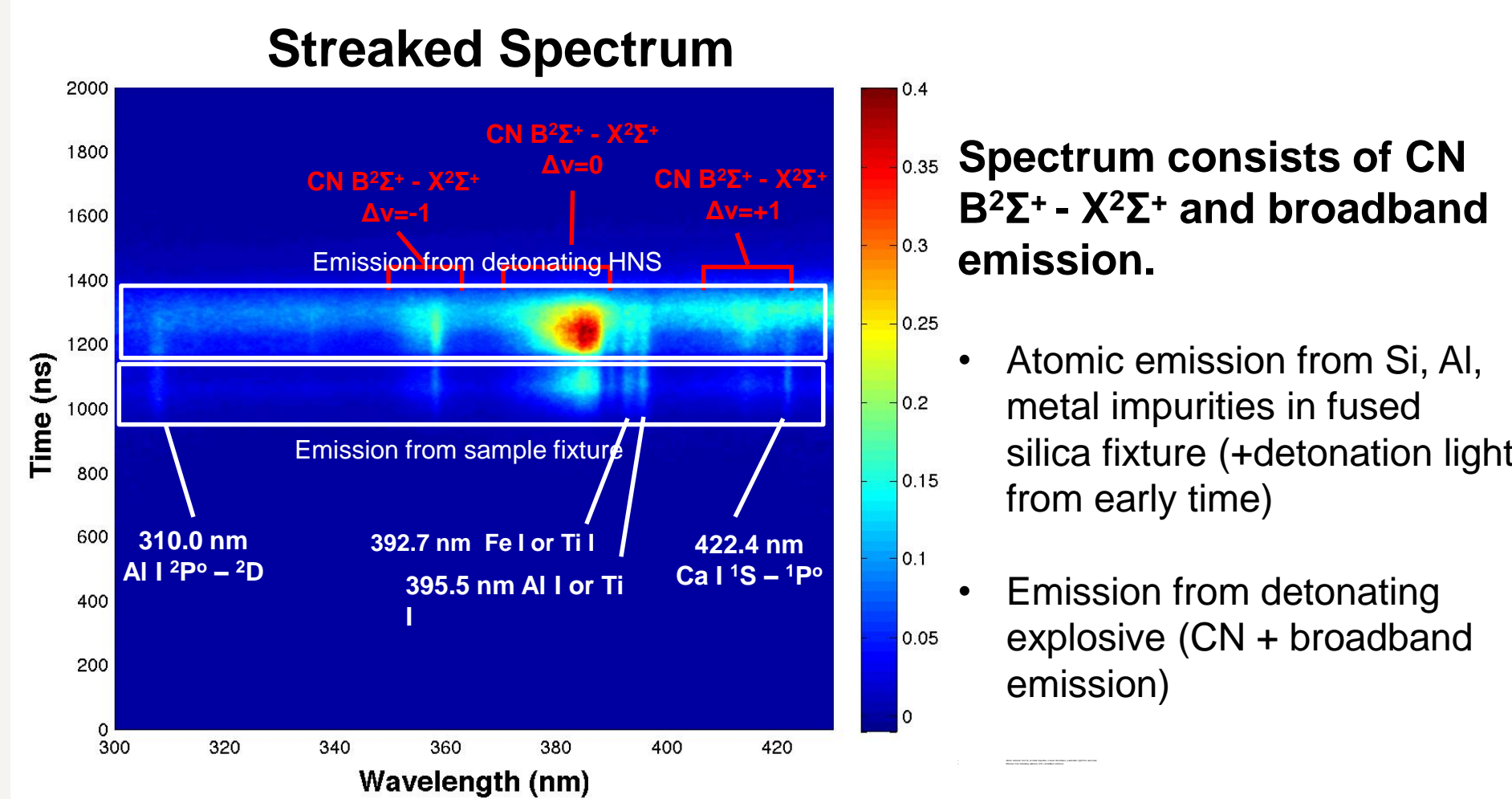
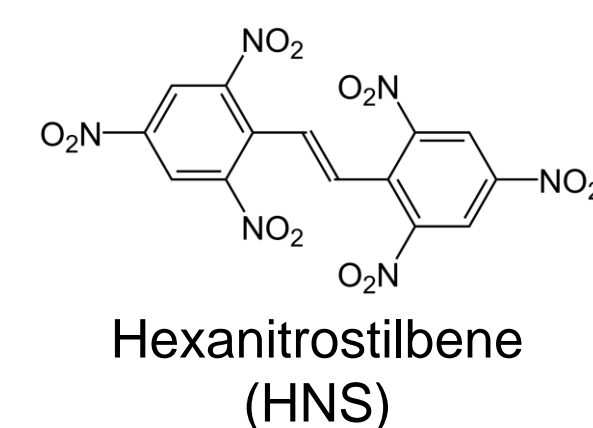
Explosive Samples

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



Detonation Measurements

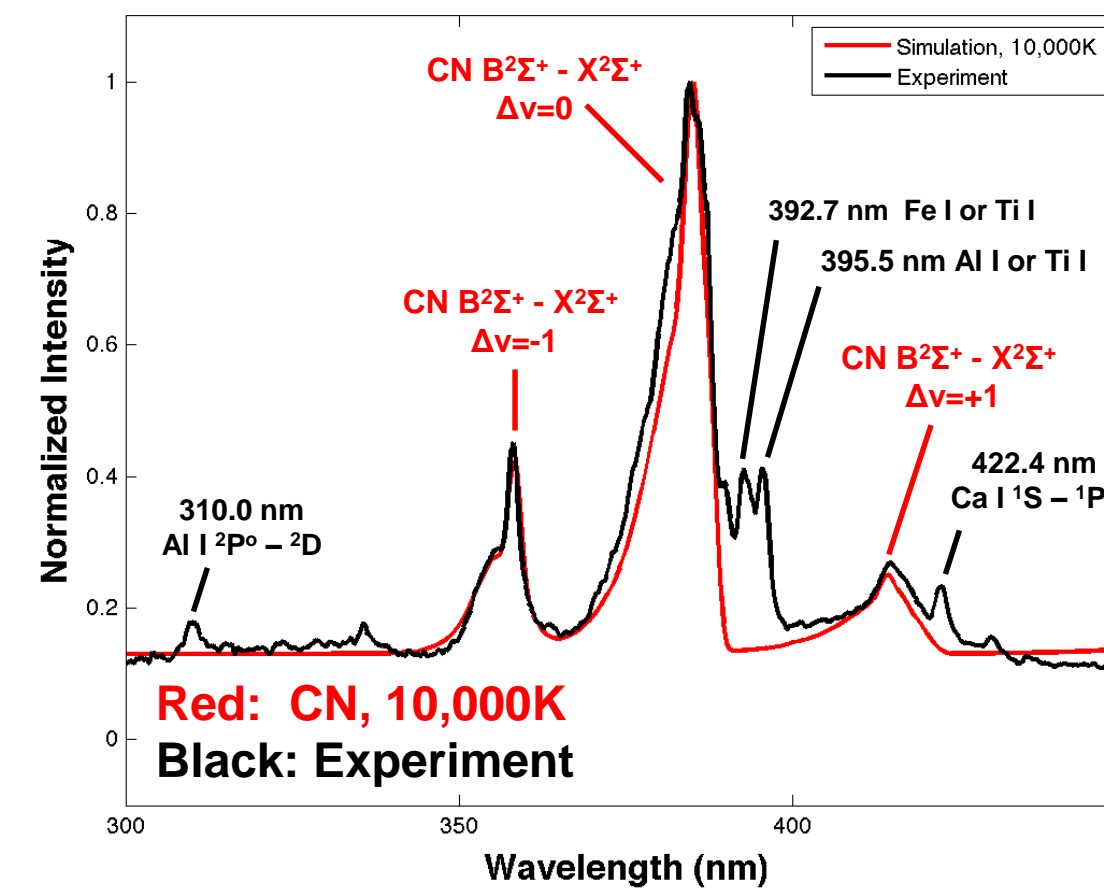
This spectrum shows ultraviolet emission from detonating HNS, with distinct molecular emission features.



Spectrum consists of CN B²Σ⁺ - X²Σ⁺ 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 Spectrum

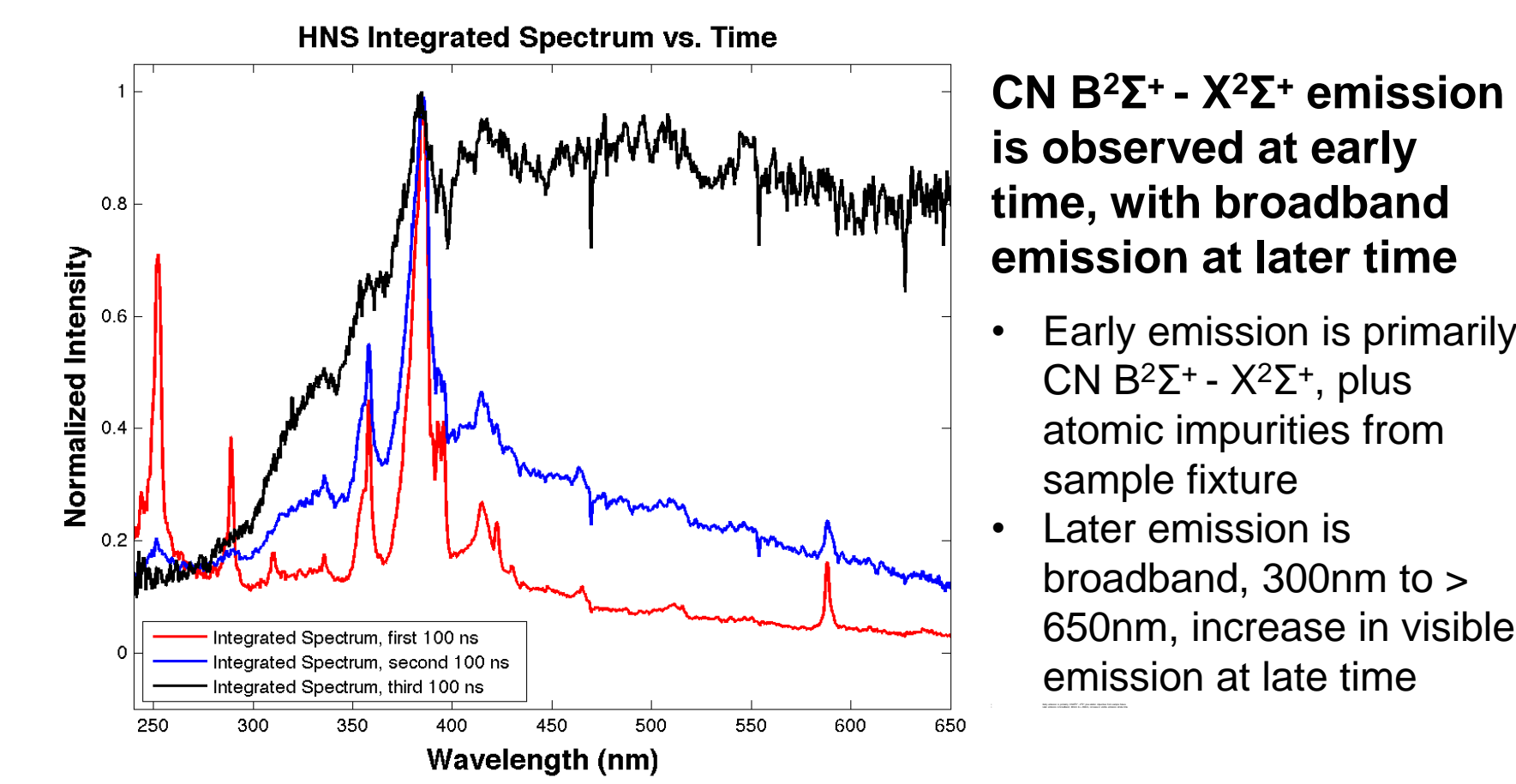


CN B²Σ⁺ - X²Σ⁺ emission is observed with high rotational and vibrational excitation.

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

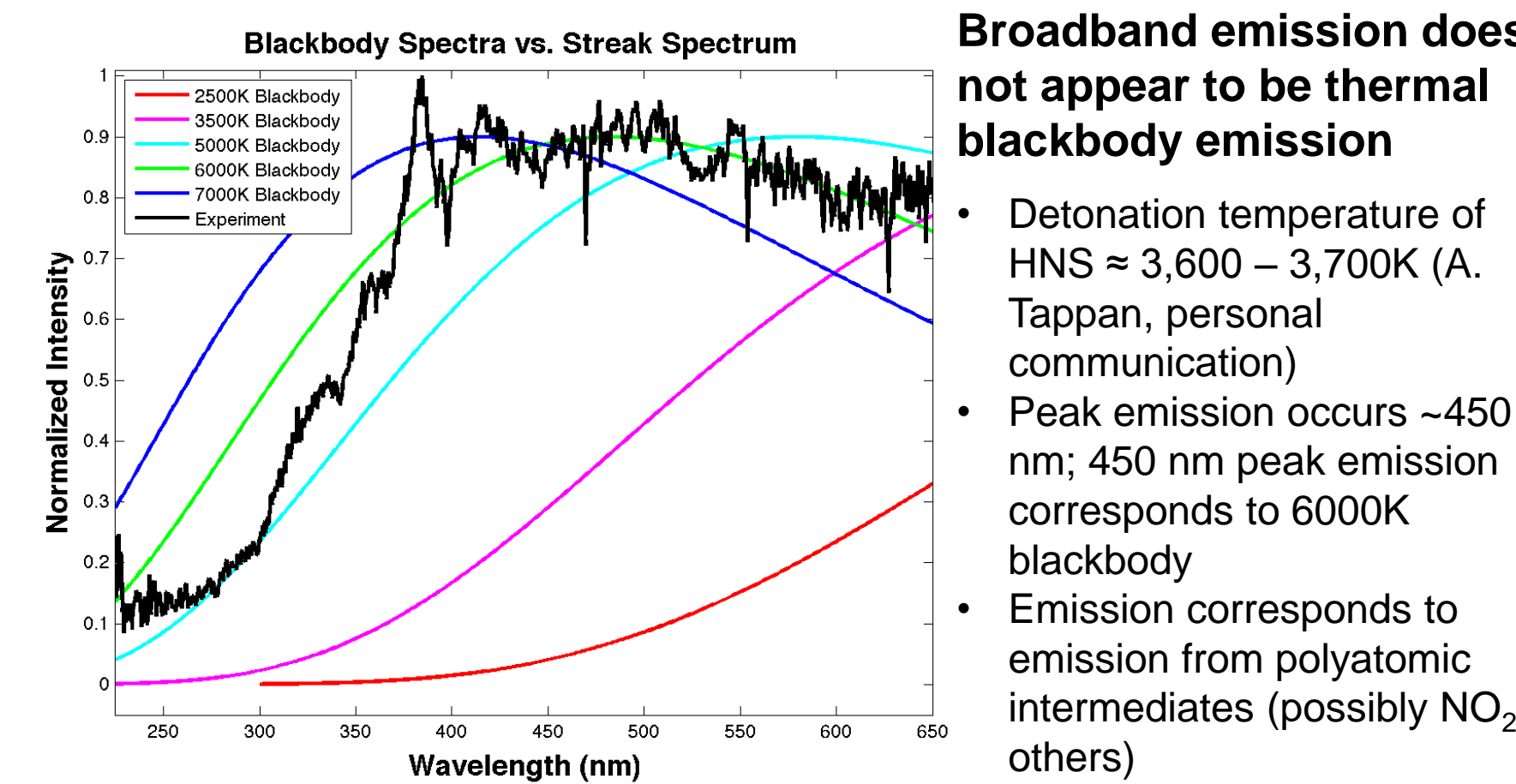
Detonation Measurements (Continued)

Spectrum shows vibrationally-resolved and broadband emission



CN B²Σ⁺ - X²Σ⁺ emission is observed at early time, with broadband emission at later time

- Early emission is primarily CN B²Σ⁺ - X²Σ⁺, plus atomic impurities from sample fixture
- Later emission is broadband, 300nm to > 650nm, increase in visible emission at late time

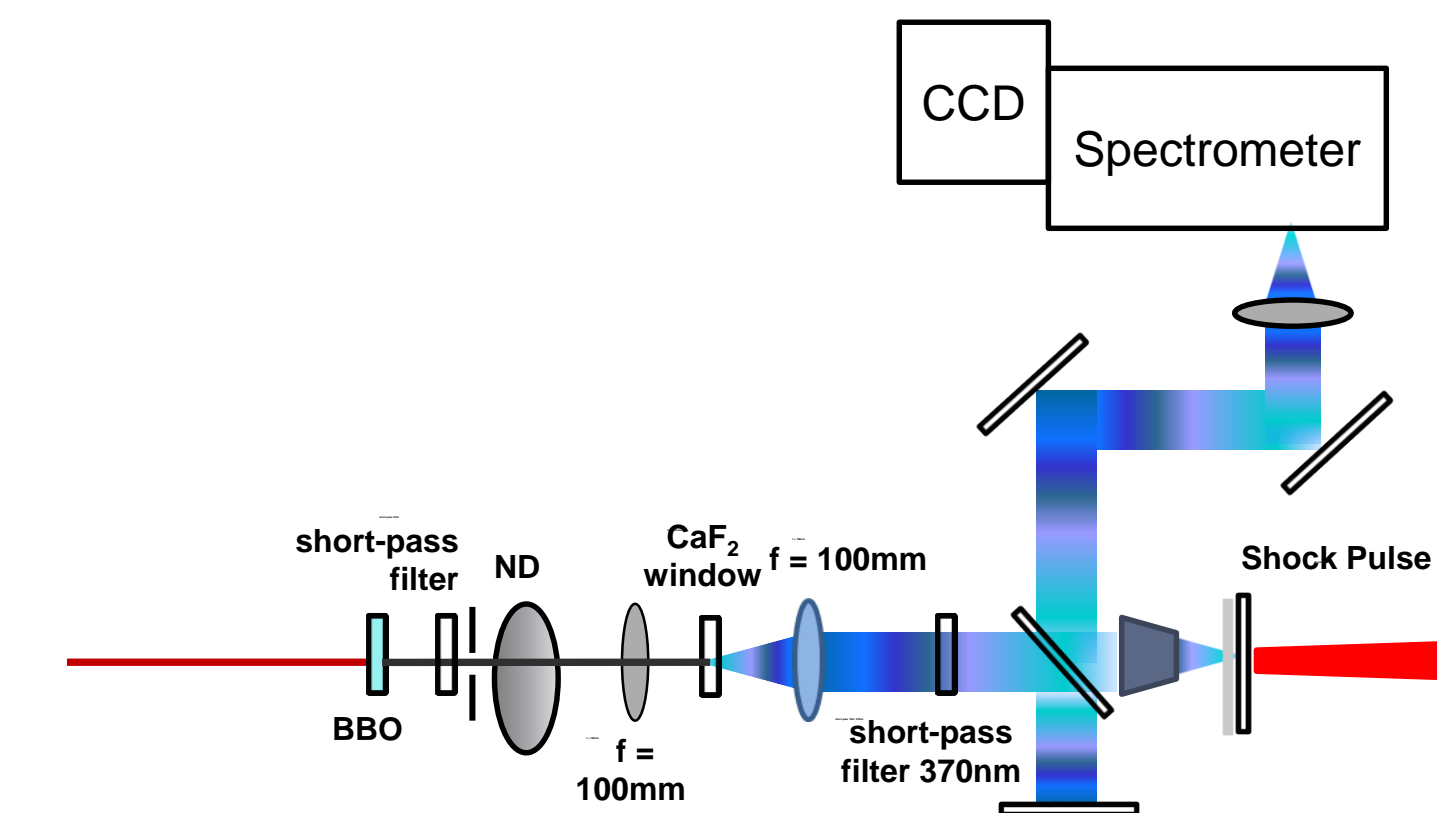


Broadband emission does not appear to be thermal blackbody emission

- 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 NO₂, others)

Transient Absorption Measurements of Electronic Structure

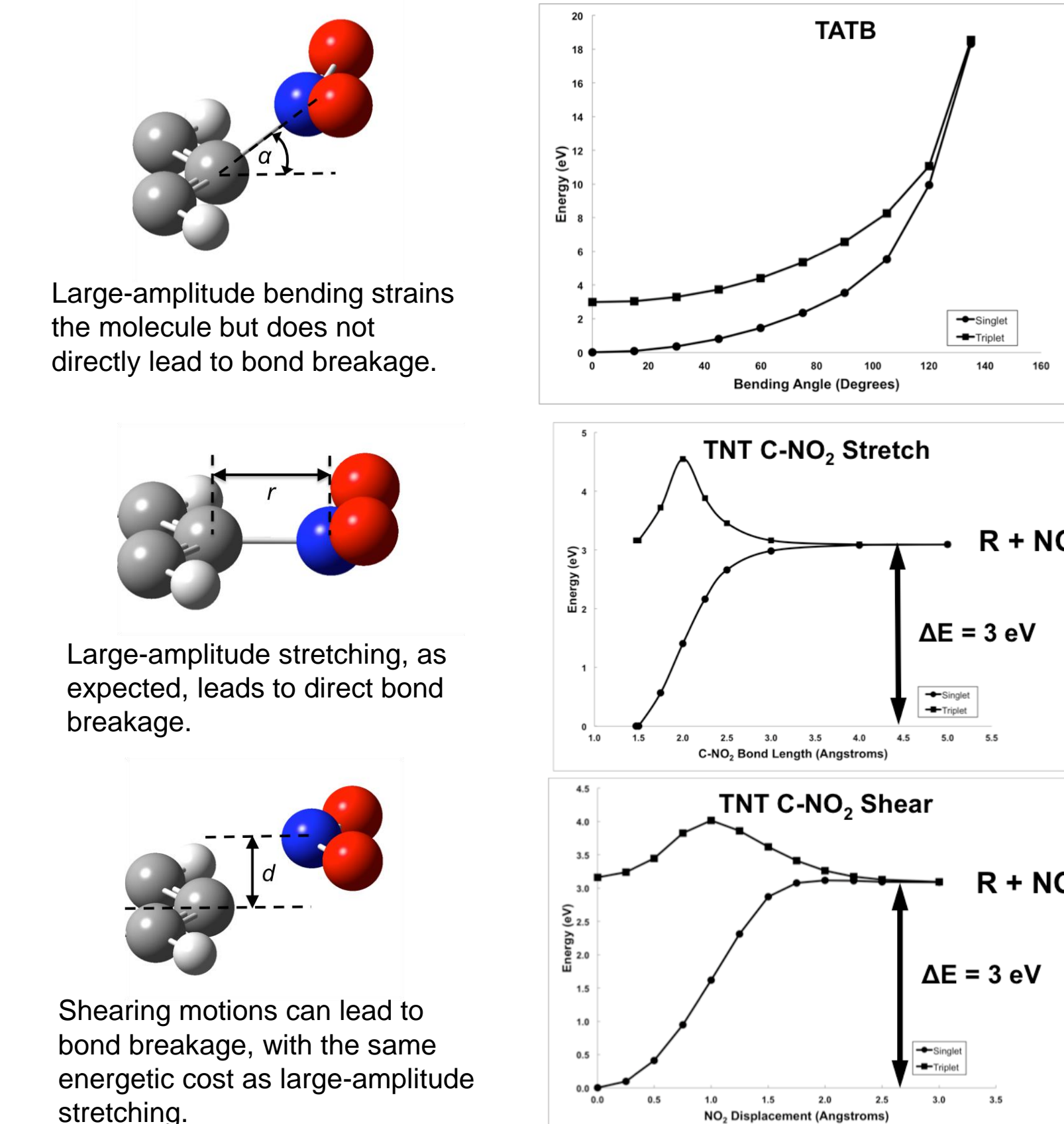
We are investigating how compression changes the properties of molecular crystals. This experiment is designed to detect change in electronic structure of crystal under shock compression.



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

Modeling Effects of Large-Amplitude Motion

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.

These results were presented at the 2015 American Physical Society Meeting on Shock Compression of Condensed Matter:

Jeffrey J. Kay, "Mechanisms of Shock-Induced Reactions in High Explosives", *AIP Conf. Proc.* (2015) (To be published)

Jeffrey J. Kay, Ryan R. Wixom, Brook A. Jilek, Robert Knepper, Alexander S. Tappan, and David L. Damm, "Spectroscopic Analysis of Time-Resolved Emission from Detonating Thin Film Explosive Samples", *AIP Conf. Proc.* (2015) (To be published)