R1-D.1: Theoretical Modeling Considerations

Abstract—During the first year, our plan was to initiate research in three different, however interrelated, directions. These research directions included:

1. Development of a new theoretical method to calculate the THz spectrum of solid explosives. The molecular dynamics based approach will allow prediction of the spectra and assignment of its features. This goal was accomplished successfully and the results were published in the Journal of Physical Chemistry Letters.

2. Reactive molecular dynamics (RMD) will be utilized to study the ablation products of an intense short laser pulse interaction with thin layers of explosive particulates. This information will be used to guide the optimization of remote detection of explosives. This part of the research is being summarized at present in the form of a research paper. We examined three different possible mechanisms and demonstrated that only one is operative at experimental conditions. In other words, only one of the mechanisms leads to the ejection of intact parent explosive molecules from the irradiated thin layer under experimental conditions.

3. Finally, the RMD approach will also be used to investigate the sensitivity and detonation characteristics of liquid explosives. In this direction of research, we started with a thorough investigation of HN₃ kinetic and thermodynamic properties using electronic structure calculations. The data obtained in these calculations was used to construct a reliable reactive force field. The new force field is being used at present to study the dynamics of thermal decomposition of liquid HN₃. During the coming year, we plan to extend this study and examine the behavior of mixtures of HN₃ with various amounts of dilution media (liquids) that could desensitize the explosive, thereby increasing its safety for handling.

I. PARTICIPANTS

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II. PROJECT OVERVIEW AND SIGNIFICANCE

The theory group has a number of long term goals. The main goals are:

- Detailed understanding of the nature of Laser-explosive interactions that will help in the development of remote detection methods.
- Understanding the details of reactions and mechanism involved in detonation of liquid explosives and their mixture with inert liquids. The main focus will be on the sensitivity to detonation variations.
- Development of a theoretical scheme to evaluate the “burning rates” of explosives during detonation.
- Development of calculation methods to study carbon clusters and soot formation during and following the detonation.

In addition to these goals, the theory group will use various theoretical methods to assist in the detailed understanding of studies performed by other groups (provided these groups will require our assistance). This assistance can include: electronic structure calculations, ab initio MD calculations and quantum mechanical studies of periodic systems at extreme conditions.

III. RESEARCH ACTIVITY

A. State-of-the-art and technical approach

Most of the theoretical research in our group is devoted to the detailed study of microscopic systems. The size of the system under investigation is limited mostly to the sub micrometer regime. Although such small regions are limited in the description of macroscopic explosives, some of the explosive behavior can be investigated in great detail. Three main types of calculations are being used: (1) Molecular Dynamics using a reactive force field, (2) Quantum Mechanical description of the system dynamics where the force field can be calculated using different levels of approximations and, (3) electronic structure calculations to obtain accurate kinetic and thermodynamic properties. The electronic structure calculations assume a stationary system while both RMD and QM approaches can be used for the study of time dependent events that are limited to a short time period, on the order of nanoseconds. Despite this limitation of the simulation duration, one can use these methods to investigate the behavior of reactive systems at extreme conditions (high temperature and pressure).

For the electronic structure calculations we use the commercial code Gaussian 09. This code includes a variety of approximate exchange-correlation functionals including some modern hybrid functionals. The calculations are aimed at obtaining lowest energy configuration, obtaining reaction pathway and the corresponding transition state geometries and energies. The level of computational accuracy is dictated, in most cases, by the size of the system investigated and the computational resources available.

The Molecular Dynamics code we employ is the open source code LAMMPS. This code incorporates a wide range of force fields, each specially designed for some tasks or types of systems. In most of the applications we use the ReaxFF, a reactive force field developed by Adri van Duin and co-workers at Caltech. LAMMPS is the basic MD code that is modified to include new developments carried out in our group (such as the approach to calculate THz spectra, hot spot simulations and extensions of the reactive force field to new systems). In a similar manner, we use an open source code for the QM calculation, the Quantum Espresso (QE) package. This code allows one to calculate, with high accuracy, the system energy at a wide range of pressure values. Thus, one can obtain the vibrational spectra of the system and its equation of state using these calculations. This approach requires quite extensive computational resources that grow rapidly as the system size increases. To study larger systems (few hundred atoms), we employ the DFTB+ semi-empirical QM approach. This method allows one to obtain information regarding reactions and their products at different temperatures and pressures.
B. Major contributions

B.1 Elucidation of the relation between structure and sensitivity in explosive materials

A long standing issue is why certain explosives are sensitive while others with very similar structure are relatively inert. We studied this problem using TNT as a prime example. We first discovered that TNT is more sensitive in solid or liquid form than in the gas phase. We related the enhanced sensitivity to a new binary reaction mechanism which involves a few steps that reduce the activation energy by a ~30% relative to the gas phase. These radical mechanisms were used to compare and predict the sensitivity of other common explosives. The RMD simulations of solid and liquid TNT allows to obtain detailed understanding of the thermal decomposition process at high temperatures and pressure. The temperature and pressure ranges examined are similar to those experienced during detonation. Variation of the thermal decomposition products during detonation like conditions are shown in Figure 1. This type of results allow to determine the mechanism responsible for the decomposition process.

![Figure 1: Initial decomposition products of solid TNT at temperatures 1800K and 3500K and volumes V0 (ambient) and 0.7V0 (30% compression). Formation of covalent dimers emphasizes the role of bimolecular association reactions.](image)

B.2 A novel detection scheme of explosives

We suggest, theoretically, a novel detection scheme using THz spectroscopy for detection of explosives. We first developed a new direct computational method to study energy absorption from a pulse in the THz frequency range. The method overcomes the problems with linear response theory and normal mode analysis. This led to a novel nonlinear spectroscopic method based on polarization correlation measurements.

B.3 Laser ablation of thin explosive layers

We have developed a theoretical model which accounts for the recent experimental findings of intact explosive molecules’ ejection under high intensity ultra-short laser pulses. The model is based on reactive molecular dynamics simulations and allows the identification of bond formation and rupture events. Three different possible physical mechanisms were investigated, however only one of them yield results that agreed with
Experimental findings: The ejection of intact molecules of explosives with the correct velocity distributions and dependence on laser parameters. A schematic description of the relation between the ejected material composition and shock wave velocity is shown in Figure 2. It can clearly be seen that the increase in shock velocity leads to reduction in the size of ejected species.

B.4 HN₃—development of reactive force field of a typical liquid explosive

Detection of liquid explosives remains a great challenge to the law enforcement communities worldwide. Some liquids, such as hydrazoic acid (HN₃), are extremely sensitive and are highly energetic and can potentially be used in improvised explosive devices. The high sensitivity of HN₃ puts its carrier at a risk of accidental detonation, unless the liquid is diluted. Dilution of HN₃ can be achieved with different media, which act as desensitizers to the explosive molecules. The study of the explosive properties of HN₃ and its mixtures with different solvents, such as water, is of paramount importance for the development of counter measures against terrorist attempts. A thorough knowledge of its detonation mechanism, initiation pathways and interaction with other inert liquids can be achieved using reactive molecular dynamics simulations of pure and mixture phases of HN₃. We have developed a new reactive force field based on accurate Quantum Chemical calculations to describe the properties, different decomposition routes and thermochemical performance of HN₃. Currently we study the thermal and shock initiation chemistry of liquid HN₃. Figure 3 shows the time evolution of decomposition products following rapid heating. This type of simulations will be carried out at different pressure values for the pure liquid. We plan to extend the force field to include the chemistry of HN₃ with different diluting media. Such extension will allow to carry out RMD simulations to mixtures of HN₃ with inert liquids.

Figure 2: Ejection of intact TNT molecules from the solid (shock induced vaporization). Different shock speeds result in different size distributions: Lower shock speeds produce "chunks" of material while higher speed shocks eject molecules and intact molecular clusters.

Figure 3: Thermal Decomposition of liquid HN₃ near CJ conditions from ReaxFF-HN₃ reactive simulations.
C. Future plans

1. Electronic structure calculations of Hexamethylene triperoxide diamine (HMTD) in order to determine its decomposition pathways. The purpose is to find the activation energy for decomposition and to correlate it with experimental findings. In addition we will study possible additives which will enhance or suppress the sensitivity to initiation.

2. Hot spot calculation (new methodology) and application for micro structure importance and sensitivity estimation.

3. Liquid explosive: HN₃, and its combination with inert liquids.

4. High pressure calculations (collaboration with other groups).

IV. PROJECT DOCUMENTATION AND DELIVERABLES

A. Peer reviewed journal articles


V. REFERENCES


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