R1-D.1: Theoretical Modeling Considerations

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II. PROJECT DESCRIPTION

A. Overview and Significance

The theoretical effort at the Hebrew University and the Ben-Gurion University is aimed at obtaining an in-depth understanding of the characteristics of new explosive materials. This is in addition to assisting the experimental investigations within ALERT in deciphering reaction mechanisms. The theoretical methods are based on ab-initio quantum chemical (QC) calculation and ab-initio molecular dynamics (AIMD). For simulating larger molecular ensembles, reactive molecular dynamics (RMD) methods were employed. These computational methods have been applied successfully in the study of explosive materials from a molecular point of view. The main sub-projects investigated at present include:

1. Understanding the influence of hot spots and shear forces on the explosive sensitivity.
2. Establishing the relationship between oxidizer-fuel ratios in homemade explosives (HMEs) detonable mixtures. The system chosen is HN₃ and its mixtures with water.
3. Calculating accurate equations of state for different HMEs using RMD and AIMD calculations. The outcome can be used as input in thermodynamic codes such as CHEETHA.
4. Employing QC calculations to understand the decomposition process of HMEs in different environments (pH dependences). These types of calculations assist in the design and assessment of additives to oxidizers (such as H₂O₂) that will prevent using these oxidizers for the synthesis of HMEs.
5. Studying spectroscopic characteristics of explosives that could assist in developing protocols for stand-off detection schemes.
6. Studying the interaction between short, intense laser pulses and thin films of explosives and understanding the basic mechanisms that lead to parent molecule ejections. This will allow optimization of detection schemes based on the laser ablation process.

During the last two years, we have laid the foundations for sub-projects number 1, 2, 3 and 6. A new ap-
approach, based on RMD, to calculate the THz spectra of two military explosives, was developed. The results suggested that a 2D spectroscopic method using polarized THz radiation can be used to obtain high specificity in explosives detection.

The study of the detonation of pure liquid explosive HN$_3$ has been initiated by the development of an accurate reactive force field. This stage required extensive QC calculations on both single and bi-molecular systems. The first step consisted of the development of RMD-based methods to study the role of hot spots (voids and grain boundaries) during the initial stages of detonation. This issue is associated with the sensitivity of energetic materials and can contribute to the design of new insensitive explosives. The reactive force field (ReaxFF) developed was used to obtain thermodynamic and kinetic parameters for this complex system. The results are being summarized as a research paper. The ReaxFF will be extended to include mixtures of water with HN$_3$.

We have developed a new methodology that allows simulation of energetic materials at their C-J conditions (the C-J temperature and pressure) for long periods of time (up to nano seconds). This approach was applied to studying the role of hot spots on the sensitivity of ETN, a new HME. The methodology will be extended to study the role of shear forces on explosive sensitivity and compare them with the existence of hot spots.

During the present year we had a very fruitful collaboration with the Oxley-Smith group at URI related to the decomposition of HMTD (sub-project number 4 above) for Project R1-A.1. The experimental study at URI was accompanied by extensive QC calculations to reveal the decomposition mechanism of HMTD in different environments. This collaboration led to a thorough understanding of HMTD decomposition routes, the energy barriers involved and the main decomposition products obtained. The results of this joint study are summarized at present as a research paper (see Section VI.A.2).

Lastly, we carried out model calculations of the short laser pulse ablation of thin explosive layers. This approach has been demonstrated experimentally to lead to ejection of parent explosive molecules without substantial decomposition. Our simulations, using RMD, revealed two main mechanisms that explain the experimental observations. The results of this study are summarized at present as a research paper (see Section VI.A.1). The results obtained in the calculations allow the optimization of molecular ejection from the irradiated film. This will assist in the design of efficient detection methods based on mass spectroscopy.

B. State-of-the-Art and Technical Approach

As described in the overview above, the research effort during the past two years led to a number of new methods and methodologies. In the case of THz spectroscopy [1 and 2], the reliable calculation of absorption bands is extremely difficult due to the complex systems involved. Moreover, no reliable method for spectral features assignment exists. The approach we developed is unique and can be easily implemented. Moreover, the use of 2D spectroscopy utilizing polarized THz light may serve as a unique and reliable method to obtain high specificity in THz spectroscopy of explosives. We do hope the new approach suggested by the theoretical calculation will be examined experimentally by one of the groups in the HSE and, if proved to work, be developed as a new detection method.

Modeling methods are based on the ReaxFF molecular dynamics approach. Currently, this is the only approach that allows to reliably model chemical reaction in the bulk at high temperatures and pressures. This method has been used by our group and others to develop an implementation for a number of new energetic materials [3-6]. The description of energetic materials at their C-J conditions requires the use of very large molecular systems, hence, very large computational power is needed for their implementation. The new methodology we suggested allows one to reach the C-J state of the energetic material studied by a short simulation. Once the C-J state is reached, one can continue the simulation for a long period to study the complex reactive events that occur at the C-J state. This methodology allows us to use much smaller system sizes in the simulation and to obtain a marked reduction in computer resources.
The development of a new reactive force field (for HN₃ and ETN so far) allows us to study new explosive compositions and mixtures and evaluate their sensitivity.

Mastering the theoretical methods based on the molecular description of the energetic materials allows us to assist the experimental groups in ALERT to obtain a better understanding of the systems studied. This is an ideal situation that allows strong collaboration between experimental and theoretical investigations.

C. Major Contributions

Contributions in Year 1 and 2:

- Development of a new methodology to study the role of structural defects on explosive sensitivity. This contribution is in its early stages and we will extend it to include shear forces.

- Development of a new computational method to calculate the THz spectra of solids. This contribution has impact in two directions: first in the assignment of the THz spectral feature to various modes of the system studied. The second direction is to develop a new detection method with high specificity of explosive using polarized THz light in a new 2D spectroscopy.

- The QC calculations allow for a detailed understanding of HMTD decomposition at different pH values.

- The development of new, improved reactive force fields for both HN₃ and ETN allows us to carry out the thorough study of two new types of systems. In addition, this is the first step of a detailed study of oxidizer-fuel mixtures in the liquid state.

D. Milestones

- The completion of the RMD methodology of simulation explosives at their C-J states needs to be extended to also include the role of shear forces on explosive sensitivity.

- The extremely rapid detonation of HN₃ together with its unique structure due to the hydrogen bonding in the system, suggests that this system may show the behavior of weak detonation. This type of detonation has been predicted to exist theoretically but was not observed yet in any realistic system.

- The development of a water-HN₃ reactive force field will enable us to study in detail the mechanism that lead to detonateability in such mixtures (mixtures up to a ratio of 1:1 are detonateable).

E. Future Plans

During Year 3, we intend to focus on the following directions:

1. Complete and summarize the sub-project number 6 (in the list above) related to laser ablation of thin explosive layers. Two mechanisms were examined: creation of a shock wave in the metal substrate and direct heating of the film-substrate interface. In both cases, one can obtain parent molecule ejections at the surface. When a shock wave is formed at the metal substrate surface, due to the rapid melting of the metal outer layer, various size clusters are ejected from the film. Most of the clusters are ejected following high compression that results in emission of molecules as shown below in Figure 1 on the next page.

   The other possible mechanism is the rapid heating of the explosive film at its interface with the metal substrate. The results obtained from the interface rapid heating to different temperatures after the 20 picoseconds (ps) simulation are presented in Figure 2 on the next page. The temperatures used here were 1500K (top), 2000K (middle) and 2500K (bottom). In all three cases, very little decomposition is observed and increasing amounts of ejected molecules are seen.
2. We intend to carry out additional simulations of hot spots in ETN and to extend the methodology developed this year to include shear forces. The induction of shear forces will be accomplished by using a non-symmetric collision between two slabs that will result in the induction of shear tension. We will employ a non-symmetric collision model along different crystallographic planes to examine the importance of shear orientation on the explosive sensitivity.

3. We plan to continue our study of HN$_3$ detonation in two directions. The first will examine the possibility that a weak detonation is developed in the solid crystal. The solid state of HN$_3$ is much denser than the liquid phase and has a highly ordered structure as shown in Figure 3 on the next page. This structure is a result of the large number of hydrogen bonds in the system. This highly ordered structure with chains of ......N$_3$-H......N$_3$-H...... (heavy-light-heavy masses) together with the extremely rapid detonation velocity constitutes a system with the high probability to show the weak detonation phenomena.

Figure 1: Clusters ejected following a shock wave with velocity of 6 km/sec. The left frame is after 20 ps and the one on the right is after 100 ps.

Figure 2: Snapshots after 20 ps simulations of the explosive film to temperatures of 1500K (top), 2000K (middle) and 2500K (bottom).
The research direction associated with HN₃ requires the extension of the ReaxFF developed to include interaction and reaction of HN₃ with water. Once this goal is accomplished, the detonation mechanism will be studied for various mixtures. This study will yield a detailed understanding of mechanism changes in the detonation of mixtures with different amounts of inhibitors (water in this case). These type of simulations are directly related to the understanding of “detonation poisoning” by inhibitors.

4. Use of AIMD calculations together with RMD calculations to obtain the equation of state of new explosives and HMEs. We will be happy to collaborate on this topic with the experimental group performing anvil diamond cell measurements, project R1-A.2 led by Choong-Shik Yoo at Washington State University.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

1. The theoretical calculations assisted the experimental group of Prof. Jimmie Oxley in understanding the mechanism of HMTD decomposition for project R1-A.1.

2. The detailed understanding of laser ablation processes is expected to assist development of efficient sampling methods.

B. Potential for Transition

The results obtained in the fundamental theoretical studies we perform have a significant transitional and collaborative relationship with users such as Prof. Jimmie Oxley and other experimental groups (i.e. in national labs) who can use our results to guide their scientific work.
C. **Data and/or IP Acquisition Strategy**

In the future data may come back from our transition partner that might assist us in our modeling. IP is more likely generated by our experimental transition partner.

D. **Transition Pathway**

The use of computer simulations can identify optimal pathways for validating fundamental properties of the new materials. Specifically these results can be used by groups that are developing experimental methods to characterize materials such as homemade explosives. Simulations are commonly used to guide experimental design. For example, we have collaborated with Prof. Jimmie Oxley and her colleagues to validate the mechanisms of synthesis and degradation of new explosives.

E. **Customer Connections**

It is not likely that our models will be commercialized, but our experimental transition partner may commercialize results that are derivative.

IV. **PROJECT DOCUMENTATION**

A. **Peer Reviewed Journal Articles**

Pending-


2. Jimmie C. Oxley; James L. Smith; Matthew Porter; Lindsay McLennan; Kevin Colizza; Yehuda Zeiri; Ronnie Kosloff; Faina Dubnikova, Mechanisms of Synthesis and Degradation of Hexamethylene triperoxide diamine (HMTD), In preparation (2015).

B. **Other Presentations**

1. Seminars
   a. Seminar by Yehuda Zeiri: Physical Chemistry seminar in the Chemistry department of Indiana State University at Bloomington (April 2, 2015).

V. **REFERENCES**


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