SAND2015-5065C

Mechanisms of Shock-Induced Reactions in High Explosives

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2015 American Physical Society
Shock Compression of Condensed Matter
Tampa, FL

17 June 2015

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Mechanisms of Shock-Induced Reactions

We are trying to understand how shock waves initiate chemical reactions in explosives

This is a challenging problem, with many unanswered questions on many levels:

- **What are first bonds to break?**
- **What molecular processes cause these bonds to break?**
- **What macroscopic variables control initiation?**
  - Temperature or Pressure? (Thermal/athermal, instantaneous vs. equilibrium)
- **How do hot spots work?**
  - Microscopic level (void collapse, jetting, friction, etc.)
  - Molecular level (vibrational heating, dissociation, etc.)
- **What are the critical properties of the material that control shock sensitivity?**
  - Microstructure / Particle size
  - Crystal structure
  - Molecular structure
- **When will material fail to initiate?**
  - Critical hot spots vs. burn-out
  - Detonation processes vs. initiation

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Ultimately, we need to understand mechanism at molecular level

Shock Sensitivity of Explosives

Recent review article by Politzer and Murray

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

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

- 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 are underlying mechanisms that we have not yet assembled.

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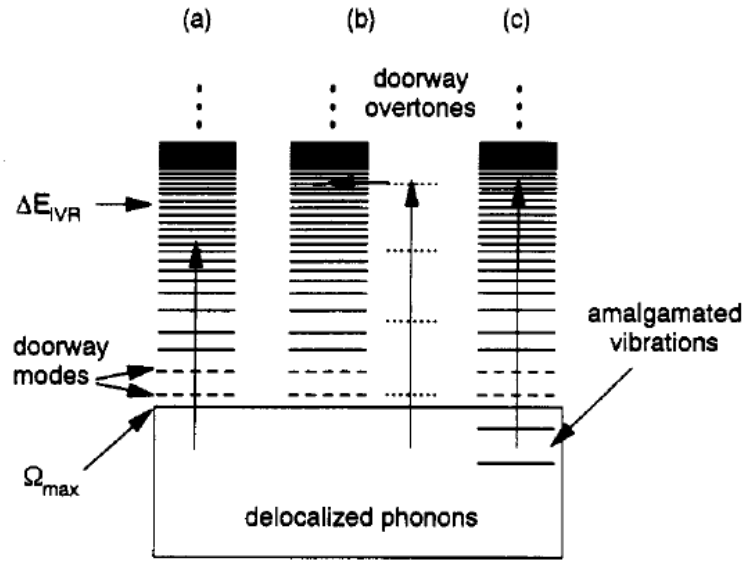
Survey of Previous Work: Theory

(Much experimental and theoretical work done in this area – brief survey)

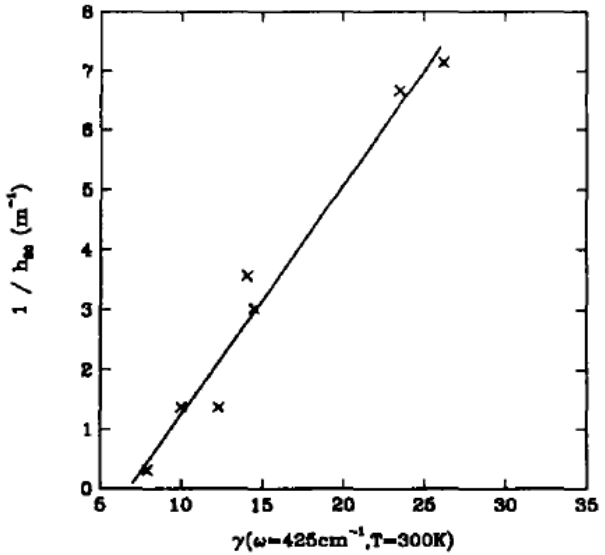
Shock heating and vibrational redistribution (Phonon up-pumping)

Schematic of vibrational degrees of freedom involved in shock heating



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

Correlation between impact sensitivity and vibrational energy transfer rates



Fried, Ruggiero *Mat. Res. Soc. Symp. Proc.* **296** (1993)

Framework for how shock waves heat material and localize energy in chemical bonds. Phonon-vibration energy transfer *via* anharmonic coupling.

Dlott, Fayer, Fried, Hooper, others

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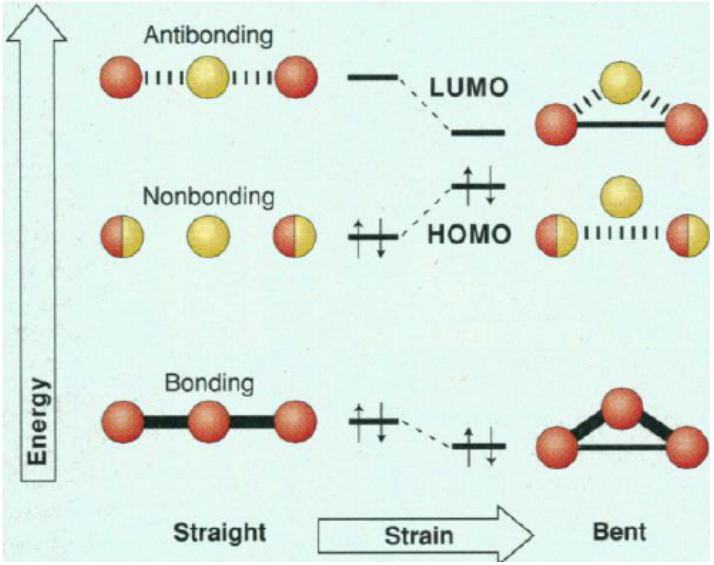
Summary of Previous Work: Theory

Initiation of reactions by electronic excitation

Changes in electronic structure caused by strain (HOMO-LUMO gap)



J. J. Gilman, *Science* **274**, 5284 (1996)

Changes in band gap in shocked solid (band gap closure)

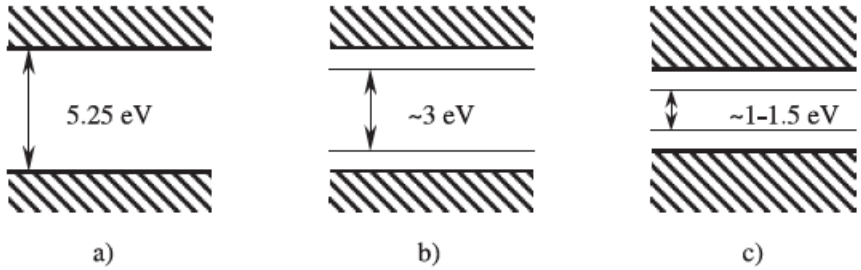


FIGURE 1 Schematic representation of the calculated bandgap of RDX: **a** perfect crystal; **b** RDX with edge dislocations; and **c** shocked RDX with edge dislocations

Kuklja, *Appl. Phys. A* **76**, 359 (2003)

Framework for how compression and strain may alter electronic structure of molecules and of solid, by enabling spontaneous reactions

Gilman, Kuklja, Kunz, Reed, Fried, Manaa

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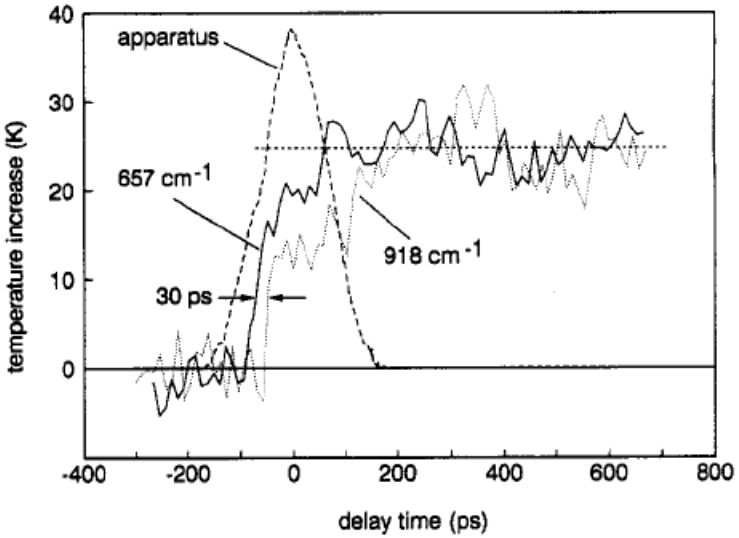
Summary of Previous Work: Experiment

Ultrafast Raman Temperature Measurements

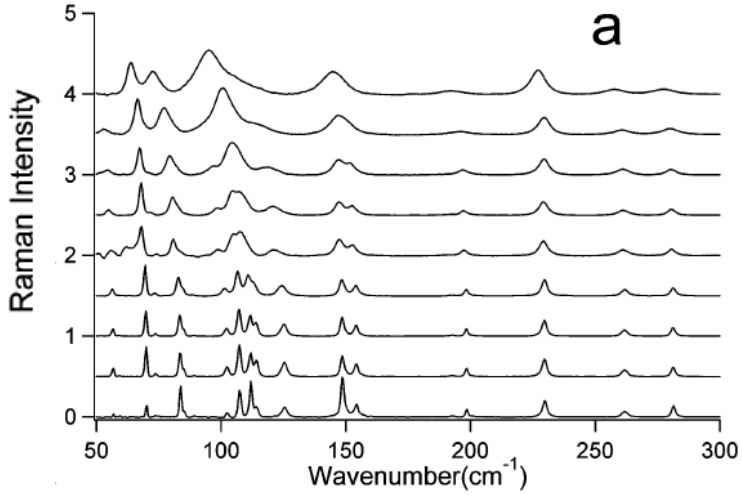


Chen, Tolbert, and Dlott,
J. Phys. Chem. **98**, 7759 (1994)

Direct measurements of shock heating and up-pumping rates

Dlott and co-workers

Temperature-Dependent Raman Measurements



McGrane, Barber, and Quenneville,
J. Phys. Chem. A, **109**, 9919 (2005)

Analysis of anharmonic couplings that govern shock heating

McGrane and co-workers

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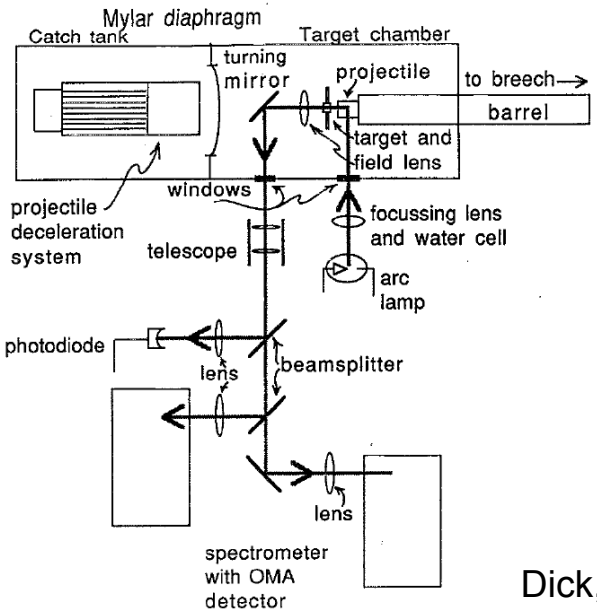
Summary of Previous Work: Experiment

Shock sensitivity vs. orientation and time-resolved emission measurements



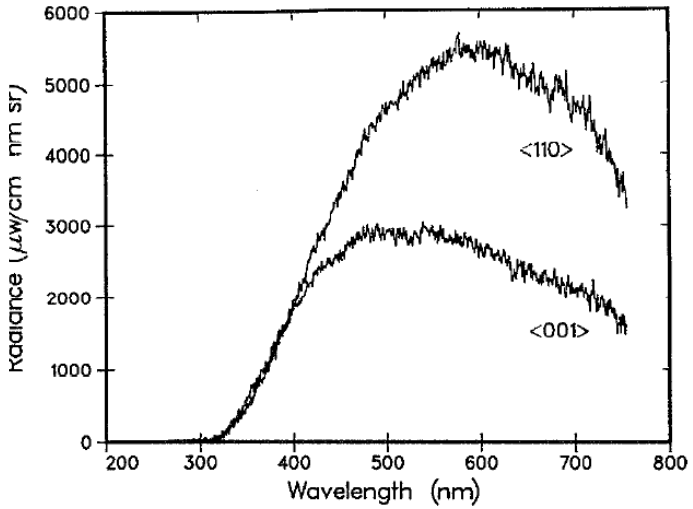


TABLE V. Atom–atom interactions.

Shock direction	MRSS slip system	Atom pair	Number of interactions	Closest approach (Å)
⟨100⟩	{110}⟨1$\bar{1}$1⟩	O-O	3	1.05
⟨101⟩	{100}⟨001⟩	O-O	4	0.78
⟨001⟩	{100}⟨$\bar{1}$01⟩	O-O	3	0.86
		C-O	4	0.71
		O-H	6	0.11
		N-H	2	1.01
		C-N	1	1.52
		N-O	1	1.38
⟨110⟩	{100}⟨011⟩	O-O	9	0.54
		N-O	5	1.01
		C-O	2	1.31
		O-H	6	0.92
		N-H	4	0.80
		H-H	2	0.99
		N-N	1	1.58
		C-N	1	1.60

Dick, Mulford, Spencer, Pettit, Garcia, and Shaw, *J. Appl. Phys.* **70**, 3572 (1991)

Development of steric hindrance model – more sensitive orientations result from interactions between nearby molecules

Dick and co-workers

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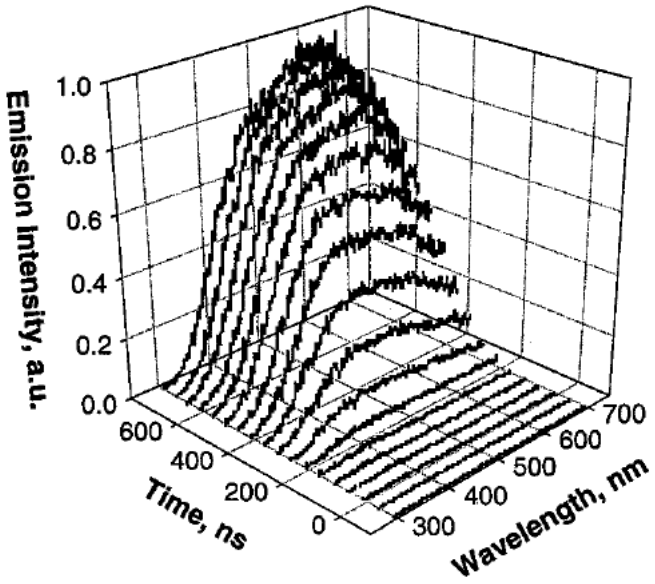
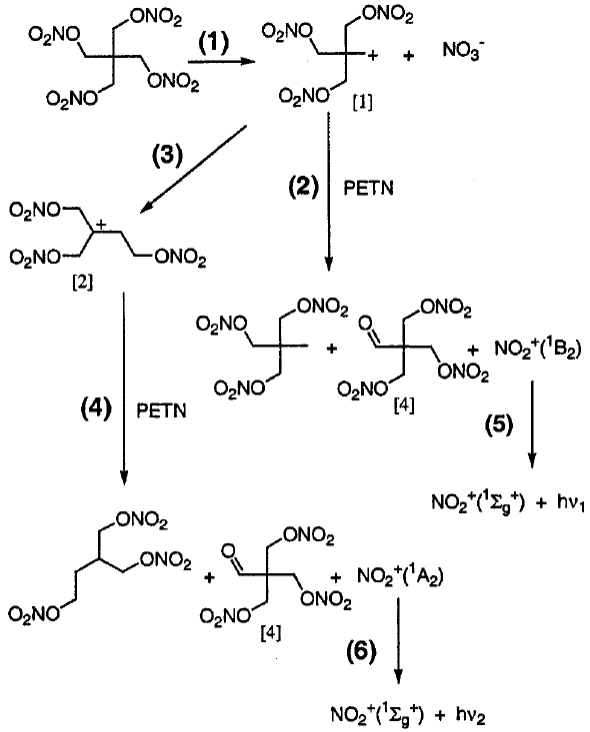
Summary of Previous Work: Experiment

Emission measurements in shocked solids



Dreger, Grudskov, Gupta, and Dick
J. Phys. Chem. B **106**, 247 (2002)



Measurements show emission from electronically excited species following shock

Dick, Dreger, Gupta, others

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Understanding Shock-Induced Reactions at the Quantum Level

We are looking for are quantum-mechanical understanding of shock-induced reactions

- Many questions still surround quantum-mechanical mechanisms of shock-induced reactions
- As a community, we have quantum theories of shock-induced reactions, and many experimental measurements, need more definitive measurements.
- Systems are complex – difficult to isolate key physics – reductionist approach difficult
- Understanding the many facets of this problem requires a diverse, multi-pronged approach:

Problem requires a diverse approach from all sides

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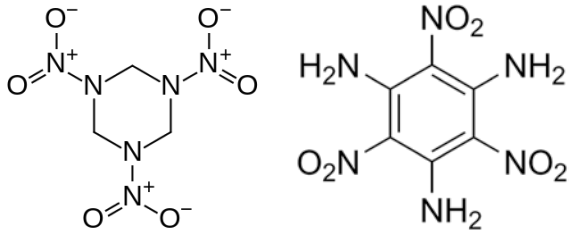
Material Properties

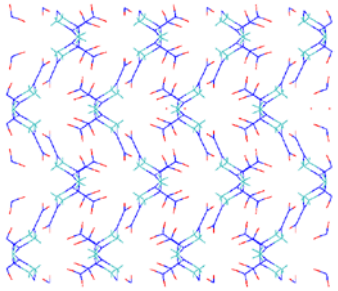
Take a step back - What material properties are important?

- ***Molecular structure***
  - Geometry and functional groups
  - Vibrational couplings
  - Electronic structure



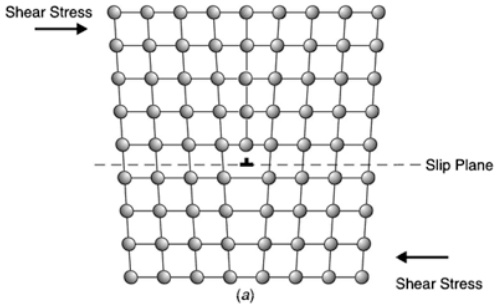
RDX and TATB

- ***Structure of the crystal lattice***
  - Geometric arrangement of molecules
  - Vibrational structure of crystal
  - Electronic structure of crystal



RDX lattice

- ***Crystal defects***
  - Dislocations
  - Volume defects
  - Surfaces
  - Steric interactions at defect sites
  - Electronic structure of defects



Lattice dislocation

R. D. Tilley, *Defects in Solids*, Wiley (2008)

Some may be “hidden” variables that control shock-induced reactions

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Temperature, Pressure, and Time

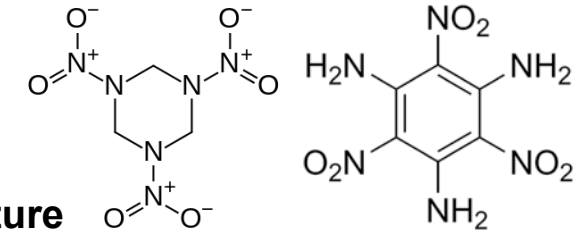
What dynamic variables control shock-induced reactions?

- ***Temperature***
  - Temperature: Measure of random thermal motion in material
  - Shock wave sets up nonequilibrium thermal distribution
  - How long does it take material to reach equilibrium?
  - Vibrational redistribution takes time
  - Truly “thermal” reactions require time for energy to redistribute
- ***Pressure***
  - Pressure: Force per unit area
  - Under shock compression, crystal is compressed, molecules are accelerated
  - Collisions between molecules occur at certain collision energy
  - Instantaneous (athermal) reactions may occur due to various effects of compression – collisions, change in electronic structure
- ***Time***
  - Difference between thermal and athermal reactions is, in some sense, dependent on how much time process takes. Equilibrium vs. nonequilibrium

Dynamic Processes

What *dynamic processes* are important?

- ***Molecular level***
  - *Compression* → **Deformation**
  - *Heating* → **Vibrational energy transfer**
  - *Compression* → **Changes in electronic structure**



RDX and TATB

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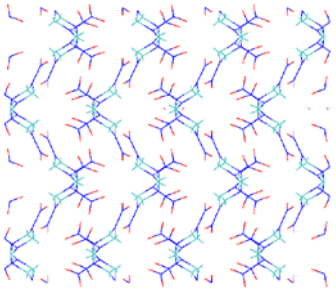
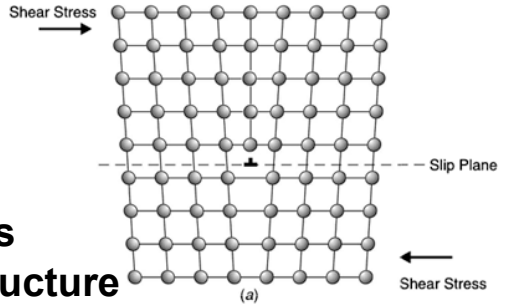


RDX lattice

- ***Crystal defects***
  - *Compression* → **Relative motion in lattice**
  - *Compression* → **Interactions between molecules**
  - *Compression* → **Local changes in electronic structure**



Lattice dislocation

R. D. Tilley, *Defects in Solids*, Wiley (2008)

What we would like to understand is how important each of these processes are, and under what conditions

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Shock-Induced Chemistry @ Sandia

Sandia has launched an extensive effort to understand many of these dynamic processes, experimentally and computationally:

- Ultrafast spectroscopic measurements**
- Optical emission measurements**
- Quantum chemical modeling**
- Molecular dynamics modeling
- Microscale characterization
- Grain scale modeling
- And more

Overarching goal is to put the puzzle together by characterizing each of the dynamically-important processes

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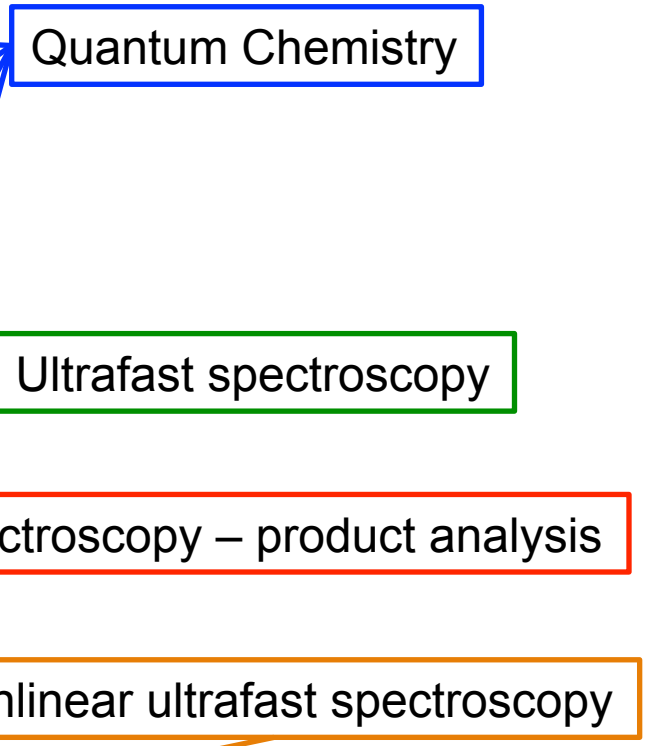

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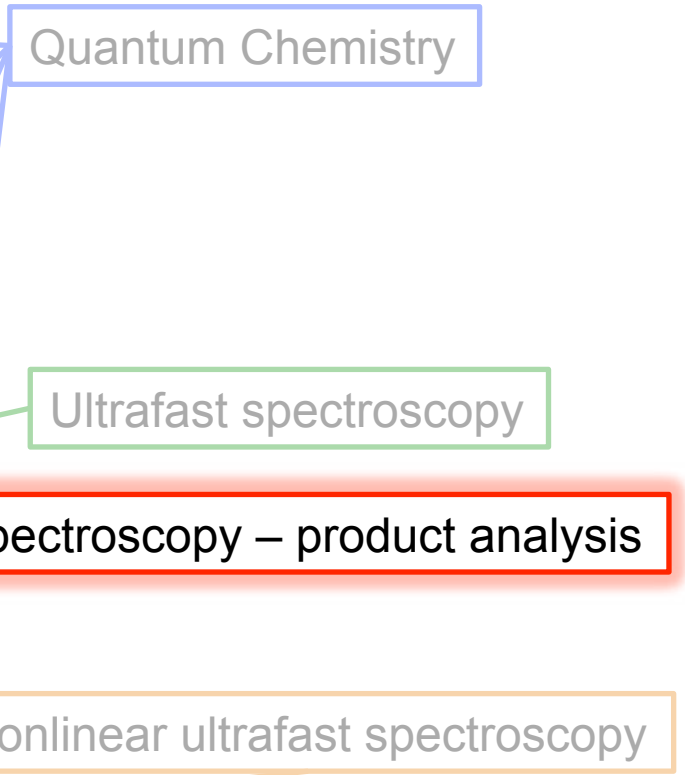

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Probing Reaction Products and State Distributions – Emission Spectroscopy

- **Shock-induced reactions are governed by forces that we can't directly measure**
  - Potential energy surfaces (+ Distortion under shock)
  - Nuclear motion (Response of molecules and lattice to shock)
  - Conical intersections

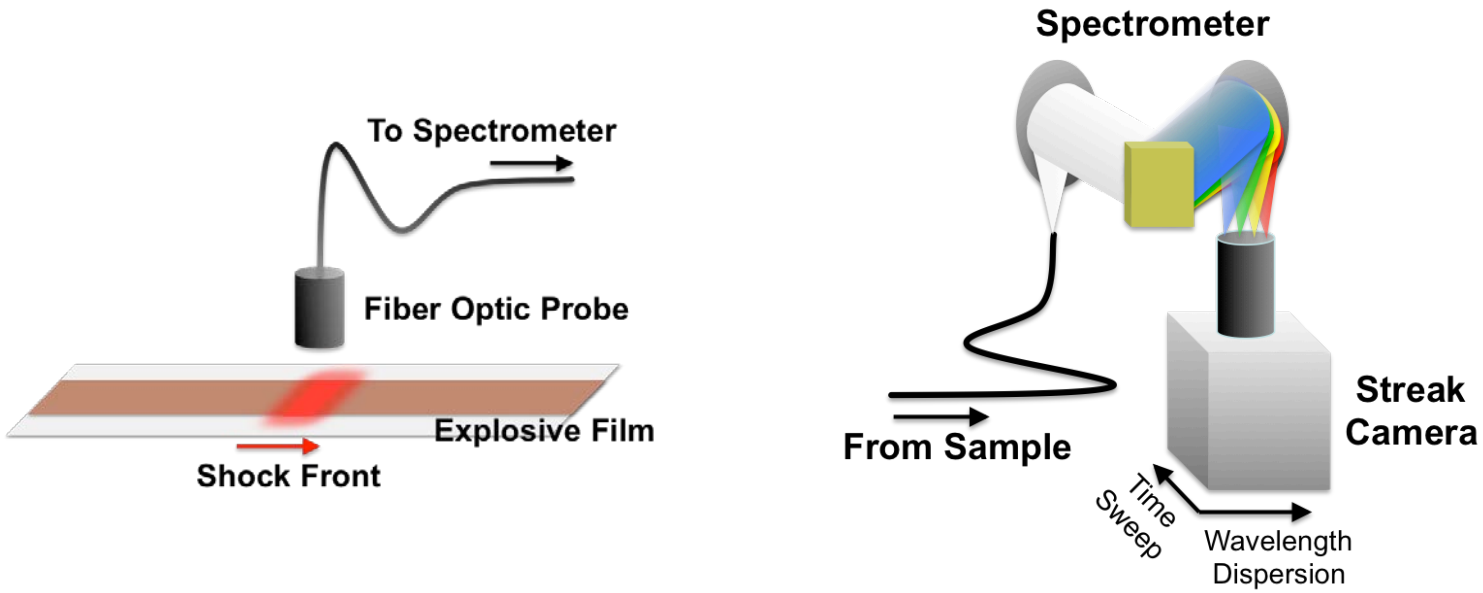
- **Spectroscopic experiments measure species and distributions**
  - Identification of product species
  - Quantum state distributions

- **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.

Experiment: Streaked Emission Spectroscopy

Streak camera and spectrometer are used in combination to analyze optical emission (wavelength vs. time)

Spectrum provides diagnostic information about species and quantum distributions



1. Dreger, Grudzkov, Gupta, and Dick, *J. Phys. Chem. B* **106**, 247 (2002)
2. J. Carney, *Rev. Sci. Instrum.* **77**, 063103 (2006)

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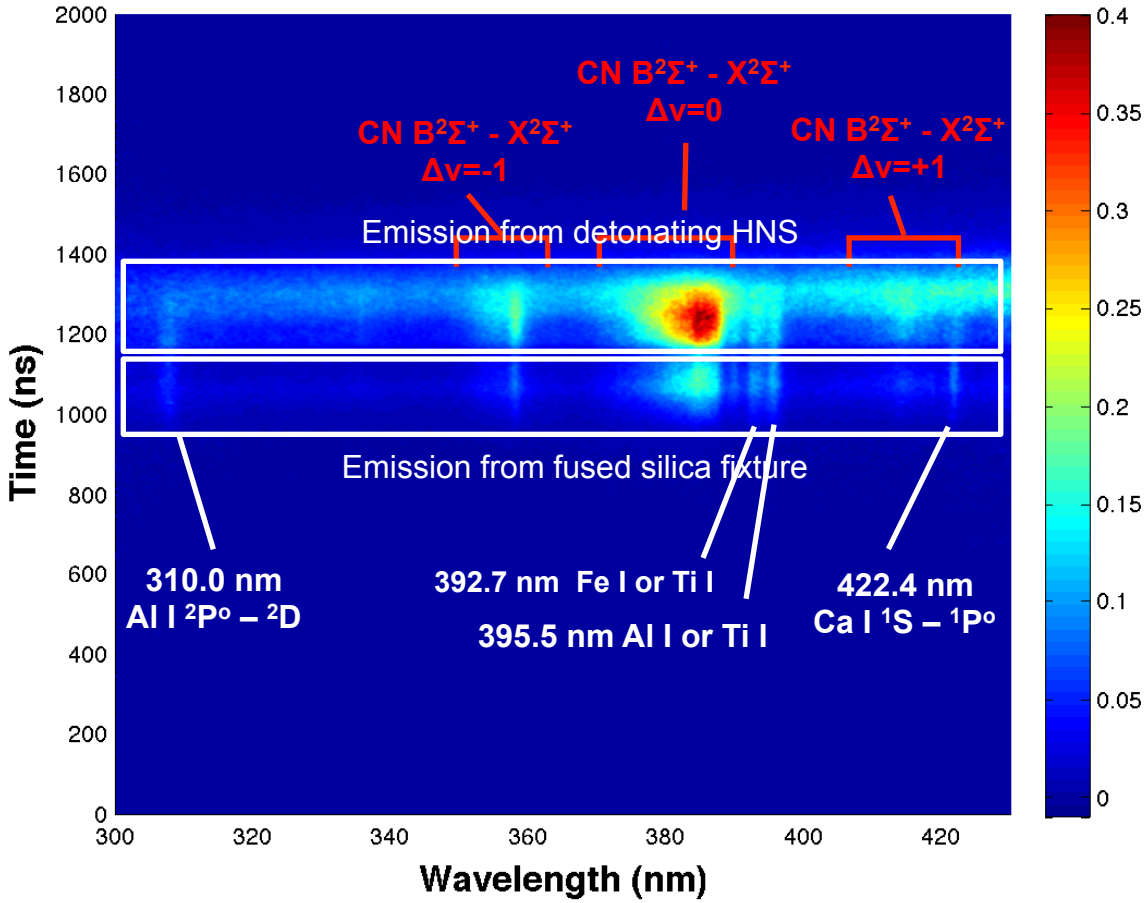
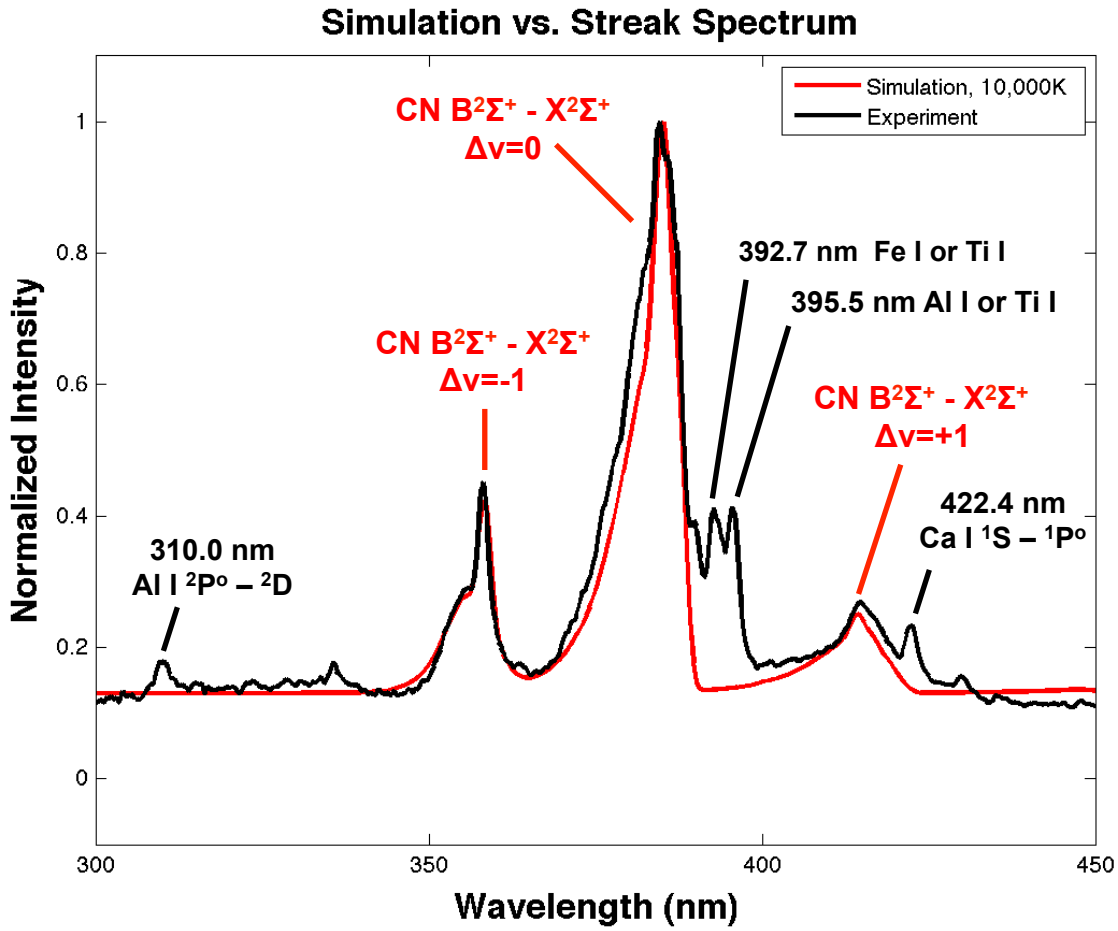
Streak Spectroscopy: HNS



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)

Streak Spectroscopy: HNS

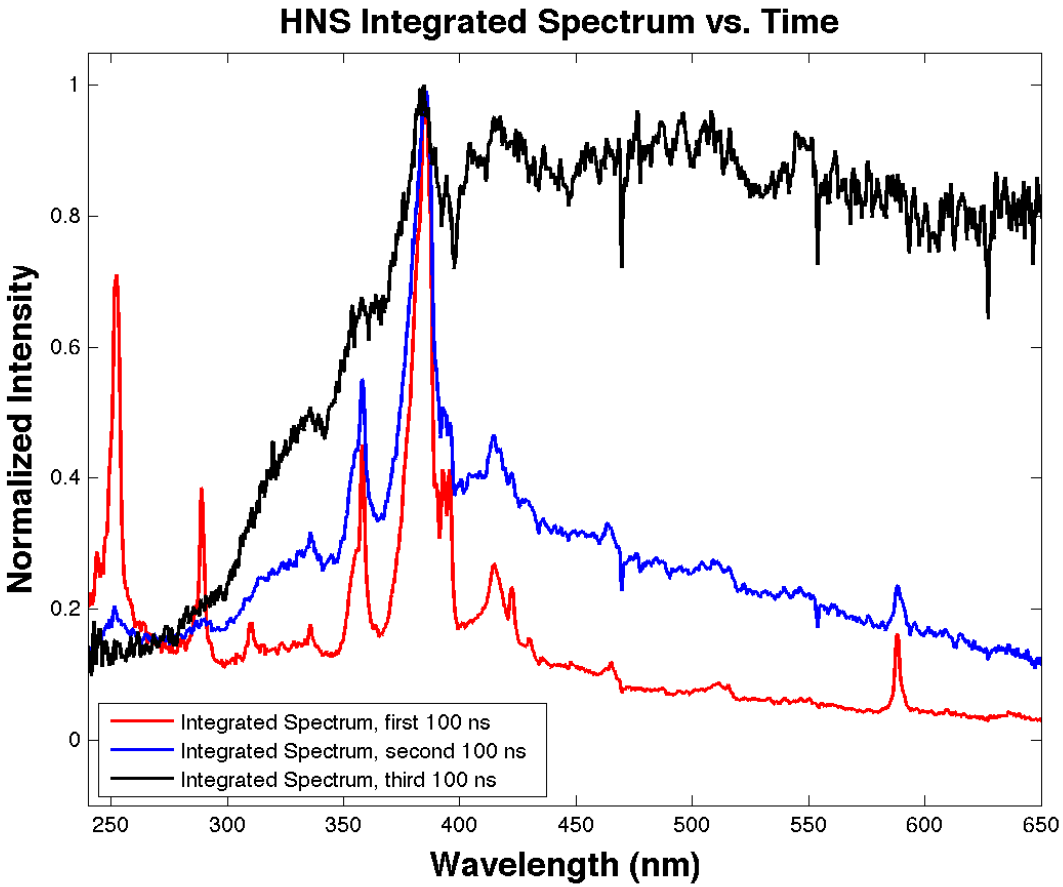


CN $B^2\Sigma^+ - X^2\Sigma^+$ emission is observed with high rotational and vibrational excitation.

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

Streak Spectroscopy: HNS

Normalized Spectra

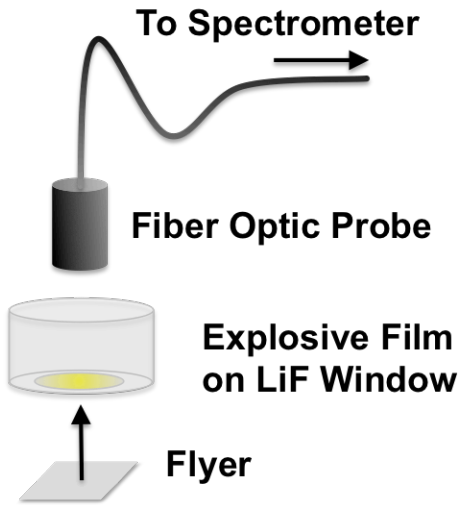


CN $B^2\Sigma^+$ - $X^2\Sigma^+$ emission is observed at early time, with broadband emission at later time

- 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

Streak Spectroscopy: Impact Experiments

Next series of shots will characterize emission across a range of impact velocities and shock pressures



Vary flyer velocity to change conditions from onset of reaction to detonation – spectroscopically characterize regimes and threshold behaviors

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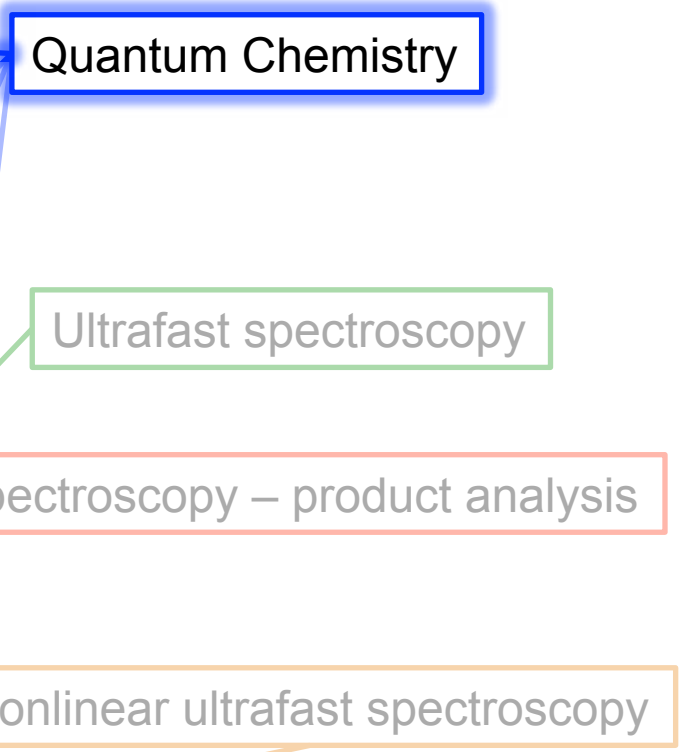

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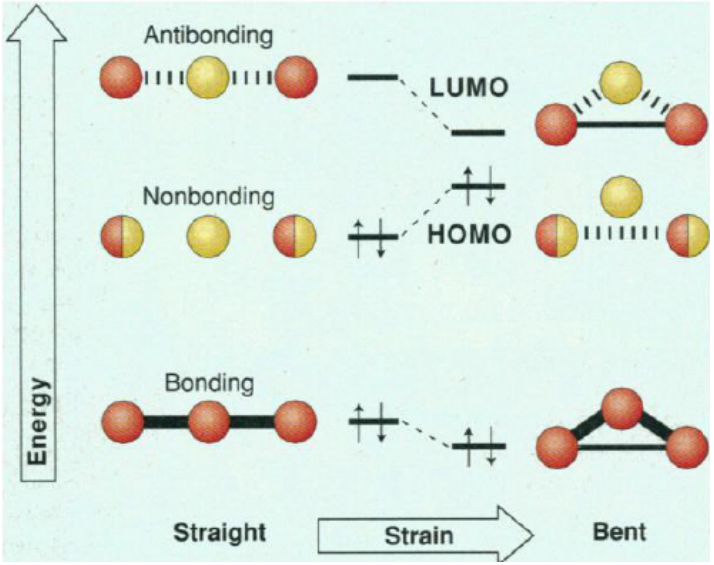
Modeling Effects of Large-Amplitude Deformation

How does electronic structure change when molecules are strained?

J. J. Gilman [*Science* **274**, 5284 (1996)] noted that strain-induced deformation of molecules can lead to changes in electronic structure that trigger reactions

Shock can induce large-amplitude deformations

What happens in larger molecules of interest?



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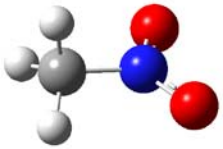
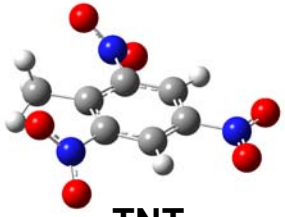
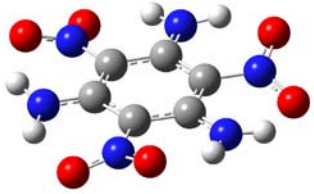


Nitromethane



TNT



TATB

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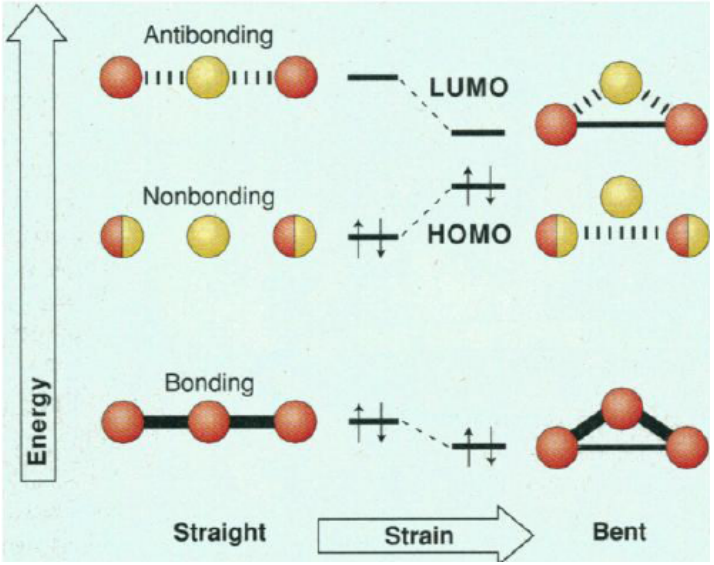

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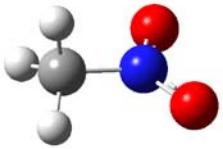
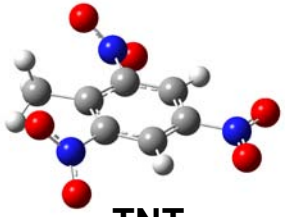


Nitromethane



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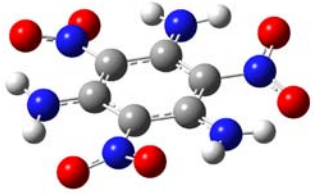

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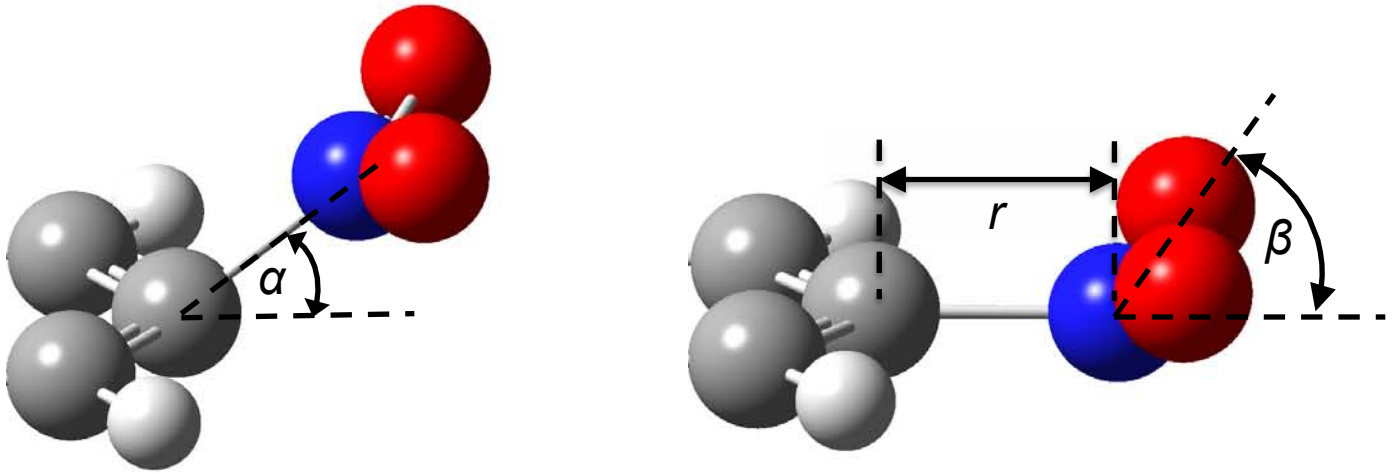
Modeling Effects of Large-Amplitude Deformation

Subject molecules to large-amplitude bending – how can we induce dissociation?



Calculate potential energy surfaces of ground singlet and first triplet states as function of bending angles

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Modeling Effects of Large-Amplitude Deformation

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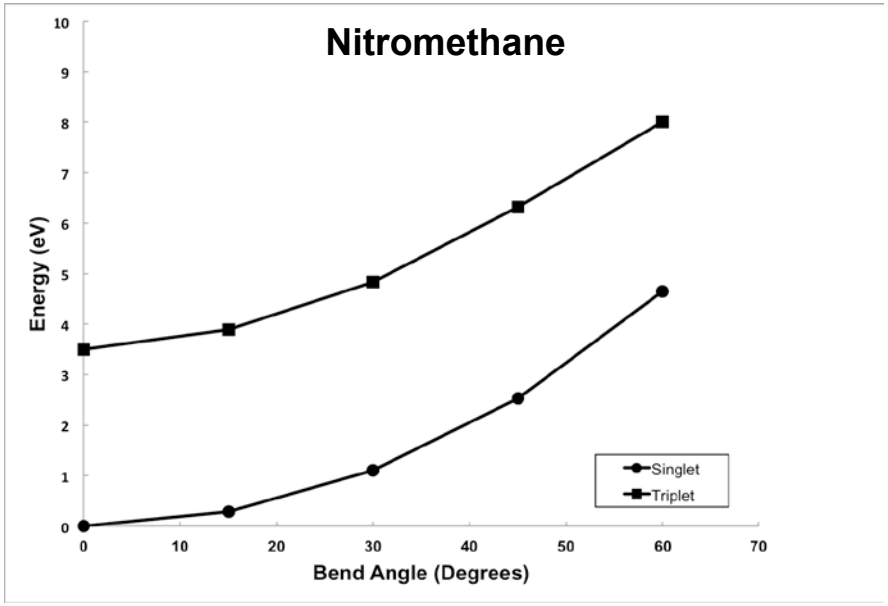

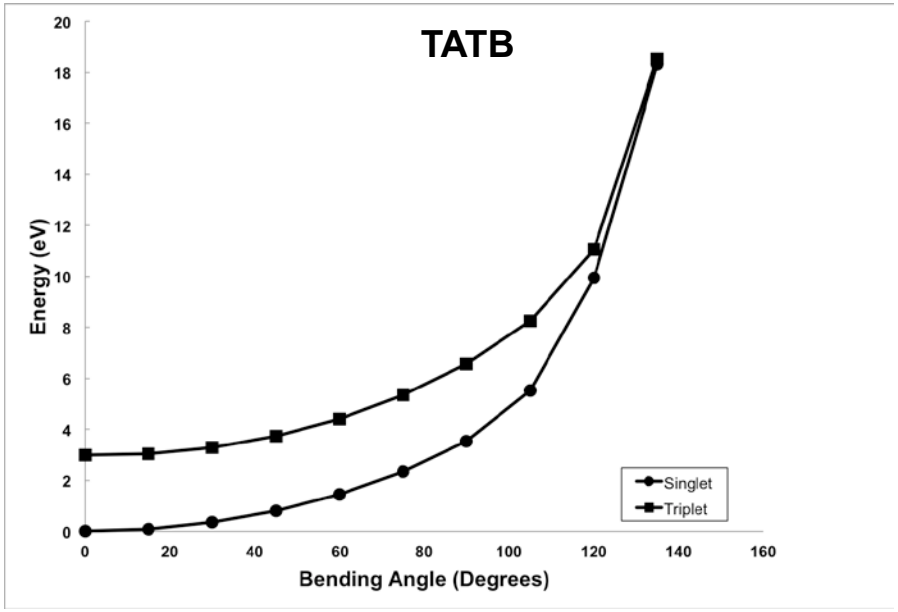

Bending doesn't really help to break bonds – singlet/triplet gap persists to high bend angles

How can we mechanically break bonds?

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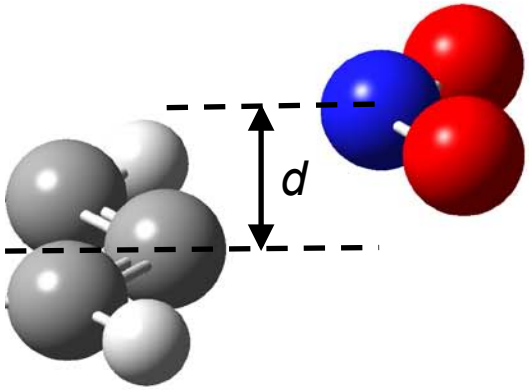
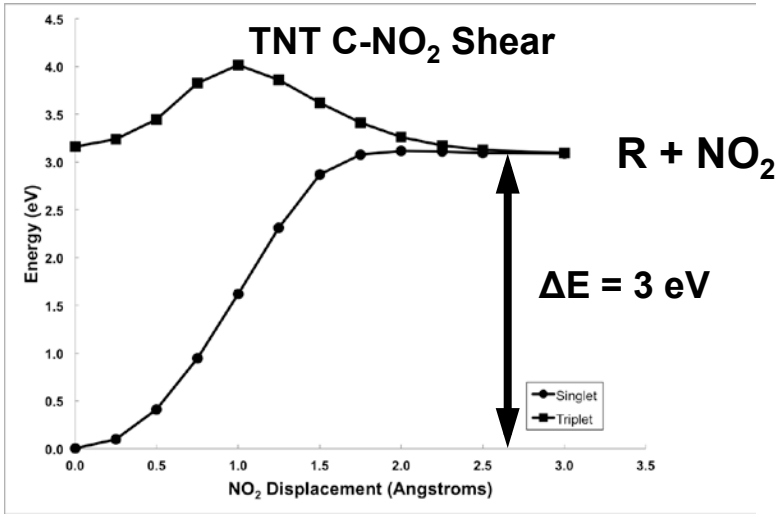
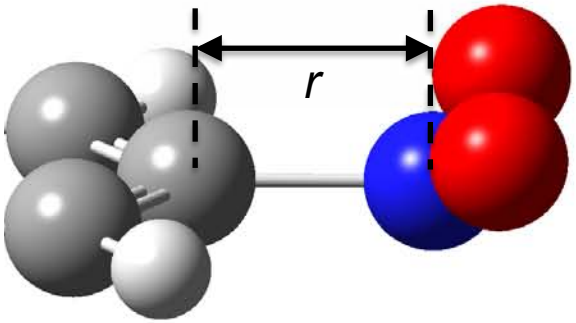
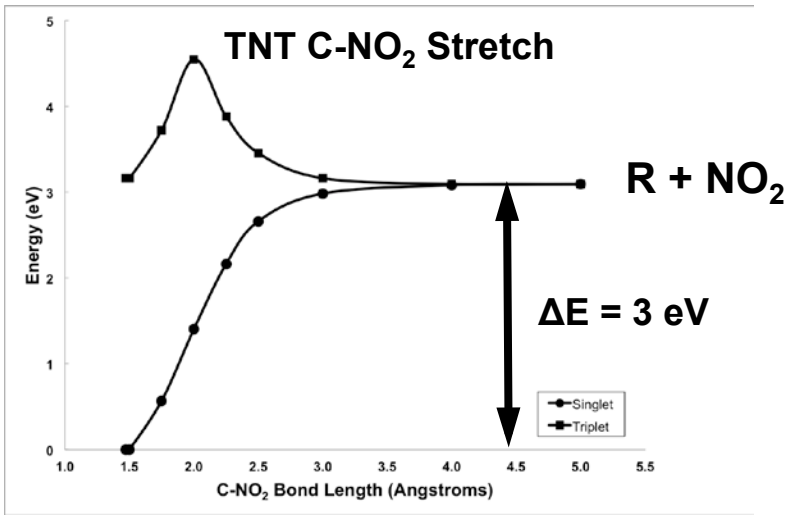
Modeling Effects of Large-Amplitude Deformation

"Shearing" bonds does lead to dissociation – just as easy as stretching









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Could occur in solid, but not in gas phase. Rarely considered

Modeling Effects of Large-Amplitude Deformation

Shear has long been thought to be important in shock-induced reactivity

Steric hindrance model: Dick *et al.*

Sensitivity in crystals is orientation-dependent

Examined steric hindrance that occurs during edge dislocation motion under shear flow

Most sensitive orientations in PETN have more *steric hindrance* – more close approaches between parts of molecules

More opportunities for mechanical deformation/impact

TABLE V. Atom–atom interactions.

Shock direction	MRSS slip system	Atom pair	Number of interactions	Closest approach (Å)	
⟨100⟩	{110}⟨1$\bar{1}$1⟩	O-O	3	1.05	Least sensitive direction
⟨101⟩	{100}⟨001⟩	O-O	4	0.78	
⟨001⟩	{100}⟨101⟩	O-O	3	0.86	
		C-O	4	0.71	
		O-H	6	0.11	
		N-H	2	1.01	
		C-N	1	1.52	
		N-O	1	1.38	
⟨110⟩	{100}⟨011⟩	O-O	9	0.54	Most sensitive direction
		N-O	5	1.01	
		C-O	2	1.31	
		O-H	6	0.92	
		N-H	4	0.80	
		H-H	2	0.99	
		N-N	1	1.58	
		C-N	1	1.60	

J. J. Dick, *et al.*, *J. Appl. Phys.* **70**, 3572 (1991)

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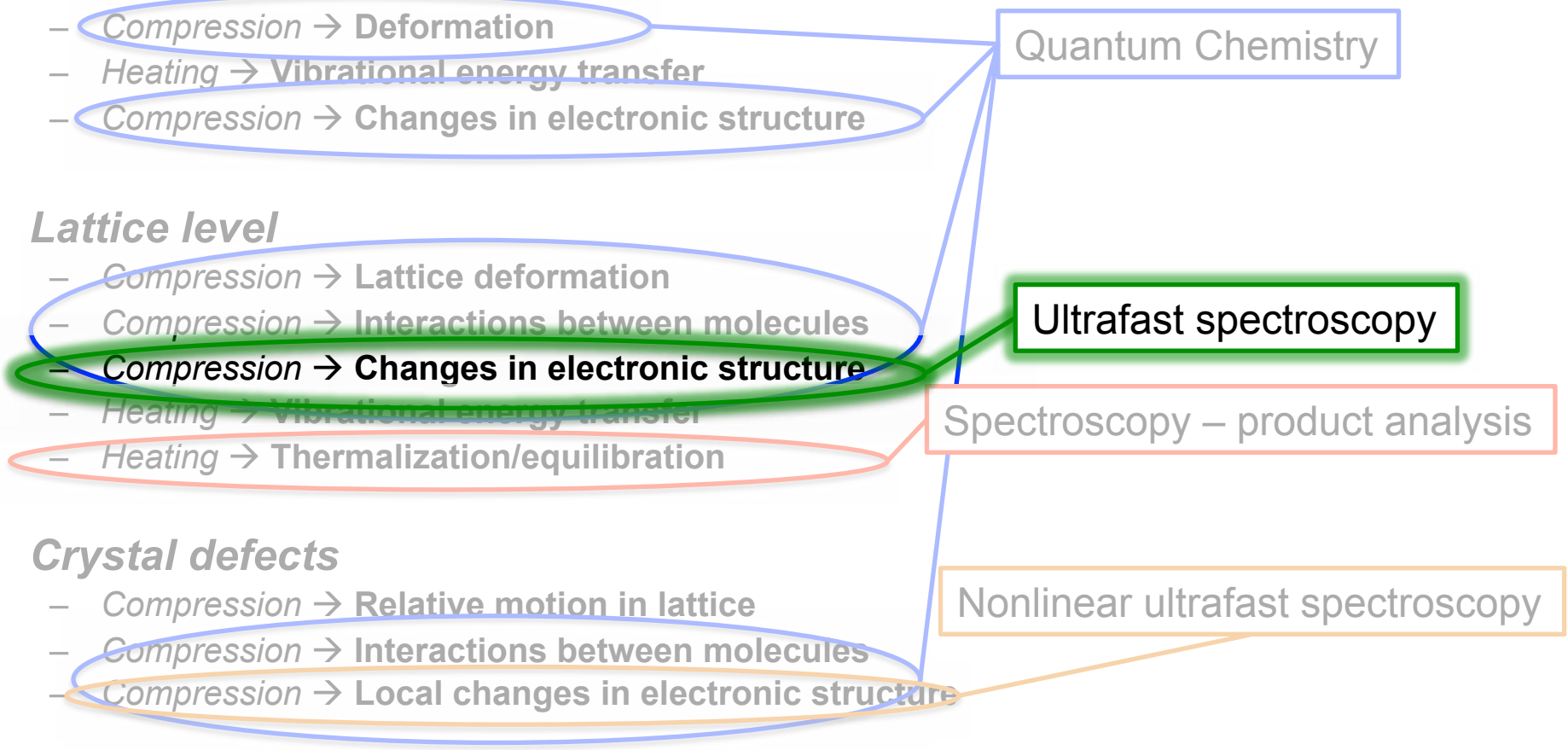
Dynamic Processes

What *dynamic processes* are important?

- ***Molecular level***
  - *Compression* → **Deformation**
  - *Heating* → **Vibrational energy transfer**
  - *Compression* → **Changes in electronic structure**
- ***Lattice level***
  - *Compression* → **Lattice deformation**
  - *Compression* → **Interactions between molecules**
  - *Compression* → **Changes in electronic structure**
  - *Heating* → **Vibrational energy transfer**
  - *Heating* → **Thermalization/equilibration**
- ***Crystal defects***
  - *Compression* → **Relative motion in lattice**
  - *Compression* → **Interactions between molecules**
  - *Compression* → **Local changes in electronic structure**



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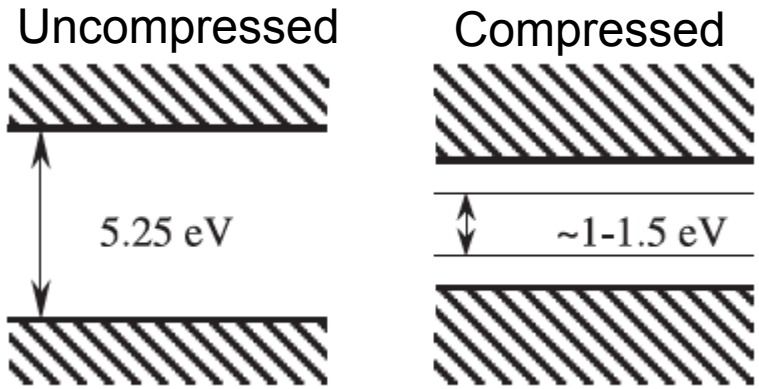
Probing Electronic Structure Under Compression – Transient Absorption

- **Shock-induced changes in electronic structure of crystal will change absorption spectrum**
- **Band gap closure theory of Kuklja *et al*. predicts strong red-shift**



Kuklja *Appl. Phys. A* **76**, 359 (2003)

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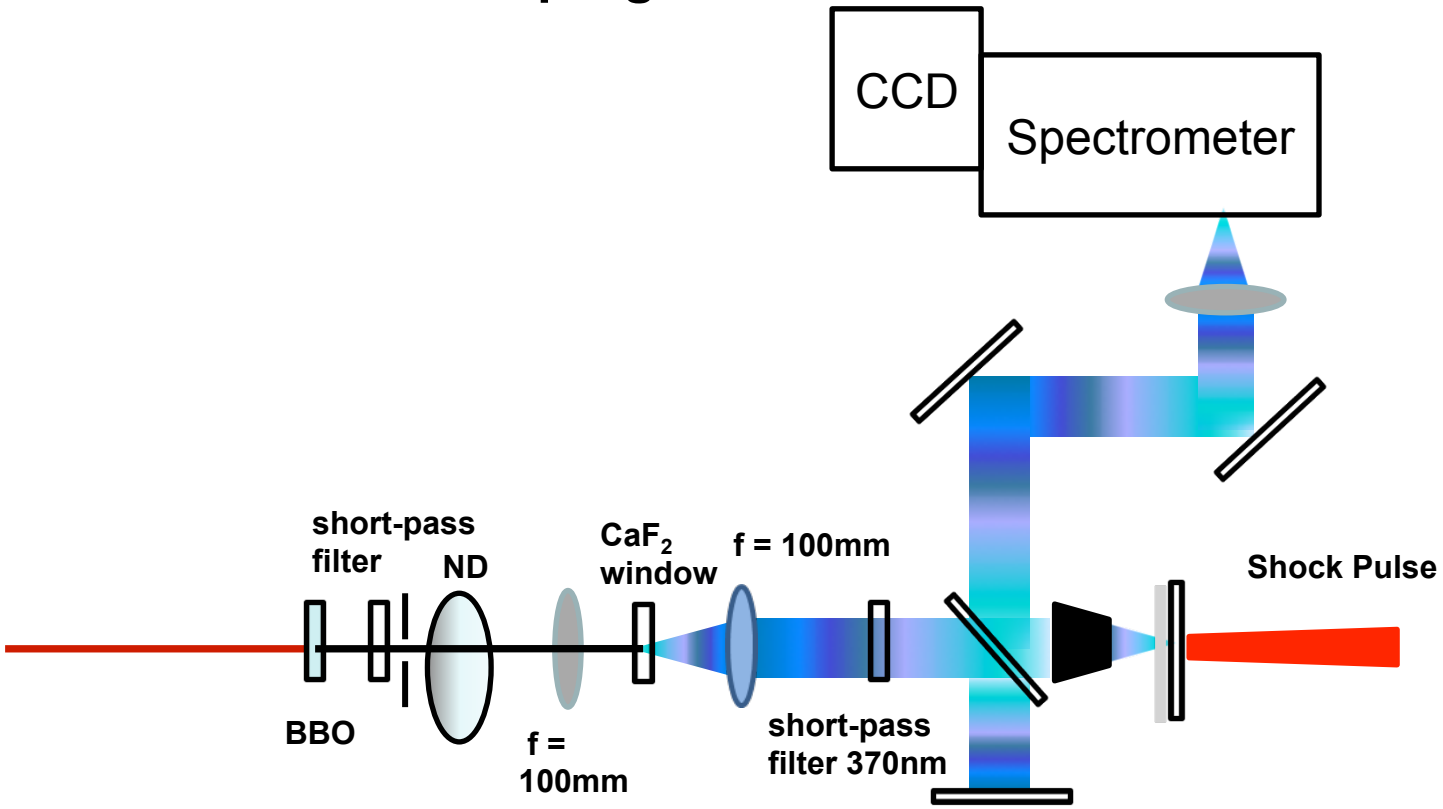
Probing Electronic Structure Under Compression – Transient Absorption

- **Experiments at Sandia for examining shock-induced changes in electronic structure in progress**



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

*** In Progress ***

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Dynamic Processes

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Quantum Chemistry

Ultrafast spectroscopy

Spectroscopy – product analysis

Nonlinear ultrafast spectroscopy

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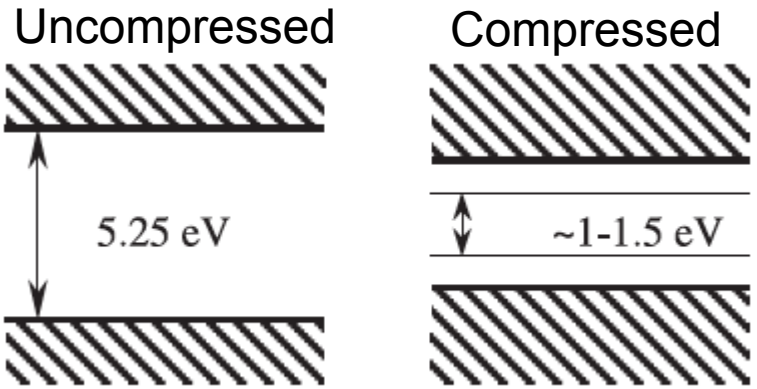
Probing Electronic Structure of Defects – Sum Frequency Spectroscopy

- **Defects in crystals have different electronic structure than pristine lattice**
- **Theory by Kuklja *et al*. predicts larger change in band gap with less compression for crystals with defects**



Kuklja *Appl. Phys. A* **76**, 359 (2003)

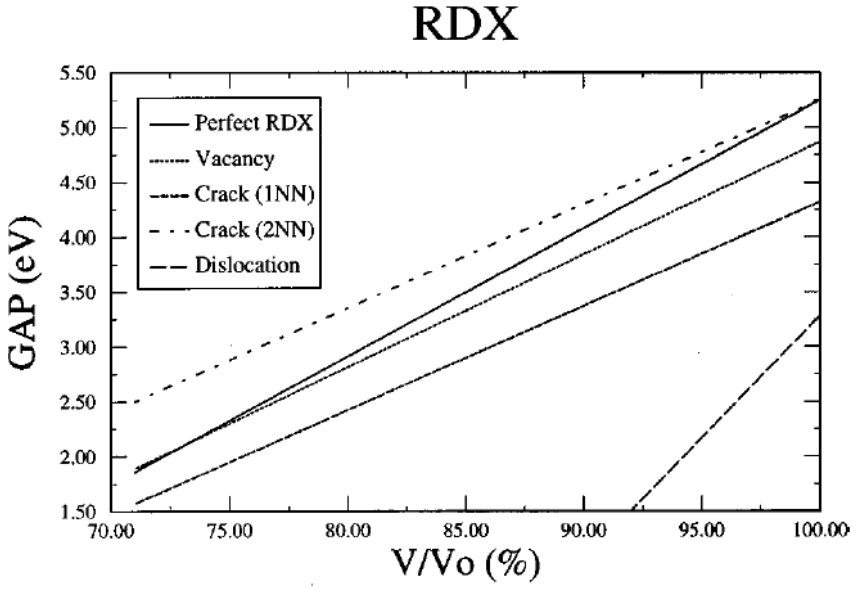


FIG. 4. The gap as a function of compression of RDX containing different defects.

Kuklja, Stefanovich, and Kunz, *J. Chem. Phys.* **112**, 3417 (2000)

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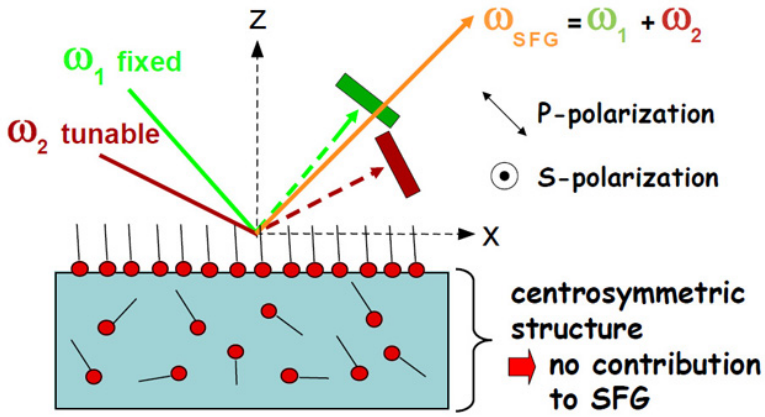
Probing Electronic Structure of Defects – Sum Frequency Spectroscopy

- **We know that crystal defects enhance reactivity of materials. How can we probe crystalline defects?**
- **$\chi^{(2)}$ nonlinear optical techniques can sensitively probe regions of crystal that do not possess inversion symmetry - can separate *anomalous regions* from *bulk.***
- **Surface is most easily probed type of crystalline defect**
- **Void is (to first order) a closed surface. What does the electronic structure look like?**



http://www.uni-regensburg.de

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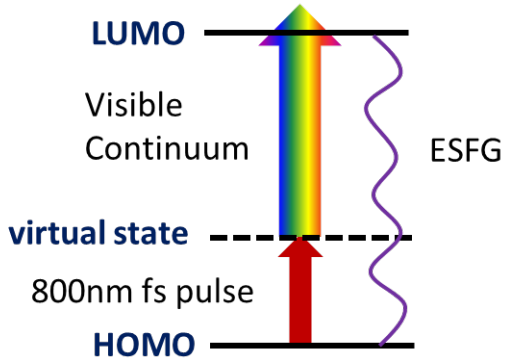
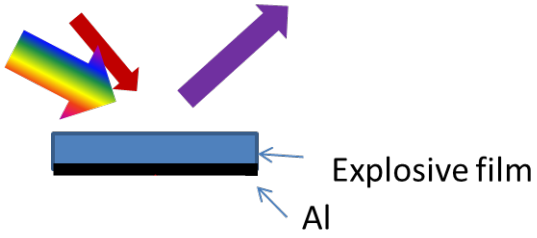
Electronic SFG At Explosive Interface

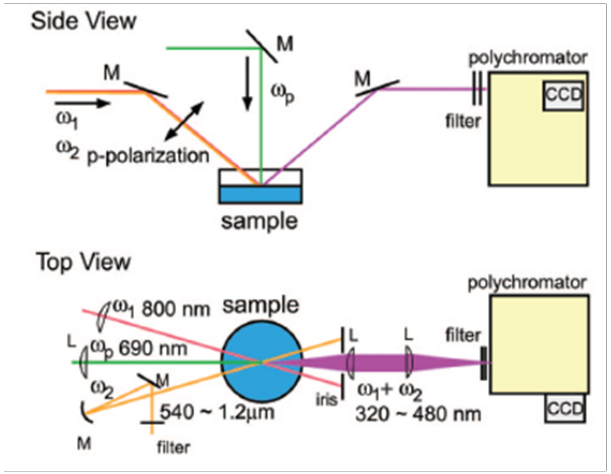
Experiment probes electronic structure of surface in comparison to bulk: *Surface is simplest type of defect, surrogate for internal void*



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.

*** In Progress ***

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Acknowledgments

Dr. Darcie Farrow (SNL)
Dr. Sean Kearney (SNL)
Ian Kohl (SNL)
Dr. Ryan Wixom (SNL)
Brook Jilek (SNL)
Alex Tappan (SNL)
Dr. Robert Knepper (SNL)
Dr. Leanna Minier (SNL)

Sandia Laboratory-Directed Research and Development (LDRD) Program