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 ALERT 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 calculation. 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). The results of the simulations prove that nanometer size 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 both cases.

A.3. New Reactive Force Fields (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. The conditions required for this process were determined and will allow optimization of molecular ejection. These results may have important implications on explosive detection methods.

A.5. Decomposition Routes of HMTD

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 of Dr. Jimmie Oxley and Dr. James Smith at the University of Rhode Island (Projects R1-A.1, R1-B.1, and R1-C.2). The joint study yielded an efficient and safe route to decompose large quantities of HMTD. The possible decomposition pathways of HMTD in different environments were examined in detail and allowed to develop an efficient destruction approach. The destruction method proposed can be used by end-users such as the police bomb squad and other law enforcement units.

A.6. Detonation of Liquid Mixtures

In 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 examined are: acetone, ethanolamine, methanol, and hydrogen peroxide (H_2O_2). The main goal of the study is to understand the role of the various additives on sensitivity and detonation performance. In Year 5, it was found that these liquid explosives exhibit an initial incubation period followed development of the detonation wave that is accompanied by temperature and pressure rise. The rate of energy release during the detonation, as characterized by the rate of temperature rise, is shown in Figure 1 for all the systems examined.
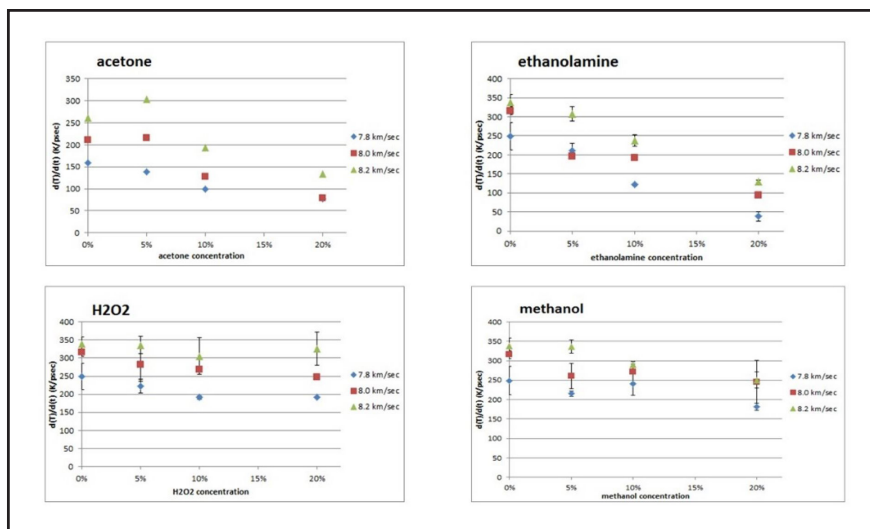
Figure 1: Rate of temperature rise during detonation at three shock velocities of nitromethane mixtures with four additives at different molar concentrations. The shock velocities examined were: 7.8, 8.0, and 8.2 km/sec.

It is clear that in all cases increasing the amount of additive leads to a reduced rate of temperature increase. For hydrogen peroxide this decrease in T rise rate is very small, while for ethanolmine it is the largest. In the case of acetone, the addition of a small amount (5%) leads to an increase in heat release rate.

It has been shown that when energetic materials are heated rapidly (as when a shock wave passes through the material), there is a short period during which translational energy is converted into molecular internal energy. This gives rise to an endothermic stage that is due to the initial steps of molecular decomposition. Examination of the potential energy of the system defines the end of this stage. Hence, the parent molecules decomposition rate during the endothermic stage allows for the obtainment of the decomposition reaction rate and further determination of an associated activation energy (E_{en}) by simulations at different elevated temperatures. The activation energies obtained for the various mixtures were examined are presented in Figure 2.
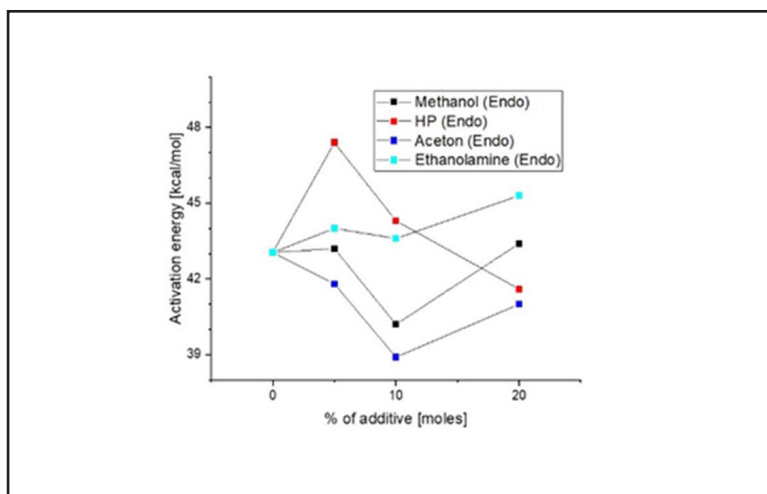

Figure 2: Activation energies of the endothermic stage obtained for the different mixtures examined.

Examination of these results shows that addition of acetone leads to marked reduction in the magnitude of E_{en}, hence, mixtures of nitromethane (NM) with acetone are expected to be more sensitive to detonation. Similar behavior is observed for the addition of 10% methanol and 20% hydrogen peroxide. The addition of ethanolamine to NM at all concentrations examined leads to a less sensitive mixture.

A.7. Mixtures of Hydrogen Peroxide with Urea and with Erythritol

The reaction pathways and energy barriers involved in detonation of hydrogen peroxide mixed with urea or erythritol were investigated using electronic structure calculations at the Density Functional Theory (DFT) level. The first system examined is a mixture of H_2O_2 and urea. The preliminary calculations show that decomposition of urea involves a first step of intramolecular rearrangement followed by the release of an ammonia molecule. The energy barriers associated with these two steps are 42 and 59 kcal/mol respectively. The interaction between urea hydrogenperoxide molecules eliminates the first energy barrier, but still requires 59 kcal/mol to produce a NH_3 molecule. In the case that two H_2O_2 molecules interact with one urea molecule, the reaction can reach completion by surpassing a barrier of only about 14 kcal/mol (see Fig. 3). 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 H_2O_2 and sugar.
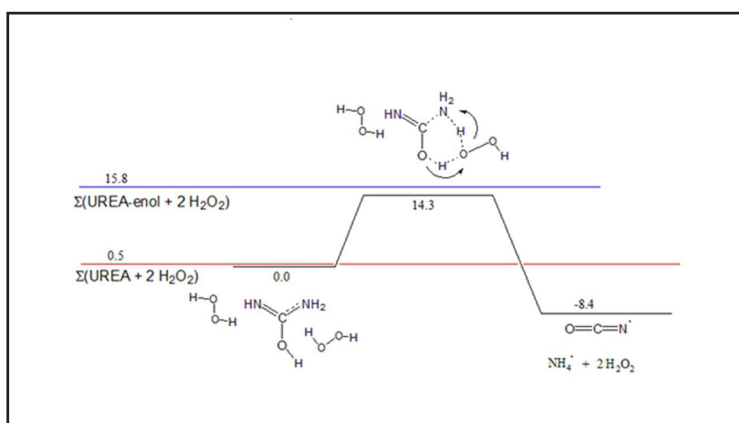

Figure 3: The reaction path for an urea molecule reacting with two H_2O_2 molecules. The red and blue lines mark the energies of the corresponding intermediate complexes.

The interaction of the two H_2O_2 molecules with urea leads to formation of an intermediate complex with an energy barrier of only 14 kcal/mol. This complex then decomposes to yield an ammonia molecule as a by-product. This first step in the decomposition is exothermic by about 8 kcal/mol. These calculations are being recalculated using a much larger basis set to substantiate these results.

It is well established that alcohols such as erythritol can undergo unimolecular decomposition to produce a water molecule (a di-hydration reaction). The energy barrier we calculated to obtain the required intermediate complex is about 46 kcal/mol. In the presence of hydrogen peroxide, a slight reduction of the energy barrier, about 5kcal/mol, is observed. However, if a different conformer of erythritol is used as a starting point, the energy barrier of erythritol decomposition to yield an H2O molecule is markedly reduced to about 17kcal/mol (see Fig. 4).
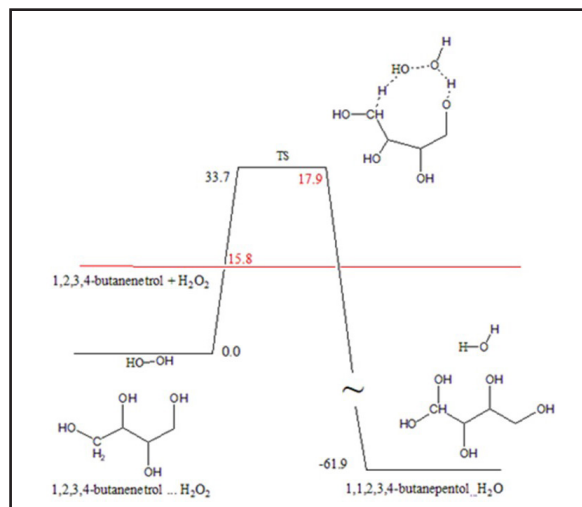
Figure 4: Erythritol decomposition route in the presence of H$_2$O$_2$. The red line marks the energy of the complex spontaneously formed among the two molecules.

It should be noted that this decomposition step is very exothermic and can supply energy for additional decomposition steps. These results are re-calculated using a much larger basis set to substantiate the preliminary calculations.

A.8.   Development of a Global Efficient Training Method for ReaxFF Parameters

Particle swarm optimization (PSO) is a powerful metaheuristic population-based global optimization algorithm. However, when applied to non-separable objective functions, its performance on multimodal landscapes is significantly degraded. A new method with significant improvement in the search quality and efficiency on multimodal functions was developed by enhancing the basic rotation-invariant particle swarm optimization algorithm with isotropic Gaussian mutation operators. The new algorithm demonstrates a superior performance across several nonlinear, multimodal benchmark functions compared to the rotation-invariant Particle Swam Optimization (PSO) algorithm and the well-established simulated annealing and sequential one-parameter parabolic interpolation methods. A search for the optimal set of parameters for the dispersion interaction model in ReaxFF-lg reactive force field is carried out with respect to accurate DFT-TS calculations. The resulting optimized force field accurately describes the equations of state of several high-energy molecular crystals where such interactions are of crucial importance. The improved algorithm also presents a better performance compared to a Genetic Algorithm optimization method in the optimization of a ReaxFF-lg correction model parameters. The computational framework is implemented in a stand-alone C++ code that allows a straightforward development of reactive force fields. The improvement in equations of state of four explosives due to the addition of improved dispersion forces to ReaxFF using the new training method is presented in Figure 5.
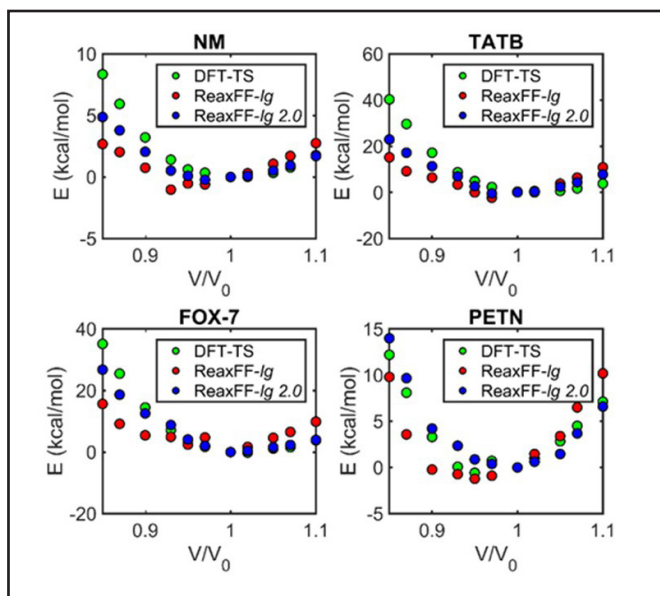
Figure 5: Calculated equations of state for energetic molecular crystals. DFT calculations (green) include the Tkatchenko-Scheffler dispersion correction. Force field values are calculated with ReaxFF-lg 2.0 obtained following the new optimization method (blue) and compared to the original ReaxFF-lg values of Liu et al (red).

Figure 6 presents a comparison between results of optimizations conducted by two variants of GARFFIELD and of our method on a compact set of previously training data. The training set contains full dissociation and compression curves for vdW bonded dimers in the S66 database including $AcNH_2$, NH_3, CH_3NH_2, CH_3NH_2, Pyridine, and HN_3 dimers. In both cases, we use exactly the same initial force field to evaluate the initial fitness. This results in an initial fitness of $2.75 \cdot 10^3$. After roughly 100 iterations, GARFFIELD improves the average fitness by a factor of about 2.5. Then a slower improvement rate can be observed until the final results are obtained. In comparison, the new method, termed RiPSOGM, using 20 agents, succeeds to dramatically lower the average fitness in the first few (about 20) iterations and then shows very slow improvement and stays almost stagnant throughout the remaining search process. This behavior stems from the randomization process where each of the optimization parameters gets a completely independent random value within its domain boundaries. Then, the member with the globally best fitness is chosen as the new force field for the next step in the search process. In contrast, GARFFIELD generates a population of 20 genes with mutation and crossover operations from the initial force field. Turning on local search (CG) after 400 iterations for the additional 100 iterations in GARFFIELD leads to further lowering of the fitness to 254.2. The addition of a local search in RiPSOGM offers a similar improvement and arrives at the final fitness value of 191.8. Thus the better performance of RiPSOGM over GARFFIELD is afforded by (a) the randomization step already at the initial stage and the selection of the globally best member as the new force field for the search process; (b) the efficient information-sharing mechanism in the swarm; and (c) the addition of local search-like characteristics to each swarm member. Overall, the RiPSOGM framework which is rotation-invariant, shows a better performance in terms of solution quality and computational cost, and is less divergent throughout the optimization path.
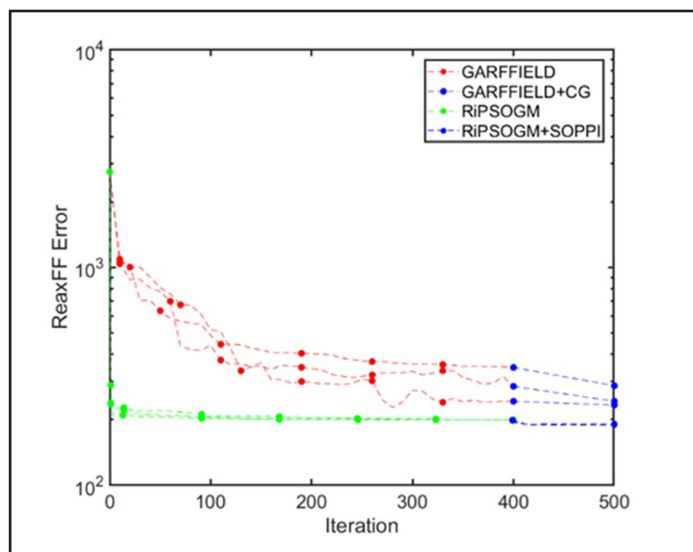
Figure 6: Comparison of our global optimization performance and the genetic algorithm based code GARFFIELD with and without a conjugate-gradient (CG) minimization. Population size in both methods is 20 agents. For each algorithm, three independent runs were performed. The y-axis is a log scale and the dots are a guide to the eye.

B. State of the Art and Technical Approach

The theoretical studies reported use mainly 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 sets 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:

- A method to calculate THz spectra of molecular crystals was developed by us and its implementation to TATP and RDX were published [3];

- 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

- 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.

At described above, recently we developed a new approach that allows for an efficient construction of reactive force fields. 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) using this data baseto train an accurate ReaxFF, namely, to obtain the parameters that reproduce accurately the QC data. This stage, in most cases, used to be extremely complex and involved 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 were the only group of researchers at ALERT that performs theoretical studies as those described here.

C.   Major Contributions

The major contributions of this project to date include:

- Year 5:
  - Summary of the detonation properties of liquid mixtures between nitromethane and four different liquid additives (acetone, ethyleamine, methanol, and hydrogenperoxide).
  - Decomposition pathways of mixtures of H_2O_2 with urea and with erythritol.
  - Development of a new, accurate, and efficient method to search for optimal ReaxFF parameters to accurately reproduce DFT data.
- Year 4:
  - New ReaxFF parametrization for solid Erythritol tetranitrate (ETN).
  - Detonation properties of liquid mixtures.
- Year 3:
  - The role of nano-size defects simulation using a new methodology.
  - Deciphering the mechanism of laser induced ejection of molecules.
- Year 2:
  - New ReaxFF parametrization for liquid HN_3.
  - Determining the decomposition routes of HMTD for safe disposal.
- Year 1:
  - Explosive detection using 2D THz Spectroscopy.
  - Characterization of TNT detonation mechanism: bimolecular pathway.

D.   Milestones

- RMD simulations of mixtures of nitromethane with four different additives: acetone, ethanolamine, methanol, and H_2O_2 were completed. Presently, we are analyzing the data with the aim to publish a paper.
- The construction of a new reactive force field for TNT was completed in Year 4. The main improvement to the existing force field is a better treatment of hydrogen bonding and dispersion forces. This improved the equilibrium density of the bulk TNT.
- The QC calculations regarding the stability, energy barrier for decomposition, and thermal decomposition pathway to obtain stable products of the three nitrified sugars were completed. The results were transferred to the experimental group of Dr. Oxley for comparison with experimental data.
- First stage of QC calculations of reactions in mixtures of H_2O_2 with urea and with erythritol were completed. The results show that in both cases, existence of enough hydrogen peroxide leads to reduced energy barriers for initial decomposition of the "fuel" molecules. These results are being substantiated at

present using more accurate calculations (i.e. using larger basis sets).

- We have not yet started the simulations of potassium chlorate mixture with wax. The study of this system will start once the calculations of H_2O_2 mixtures will end.

- The influence of nano-Al particles' addition on detonation characteristics of some of the HMEs has not started yet.

- A new efficient global search method was developed and implemented to obtain ReaxFF parameters for new systems to be used. The new approach was applied to the addition of dispersive forces to the force field for HN_3 developed by us earlier. The new force field allows to reproduce the very large difference (about 30%) between solid and liquid HN_3. The new ReaxFF is being used at present to understand the origin of this anomalous density difference.

E.   Future Plans (Year 6)

As a result of the ALERT Biennial Review conducted in March of 2018, this project has been concluded and will not be funded in Year 6. As much as possible, we will complete the investigations currently in progress with the following specific objectives:

- Past Year 5, additional time and resources will be required to complete the planned study of the different improvised explosives. In particular, RMD simulations of hydrogen peroxide mixtures with urea and with sugar will be performed. These simulations will focus on the sensitivity and detonation mechanism of these mixtures.

- Our goal is to be able to simulate and predict the explosive characteristics of all improvised explosives and simulate spectroscopic characteristics for remote detection from first principles. These type of simulations require appropriate force fields. The new global optimization method we developed will allow efficient and accurate parametrization of ReaxFF for different systems. The new optimization method was already applied to improve the ReaxFF parametrization of the HN_3 system. The improvement consist of proper addition of dispersion forces and hydrogen bonding to the ReaxFF. This addition will allow to calculate accurately the vibrational characteristics of liquid and solid HN_3.

- In addition to the QC calculations related to mixtures of H_2O_2 with urea and with erythritol, we also plan to carry out RMD simulations of these systems. Reactive molecular dynamics study of oxidizer-fuel mixtures will allow for greater understanding of the sensitivity, thermodynamics, and kinetics of the detonation of these mixtures.

- We plan to initiate the study of hydrogen azide as the first member of a new family of potential improvised explosives.

- During the last 3-4 years, we studied different families of improvised explosives (i.e. peroxides, liquids, mixture of oxidizers, and fuels). The theoretical study accompanied the experimental investigation by the research group of Dr. Oxley at the University of Rhode Island. We propose that the two groups will compose a comprehensive overview of improvised explosives. This review will serve the Department of Homeland Security as a technical guide to these systems.

III.   RELEVANCE AND TRANSITION

A.   Relevance of Research to the DHS Enterprise

1. One of the main challenges in dealing with the threat of terror is the appearance of unknown im-

provised 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.

2. 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, Dr. 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 supplemental material.

D. Transition Pathway

Computer simulations are essential for rapid response to unknown improvised explosives. Such simulations can identify fundamental properties, such as the 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

1. Fisher, D., Zach, R., Matana, Y., Elia, P., Shustack, S., Yarden, S., & Zeiri, Y. "Bomb Swab: Can Trace Explosive Particles Detection Be Improved?" Talanta, *174*, 1 November 2017, pp. 92–99. DOI: 10.1016/j.talanta.2017.05.085

2. Oxley, J.C., Furman, D., Brown, A.C., Dubnikova, F., Smith, J.L., Kosloff, R., & Zeiri, Y. "Thermal Decomposition of Erythritol Tetranitrate: A Joint Experimental and Computational Study." *Journal of Physical Chemistry C*, *121(30)*, 6 July 2017, pp. 16145-16157. DOI: 10.1021/acs.jpcc.7b04668

3. Kalson, N.H., Furman, D., & Zeiri, Y. "Cavitation-Induced Synthesis of Biogenic Molecules on Primordial Earth." *ACS Cent. Sci., 3*(9), 11 September 2017, pp. 1041-1049. DOI: 10.1021/acscentsci.7b00325

Pending-

1. Furman, D., Carmeli, B., Zeiri, Y., & Kosloff, R. "Enhanced Particle Swarm Optimization Algorithm: Efficient Training of ReaxFF Reactive Force Fields." *Journal of Chemical Theory and Computation.* In press.

B.   Conference Proceedings

1. Kosloff, R., Zeiri, Y., & Furman, D. "Molecular Dynamical Simulations of Energetic Materials: Mechanism, THz Spectroscopy and Laser Ablation." *The 83rd Annual Meeting of the Israel Chemical Society*, Tel Aviv, Israel, February 13-14, 2018.

V.   REFERENCES

[1] Frisch, M. J.; Trucks, G. W.; et al. Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

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[3] G. Katz, S. Zybin, W. A. Goddard III, Y. Zeiri, and R. Kosloff. "Direct MD Simulations of Terahertz Absorption and 2-D Spectroscopy Applied to Explosive Crystals." J. Phys. Chem. Lett., 5, 772 (2014).

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[5] David Furman, Faina Dubnikova, Adri C.T. van Duin, Yehuda Zeiri and Ronnie Kosloff. "Reactive Force Field for Liquid Hydrazoic Acid with Applications to Detonation Chemistry." J. Phys. Chem. C, (2016), 120, 4744-4752.

[6] Jimmie C. Oxley, David Furman, Austin C. Brown, Faina Dubnikova, James L. Smith, Ronnie Kosloff, and Yehuda Zeiri. "Thermal Decomposition of Erythritol Tetranitrate: A Joint Experimental and Computational Study." J. Phys. Chem. C, submitted for publication.

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