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SAND2016-2208C

Sandia National Laboratories

# Ultrafast Laser Diagnostics for Understanding Hot Spot Initiation in Energetic 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 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**

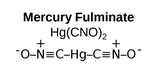
## Types of Explosives

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

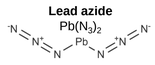
**Primary Explosives**
Very sensitive to heat, light, friction
Detonates easily
Unstable molecules

**Secondary Explosives**
Not sensitive to heat, light, friction
Requires shock wave to detonate
Stable molecules

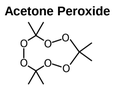
**Mercury Fulminate** $Hg(CNO)_2$



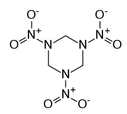
**Lead azide** $Pb(N_3)_2$



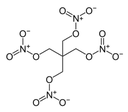
**Acetone Peroxide**



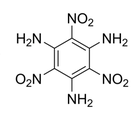
**Trinitrotoluene** (TNT)



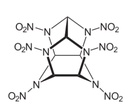
**RDX**



**Pentaerythitol Tetranitrate** (PETN)



**Triaminotrinitrobenzene** (TATB)



**CL-20**

## 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:**

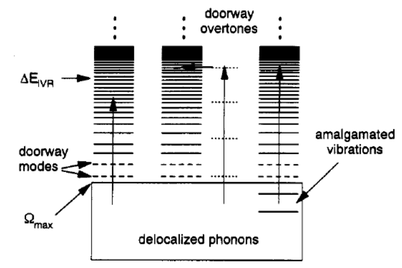
**Thermal: Phonon up-pumping** (Dlott, Fayer, Tokmakoff, *et al.*)
- Energy transferred from phonons to molecular vibrations
- Thermal process
- Temperature is controlling variable
- Predicts thermal distribution of quantum states

**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.



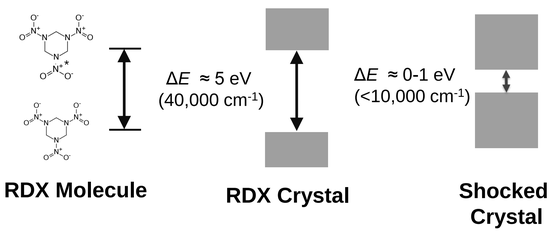

Tokmakoff, Fayer, and Dlott, *J. Phys. Chem.* **97**, 1901 (1993)

Anharmonic coupling couples the molecular vibrations with phonon modes of crystal

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

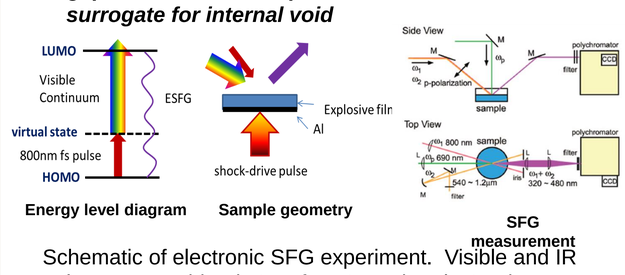
## Athermal Reactions

**Electronic changes and band gap closure:**
Compression is expected to reduce band gap of material, placing excited states within energetic reach.



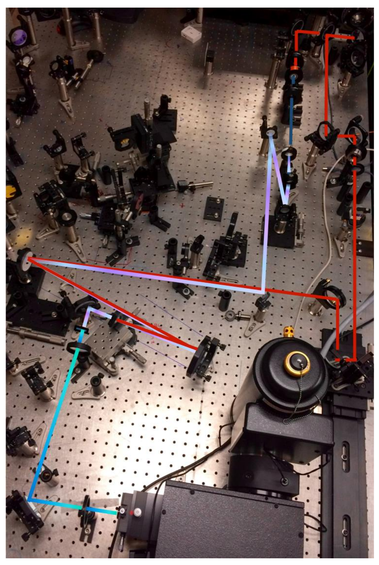

## Electronic Sum Frequency Generation at Explosive Interface

**Experiment is designed to detect difference in band gap of surface in comparison to bulk: *Surface is surrogate for internal void***

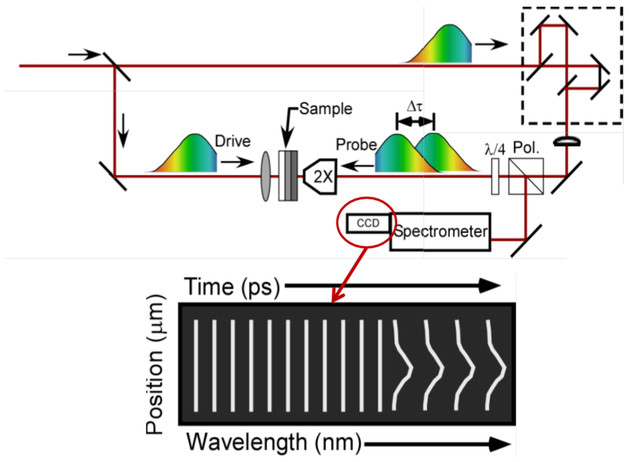



**Energy level diagram** **Sample geometry** **SFG measurement**

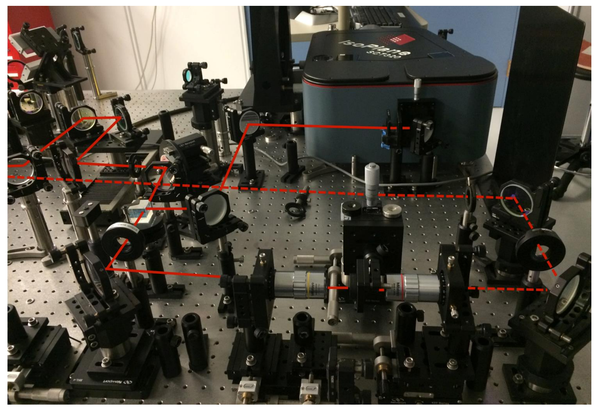
Schematic of electronic SFG experiment. Visible and IR pulses are combined at surface to probe electronic structure of interface. Sum frequency signal is emitted in unique spatial direction. Signal is produced by nonzero $X^{(2)}$ susceptibility within few molecular layers of surface.



## Ultrafast Shock Interrogation Measurements

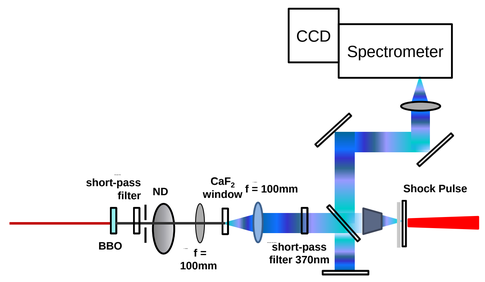



Schematic of USI setup. Technique developed at LLNL and implemented at Sandia for Shock Characterization

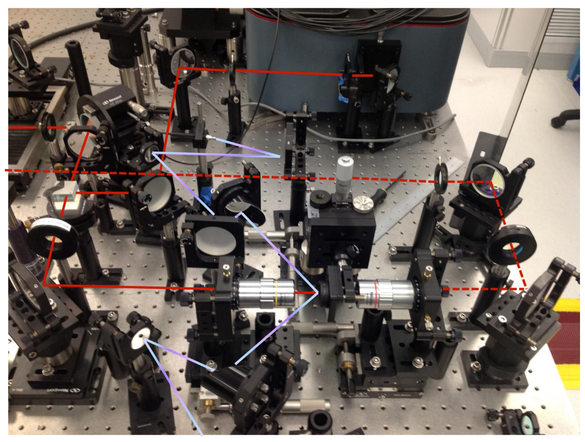


## Transient Absorption Measurements of Electronic Structure

**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.



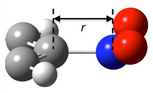
## Modeling Effects of Large-Amplitude Motion

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

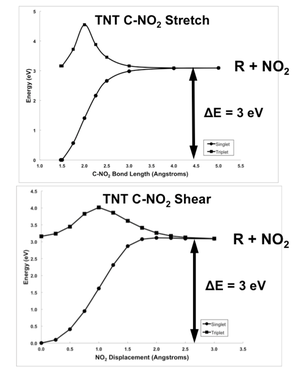


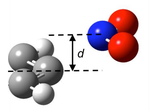
Large-amplitude bending strains the molecule but does not directly lead to bond breakage.



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.




***Results from this work were presented at the 2014 International Detonation Symposium:***

Brook A. Jilek, Ian T. Kohl, Darcie A. Farrow, Junji Urayama, Robert Knepper, Sean P. Kearney, Michael R. Armstrong, Jonathan C. Crowhurst, James Lewicki, and Joseph M. Zaug, "Unreacted Equations of State of Sylgard and Hexanitroazobenzene Determined by Ultrafast Time Domain Interferometry", Proceedings – 15th International Detonation Symposium, IDS 2014

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