R1-D.1: Theoretical Modeling Considerations

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II. PROJECT DESCRIPTION

A. Project Overview

Since July 2013, we have significantly enhanced our understanding of improvised explosives and improved our simulation capabilities. The main topics we studied in this project are described below:

A.1. Explosive Detection Using 2D THz Spectroscopy

The theoretical research effort during the first two years (of Phase II) resulted in a few suggestions of new methods and methodologies. For example, a novel THz spectroscopy signature for explosive materials was described. The method is based on a new and reliable methodology of simulation based on calculation of the absorption bands of complex molecular crystals. The new detection method suggested by this theoretical study employs 2D spectroscopy using polarized THz light as a unique and reliable method to obtain high specificity in the THz spectroscopy of explosives. This study is a first of its kind and we hope that its predictions will be examined experimentally.

A.2. The Role of Nanometer Size Defects-Simulations Using a New Efficient Methodology

Another new methodology developed in this project is an approach to accurately describe energetic materials (solid or liquid) at their Chapman-Jouguet (C-J) conditions. This task usually requires use of very large molecular systems; consequently, very large computational power is required. The newly developed methodology allows the simulated explosive to reach the C-J state of the energetic material using a very short simulation. Once the C-J state is reached, the simulation continues for a relatively long period that allows us to study the complex reactive events occurring at the C-J state. Additionally, the new methodology can be applied to a much smaller system. This methodology was applied to study the role of nanometer size cavities...
in Erythritol tetranitrate (ETN). Schematic description of the ETN system studied and the new methodology are shown in Figure 1.

![Figure 1: Cut-plane view of the initial equilibrated state (left). The system is composed of two identical slabs of material 2 Å apart from each other. In each slab, all the molecules residing within a sphere of a defined diameter (5 nm) are removed to form a nanoscale spherical void and the symmetric plate impact methodology is carried out. Cut-plane view of the system a few picoseconds after the two identical slabs collided and generated two oppositely propagating shock waves (right). Atoms are colored by the magnitude of their velocity, and shock propagation is in the (100) direction.](image)

The results of the simulations (see Fig. 2 below) prove that these small cavities act as hot spots just like much larger (1-100 micrometer) cavities. Moreover, the same mechanism is responsible for the overheating of the cavity region in the two cases.

![Figure 2: Temperature evolution during shock initiation of ETN: Single crystal ETN (left); and ETN with a nanovoid of 5 nm diameter (right). Black dots mark the position of the nanovoid in both parts of material.](image)

A.3. New ReaxFF Parameters for Two Explosives

New reactive force fields (for both HN$_3$ and ETN) were developed and allowed us to study the detonation dynamics of these two explosives. The theoretical study of these explosives yields results related to these explosives' thermodynamic, kinetic, and spectroscopic characteristics, as well as evaluation of their detonation sensitivity and performance.

A.4. Laser Pulse-Induced Ejection of Molecules

A model describing the mechanism that operates during the interaction of intense short laser pulses with thin explosive layers on a solid substrate was developed. The model allowed us to understand the mechanism that is responsible for the ejection of intact explosive molecules upon laser irradiation. The simulations show that a model in which the laser irradiation induces a shock wave that hits the thin film correctly describes the experimental data. A schematic illustration of the mechanism is presented in Figure 3 (on the next page). The conditions required for this process were determined and will allow an optimization of molecular ejection. These results may have important implications on explosive detection methods.
A.5. **Decomposition Routes of HMTD**

![Diagram of HMTD decomposition](image)

Figure 3: Interaction of an intense, non-resonant, ultrashort laser pulse with a metal surface generates an outward propagating shockwave. A solid TNT sample, transparent to the laser, experiences a mechanical impact on a femtosecond time scale due to a plasma plume formation and supersonic expansion.

Extensive QC calculations on the decomposition of Hexamethylene triperoxide diamine (HMTD) in different environments has been carried out. This study was part of a collaboration with the ALERT projects (R1-A.1, R1-B.1, and R1-C.2) of Dr. Jimmie Oxley and Dr. James Smith. The joint study yielded an efficient and safe route to decompose large quantities of HMTD. The possible decomposition pathways of HMTD in different environments are shown, with the energy barriers involved, in Figure 4 below. The destruction method proposed can be used by end-users such as the police bomb squad and other law enforcement units.

![Diagram of HMTD decomposition pathways](image)

Figure 4: Scheme showing all the possible initial decomposition steps of a HMTD molecule in different environments.

A.6. **Detonation of Liquid Mixtures**

During Year 4, we started a comprehensive study of liquid explosive detonation. The study considers pure nitromethane as well as its mixture with other liquids (both oxidizers and fuels) at various ratios. The additives considered are: acetone, ethanolamine, methanol and hydrogen peroxide. The main goal of this study is to understand the role of the various additives on sensitivity and detonation performance. The simulations, performed at the C-J states of these mixtures using the methodology described above, show that prior to detonation these systems have an incubation period. During this incubation period, low rate decomposition reactions are observed; at the end of this period, the reaction rates increase dramatically resulting in large energy release. This starts the detonation stage. However, the incubation periods observed for identical systems with different initial atomic positions and velocities can vary appreciably. This is manifested in the rate of parent nitromethane decomposition of an 80:20% mixture of NM and acetone (see Fig. 5 on the next page). To examine the local temperature in the system at various regions and its variation with time, the simulation volume was divided into 3x3x3=27 sub-volumes and the local effective temperature in each was evaluated.
The 27 sub-volumes are presented along the horizontal axis in Figure 6 while time evolution is along the vertical axis. The 2D distributions obtained for the 9 systems shown in Figure 5 are presented in Figure 6 below. The incubation periods and their variation are clearly seen as the width of the green regions. Also, the transition to detonation is clearly observed as the boundary between the green and yellow regions.

Figure 5: NM disappearance during three shock velocities. For each shock velocity, three identical simulations are shown.

Figure 6: 2D description of the local temperature variation in the reaction volume during the simulation. Three identical simulations using shock velocity of $v_{\text{shock}} = 7.8$ Km/sec (top row), $v_{\text{shock}} = 8.0$ Km/sec (middle row), and $v_{\text{shock}} = 8.2$ Km/sec (bottom row). The temperature scales are identical and span the range of 300K (blue) up to 5300K (red).

It is clear that decomposition reaction of NM should start simultaneously in a few cells to obtain the transi-
tion into detonation stage. Thus, it seems that these liquid mixtures exhibit a similar behavior to solid explosives and require hot-spot formation to transform from burning to the detonation stage. At present, we are trying to understand the physical/chemical nature of these “hot spots” in the liquid.

We recently began to investigate the reaction pathways and energy barriers involved in detonation of hydrogen peroxide mixed with different fuels. The first system we examined is a mixture of $\text{H}_2\text{O}_2$ and urea. The system was studied using QC calculations at the Density Functional Theory (DFT) level of theory. The first system examined is a mixture of hydrogen peroxide with urea. The calculations were aimed at the understanding of the reaction mechanism that is responsible for the urea decomposition and formation of detonation products. Preliminary results indicate that the decomposition of a urea molecule is required to overcome an initial energy barrier of about 42 kcal/mol to obtain intermediates. This is followed by an additional barrier of 59 kcal/mol to achieve further decomposition. The reaction between one urea and one $\text{H}_2\text{O}_2$ molecule is required to overcome an initial energy barrier of only about 11 kcal/mol; however, further steps to obtain stable product are required to overcome a high energy barrier of approximately 60 kcal/mol. In the case that two $\text{H}_2\text{O}_2$ molecules react with one urea molecule, the reaction can reach completion by surpassing a barrier of only about 14 kcal/mol. These results indicate that detonation can easily occur when the molar ratios of hydrogen peroxide and urea exceed 2:1. This study continues at present and will be extended to mixtures of $\text{H}_2\text{O}_2$ and sugar.

A.7. Homemade Plastic Explosives

An additional system we plan to study in the near future involves the mixture of potassium chlorate and wax. Through simple procedures, potassium chlorate can be used to synthesize homemade plastic explosives when mixed with wax. This homemade explosive (HME) is a high-energy material that can be molded to the desired shape with a density of about 1.3 g/cm$^3$. A milestone to be achieved in this case will be the determination of the detonation characteristics of mixtures of hydrogen peroxide with urea and formaldehyde at a variety of compositions. These two types of mixtures are detonable and our main focus will be on understanding the mechanism governing the process and the variation of sensitivity to detonation as a function of mixture type and components ratio.

B. Year Two (July 2014 through June 2015) Biennial Review Results and Related Actions to Address

The previous Biennial Review indicated that DHS has no interest in THz spectroscopy, hence, this aspect of the project was suspended. All our efforts were channeled, according to the interest of DHS, into the study of HMEs. The advancement of these directions are described above.

C. State of the Art and Technical Approach

The theoretical studies concentrated on two methods: quantum chemical (QC) calculations and reactive molecular dynamics (RMD). These methodologies are constantly being developed and can be implemented using either commercial (QC) or open source (RMD) codes. For the QC calculations, we primarily used the Gaussian 09 commercial code [1]. In most of the implementations in this project, we employed DFT level theory with various functionals and basis set that are suitable for the problem studied. We did comparative studies using different functionals.

In the case of RMS simulations, considerable methodological development was required. In all our studies the open source code LAMMPS was used [2]. Here one has in many cases to develop new implementation methodologies or force fields that are suitable to investigate the problem in question. A number of such new methodologies were developed by us during this project. Some of these were already described above: 1) a method to calculate THz spectra of molecular crystals was developed by us and its implementation to TATP and RDX were published [3]; 2) A simple scheme that allowed us to obtain the C-J state of explosive materials rapidly and using relatively small systems was applied in the study of nanometer vacancies in ETN [4] and
is also implemented in the study of liquid explosives; and 3) two new reactive force fields were developed in this project, one for the HN$_3$ system [5] and the other for ETN [4,6]. In addition to these, we have developed a new code for the efficient analysis of RMD data. This approach is based on graph theory and allows us to search the LAMMPS output to identify the species at any given moment of the simulation. This method allows for efficient analysis and search capability of the very large amounts of data obtained in big simulations of the detonation of energetic materials.

At present, we are in the process of developing a new approach that will allow for an efficient construction of reactive force fields (ReaxFF). At the moment, the development of ReaxFF for new systems constitutes two stages: 1) QC calculations of geometries, and energies of a large number of reactant configurations, intermediates, bi- and tri-molecular processes, etc; and 2) the development of an accurate ReaxFF, namely, to obtain the parameters that reproduce the QC data. This stage, in most cases, is extremely complex and involves a very long development period. Our new approach is based on the use of population to search parameter space to obtain the global minimum. The search is based on the Particle Swarm Optimization (PSO) algorithm with a number of improvements that markedly reduce search time and increase the probability to locate the lowest minimum.

As far as we know, we are the only group in ALERT that performs theoretical studies as those described here.

D. Major Contributions

The major contributions of this project to date include:

- Year 4:
  o New ReaxFF parametrization for solid Erythritol tetranitrate (ETN) HME.
  o Detonation properties of liquid mixtures.

- Year 3:
  o The role of nano-size defects simulation using a new methodology.
  o Deciphering the mechanism of laser induced ejection of molecules.

- Year 2:
  o New ReaxFF parametrization for liquid HN$_3$.
  o Determining the decomposition routes of HMTD for safe disposal.

- Year 1:
  o Explosive detection using 2D THz Spectroscopy.
  o Characterization of TNT detonation mechanism: bimolecular pathway.

E. Milestones

Milestones accomplished in Year 4 include:

- ReaxFF parametrization for solid Erythritol tetranitrate (ETN) HME.
- Theoretical and experimental characterization of Erythritol tetranitrate (ETN) HME detonation.
- Study of liquid HME mixtures based on nitromethane (in progress; will complete in Year 5).

Milestones to be achieved in Year 5:

- Complete the study of liquid HME mixtures based on nitromethane.
- Theoretical and experimental study of the stability and decomposition mechanism of improvised explo-
sives based on nitrated sugars.

- Development of a new methodology for ReaxFF parametrization and its implementation to include dispersion forces in the force field for HN$_3$.
- Sensitivity and decomposition mechanism of HMEs based on hydrogen peroxide mixtures with urea or sugar.

F. Future Plans

If additional funding for this project becomes available (Year 6), we plan to address the following issues:

- Characterize, using theoretical methods, the sensitivity and detonation mechanism of homemade plastic explosives: mixture of wax with KClO$_4$.
- Write a comprehensive overview of the physical and chemical properties of HMEs studied during the period of this research (jointly with Dr. Jimmie Oxley's group). This overview will address information required by law enforcement units (bomb squads, etc.).

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

One of the main challenges in dealing with the threat of terror is the appearance of unknown improvised explosives. There is a need for rapid assessment of the yield, sensitivity, and safe disposal of these explosives. In addition, procedures for detection, specifically, remote detection if possible, are needed. We suggest using computational methods as a first rapid response to these threats. We have the capability to supply such data without having to synthesize the hazardous material, which is time consuming and dangerous.

Our immediate goal is to advance our computational methods to address the potential hazard of explosive liquid mixtures. Currently, these liquids are hard to detect and their explosive properties are difficult to predict.

B. Potential for Transition

As a theory group, our task is to develop simulation and computational tools to be used as a base for rational design. Our tools will support experimental efforts. Our end-users are researchers, government agencies and companies involved in security.

Computer simulations are, in most cases, the fast lane for the evaluation of unknown improvised explosives and compositions (IECs). QC and RMD calculations can identify fundamental properties, such as the detonation mechanism and yield of new materials. Experimental studies are time consuming, expensive, and potentially dangerous. Specifically, the results of the theoretical research described above can be used to guide and focus experimental efforts to synthesize, characterize, and detect materials such as IECs. For example, we have collaborated with R1 Thrust Leader, Prof. Jimmie Oxley and her colleagues to validate the mechanisms of synthesis and degradation of new explosives by combining simulations and experiments.

C. Data and/or IP Acquisition Strategy

The datasets developed for modeling will be put in public domain as supplement material.

D. Transition Pathway

Computer simulations are essential for rapid response to unknown improvised explosives. Such simulations can identify fundamental properties, such a detonation mechanism and yield of new materials. Experimental
studies are time consuming, expensive, and dangerous. Specifically, the computational results can be used to guide and focus experimental efforts to characterize materials such as HMEs. The direct outcome will be potential parameters which can be used with standard simulation platforms such as LAMPS.

E. Customer Connections

The connections to DHS, TSL, and TSA are strong. To date, the FBI is the major agency outside of DHS which is aware of the details of this project.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Peer Reviewed Journal Articles


Pending-


B. Peer Reviewed Conference Proceedings


C. Software Developed


V. REFERENCES


