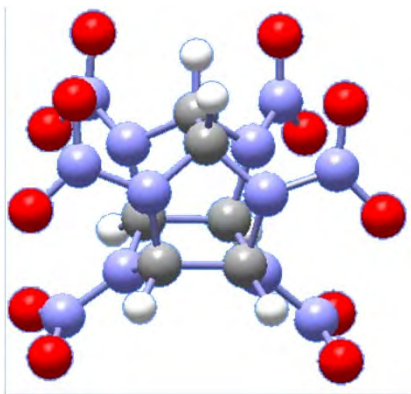


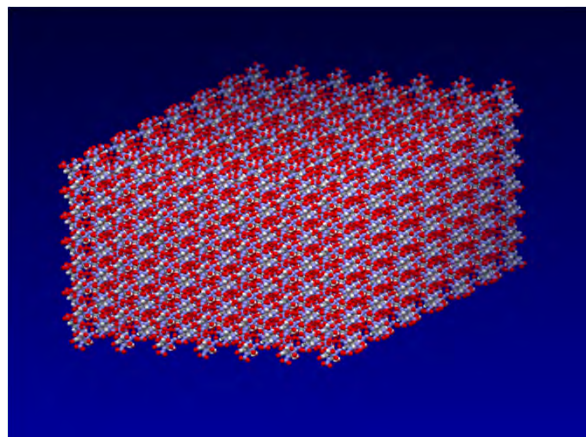
Fundamental Energetic Materials Initiative

Combat Safe Energetic Ingredients Based on
Molecular Design and Crystal Morphology

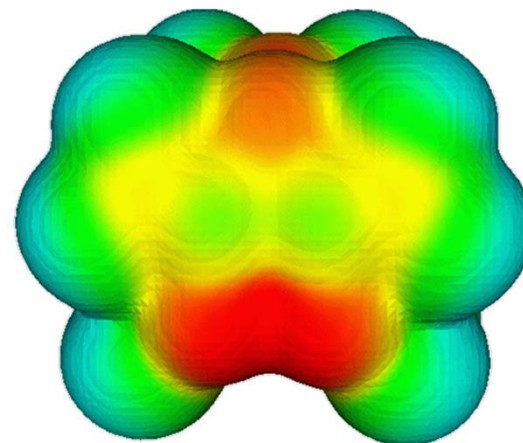
Molecular Synthesis
CL20



Crystal Structure/
Morphology



Electrostatic Potential



Clifford Bedford, Ph.D.

Partners in Environmental Technology Technical Symposium & Workshop
30 November 2011

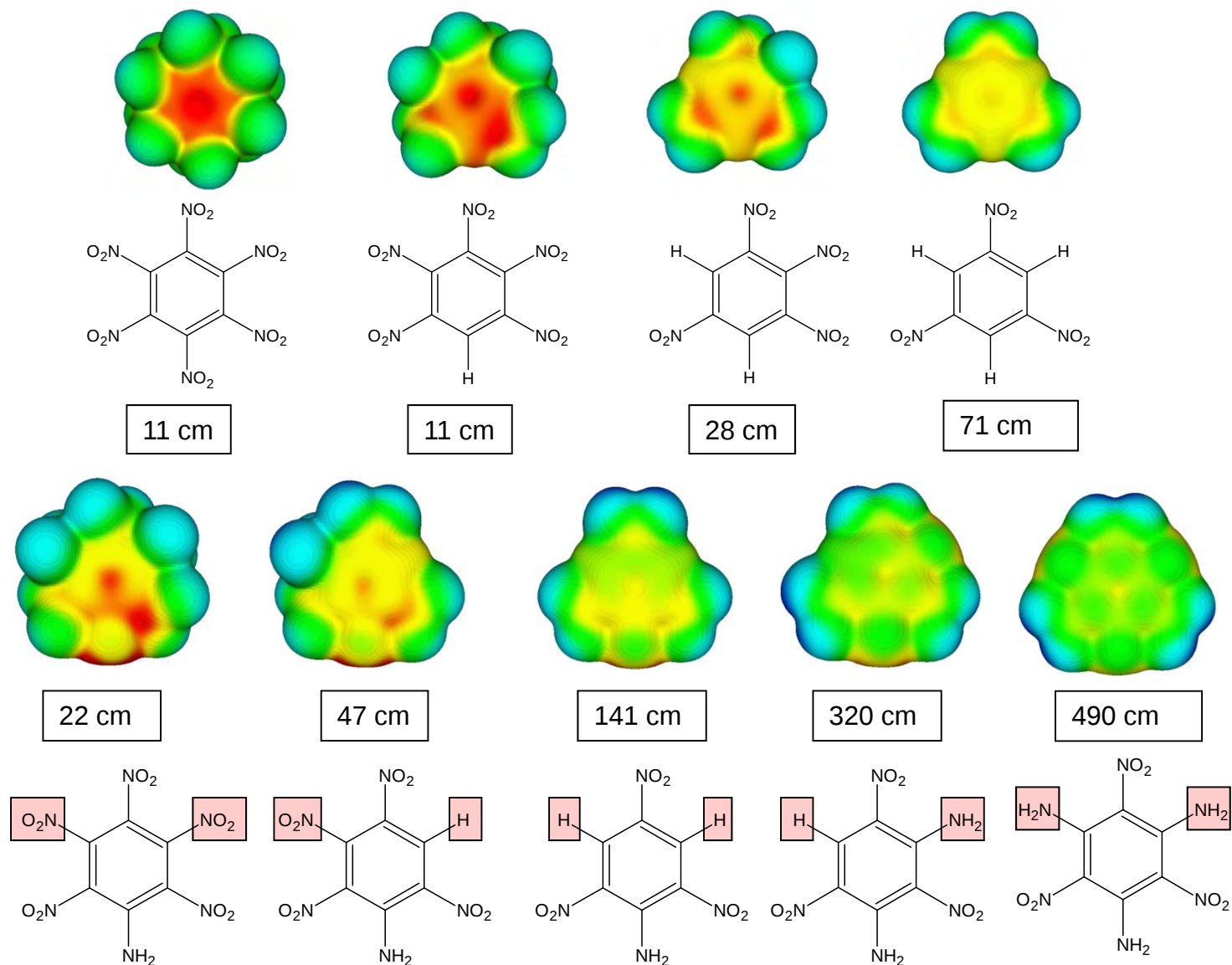
Report Documentation Page				Form Approved OMB No. 0704-0188	
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Background

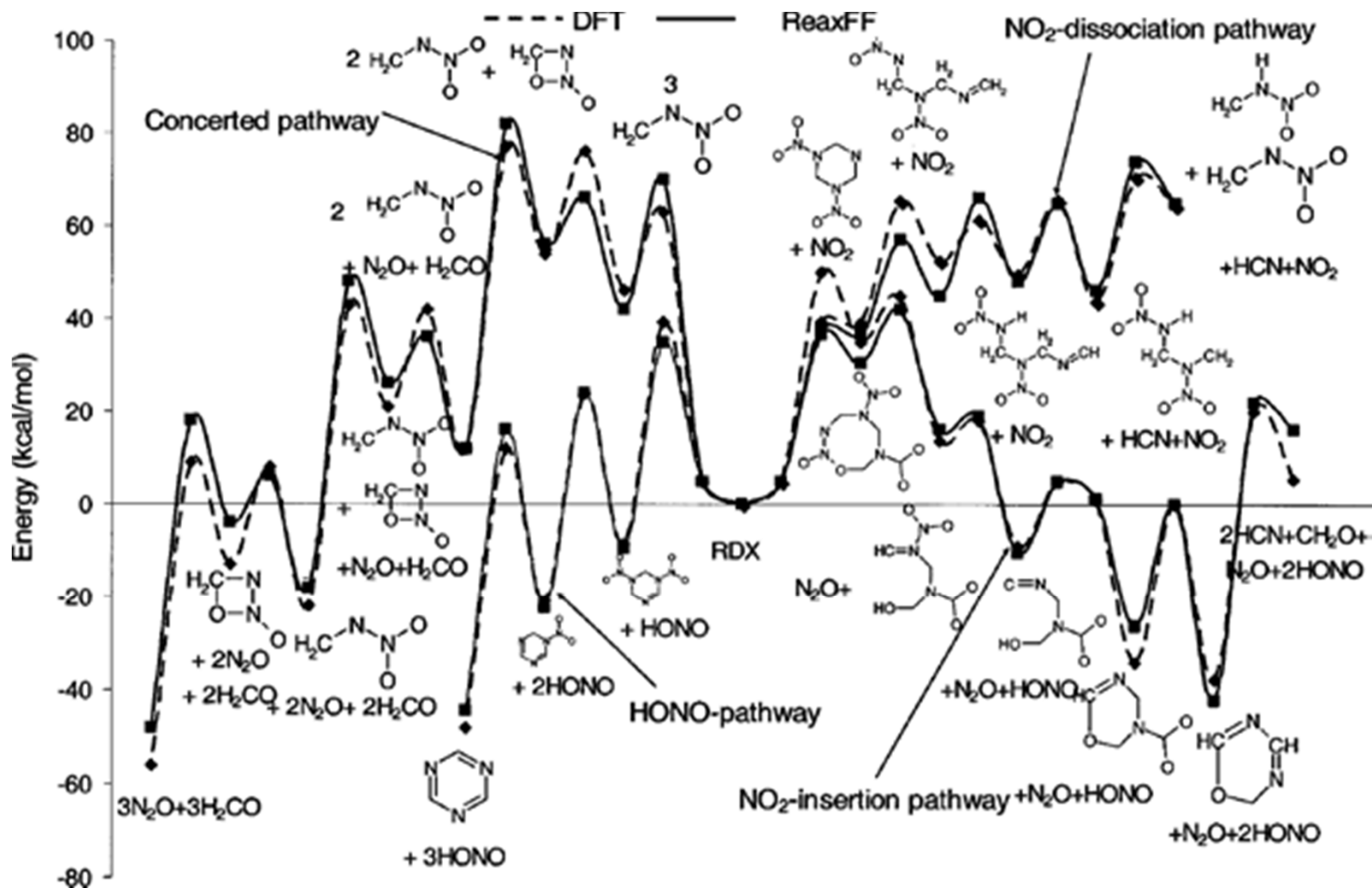
- Couple the molecular and structural nature of energetic materials to their respective properties and predict ingredient targets based on rational sensitivity and performance objectives.
- Diagnostic methods and measurements of performance and safety characteristics under detonation conditions are extremely limited, (ps/ns time frames, 300KBar pressures, 5,500 degree temperatures).
- The electronic and crystalline nature of today's bulk explosive ingredients cannot be altered, the materials must be replaced in order to achieve acceptable performance and mandated IM safety standards.
- Integrating energetic ingredient synthesis knowledge management, molecular design, and the nature of crystal packing/morphology prediction will provide target materials that resist extreme thermal or shock loading conditions at the molecular and crystal levels.
- Replace one of the six bulk commodity chemicals currently used in all military propellant and explosive applications (ammonium perchlorate (AP), trinitrotoluene (TNT), 1,3,5-trinitrohexahydro-s-triazine (RDX), 1,3,5,7-tetranitrooctahydro -tetrazocine (HMX), nitroglycerin (NG), nitrocellulose (NC)) is the only way to achieve IM compliance.

Relationships Between Molecular Dynamics and Bulk Material Sensitivity Emerging



B. M. Rice and J. J. Hare, "A Quantum Mechanical Investigation of the Relation Between Impact Sensitivity and the Charge Distribution in Energetic Molecules", B. M. Rice and J. J. Hare, *Journal of Physical Chemistry*, Vol. 106, 1770 (2002).

Energetics of Unimolecular RDX Decomposition Mechanisms



Energetics of unimolecular decomposition mechanisms in RDX obtained using the Goddard W.A, et.al. "Thermal decomposition of RDX from reactive molecular dynamics", J. Chem. Phys., 122 (5), 054502, (2005).



Empirically Derived Synthesis Hypotheses

Couple Empirical Hypotheses with Crystal and Molecular Modeling capabilities

- 1. Increase Inter and Intra Molecular Hydrogen Bonding:**
 - I. Challenge:** Impart high levels of hydrogen bonding/ Dipole inter to increase the molecular heat capacity and enhance Van der Waals molecular interactions.
 - II. Results:** This should allow the materials to dissipate the heat and shock loading in a manner other than covalent bond breaking and consequent hot spot formation leading to crystal deflagration/detonating.
- 2. Delocalize Electron Density in Nitro Groups:**
 - I. Challenge:** Design compounds in which the electron density is spread from the nitro groups to surrounding groups or atoms.
 - II. Results:** This increases bond order between the nitro group and the atom to which it is bonded; the resulting dissipation of localized charge density or distribution should render the molecule more stable.
- 3. Utilize Coulombic Attractions to Stabilize the Ground-State Structure:**
 - I. Challenge:** Stabilize the ground-state geometry by designing structures whose sigma or pi framework have alternating positive and negative charges.
 - II. Results:** Again this hypothesis will increase bond order throughout the atomic arrangement further stabilizing ground state energy



Empirically Derived Synthesis Hypotheses

Couple Empirical Hypotheses with Crystal and Molecular Modeling capabilities

4. Reduce the Number of Nitro Groups:

- I. **Challenge:** Impart stability to molecules, by including energetic oxygen functionality in groups other than nitro groups, such as N-Oxides.
- II. **Results:** The carbon/nitrogen/oxygen-nitrogen bond of a nitro group (nitrocarbon, nitramine, nitrate ester, respectively) is generally the weakest bond within and energetic molecule. Reduction or elimination of this functional group in favor of other nitrogen-oxygen combinations will afford improved molecular stability

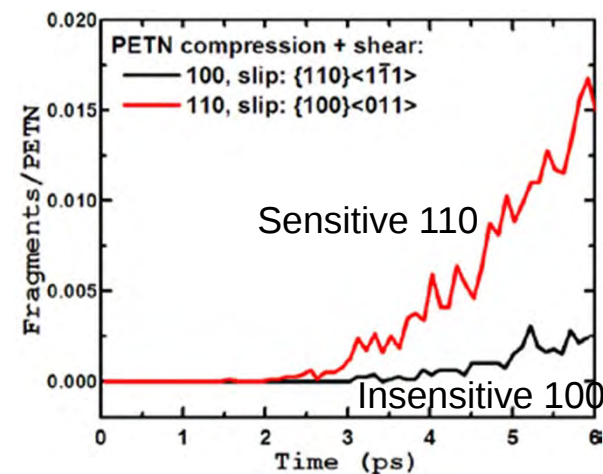
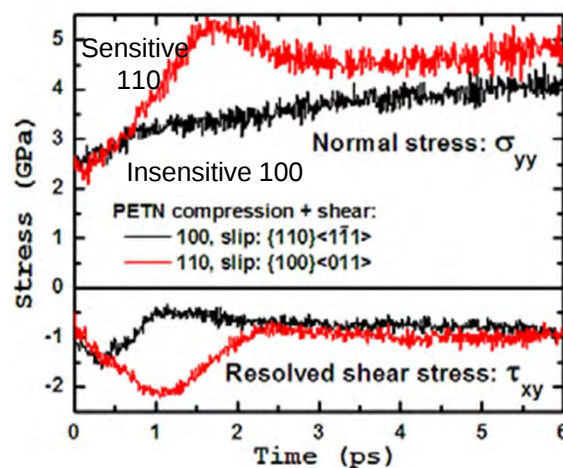
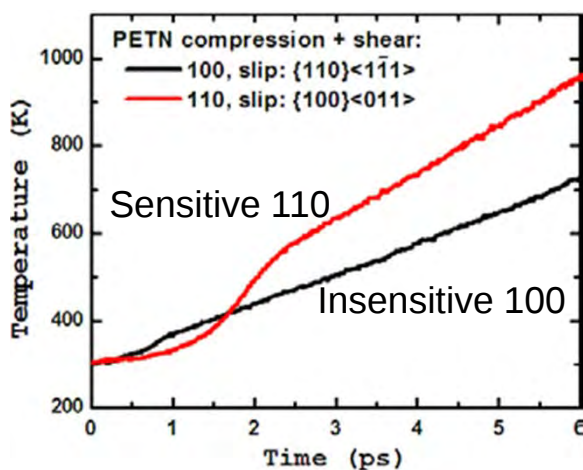
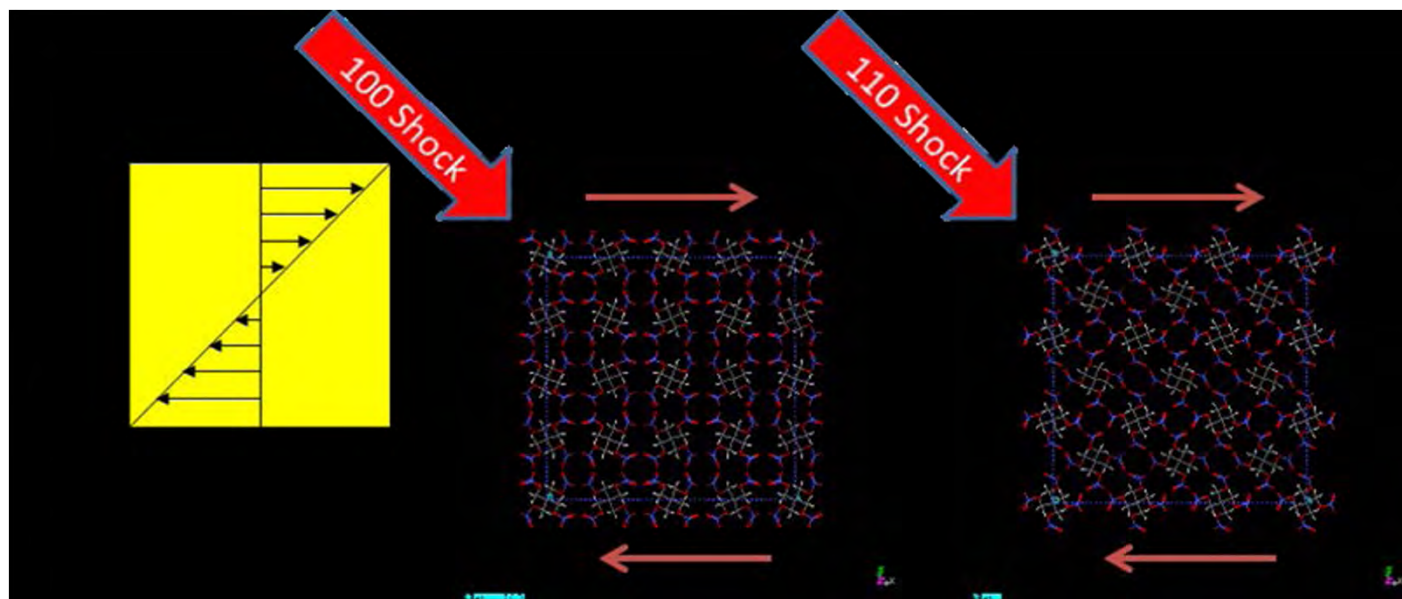
5. Avoid High Acidity:

- I. **Challenge:** Avoid high acidity by using imidazole, triazoles, tetrazoles and their six-membered ring counterparts rings and amination to block hydrogen.
- II. **Results:** Acidic hydrogen induce compatibility issues during formulation and processing stages.

6. Maximize Crystal Packing Planarity:

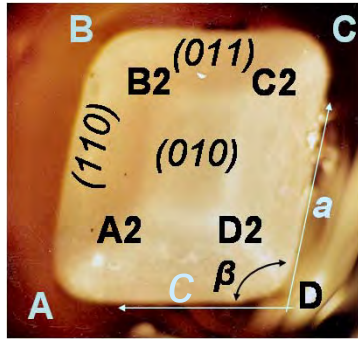
- I. **Challenge:** Design compounds with linear planar two dimensional atomic arrangements to minimize slip plane resistance to shock and shear ignition mechanisms.
- II. **Results:** Improved dynamic slipping will minimize atom/atom interactions significantly reducing the hot spot formation and heat dissipation into the crystal structure.

The Role of Crystal Anisotropic Shock Induced Effects Calculated and Validated

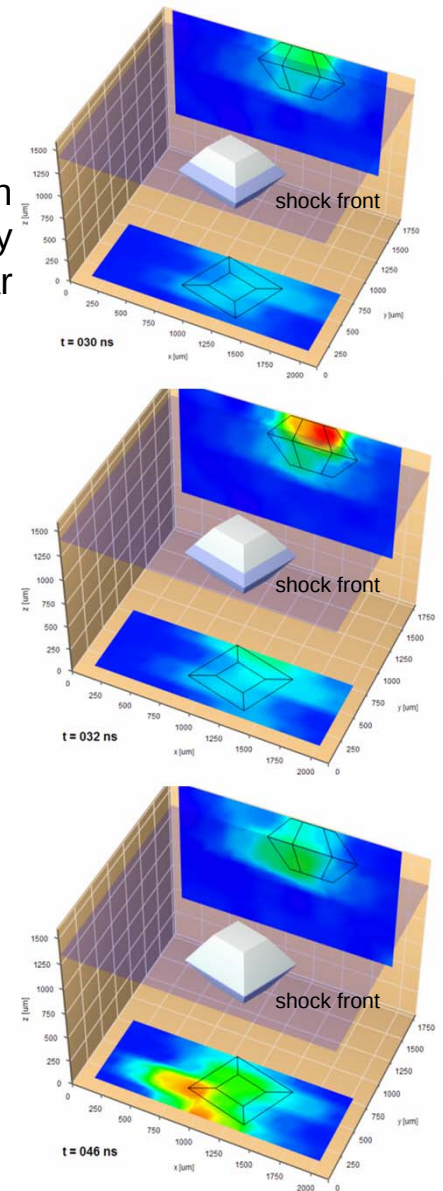
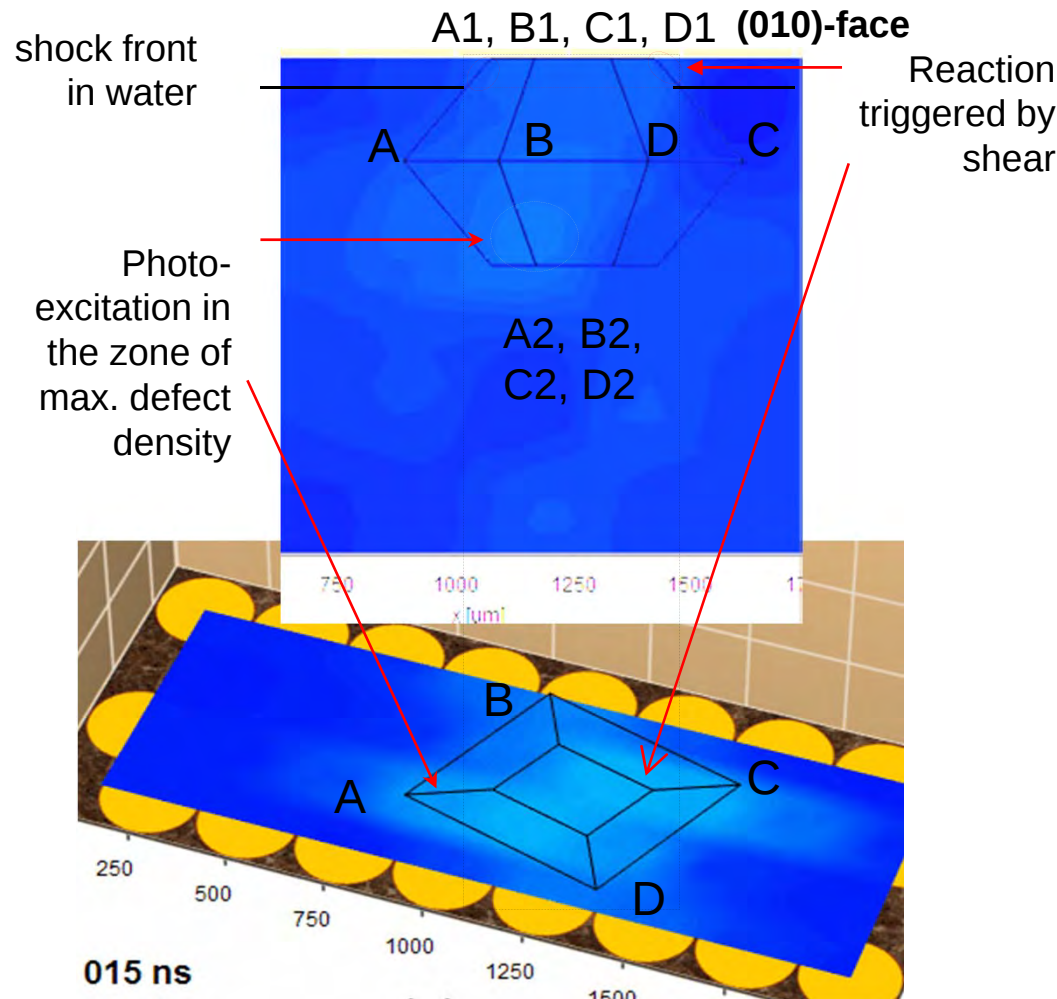


Dick et. al. J.Appl.Phys. 70, 3572 (1991); 76, 2726 (1994); Gupta et. al. J of Physical Chem., 114, 7038, 8099 (2010).

New Diagnostic Developments Offer Real Time Insights into Detonation and Propagation within EM crystals



Class-3 HMX particles,
 β -HMX crystal
 AB = 500-800 μ m
 A1A2 = 400-700 μ m (height)
 $\beta = 102^\circ \pm 1^\circ$ (exp.)



Igor E. Plaksin, et.al. numerous publications 2000-2010

Validation of the Hypothesis of Light Induced Band Gap Propagation of Detonation?



Coupling Computational Chemistry and Material Synthesis Meeting 21st Century Navy Requirements

Proposed Program Overview

- **Objective:**

- This Program Will Establish the Computational and Synthetic Chemistry Foundations Required to Target the Next Generation of Energetic Ingredients Capable of Resisting Inadvertent Thermal and Shock Loading Conditions.

- **Approach:**

- Couple Predictive Molecular Design, the Nature of Crystal Packing and Energy Dissipation Within Molecular Crystals (Hot Spot Formation) with the Expert Knowledge Base Existing in Organic, Organometallic and Inorganic Synthesis Chemistry of Energetic Materials Functionality.
- An iterative process will be developed through:
 - Step 1: Mature MD processes to include molecular thermal and conformational stability optimization at elevated temperatures. Predict energy levels for degradation process based on functional group analysis. Define crystal morphology at operational levels
 - Step 2: Integrate MD processes with Crystal lattice and Crystal morphology prediction through Crystal structure validation to minimize shock and thermal initiation mechanisms and effects in future EM material designs.
 - Step 3: Combine synthetic chemistry knowledge management and compound synthesis validation with MD computational support for future EM target selection.



Coupling Computational Chemistry and Material Synthesis Meeting 21st Century Navy Requirements

Proposed Program Overview

- **Purpose:**

- Establish the fundamental science to provide the Navy with Safe, Cost-effective Ordnance; Ordnance with Precision and Adaptable Effects to Enable Smaller Weapon Systems

- **Challenges:**

- Establish the Connectivity Between Molecular Structure, Crystal Morphology prediction and Synthesis Chemistry to Provide IM Compliant Energetic Ingredients Shock and Thermal Sensitivity.
- Focus MD Modeling and Simulation to Prediction Stable Crystal Structures/ Crystal Morphology which are Currently Poorly Understood
- Establish Methodologies to Model, Measure and Predict Molecular and Crystal EM Response to External Shock and Thermal Modeling
- Nascent Validation of Design Criteria for Molecular Stability as a Function of Insensitivity

- **Status Of Current Technology:**

- There are Currently No Munitions In The Department Of Defense Which Meet The Insensitive Munitions Requirements Of Mil-std-2105d



Technology Is Applicable To Reduce Sensitivity For All Classes Of Weapons In The Fleet

Significant Breakthroughs Will Provide Industry and The Service PEOs Ingredients That Meet 21th Century Warfighting Needs And

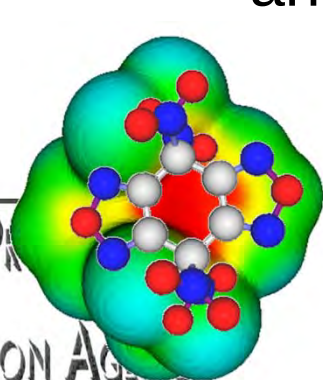
- Provide the weapons safety mandated by the MIL-STD-2105D
 - ✓ Ensure energetic materials are insensitive to external stimuli
- Maintain weapon lethality requirements.
 - ✓ Ensure Detonation pressures are maintained
- Increase Range and first strike capabilities
 - ✓ Maintain or Increase I_{sp}
- Provide substantial life cycle cost savings
 - ✓ Eliminate Exotic Packaging, Handling and Storage Requirements

Enable Design Technologies to Predict Chemical and Physical Properties of EM

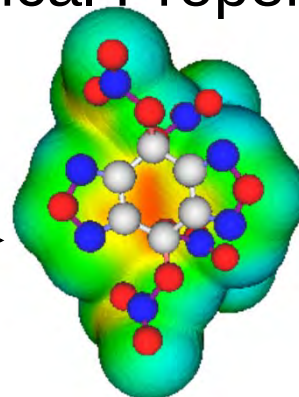


CHEMICAL PHYSICS
INFORMATION AGENCY

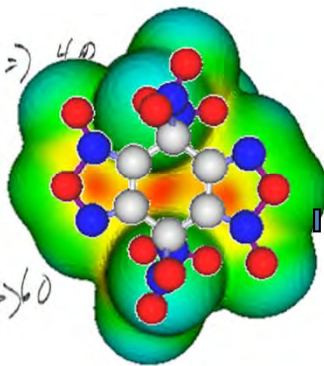
ΔH_{CH}



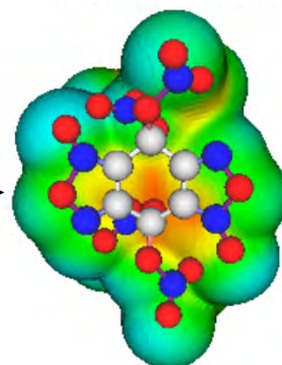
$\rho \text{ (g/cc)} = 2.002$
 $\Delta H_f = 107.7 \text{ kcal/mol}$



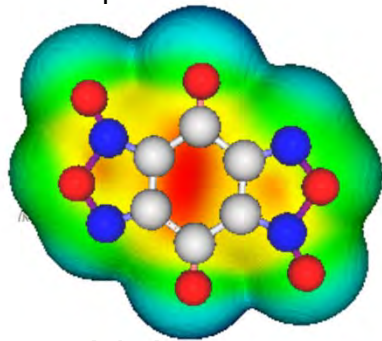
$\rho \text{ (g/cc)} = 2.045$
 $\Delta H_f = 49.8 \text{ kcal/mol}$



$\rho \text{ (g/cc)} = 2.045$
 $\Delta H_f = 98.4 \text{ kcal/mol}$



$\rho \text{ (g/cc)} = 2.088$
 $\Delta H_f = 43.0 \text{ kcal/mol}$



$\rho \text{ (g/cc)} = 1.912$
 $\Delta H_f = 32.5 \text{ kcal/mol}$

Initial Concept:
 Comparatively easy to
 predict molecular stability
 to determine if synthesis is
 warranted.

Postulation:
 Replace Nitro NO_2 Functional
 Group with Nitrato ONO_2
 Functional Group

Results:
 Molecular Dynamic Conclusion
 Improved Electron density
 distribution in Molecule

Challenge:
 Activation energy for N_2O_5
 Formation from Geminal Dinitrato
 Functional Arrangement
 Not Consider in MD Assessment

Solution:
 Couple Synthesis and Quantum
 Chemistry to Resolve Temperature
 And Fundamental Knowledge
 Management Issues



Establish Teaming Groups that Bridge Both Fundamental Research Environments

Organic, Organometallic, Inorganic
Synthesis Chemists



University of Idaho

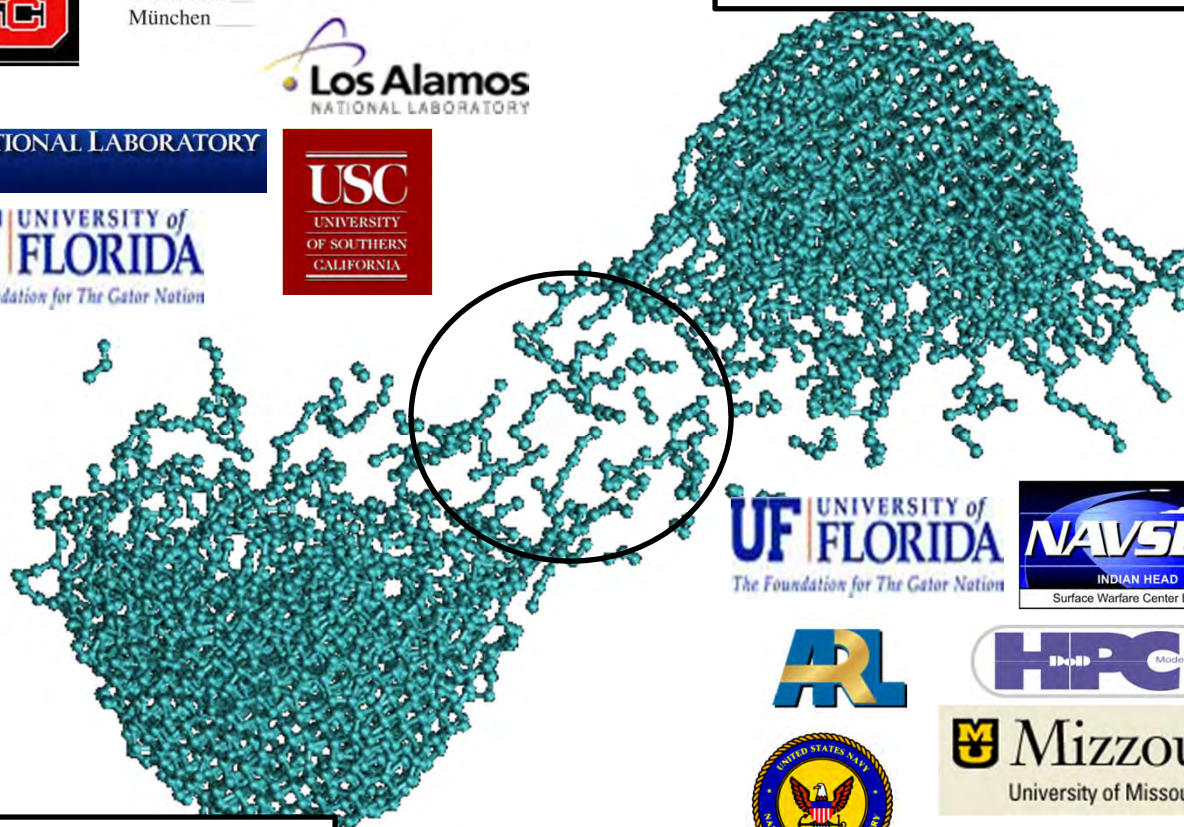


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Modeling and Simulation
Chemists and Physicist



CALTECH



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Questions