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First-Principles Atomistic Simulations of Energetic Materials

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Dedication

I am forever indebted to my mother Victoria, my brother Paul, and mother-in-law Kristen for all of their encouragement and support, both morally and financially; as well as to my extended family and friends who always held out hope for my success. Finally, I am eternally grateful to my beautiful wife Meredith and daughters Eleanor and Dinah, who endured the brunt of my trials and frustrations, and who provided me with ample love, encouragement, optimism, and motivation to complete my work despite their sacrifices.
Acknowledgments

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Abstract

This dissertation is concerned with the understanding of physico-chemical properties of energetic materials (EMs). Recently, a substantial amount of work has been directed towards calculations of equations of state and structural changes upon compression of existing EMs, as well as elucidating the underlying chemistry of initiation in detonating EMs. This work contributes to this effort by 1) predicting equations of state and thermo-physical properties of EMs, 2) predicting new phases of novel EMs, and 3) examining the initial stages of chemistry that result in detonation in EMs. The motivation for the first thrust, is to provide thermodynamic properties as input parameters for mesoscale modeling. Such properties are urgently sought for a wide range of temperatures and pressures, and are often difficult or even impossible to obtain from experiment. However, thermo-physical properties are obtained by calculating structural properties and vibration spectra using density function theory and employing the quasi-harmonic approximation. The second thrust is directed towards the prediction and investigation of novel polymorphs of known azide compounds to identify precursor materials for synthesis of polymeric nitrogen EMs. Structural searches are used to identify new polymorphs, while theoretical Raman spectra for these polymorphs are calculated to aid experimentalists in identifying the appearance of these azide compounds under high pressure. The final thrust is concerned with elucidating the initial chemical events that lead to detonation through hypervelocity collision simulations using first-principles molecular dynamics. The chemical mechanisms of initiation are determined from the atomic trajectory data, while heats of reaction are calculated to quantify energy trends of chemical transformations.
1 Introduction

1.1 Note to Reader

This dissertation is composed of three published articles from peer-reviewed journals, one peer-reviewed conference proceedings, and three articles submitted for peer-review. All articles, both published and in review, are included as appendices. The chapters within this dissertation serve to highlight particular results from the peer-reviewed articles, and are not meant to stand alone; hence all details should be sought in the peer-reviewed articles for a comprehensive understanding of the research.

Figures within this dissertation contain color, which greatly enhances the ease with which the concepts and data depicted may be understood. The original dissertation is available from the University of South Florida in Tampa, Florida.

1.2 Energetic Materials and Detonation

An energetic material (EM) is a crystalline material containing large quantities of chemical energy, which is released upon initiation of chemical reactions. Such materials may include anything that is readily combustible, or that will explode with the right stimulus, including any explosive, propellant, or combustible fuel. Of particular interest for industrial and military applications is a class of EM known as insensitive munitions, generally composed of nitro compounds. As their classification suggests, these EMs are extremely insensitive to indirect mechanical or thermal stimulus, and typically require a less sensitive explosive charge to initiate detonation. As one might expect this is an advantageous trait since it makes a material with extremely high
destructive potential relatively safe to handle as casual contact and accidental mechanical or thermal stimuli often will leave the material unperturbed. However, once an intentional directed shock is delivered to such a material, a series of endothermic reactions ensue that prime the system towards a violent exothermic release of energy that propagates through the system at supersonic speeds [1, 2]. This process is known as detonation initiation.

Detonation initiation is characterized by the delivery of a shock wave into the material that leads to strong compression of the crystalline lattice (induction) resulting in mechanical distortions of chemical bonds that overcome the high energy barriers to bond breaking (reaction). Once the initial barriers to reactions are overcome, the combination of high pressure, mechanical distortion, and dissociated chemical radicals leads to very rapid chemical decomposition of the material at rates up to two orders of magnitude faster than those described by thermal chemistry [3]. In such a reacting material, chemistry is believed to be initiated within a few hundred femtoseconds [4–6], leaving no time for the equilibration of the mechanical energy locally deposited into the material across all normal modes, or degrees of freedom, within the system. While this may offer challenges to experimentalists towards understanding the unconventional nature of initiation chemistry, modern theory and simulation techniques offer a means to fill the gaps in knowledge on what mechanisms contribute to the initiation of a detonation process.

In the late 1800’s researchers first recognized the detonation phenomenon while investigating supersonic flame propagation through tubes filled with gas. These flame fronts were enigmatic in that not only did they move supersonically, but their velocities would decrease when the initial, pre-ignition temperature of the gas was increased, defying intuition. By 1899, D.L. Chapman published his work [7] on predicting the speed of flame propagation, using conservation of mass, momentum, and energy, which was expanded upon by J.C.E. Jouguet in 1906 [8]. Together, their works created the
notion of the Chapman-Jouguet (CJ) point, the position along the detonation front profile after which all reactants have been converted to products. However, this idea was limited by the notion that reactions take place instantaneously. By 1943, Zel’rovich, von Neumann and Doring (ZND) [9-11] added an induction and a reaction zone ahead of the CJ point. At the very front of the detonation profile was the von Neumann spike, at which pressure was at a maximum, preceded only by an instantaneous jump from ambient pressure.

While this ZND theory worked well to predict detonation velocities, it still was only a 1-dimensional model, and thus truly applicable to only planar detonation waves. By the 1960s evidence began to mount that planar detonation wave structure in gases was actually the exception and not the norm; new complex 3-dimensional regimes of detonation fronts, such as transverse, pulsating, spinning, and turbulent detonations, were being observed in gas phase as imaging technology improved [12-18], while theoretical studies [19-24] of these regimes ensued with increasing computational capabilities. Despite this, the classical ZND model is still used as a simple means to estimate detonation velocity, as it does so quite well.

As alluded to above, detonation is a complex process that requires understanding from the atomic scale to the macroscopic scale. Factors such as chemical composition, atomic/molecular arrangement, thermodynamic properties, and the boundary conditions along the periphery of the system all contribute to the character of the detonation front. However, typical detonating systems are far too large to simulate at the atomic scale. Therefore, mesoscale modeling (i.e. models that consider grains of material much smaller than important features such as hot spots, voids, etc.) of the detonation phenomenon are performed to understand the macroscopic processes involved, as well as to predict performance under a wide range of environments and conditions.

To achieve proper prediction of detonation processes, however, the model must
correctly describe both thermo-physical properties and chemistry. This can only be achieved by providing such properties over a wide range of pressures and temperatures, while also having detailed knowledge of the chemical mechanisms that initiate detonation; neither of which can be readily obtained from experiment. It is the goal of this dissertation to use first-principles density functional theory (DFT) calculations to predict the thermo-physical properties of condensed phase EMs over an applicable range of pressures and temperatures, while also investigating the mechanisms that initiate the chemistry of detonation using first-principles molecular dynamics (MD).

1.3 Thermo-Physical Properties of Energetic Materials from First-Principles

As already stated, atomic-scale description of the EMs is limited by system size, typically \( \sim 100 \) atoms. In contrast, ‘real-world’ performance and characterization often depends on macroscopic material properties. Towards the engineering and prediction of ‘real-world’ explosive performance for known EMs, intensive relationships such as the equation of state (EOS) (relationship between pressure, volume and temperature), as well as thermo-physical properties such as compressibility, and heat capacities, should be available [25]. These quantities are urgently sought to model EMs on the mesoscale, which takes into account grains that are small enough to properly resolve hot spots, zones of chemically degraded material, plastic binder grains, voids, and other defects. In contrast to experiment, the necessary physico-chemical properties for mesoscale modeling of EMs can be obtained using first-principles calculations with corrections to account for weak van der Waals (vdW) dispersive forces, as well as corrections to account for zero-point and thermal contributions to the total energy. Within this dissertation a comprehensive modeling of these properties over a wide range of temperatures and pressures is performed for a set of important EMs.
1.4 First-Principles Investigation of High Nitrogen Content Energetic Materials

While nitro compound explosives dominate in both industrial and military applications, attention has recently turned towards high- or all-nitrogen EMs, specifically polymeric forms of nitrogen including the cubic-gauche (cg) phase of crystalline nitrogen [26–37]. The motivation behind this interest is that the decomposition of single/double bonded nitrogen to triple bonded $N_2$ gas releases a substantial amount of energy which can provide twice the impulse and several times the explosive pressure compared to even the most powerful nitramine EMs, such as HMX, in use today [38]. While cg-nitrogen has been observed to form under high pressure and temperature in diamond anvil cell (DAC) experiments, it has yet to be recovered at ambient conditions [28–33, 35–37]. This has prompted many to look beyond $N_2$ gas as a precursor to such high-nitrogen compounds, and instead investigate azide containing compounds such as sodium-azide [39–41] or ammonium-azide [42–45].

It has been suggested [46] that non-nitrogen impurities from such precursors may help to stabilize singly bonded nitrogen complexes, leading to new materials not yet conceived. Challenges facing such endeavors include the relative blindness in experiment to the mechanical processes leading to polymorphic and chemical transitions upon pressure loading, as well as the expense and difficulties in performing experiments at such high pressures at which transitions occur. Fortunately, theory offers far less expense in elucidating the mechanisms behind materials transformation, and can go further by predicting candidate structures and their properties, and guiding experiment towards their realization. As such, a portion of this dissertation serves to demonstrate how first-principles calculations of EOSs, as well as Raman spectra, can be complimentary to experiments by predicting structures and material transformations at the atomistic scale.
1.5 Gas Phase Hypervelocity Bi-Molecular Collisions

To understand the chemical mechanisms that initiate detonation in condensed phase EMs due to a rapidly passing shock wave, hypervelocity bi-molecular collisions of energetic molecules with initial positions corresponding to those within the crystalline lattice, are simulated using first-principles molecular dynamics (MD). Included within this simulation effort are hypervelocity collisions of Pentaerythritol tetranitrate (PETN) molecules, as well as Sila-Pentaerythritol tetranitrate (Si-PETN), 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX), Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and triaminotrinitrobenzene or 2,4,6-triamino-1,3,5-trinitrobenzene (TATB). For PETN, qualitative correlations are made between the known anisotropic sensitivities [47–51] and bi-molecular collisions of corresponding orientations by investigating the minimum collision velocity to initiate chemical reactions for each crystallographic direction. Discussions on simulations for other EMs are specifically focused on the formation of exotic reaction products that are predicted to occur in real systems, while heats of reaction for these products are calculated to show how initiation tends towards endothermic steps with the lowest change in energy, while those of exothermic steps demonstrate the rapid release of energy that can occur for various pathways during initiation.
2 Thermo-Physical Properties of Energetic Materials

2.1 Motivation

The equation of state (EOS) is essentially the relationship between the volume of some predefined quantity of atoms (often the unit cell) and the pressure associated with that volume for a particular crystalline material under compression at a given constant temperature. The EOS gives the bulk modulus, or inverse of compressibility, at any pressure as \( B = V(P) \frac{dP}{dV} \), where \( V(P) \) is the volume at the pressure of interest \( P \). Usually this value is obtained for ambient conditions, and is calculated by fitting \( PV \) data points to a particular analytical form such as the Birch-Murnaghan EOS [52] given by

\[
P(V) = \frac{3B_0}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{7/3} \right] \left\{ 1 + \frac{3}{4} \left( B'_0 - 4 \right) \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\},
\]

\[
E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^3 B'_0 + \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{2/3} \right] \right\},
\]

where \( V_0, E_0, \) and \( B_0 \) are the volume, energy and bulk modulus at zero pressure, and \( B'_0 \) is the derivative of the bulk modulus with respect to pressure at zero pressure, all of which being parameters fit to the \( PV \) data. While EOSs and bulk moduli for EMs are urgently sought for mesoscale modeling, a major challenge remains: finding agreement between the fits to data generated by different experiments and calcula-
tions. Experimentalists acquire $PV$ data by loading a sample into a diamond anvil cell (DAC) and compressing it while taking x-ray diffraction data for structure determination. For the material to be compressed hydrostatically, however, a fluid medium must encapsulate the material to provide uniform pressure, which becomes problematic if the pressure medium begins to crystallize or exhibit anisotropic behavior at high pressure [53, 54]. Therefore, the choice of pressure medium can either lead to inaccuracies at high pressure or noisy data at low pressure; either of which may greatly affect the fit to a particular form of the EOS. In fact, $B_0$ reported for the same material in different experiments have varied by more than 30%, especially for complex molecular solids, which include many EMs [53].

To overcome the difficulties associated with DAC experiments, and compliment the associated data towards providing input for mesoscale modeling, static compression calculations are performed using DFT. These are done by simply relaxing the lattice parameters, volume, and atomic positions of a reference structure, and then sequentially reducing the volume by some amount while relaxing the lattice parameters and atomic positions at a given volume. The end result is often a very smooth set of $PV$ data, but there are two serious limitations to this method. First of all, EMs, being molecular crystals, are weakly bound by long range dispersive van der Waals (vdW) forces. These vdW forces are not well described by DFT, and must be added through some artificial means, usually by some empirical correction to energy that has a $C_6/R^6$ dependence. In addition, the singularities at $R = 0$ are avoided by multiplying the $C_6/R^6$ dependence by a switching function as was done by Grimme [55], as well as Neumann and Perrin [56].

Provided the empirical term is fit properly, vdW should provide slight over-binding, which can be further corrected by the addition of thermal affects. In fact, most of the reported EOS calculated using DFT have no temperature and no zero point energy contributions that would typically cause expansion of the unit cell at a particular
pressure. This poses problems when comparing calculated and experimental data as experiments are done at finite temperature. In addition, zero point energy is always present, even at $T = 0$. However, thermal and zero point energy contributions to pressure can be easily obtained by DFT through the calculation of the vibration spectrum and use of the quasi-harmonic approximation (QHA), which approximates the vibrational normal modes within a crystal as harmonic oscillators, while also taking into account thermal expansion by the fact that for each volume of the crystal there is a unique set of normal modes [57]. Once the vibration spectrum is obtained for several volumes of a given polymorph, for each volume the free energy is calculated as

$$A = \sum_i \left\{ \frac{1}{2} h\nu_i + kT \ln \left[ 1 - \exp \left( \frac{-h\nu_i}{kT} \right) \right] \right\},$$

where $T$ is the specified temperature and $\nu_i$ is the frequency of the $i^{th}$ normal mode at a given $V$. For the entire range of volumes calculated, the relationship between the free energy and associated volume can be fit to a quadratic dependence, giving the pressure contribution of the free energy as the analytical derivative $P = \left( \frac{\partial A}{\partial T} \right)_T$. This pressure contribution can then be added to the DFT “cold” pressure to give the thermally corrected pressure at a specified volume and temperature: $P(V, T) = P_A(V, T) + P_{DFT}(V)$. Thus, it is possible to provide a reasonable prediction of EOSs over a range of temperatures, as well as provide estimations of other thermodynamic properties necessary for mesoscale modeling.

2.2 Prediction of Equations of State for Various Energetic Materials

When the empirical vdW correction of Neumann and Perrin [56] is used to predict the EOSs for PETN, RDX, HMX, TATB, FOX-7, and nitromethane, it was found to cause over binding, resulting in an error of about -3% in volume compared to
experiment. This error is to be expected since thermal and zero-point energy contributions are neglected in DFT. To include these contributions, the quasi-harmonic approximation is employed. Since the quasi-harmonic approximation depends on mode frequencies as functions of volume, the vibration spectrum of each material is needed over the range of pressures applicable to the particular polymorph of interest. To this end, the frozen-phonon method is employed on supercells of each material.

For each atom three positive displacements and three negative displacement of 0.05 Å along x, y, and z (denoted by α and β) are performed. The resulting forces on each atom (denoted by i and j) due to the small atomic displacements with magnitude ∆d are used to construct two force constants matrices – one for positive displacements $F^+_{iα,jβ}$, and one for negative displacements $F^-_{iα,jβ}$. Finite differencing is performed on the corresponding elements of the two matrices, leading to the dynamical matrix given by

$$
\Omega_{iα,jβ} = \frac{1}{\sqrt{m_i m_j}} \left[ \frac{F^+_{iα,jβ} - F^-_{iα,jβ}}{2∆d} \right],
$$

which is then diagonalized to give the eigenvalues that define the square of the frequencies, and the eigenvectors that define the atomic displacements of the associated normal modes. The frequencies are then used to calculate both the thermal and zero point contributions to the free energy at finite temperature defined by experiments. The free energy as a function of cell volume is then fit to a quadratic dependence, the negative analytical derivative of which being the contribution to pressure due to temperature and ZPE, which is then added to the DFT cold pressure.

These additional contributions to pressure result in agreement of better than 1% in cell volume as compared to experiments at corresponding temperatures; see Table 1. The DFT+vdW+T EOSs of the EMs studied are also shifted upward from those of DFT+vdW into better agreement with experiment as seen in Figure 1. Despite the success of this method, future work is required to further validate calculated results against experimentally determined dependance of volume on temperature, as
Table 1: Comparison of calculated unit cell volumes to those of experiment for various EMs. Calculated values for DFT+vdW+T correspond to temperature shown for each EM.

<table>
<thead>
<tr>
<th>System</th>
<th>T (K)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$V_0$</th>
<th>% Diff</th>
<th>$V_0$</th>
<th>% Diff</th>
<th>$V_0$</th>
<th>% Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-FOX-7</td>
<td>173</td>
<td>515.89$a$</td>
<td>513.72</td>
<td>-0.42</td>
<td>502.87</td>
<td>-2.52</td>
<td>585.08</td>
<td>+13.41</td>
</tr>
<tr>
<td>β-HMX</td>
<td>RT</td>
<td>519.39$b$</td>
<td>519.57</td>
<td>+0.03</td>
<td>500.77</td>
<td>-3.58</td>
<td>556.07</td>
<td>+7.06</td>
</tr>
<tr>
<td>NM</td>
<td>4.2</td>
<td>275.31$c$</td>
<td>275.37</td>
<td>+0.02</td>
<td>270.00</td>
<td>-1.93</td>
<td>304.22</td>
<td>+10.5</td>
</tr>
<tr>
<td>PETN-I</td>
<td>RT</td>
<td>589.49$d$</td>
<td>590.65</td>
<td>+0.20</td>
<td>567.27</td>
<td>-3.77</td>
<td>620.11</td>
<td>+5.19</td>
</tr>
<tr>
<td>α-RDX</td>
<td>293</td>
<td>1633.86$e$</td>
<td>1650.13</td>
<td>+1.00</td>
<td>1591.21</td>
<td>-2.61</td>
<td>1775.95</td>
<td>+8.7</td>
</tr>
<tr>
<td>TATB</td>
<td>RT</td>
<td>442.34$f$</td>
<td>446.02</td>
<td>+0.83</td>
<td>428.76</td>
<td>-3.07</td>
<td>505.69</td>
<td>+14.32</td>
</tr>
</tbody>
</table>

$a$Ref. [58], $b$Ref. [59], $c$Ref. [60], $d$Ref. [61], $e$Ref. [62], $f$Ref. [63]

well as the accuracy of other thermodynamic properties that can be calculated in this framework. Additionally, it is believed that this method for calculating thermophysical quantities may benefit from future improvements to vdW corrections and anharmonic contributions, the latter likely being too small to warrant the needed computational effort. A more detailed description of this work is presented in the peer-reviewed journal article found in Appendix 1.

### 2.3 Predicted Equation of State for a Recently Synthesized Nitrate Ester

While DAC experiments yielding the EOSs for various widely used EMs are numerous throughout the literature [64-71], one opportunity for theory is to characterize a new material before costly experiments are done. Using DFT with the empirical vdW correction of Neumann and Perrin [56], the EOS was calculated for a nitrate-ester, shown in Figure 2, that was synthesized in 2008 by Chavez et al. [72]. It has a form similar to that of PETN, as well as sensitivity and explosive performance similar to that of HMX. Its ignition temperature exceeds its melting point, indicating that it
Figure 1: EOSs for various EMs compared to those of experiments performed at temperatures shown for FOX-7 [64], β-HMX [65, 66], nitromethane [67, 68], PETN-I [69], α-RDX [69], and TATB [70, 71]. Red lines are Birch-Murnaghan fits for DFT+vdW+T data.
can be cast in a mold [72]. The calculations of the equilibrium lattice constants using pure DFT give an error between $+4\%$ and $+5\%$, while the error in volume is in excess of $13\%$; see Table 2. When the Neumann and Perrin vdW correction is added, the error in lattice constants and volume all fall well below $1\%$. While this seems to be a startling improvement, there is still an important piece missing – thermal and zero point effects. Unfortunately, the empirical vdW method failed to provide enough over binding to allow for the addition of these contributions to the free energy even though substantial improvement over pure DFT was achieved. Nonetheless, the prediction of the EOS for this nitrate-ester, seen in Figure 3, demonstrates the necessity for the addition of vdW interactions, while also suggesting that when using such empirical corrections, caution must always be used. Calculations for this nitrate-ester may be improved by a reparametrization of the empirical vdW treatment used, which is not addressed in this work. A more detailed description of this work is presented in the peer-reviewed journal article found in Appendix 2.
Table 2: Calculated structural properties of nitrate ester compared to experiment.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>Volume (Å³)</th>
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<tr>
<td>Chavez et al. [72]</td>
<td>8.1228</td>
<td>23.0560</td>
<td>8.5072</td>
<td>90</td>
<td>113.953</td>
<td>90</td>
<td>1456.01</td>
</tr>
<tr>
<td>vDW-DFT</td>
<td>8.1894</td>
<td>23.0608</td>
<td>8.5166</td>
<td>90.00</td>
<td>114.449</td>
<td>90.00</td>
<td>1464.18</td>
</tr>
<tr>
<td>% Diff vDW-DFT</td>
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<td>0.02%</td>
<td>0.11%</td>
<td>0%</td>
<td>0.44%</td>
<td>0%</td>
<td>0.56%</td>
</tr>
<tr>
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<td>24.0160</td>
<td>8.9550</td>
<td>90.00</td>
<td>115.295</td>
<td>90.00</td>
<td>1649.48</td>
</tr>
<tr>
<td>% Diff Pure DFT</td>
<td>4.44%</td>
<td>4.16%</td>
<td>5.26%</td>
<td>0%</td>
<td>1.18%</td>
<td>0%</td>
<td>13.29%</td>
</tr>
</tbody>
</table>

Figure 3: EOSs for Nitrate Ester with vDW correction (blue circles) and without (red squares). Lines drawn through data points are Birch-Murnaghan fits.
3 Nitrogen-Rich and All-Nitrogen Energetic Materials

3.1 Motivation and Goals

Recently, intense experimental effort [28–30, 32, 73] has gone into the recovery of novel polymeric nitrogen EMs, composed of chains of singly bonded N atoms, from nitrogen-rich precursors subjected to high pressures. This is due to the perceived notion that polymeric nitrogen EMs should release enormous amounts of energy upon decomposing from their singly bonded state to triply bonded N$_2$ gas. While polymeric nitrogen has been synthesized above 100 GPa and 2000 K [28–33, 35–37], there have been no successful attempts to quench the material to ambient conditions. To surmount this challenge, intensified focus has been given to the synthesis of polymeric nitrogen from nitrogen-rich azide compounds containing N$_3$ chains [29, 43–45, 74, 75].

One of the representative examples is ammonium azide [43–45] shown in Figure 4. Ammonium azide (NH$_4$N$_3$) seems an almost obvious choice for a precursor due to the fact that it is over 90% nitrogen by weight, and since it has been predicted to undergo a phase transition into trans-tetrazine (TTZ) above 36 GPa, or a hydronitrogen solid (HNS) at 55 GPa [42]. However, while Raman characterization of NH$_4$N$_3$ has been performed at high pressure [43, 44], determination of its Phase II structure beyond its first known polymorphic phase transition at $\sim$3 GPa has been wrought with difficulties. An XRD study [45] of NH$_4$N$_3$ was recently performed, but no structure could be resolved beyond $\sim$3 GPa. It is therefore the goal of this work to predict structures of NH$_4$N$_3$ that form beyond the first Phase I to Phase II polymorphic transition to aid experimentalist towards reaching the correct conditions of pressure and temperature.
3.2 Structural Properties and Equation of State for Ammonium Azide

First-principles DFT calculations were performed with the semi-empirical DFT-D2 vdW correction [55] to investigate structural changes of NH$_4$N$_3$ upon hydrostatic compression. The zero pressure structure experimentally determined by Prince and Choi [76] was optimized both with and without the vdW correction and found to have an error of -6.5% and +2.7%, respectively, in comparison with experiment; see Table 3. The thermally corrected structure with the vdW contribution has an error in volume of -3.3%. Thermal corrections typically increase the zero pressure volume by 3%, resulting in an error of ~6% were the vdW correction not used.

Hydrostatic compression calculations were performed up to 72 GPa, and show a smooth EOS throughout the range of compressions shown in Figure 5. The fundamental feature of structural change upon hydrostatic compression within NH$_4$N$_3$ is the rotation of the azides within the $b-c$ plane. Structural data from hydrostatic calculations show the angle that the azides make with the $a-c$ plane at a thermally corrected pressure near 0.25 GPa to be 22.3°, which is in excellent agreement with
Table 3: Comparison of experimental zero pressure unit-cell volume with those calculated using DFT, DFT-D2, and DFT-D2+T at 300 K.

<table>
<thead>
<tr>
<th></th>
<th>Volume ($\text{Å}^3$)</th>
<th>% Error</th>
</tr>
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<tr>
<td>DFT</td>
<td>303.6</td>
<td>+2.7%</td>
</tr>
<tr>
<td>DFT+vdW</td>
<td>275.9</td>
<td>-6.5%</td>
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<tr>
<td>DFT+vdW+300K</td>
<td>285.4</td>
<td>-3.3%</td>
</tr>
</tbody>
</table>

Figure 5: EOS for ammonium azide.

the angle of $22.4^\circ$ found in the XRD study of Wu et al. [45] at the same pressure. However, at ~2.5 GPa, the calculated angle is $15.9^\circ$ versus the angle of $21.6^\circ$ seen in experiment [45]. This disparity between theory and experiment on the angle that the azides make with the $a-c$ plane indicates either a failure on the part of DFT to accurately describe hydrogen bonding, or that the polymorphic phase transition is occurring much sooner and much more gradually than originally believed. Nonetheless, there still remains the issue of the structure of Phase II, which the XRD study of Wu et al. was unable to resolve. A more detailed description of this work is presented in the peer-reviewed conference proceedings article found in Appendix 3.
3.3 Raman Spectra of Ammonium Azide

The Phase I to Phase II transition in NH₄N₃ was characterized by Raman spectra alone [43, 44] as it was reflected in sudden behavioral changes of Raman-active modes at ~3 GPa. Using first-principles DFT perturbation theory, Raman active modes were determined for the structures previously found in hydrostatic compression calculations. Given the disparity between calculated and experimentally determined structures up to ~3 GPa, it is no surprise that while calculated Raman spectra are in good agreement with experiment at zero pressure, as seen in Figure 6, the agreement gradually diminishes with increasing pressure, which is apparent in the comparison of calculated and experimental Raman spectra at ~5.5 GPa shown in Figure 7. Despite this trend, Raman spectra calculations were at least able to offer evidence invalidating the prediction that NH₄N₃ should undergo a transition to TTZ at 36 GPa and then HNS at 75 GPa [42]. To show this, the Raman spectra for NH₄N₃ was experimentally determined up to 71 GPa. Raman spectra for both TTZ and HNS were then calculated for ~71 GPa and compared to the experimentally determined Raman spectrum of NH₄N₃ at the same pressure. Neither the number of modes nor the frequencies calculated up to 2000 cm⁻¹ for either TTZ or HNS were consistent to the experimental Raman spectrum of NH₄N₃, indicating that a transition to either of these materials had not occurred at least up to 71 GPa; see Figure 8. The lack of a transition to TTZ or HNS, despite both being more energetically favorable at 71 GPa, likely indicates some high barrier to transition, and thus NH₄N₃ would need to be heated under high pressure to be transformed into either material. A more detailed description of this work is presented in the paper, submitted for peer-review to the Journal of Physical Chemistry A, found in Appendix 4.
Figure 6: Comparison of calculated (top) and experimental [43] (bottom) Raman spectrum for NH$_4$N$_3$ at 0.25 GPa.

Figure 7: Comparison of calculated (top) and experimental [43] (bottom) Raman spectrum for NH$_4$N$_3$ at ~5.5 GPa.
Figure 8: Raman Spectra for HNS (top), TTZ (middle), and NH$_4$N$_3$ (bottom) at 71 GPa.

3.4 Predicted Phases of Ammonium Azide

To predict potential high pressure phases of NH$_4$N$_3$, a simple atomic randomization scheme was used to displace each atom within the original Phase I structure by a small random displacement of no more than 0.1 Å, followed by relaxation of lattice vectors and atomic positions with unit cell volume held constant. Because of the ambiguity of the Phase II structure in experiment, the original Phase I structure at zero pressure and all of its hydrostatically compressed structures up to and beyond 3 GPa, as determined by DFT calculations, will hence forth be referred to as Phase A. The hydrostatically compressed structures remained identical to the Phase A structures calculated originally by DFT, without randomization, up to \(-50\) GPa, at which point the structure began to diverge from that of Phase A. By 64 GPa, a completely new Phase B structure is formed such that non-randomized expansion of the structure back to low pressure did not coincide with the original NH$_4$N$_3$ Phase A structure. This new monoclinic Phase B structure is characterized by a completely different reconformation of the azides, as seen in Figure 9, and is found to be lower in enthalpy.
than Phase A beyond 5 GPa, which is shown in Figure 10 along with the enthalpy of the randomization structures leading to Phase B. As Phase B is expanded to 1.04 times the volume of the originally optimized Phase A at zero pressure $V_{0A}$, the unit cell switches from monoclinic to orthorhombic symmetry, indicating yet another polymorphic transition to a new Phase C; see Figure 9. Non-randomized hydrostatic compressions of this new Phase C results in yet another polymorph transition at ~1.5 GPa into a triclinic Phase D, in which all azides are parallel; see Figures 9 and 10. The transition itself is caused by the azides pushing against one another head on, which seemingly could result in the zigzag azide conformation seen in Phase B, or the parallel conformation seen in Phase D, the effect of which on the energy and pressure is visible as the non-monotonic behavior from the Phase C to Phase D lines in plots of the EOS in Figure 11. Interestingly, Phase B and Phase C have nearly identical enthalpy plots, indicating that should either Phase B or D be produced in experiment, both states would likely coexist; see Figure 10.

Despite the theoretical prediction of the new phases of NH$_4$N$_3$ found by the simple atomic randomization technique, comparison of their respective Raman spectra offered no evidence that these phases have been produced in DAC experiments. Further, it should be noted that Phase B was produced from a high pressure structure obtained in hydrostatic compressions of the original Phase I structure found by Prince and Choi [76], but which does not seem to match the evolution with pressure of Phase I as determined by Wu et al. [45], leading to the conclusion that the behavior of Phase I upon compression to 3 GPa, as well as the resulting high pressure structure of Phase II, the existence of which proposed by Medvedev et al. [43, 44], have yet to be ascertained. A more detailed description of this work is presented in the peer-reviewed conference proceedings found in Appendix 3.
Figure 9: Crystal structure comparison of Phases A, B, and D at $0.90 V^A_0$ (volume of Phase A at zero pressure). Phase C is also shown at $1.10 V^A_0$. For each row, $a - b$ (left), $c - a$ (middle), and $c - b$ (right) projections of the corresponding crystal are shown.
Figure 10: Enthalpy plots for Phases A, B, D for NH$_4$N$_3$ shown with enthalpy plot of atomic randomization (green hashed line). Phase C not shown due to low pressure range and scale of plot.

Figure 11: EOS for Phases A, B, C, and D for NH$_4$N$_3$. PV and EV curves are shown in the left and right plots respectively.
4 Hypervelocity Bi-Molecular Collisions of Energetic Compounds

4.1 Motivation

The mode of chemical decomposition of EMs known as detonation is fundamental to both explosive performance and safe handling. The speed at which detonation is initiated obfuscates the resulting chemical pathways in that decomposition occurs at time scales $\sim 10^{-13}$ s, much too short to obey Arrhenius reaction kinetics [4–6]. Ideally, experiments could be set up to determine reaction intermediates upon initiation; however, to do so would require a capability to investigate violent chemical phenomena with extremely high fidelity at the femtosecond time scale. Therefore, perhaps the most practical method available to investigate such reactions is molecular dynamics.

Molecular dynamics is a numerical technique to integrate Newton’s equations of motion for atoms interacting with one another. The forces on each atom are calculated as the corresponding negative gradient of the potential energy of interaction with respect to the radius vector of the atomic position. For first-principles MD, this potential is the total energy of the system as calculated using DFT. This approach is considered valid since under the Borne-Oppenheimer approximation, the electronic subsystem moves at such great speed relative to the atomic cores that they instantaneously adjust to the slow motion of the nuclei. Therefore, the DFT energy is calculated at fixed positions of the nuclei. However, this is only valid provided the electronic subsystem is expected to remain in its ground state. Therefore, care must be taken in modeling hypervelocity collisions in order to be sure that excited states would be improbable in such a system. This can be determined by considering
the Massey parameter, defined as $\xi = a\Delta E/\hbar v$, where $\Delta E$ is the energy difference between the ground and first excited state, $v$ is the collision velocity, and $a$ is a characteristic intermolecular range of interaction between two molecules. For $\xi > 1$, there is little probability of non-adiabatic processes. Reasonably conservative estimations of $a$ and $v$ would be $5\text{Å}$ and $10\text{ km/s}$, respectively. For $\xi > 1$, $\Delta E \gg 0.01$; however, previous studies [77–80] of bulk compression of the various EMs investigated in collision studies have found the band gaps to be $\Delta E \sim 1\text{ eV}$ at pressures approaching $\sim 100\ \text{GPa}$. Hence, non-adiabatic electronic excitation processes are highly unlikely in bi-molecular collision simulations up to $10\ \text{km/s}$.

As molecules collide at speeds $> 3\text{km/s}$, collisional kinetic energy is loaded locally onto the incident complexes. The result is that atoms can not adjust their positions quickly enough to evenly disperse the energy to all internal degrees of freedom, leading to severe deformation and subsequent bond breaking as chemical groups are sheared or repelled away. As a result, several coincident events can occur, some being concerted, while others are not; and which events are related can be very ambiguous. Unfortunately, there are no as yet useful analytical techniques to quantify the flow of energy through the molecular complexes, and thus any analysis is limited to visual inspection of the system throughout it’s time course; i.e. watching animations and noting what happens. From these animations it is possible to qualitatively predict how reactions might proceed by tracking the energy change from reactants to products. This is done by isolating reactants and products at various reaction steps seen within the simulations, optimizing the structures so that the forces on the atoms are zero, and then comparing the internal energies. While this technique can not be used to determine absolute barriers to the reaction, it can offer insight into predicting the typical order in which reactions take place.

Essentially, initial endothermic steps, such as homolysis, that have the lowest change in energy will be preferred. Also, one might intuit which complexes are most
likely to react based on both heats of reaction, and geometry (i.e. which complexes are incident). Hypervelocity MD simulations of colliding molecules are rich in details that illustrate deviations from Arrhenius kinetics as the chemical reactions occur very rapidly, thus allowing many reaction pathways to be observed for the first time. The latter point is of great importance to the simulation community as large scale MD is often performed using atomic potentials that are trained to known chemistry. Essentially, such models may tend to show reactions for which they were trained, thus not accurately describing the real chemistry. By using first-principles DFT, however, the real reaction mechanism of initiation can be found, thus providing important insights into initiation chemistry as well as providing important information for training reactive force fields used for large-scale MD simulations of detonation.

4.2 PETN Collisions

Hypervelocity bi-molecular collision simulations of PETN molecules were performed within the range of velocities $3 \text{ km/s} - 7 \text{ km/s}$ to elucidate the chemical mechanisms of initiation of detonation. The initial positions of molecules were taken from the solid state environment, see Figure 12, so as to test whether the anisotropic sensitivities uncovered by Dick et al. [47, 48] could be correlated to the minimum threshold collision velocities for specific collision directions at which initiation would occur. The directions normal to the (001) and (110) planes, which were found to be most sensitive by experiment, had some of the lowest threshold velocities to initiate chemistry in simulations, being $3.3 \text{ km/s}$ and $3.9 \text{ km/s}$ respectively; see Table. Additionally, the prediction was made that the direction normal to the (011) plane should also be a direction of enhanced sensitivity for PETN due to the low threshold velocity of $3.2 \text{ km/s}$ found for this direction in simulations.

Another conclusion from the bi-molecular collision work for PETN was the short time needed to induce chemistry; see Table 4. For thermally driven chemistry to
Table 4: Threshold velocities to initiate chemical reactions for various collision orientations of PETN. Molecules indexed for a particular collision correspond to those in Figure 12. Also shown are products, time to reaction $t_{Rx}$, and experimentally determined detonation pressure. PETN is believed to detonate above the Chapman – Jouguet pressure of 31 GPa for the friction normal to the (101) plane.

<table>
<thead>
<tr>
<th>h k l</th>
<th>Type</th>
<th>Mol.</th>
<th>$V_{Th}$ (km/s)</th>
<th>Species</th>
<th>$t_{Rx}$ (fs)</th>
<th>Exp. Press. (GPa)</th>
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</thead>
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<tr>
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Figure 12: Schematic of crystalline environment for PETN using indexed spheres to indicate molecular positions (left). Molecules are selected from crystalline environment and then collided in directions normal to (001), (010), (011), (100), (101), (110), and (111) planes by applying half the collision velocity to each molecule as depicted on right.

occur, the energy of collision would need to be equilibrated throughout the entire molecular complex, requiring $\sim 10^{-11}$ s [3]. In collision simulations of PETN, reactions occur typically $\sim 10^{-13}$ s, as was originally predicted by Walker et al. [5, 6] This is an indication of a non-equilibrium mechano-chemical regime of chemistry that is characterized by direct bond breaking due to the localized loading of collision energy caused by rapid uniaxial compression brought on by a passing shock wave – a concept first proposed by Dremin [81] and Walker [5, 6].

Finally, the bi-molecular collisions of PETN gave the first hint that the mechano-chemical regime of initiation is characterized by unexpected reaction mechanisms. While nitro group dissociation has always been believed to be the first step of initiation chemistry, H elimination from the formaldehyde groups to form HONO was suspected as being the mechanism for further decomposition. What was seen in hypervelocity simulations was completely unexpected, however, as H elimination was observed occurring from a dissociated formaldehyde to a partially decomposed PETN molecule, as well as to a nitro group to form HONO; see top panel of Figure 13. Additionally, another exotic reaction was observed involving the formation of a C–O bond between the central C atom of a partially decomposed PETN molecule and the O
atom of a formaldehyde group still attached; see bottom panel of Figure 13. Essentially, the discovery of such reactions, never before considered in initiation chemistry, sparked the need to investigate other EMs so that future models may properly describe initiation chemistry. A more detailed description of this work is presented in the peer-reviewed journal article found in Appendix 5.

4.3 Si-PETN Collisions

An analogue of PETN, in which the central C atom is replaced by a Si atom, was synthesized by Klapötke et al. [82] in 2007. Interestingly, this Sila-pentaerythritol tetranitrate, or Si-PETN, exhibited extreme sensitivity to mechanical stimulus, exploding upon the slightest contact with a spatula, or upon reduction of solvent while in solution. The source of this hypersensitivity of Si-PETN, as compared to that of PETN, became a challenging problem for theory as experimental characterization of the underlying chemistry was all but impossible. As a result, several studies [83–85] surfaced to explain the underlying chemical mechanism based on the standard concept
of transition state theory. First, Liu et al. [83] proposed the oxygen-attack reaction characterized by a five-coordinated transition state for Si-PETN in which the O atom of a formaldehyde group enters the coordination sphere of the central Si atom, which causes nitro group dissociation, after which the formaldehyde group flips leaving the central Si atom bonded to three C atoms and one O atom, while the C atom of the flipped formaldehyde group bonds to an O atom of the formerly dissociated nitro group; see Figure 14. The whole process was found to be highly exothermic with a much lower activation barrier as compared to PETN [83]. A subsequent study by Murray et al. [84] offered reason as to why the approach of the O atom was so much easier in the case of Si-PETN than in PETN; that being the existence of a $\sigma$-hole, or surface of low electron density, about the Si atom that attracted the O atom. This $\sigma$-hole is simply the consequence of the relative size of the Si atom compared to the C atom, where Si–C bonding is typically $\sim 1.9\,\text{Å}$ as opposed to C–C bonding in PETN $\sim 1.5\,\text{Å}$. The oxygen attack reaction was then used by An et al. [85] to train reactive force field (ReaxFF) potentials to be used in large scale, MD shock study on Si-PETN, which resulted in many instances of formaldehyde flipping as seen in the oxygen-attack reaction.

While, the oxygen attack reaction may seem to offer a satisfactory explanation of why Si-PETN is so much more sensitive to mechanical stimulus than PETN, it does not preclude the existence of other reaction mechanisms that may also con-
tribute to its high sensitivity. To determine whether other chemical mechanisms are at play, first-principles MD simulations of hypervelocity bi-molecular collisions were performed for Si-PETN in exactly the same way as was done for PETN. The threshold velocities to initiate chemical reactions are surprisingly similar to those for PETN, as seen in Table 5, indicating that these threshold velocities can not be directly correlated to the amount of mechanical stimulus required for initiation in the bulk, as in flyer plate experiments; rather, they are more an indicator of the amount of kinetic energy required locally at the molecular level for chemistry to occur. Despite similarities in threshold velocities, completely different reaction mechanisms are seen for Si-PETN as opposed to PETN, while a substantial variety of reactions are seen in hypervelocity collisions of Si-PETN that go beyond the simple oxygen-attack reaction addressed in previous studies [83–85]. Though it is true that a great number of these reaction mechanisms begin with an O atom from a formaldehyde group passing into the coordination sphere of the central Si atom, many other reactions involve O atoms from nitro groups or the central Si atom from the second molecule doing the same. The resulting chemistry is diverse, producing orientationally dependent intermediates never before considered; see Figure 15.

Some of the more exotic intermediates involve bonding of adjacent formaldehyde groups on the same molecule (Figure 15 a), while others involve intermolecular binding, either with a formaldehyde group acting as a bridge between the central Si atoms of the two molecules (Figure 15 b), or with direct Si–Si bonding (Figure 15 c). Also, the formation of many of these intermediates, particularly those involving intermolecular binding, tends to be highly exothermic, which can undoubtedly lead to further reactions within the bulk. The exothermicity of Si-PETN seems the most likely reason for it’s high sensitivity to mechanical stimulus. In contrast, reactions involving PETN tend to be mostly endothermic. Thus, subjecting the two EMs to the same stimulus may result in some chemical decomposition at the local, molecular scale,
Table 5: Threshold collision velocities to initiate chemistry for Si-PETN with comparison to those of PETN for the same collision orientations. The type of collisions are denoted as 'h' for head-on and 'g' for glancing.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Type</th>
<th>Mol.</th>
<th>PETN $V_{thr}$</th>
<th>Si-PETN $V_{thr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>head-on</td>
<td>1 - 3</td>
<td>3.30</td>
<td>3.10</td>
</tr>
<tr>
<td>010</td>
<td>glancing</td>
<td>1 - 2</td>
<td>4.70</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td>head-on</td>
<td>1 - 4</td>
<td>4.40</td>
<td>4.00</td>
</tr>
<tr>
<td>011</td>
<td>glancing</td>
<td>1 - 2</td>
<td>5.30</td>
<td>5.80</td>
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<tr>
<td></td>
<td></td>
<td>1 - 3</td>
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<td>1 - 5</td>
<td>3.20</td>
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<td>4.70</td>
<td>4.10</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
<td>101</td>
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<td>4.60</td>
<td>3.50</td>
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<tr>
<td></td>
<td></td>
<td>1 - 7</td>
<td>4.40</td>
<td>3.50</td>
</tr>
<tr>
<td>110</td>
<td>glancing</td>
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<td>4.50</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 - 3</td>
<td>-</td>
<td>4.50</td>
</tr>
<tr>
<td>111</td>
<td>head-on</td>
<td>1 - 8</td>
<td>3.90</td>
<td>3.00</td>
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</tbody>
</table>

which would be short-lived in PETN, but perhaps would lead to a cascade of reaction events in Si-PETN. A more detailed description of this work is presented in the paper, submitted to the Journal of Physical Chemistry A for peer-review, found in Appendix 6.

4.4 RDX, HMX, and TATB Collisions

RDX (1,3,5-Trinitrohydro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), and TATB (1,3,5-triamino-2,4,6-trinitrobenzene) are all very important EMs, used in a variety of applications both military and industrial. Each of these EMs is composed of a ring functionalized with nitro groups, for which decomposition occurs by nitro group dissociation, followed by subsequent H elimination and ring breaking reactions. Little is known, however, about how reactions beyond nitro group dissociation occur in the non-equilibrium mechano-chemistry regime. To develop a comprehensive understanding of the initiation chemistry in these ringed ni-
tro compound EMs, hypervelocity bi-molecular collisions were performed in a similar fashion to those in the studies done for PETN and Si-PETN. However, less emphasis is placed on the threshold velocities to initiate chemistry, while more is placed on cataloging the reactions themselves for the purpose of providing insight into initiation chemistry of these EMs.

As is typically agreed upon by the scientific community, nitro group dissociation is the most likely first reaction step in the initiation chemistry of RDX [86–91]. Further, as seen in collision simulations, H elimination to form HONO after nitro group dissociation is fairly common and usually highly exothermic. Several other reaction mechanisms occur in our simulations that have not been considered. Among these are intra- and inter-molecular H transfer to N atoms on the ring that are no longer bonded to nitro groups, which happen to be highly exothermic, and may lead to ring cleavage. However, the most interesting and perhaps least expected reactions that commonly occur for RDX in collision simulations involve a reconformation of the ring into a ‘3/5’ configuration such that two N atoms on the ring bond after both having undergone nitro group dissociations; see Figure 16. This ’3/5’ conformation invariably leads to ring cleavage once the final nitro group dissociates, and has never before been considered, despite being a more common pathway observed in collision simu-
Figure 16: Formation of RDX '3/5' ring conformation. Values over bold arrows are heats of reaction from previous step. Small value pointing to bond is heat of reaction for breaking that one bond. Hashed lines indicate from where products came. \( \Delta E \) is the net heat of reaction from unreacted RDX to final product shown.

Additional, for some cases in which the '3/5' conformation occurred, water was formed within the 0.5 ps simulation time frame, which is believed to catalyze further decomposition and lead to enhanced exothermicity.

Similar to RDX, HMX is composed of the same \( \text{H}_2\text{CONN}_2 \) building blocks; the main difference being that HMX has four of these as opposed to three in the case of RDX. As such, HMX possesses some superficial chemical similarities to RDX in terms of energy required to dissociate nitro groups, or energy released due to H elimination reactions. However, the larger size and complexity of HMX allows for two distinct ring reconformations shown in Figure 17, as opposed to just one for RDX. These ring reconformations are label the 'Mask' (Figure 17 a) and the '3/7' (Figure 17 b) conformations. The '3/7' conformation occurs when two adjacent nitro groups dissociate, allowing the N atoms on the ring to bond, forming a three-member ring and a seven-member ring. The 'Mask' conformation, on the other hand, occurs when opposing nitro groups dissociate, allowing the opposing N atoms on the ring to bond, forming two five-member rings. As in RDX, the asymmetric '3/7' conformation ultimately leads to ring cleavage in collision simulations; whereas the 'Mask' conformation was observed to lead only to further nitro group dissociations. Interestingly, the products resulting from the '3/7' conformation have only endothermic H elimination reactions; while H elimination reactions for the 'Mask' conformation are highly exothermic after
Figure 17: HMX ring reconformations: a) formation of 'Mask' conformation; b) formation of '3/7' conformation. Values above bold arrows are heats of reaction from previous step. Small values near bonds are heats of reaction for bond breaking, while values near H atoms are heats of reaction for H elimination by NO$_2$ to form HONO. ΔE values are net heats of reaction from unreacted HMX molecules to final products shown.

one additional nitro group dissociation, and should lead to ring cleavage, though no such reactions were observed within the simulation time frame.

In addition to the unimolecular reactions mentioned above, bi-molecular reactions, including inter-molecular H transfer and inter-ring bonding, are also observed. For orientations in which nitro groups on both HMX molecules are aligned to collide, one of two things will occur beyond simple nitro group dissociation: either an H atom transfers from one molecule to the N atom on the ring of the other, or the two vacant N atoms on each ring will form a bond as seen in Figure 18 a. So long as one of the rings does not reconform into a 'Mask' conformation seen in Figure 18 c, there seems to always be a preference for the bonded N atoms to increase bond order, thus sacrificing other bonds within the rings and leading to ring cleavage of both rings. The end result is two long chains, each containing one nitro group, and a nitrogen molecule as shown in Figure 18 b. The resulting chains are observed to decompose further into N(CH$_2$)$_2$ and H$_2$CNH$_2$CONN$_2$.

TATB is yet another ringed nitro compound EM, but is distinct from the nitramine explosives RDX and HMX in that rather than possessing a cyclic ring of alternating
Figure 18: HMX bi-molecular reactions: a) bonded HMX rings that lead to either b) formation of N$_2$ and chains, or c) formation of 'Mask' conformation. Values above bold arrows are heats of reaction from previous step; while $\Delta E$ values are net heats of reaction from initial HMX molecules to products shown.

N and C atoms, it has an aromatic ring of carbon, making it far more insensitive to shock as compared to RDX and HMX due to its high resistance to ring cleavage. Additionally, the C–N bond in TATB is much stronger than the N–N bonds in RDX and HMX, meaning that much more energy is required to cause nitro group dissociation. Also, TATB molecules are planar and somewhat stiffer than RDX or HMX, which caused some issues when simulating hypervelocity bi-molecular collisions without the steric constraints imposed by the crystalline environment: most lower velocity collisions resulted in molecules imparting only rotation to and glancing off one another. To surmount these challenges, TATB collisions were performed up to collision velocities of 10 km/s, which yielded some surprising initiation chemistry. While the predicted mode of initiation for TATB involved ring closure [92] – that is an H atom from an amine group transferring to an O atom of a neighboring nitro group leading to the dissociation of HONO – this was only seen in one case. Further, one experimental study [93] revealed the disappearance of a spectral line associated with the all-carbon
Figure 19: Formation of TATB ’3/5’ ring conformation. Heats of reaction from each step are shown above bold arrows; net heat of reaction is given by $\Delta E$. Small values pointing to bonds are heats of reaction for bond breaking, while those near H atoms are heats of reaction for H elimination by NO$_2$ to form HONO.

ring within the range of their probe. This change in spectrum was attributed to some unknown ring deformation as ring cleavage was deemed unlikely due to the energy imparted to the molecules. In fact, collision simulations of TATB reveal the prevalence of just such a ring deformation in which the TATB ring reconfigures into a ’3/5’ ring, as seen for RDX, after nitro group dissociation; see Figure 19. While still endothermic, this ring reconfiguration reaction has a heat of reaction that is a little over half that of nitro group dissociation. Additionally, nitro group dissociation is reduced to less than a third of what it is without ring reconfiguration. Hence, the ’3/5’ ring conformation in TATB is an essential mechanism for unimolecular decomposition.

In addition to the ’3/5’ ring conformation, a bi-molecular ring reduction pathway was observed for a couple of collision cases normal to the (100) plane. This pathway involves the transfer of a nitro group from one molecule to a C atom bonded to an amino group on the other molecule; see Figure 20 a. This causes NO to dissociate from the transferred nitro group, leaving an O atom bonded to the C atom on the ring with an amino group. This configuration changes the local bond order on the ring, causing the C atom to dissociate from one of the other C atoms, leading to exothermic collapse into a five-member ring and an HNCO group. The O atom of the HNCO group then forms a bond with the C atom that is still part of the ring, which results in the dissociation of CO and HNC, as well as exothermic collapse into...
a) bi-molecular reactions leading to five-member ring; b) unimolecular reactions starting from five-member ring leading to four-member ring. Thin arrows show where species will go, while hashed line show from where products came. Values above bold arrows are heats of reaction from previous step; $\Delta E$ represents net heat of reaction from unreacted TATB molecules to final products shown.

a four-member ring bonded to two amino and two nitro groups; see Figure 20 b. The high exothermicity of the ring collapse reactions results in a net heat of reaction on the order of one nitro group dissociation. Other bi-molecular reaction mechanisms resulting in ring cleavage were observed in collision simulations of TATB, but none had as low a net heat of reaction as the one just described.

A more detailed description of this work on RDX, HMX, and TATB bi-molecular hypervelocity collisions is presented in the paper, submitted to the Journal of Physical Chemistry A for peer-review, found in Appendix 7.
5 Conclusion

The research performed during this PhD project addresses several critical challenges within the EM and detonation community: the theoretical prediction of thermo-physical properties of EMs to be used by the mesoscale simulation community to develop more robust models of detonation performance under a variety of conditions; the theoretical investigation of potential polymeric nitrogen precursors and how these may be transformed into novel, recoverable high nitrogen EMs; and the investigation of EM initiation chemistry towards building a catalog of never before considered reaction mechanisms that can be used to train improved reactive potentials for building more sophisticated and predictive models of detonation. The first thrust of predicting thermo-physical properties demonstrates the feasibility of using first-principles DFT hydrostatic compression simulations with DFPT and the quasi-harmonic approximation to provide reasonably accurate properties over a wide range of applicable pressures and temperatures, which may further increase the capabilities of mesoscale modeling to aid the engineering of EM performance and safety, while also providing better understanding of the macroscopic behavior of EM detonation. The second thrust, investigation of a potential azide precursor of novel polymeric nitrogen EMs, outlines the initial steps towards understanding the behavior of NH$_4$N$_3$ under hydrostatic pressure loading, which may one day lead to the viable manufacture of more powerful and cleaner burning high nitrogen EM compounds that will provide great benefit for both military and industrial applications, ranging from munitions to propellents. Finally, the third thrust, first-principles hypervelocity bi-molecular collision simulations of EM molecules, demonstrates the fundamental nature of initiation
chemistry as a rapid mechano-chemical process that produces a variety of intermediates never before considered, which should be included in the training of reactive potentials for large scale MD simulations.

Future work involves refinement of predictions of thermo-physical properties of EMs, complete characterization of the polymorphs of NH$_4$N$_3$ under hydrostatic loading and investigation of the dynamics involved in polymorphic phase transitions, and further expansion of hypervelocity collision simulations to catalog chemical initiation intermediates of other EMs. The refinement of predicted thermo-physical properties of EMs will require improvements to the description of weak dispersive forces, including vdW interaction, to predict structures more commensurate with those found in nature. Further prediction of thermodynamic properties such as heat capacities, thermal expansion coefficients, and Gruneisen parameters as functions of pressure and temperature will also be required, and may be refined by inclusion of anharmonic effects within calculated spectra. These improvements to the prediction of thermo-physical properties of EMs will also serve to aid theoretical efforts towards better characterization of polymeric nitrogen precursors and polymorph searches which may one day guide experimentalist to the recovery of novel polymeric nitrogen EMs. Lastly, catalogs of the chemical intermediates of initiation should be expanded to include more EMs, while transition state theory studies need to be performed to calculate the theoretical barriers of reactions for these intermediates, which will make possible the development of more robust reactive potentials. Additionally, further investigation of the rapid local energy deposition of collision energy into the colliding molecular complex is warranted pending the development of techniques to analyze such phenomena.
References


Appendix 1: Equations of state for energetic materials from density functional theory with van der Waals, thermal, and zero-point energy corrections

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Related Publications

Equations of state for energetic materials from density functional theory with van der Waals, thermal, and zero-point energy corrections


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It is shown that the introduction of zero-point energy and thermal effects to density functional theory with an empirical van der Waals correction results in a significant improvement in the prediction of equilibrium volumes and isothermal equations of state for hydrostatic compressions of energetic materials at nonzero temperatures. This method can be used to predict the thermophysical properties of these materials for a wide range of pressures and temperatures. © 2010 American Institute of Physics [doi:10.1063/1.3526754]

Equations of state (EOS), which establish fundamental relationships between thermodynamic variables, are important because they provide necessary input for the description of materials at the mesoscopic and continuum levels. In the case of energetic materials (EMs), experiment faces difficulties in accurately measuring EOSs due to problems associated with the compressive medium in static high pressure experiments. Theory, on the other hand, can provide a viable alternative to costly experimentation. However, the straightforward application of density functional theory (DFT) to calculate the EOSs of EMs has failed to deliver accurate results partially due to a poor description of van der Waals (vdW) interactions in molecular crystals. Recently, substantial efforts within the DFT community have been directed toward fixing the vdW problem either by modifying exchange-correlation functionals, or through empirical corrections added to DFT (DFT+vdW). While it has been demonstrated that the latter approach yields improved results, the error in the calculated equilibrium volumes of EM crystals is still appreciable. In this work it is shown that the introduction of zero-point energy (ZPE) and thermal effects to DFT+vdW not only largely removes this error, but also significantly improves the prediction of isothermal EOSs for hydrostatic compressions of EMs.

The approach is based on standard DFT using the Perdew–Burke–Ernzerhof exchange-correlation functional with empirical vdW C_{6}/r^{6} type atom-atom potentials added to DFT using damping functions to switch off diverging vdW contributions at small interatomic distances. We use the specific parametrization of Neuman and Perrin, which is similar to the DFT-D approach of Grimme. Both compressed and expanded structures were optimized within the DFT+vdW framework at fixed volume V. Then, ZPE and thermal effects were included by adding their contributions to the “cold pressure” calculated by DFT+vdW. Expansion calculations, corresponding to negative “cold pressure” (see Fig. 1), were performed to obtain more low-pressure points when positive ZPE and thermal contributions are added to DFT+vdW. The ZPE and thermal pressure contributions were determined using the quasiharmonic approximation, which takes into account anharmonic effects that result in the dependence of the frequencies on the volume. Therefore, the vibration spectrum was obtained for each compression or expansion corresponding to volume V. Then, the crystal free energy A at a given temperature T and volume V was calculated using the vibration spectrum and energy expression for the quantum harmonic oscillator from statistical mechanics. Finally, an analytical form for the free energy as a function of volume A(V) (at a given T) was determined by a polynomial fit to numerical values of A, thereby enabling the thermal and ZPE pressure contributions to be calculated as P_{A}(V) = −[\partial A(V)/\partial V]. The entire computational framework is referred to as DFT+vdW+T.

The accuracy of the DFT+vdW+T approach for EMs was tested by comparing predicted equilibrium volumes \(v_{0}\), the isothermal EOSs \(P(V)\), bulk moduli \(B_{0}\), and their pressure derivatives \(B_{0}'\) to available experimental data. To extract \(v_{0}\), \(B_{0}\), and \(B_{0}'\), we followed the standard procedure used by experimentalists: the computed \(P,V\) data points, obtained at a given \(T\), were fitted to the Birch–Murnaghan EOS (Ref. 12)

\[
P(V,T) = \frac{2}{3} B_{0}(T) \left( \frac{\eta(T)}{\eta(T)_{0}} \right)^{7/3} - \frac{1}{3} \left( \frac{\eta(T)}{\eta(T)_{0}} \right)^{5/3} \times \left\{1 + \frac{2}{3} \left[ B_{0}'(T) - 4 \frac{\eta(T)}{\eta(T)_{0}} \right] \right\}
\]

\(\eta(T) = V/V_{0}(T)\),

(1)

with \(V_{0}(T)\), \(B_{0}(T)\), and \(B_{0}'(T)\) treated as fitting parameters.

As shown in Table 1, pure DFT overpredicts unit-cell volumes for the entire set of EM crystals by +9.8% on average compared to experiment, while DFT+vdW underpredicts volumes by −2.9%. On the other hand, the equilibrium volumes calculated using DFT+vdW+T, also shown in Table 1, have an average error of only 0.41%. Note that the equilibrium volume of solid nitromethane (NM) obtained by DFT+vdW+T, having an error of only 0.02%, is underpredicted by DFT+vdW by −1.93%. The NM case demonstrates the importance of the ZPE contributions, because its crystal structure was determined at 4.2 K, where the thermal pressure is negligible.

The isothermal EOSs for hydrostatic compressions of the EMs in this study, shown in Fig. 1, were also calculated using the DFT+vdW+T method at temperatures corresponding to those of the experiments. For each plot in Fig. 1,
DFT+vdW shows increased binding within the crystal, resulting in a drop in pressure relative to pure DFT. This is especially pronounced for the layered crystalline structures of FOX-7 and TATB, where pure DFT offers a poor description of interlayer dispersive interactions. The $P, V$ data produced by DFT+vdW+T lie between those of DFT+vdW and pure DFT. A comparison of the three with experiment demonstrates the good accuracy of the DFT+vdW+T method.

Also shown in Fig. 1 as solid lines is the Birch-Murnaghan EOS for each EM [Eq. (1)] with the values for $V_0$, $B_0$, and $B'_0$ given in Table II, obtained from three parameter fits of this EOS to the $P, V$ data calculated using DFT+vdW+T. Fitting was done from 0 to 4 GPa for FOX-7, to 12 GPa for HMX, to 7 GPa for NM, to 10 GPa for PETN, to 4 GPa for RDX, and to 8 GPa for TATB so that the fitting ranges were comparable to those of compression experiments, which included pressures up to the first polymorphic phase transition. The temperatures given in Table II do not necessarily coincide with those shown in Table I, which involve a different set of experimental studies aimed at determining crystal structure only. While values for $V_0$ from DFT+vdW+T calculations are in excellent agreement with experiment (Table I), it is difficult to make similar comparisons for $B_0$ and $B'_0$ since the experimental results can vary by more than 50% between studies due to differences in compressive media, inconsistencies in fitting ranges and fitting schemes, and noise inherent within each experimental data set. Nonetheless, agreement between theory and experiment of better than 10% for $B'_0$ was found with at least one experimental compression study for each EM, and arguably fair agreement was also found for $B'_0$. It should be noted that the experimental data of Yoo and Cynn\cite{14} for HMX had to be refitted. The original experimental range 0–27 GPa includes the $\beta\rightarrow\epsilon$ phase transition around 12 GPa; therefore, their data were processed in the pressure interval up to 12 GPa, which resulted in better agreement between DFT+vdW+T and their experiment. Finally, the relatively smooth nature of the

**TABLE I.** Equilibrium unit-cell volumes ($V_0$), as calculated using pure DFT, DFT+vdW, and DFT+vdW+T, are compared to experimental values determined at the temperatures shown. The error is given under each calculated value.

<table>
<thead>
<tr>
<th>System</th>
<th>$T$ (K)</th>
<th>$V_0$ Exp. ($\text{Å}^3$)</th>
<th>$V_0$ pure DFT ($\text{Å}^3$)</th>
<th>$V_0$ DFT+vdW ($\text{Å}^3$)</th>
<th>$V_0$ DFT+vdW+T ($\text{Å}^3$)</th>
</tr>
</thead>
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<td>$-3.07%$</td>
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\cite{15} Reference 15.  
\cite{16} Reference 16.  
\cite{17} Reference 17.  
\cite{18} Reference 18.  
\cite{19} Reference 19.  
\cite{20} Reference 20.
TABLE II. $B_0$, $B_0'$, and $V_0$ for each EM at specified temperatures $T$ of experiments obtained by fits to the Birch–Murnaghan EOS. The percent difference between theory and experiment is given under calculated values of $B_0$ and $B_0'$.  

<table>
<thead>
<tr>
<th>System</th>
<th>$T$ (K)</th>
<th>$B_0$ Expt. (GPa)</th>
<th>$B_0'$ Expt. (GPa)</th>
<th>$B_0$ Theory (GPa)</th>
<th>$B_0'$ Theory (GPa)</th>
<th>$V_0$ Theory ($\AA^3$)</th>
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DFT+vdW+T data, as compared to experiment, results in a fluctuation in values for $B_0$ and $B_0'$ not more than 5% when the fitting range is changed.  

As shown in this work, DFT+vdW+T, incorporating temperature and ZPE effects, can achieve excellent agreement with experiment. This improved capability should make possible reliable prediction of various thermophysical properties for a wide range of temperatures and pressures not easily obtainable in costly experiments, thus providing fundamental input for mesoscale and continuum simulations for EMs.  

The work at the USF and NRL was supported by the Office of Naval Research (ONR) and NRL. In addition, USF received a partial support from ARO within MURI on insensitive munitions. Calculations were performed using NSF TeraGrid facilities, USF Research Computing Cluster, and computational facilities of Materials Simulation Laboratory at the University of South Florida.

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Appendix 2: Prediction of Isothermal Equation of State of an Explosive Nitrate Ester by van der Waals Density Functional Theory

Publication Record


http://dx.doi.org/10.1021/jz900026j

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Prediction of Isothermal Equation of State of an Explosive Nitrate Ester by van der Waals Density Functional Theory

Aaron C. Landerville,*† Michael W. Conroy,‡ Ivan I. Oleynik,† and Carter T. White‡

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ABSTRACT A new energetic material, nitrate ester 1 (NEST-1), has shown promise as a powerful, technologically attractive explosive. Its physical properties under compression, however, are currently unknown. Accurate density functional calculations together with a reliable empirical van der Waals correction are employed to predict the isothermal hydrostatic equation of state for this material prior to any known experimental results. The accuracy of results obtained from this approach was tested against experimentally known NEST-1 equilibrium properties and found to be excellent.

SECTION Statistical Mechanics, Thermodynamics, Medium Effects

R

cently synthesized by Chavez et al., 1 a novel energetic nitrate ester, 2,3-bis-hydroxymethyl-2,3-dinitro-1,4-butanediol tetranitrate, shows promising properties for use in explosives applications. Herein, this new material will be referred to as NEST-1 (Nitrate ESTer-1), although it has also been termed nitrate ester molecule 1. 1

NEST-1 exhibits sensitivity properties similar to those of pentaerythritol tetranitrate (PETN), and predictions of its performance properties indicate that it is at least as powerful an explosive as cyclotetramethylene tetranitramine (HMX). 1 Importantly, NEST-1 has a relatively low melting point of 85–86 °C as compared to its decomposition point of 141 °C. This means that NEST-1 can be safely melted and cast into a mold, potentially making it useful for a wide variety of applications. Further characterization is required to investigate the potential use of this material.

NEST-1 has a molecular structure similar to that of PETN. However, instead of five carbon atoms, it has six. Two connected carbon atoms constitute the center of the molecule, each bound by one NO2 group and two CH2ONO2 groups, as depicted in Figure 1, giving it the overall chemical formula of C6H8N6O16.

Figure 1. Schematic of a NEST-1 molecule.

The Vienna Ab-initio Simulation Package 3,4 was used to perform all DFT calculations using the Perdew–Burke–Ernzerhof functional 5 with projector-augmented wave potentials 6,7 and the Neumann-Perrin vdW correction. 2 Only the gamma point was used to sample the Brillouin zone because of the large unit cell size. 6 The DFT calculations were performed using an energy cutoff of 700 eV and an electronic energy convergence tolerance of 10−6 eV, which, when compared with calculations using a range of cutoffs from 400–1000 e V, yielded a convergence better than 0.0015 eV for energy per atom, and 0.015 eV/Å for forces. The conjugate-gradient algorithm was employed to relax all structures until the maximum force on any atom in the unit cell was less than 0.03 eV/Å.

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The experimental structure at ambient conditions was relaxed without constraints to determine the calculated equilibrium structure. Hydrostatic-compression simulations were performed by scaling the volume of the unit cell from 100% to 60% of the calculated equilibrium volume. Relaxations of the unit-cell shape and atomic coordinates were performed at intermediate steps of 2%. The calculated unit-cell properties at equilibrium were obtained from a fit to experimental results when they become well reproduced. Hydrostatic-compression simulations were performed by scaling the volume of the unit cell from 100% to 60% of the calculated equilibrium volume. Relaxations of the unit-cell shape and atomic coordinates were performed at intermediate steps of 2%. The calculated unit-cell properties at equilibrium were obtained from a fit to experimental results when they become well reproduced. Hydrostatic-compression simulations were performed by scaling the volume of the unit cell from 100% to 60% of the calculated equilibrium volume. Relaxations of the unit-cell shape and atomic coordinates were performed at intermediate steps of 2%. The calculated unit-cell properties at equilibrium were obtained from a fit to experimental results when they become well reproduced.

The lattice constants $a$, $b$, and $c$ are reported in Figure 2 as a function of pressure. The $b$ and $c$ lattice constants exhibit a relatively smooth monotonic behavior, but the $a$ lattice constant, while still monotonic, first descends more steeply with increasing pressure and then plateaus in the range of 22 to 32 GPa. This plateau occurs over a region where further compression along the $a$ axis is difficult without a rotation and bending of the nitro groups primarily with respect to the $b$ axis. Completion of this required change, however, is not favored until the pressure reaches around 32 GPa, whereupon compression along the $a$ axis becomes easier. Up to 27 GPa, the computational results for all three lattice constants are well reproduced using fifth-degree polynomials with the fitting coefficients given in Table 2. Although these polynomials provide a compact way of numerically summarizing the computational results up to 27 GPa, they should not be used for greater pressures.

![Figure 2. Lattice constants as a function of pressure within the volume compression ratio range of $\eta = V/V_0 = 0.60$–1.00. The solid lines are included as guides to the eye.](image)

<table>
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<th>Parameter</th>
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<td>$c$</td>
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*Each constant $C_n$ has units of Å/(GPa)$^n$*.

From the hydrostatic compression simulations, the iso-thermal EOS was obtained and is shown in Figure 3 as a function of the volume compression ratio, $\eta = V/V_0$, where $V$ and $V_0$ are the compressed and uncompressed volumes, respectively. It is a common practice to fit the EOS data points (either experimental or calculated) by an analytic function of pressure, $P$, versus $\eta$, assuming as parameters the zero pressure isothermal bulk modulus $B_0$ and its pressure derivative $B'_0$. Such fits can be used to conveniently represent the whole set of numerical data points. In some cases, fitting to an analytic EOS is also used to smooth the experimental data. In addition, if the functional form is physically viable, the analytic EOS obtained from a fit to the data over some lower pressure and compression range can be successfully used to extrapolate the results to higher pressures and compressions. In this work, we fit the vdW-DFT data points using the analytic Birch–Murnaghan EOS,

$$P = \frac{3}{2} B_0 (\eta^{-7/3} - \eta^{-5/3}) \left[ 1 + \frac{3}{4} (B'_0 - 4) (\eta^{-5/3} - 1) \right] \quad \text{(1)}$$

for pressures up to the point closest to 5 GPa, and found that $B_0 = 15.9$ GPa, and $B'_0 = 7.1$. Figure 3 shows that this fit yields good agreement with the calculated pressure versus volume data, not only for pressures up to 5 GPa but also throughout the entire range of compressions studied, this range extends up to 44 GPa—well above the Chapman-Jouguet pressure of 40 GPa. Note, however, that care should be exercised when comparing values of $B_0$ and $B'_0$ obtained from this fit to those obtained from a fit to experimental results when they become...
available. One problem is that the values of $B_0$ and $B'_0$ depend on both the functional form of the EOS assumed\textsuperscript{10–12} and the pressure range of the fit. This point, as well as other problems that can arise in the analysis of the experimental and theoretical data, is discussed in detail by Menikoff and Sewell.\textsuperscript{12} Moreover, in the case of NEST-1, we have found that increasing $B_0$ can often be largely compensated by decreasing $B'_0$. For example, both sets [$B_0 = 15.9$ GPa and $B'_0 = 7.1$] and [$B_0 = 17.7$ GPa and $B'_0 = 6.4$] provide good fits to the computed data, when used with the analytic Birch–Murnaghan EOS, as shown in Figure 3. Therefore, it is the $P$–$V$ curves depicted in Figure 3, which are all much the same in the higher pressure region of interest, that should be tested experimentally rather than the precise values of $B_0$ and $B'_0$ that can be used to generate these curves assuming the Birch–Murnaghan EOS.

![Figure 3. Computed vdw-DFT points (open squares) for the isothermal EOS for NEST-I compared to values obtained from the Birch–Murnaghan EOS, assuming $B_0 = 15.9$ GPa and $B'_0 = 7.1$ (solid line) and $B_0 = 17.7$ GPa and $B'_0 = 6.4$ (dashed line). The range in the volume compression ratio shown is $\eta = V/V_0 = 0.60$–1.00.](image)

In summary, the hydrostatic EOS of the new energetic material NEST-I was predicted by performing accurate calculations using vdW-corrected DFT. The results were successfully tested by comparing the equilibrium structural parameters with experiment. The high pressure data will be important for future mesoscale modeling of NEST-I, and should help stimulate experimental measurements of its EOS.

SUPPORTING INFORMATION AVAILABLE Figure and caption showing comparison of computed vdw-DFT data to corresponding experimental results for β-HMX, PETN-1, and α-RDX. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT The work at USF and NRL was supported by the Office of Naval Research (ONR) and NRL. Calculations were performed using NSF TeraGrid facilities. USF Research Computing Cluster, and computational facilities of Materials Simulation Laboratory at the University of South Florida funded by ARO DURIP.

REFERENCES

Appendix 3: Ammonium azide under hydrostatic compression

Publication Record


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Related Publications

Ammonium azide under hydrostatic compression

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Email: alanderv@mail.usf.edu

Abstract. The properties of ammonium azide NH₄N₃ upon compression were investigated using first-principles density functional theory. The equation of state was calculated and the mechanism of a phase transition experimentally observed at 3.3 GPa is elucidated. Novel polymorphs of NH₄N₃ were found using a simple structure search algorithm employing random atomic displacements upon static compression. The structures of three new polymorphs, labelled as B, C, and D, are similar to those of other metal azides.

1. Introduction

Polymeric nitrogen compounds hold tremendous potential as energetic materials due to extremely high energy release upon conversion of singly-bonded material to triply-bonded N₂ molecules, with the expectation of exceeding the explosive performance of HMX by several times [1]. It has been proposed by Hu and Zhang [2] that hydro-nitrogen solid may offer a convenient pathway to polymeric nitrogen. Further, the computational study of Hu and Zhang suggests that hydro-nitrogen solid should be produced upon compression of ammonium azide (NH₄N₃) to 36 GPa [2]. However, experimental studies of NH₄N₃ have established that a polymorphic transition from Phase I to Phase II, referred to in this work as Phase A-I and A-II, occurs at ~3.3 GPa and Phase A-II of NH₄N₃ seems to persist at least up to 55 GPa [3–5]. Therefore, no phase transition to hydro-nitrogen solid has been detected so far with pressure loading at 300 K. Usually, the material transformation upon compression is experimentally probed using Raman spectroscopy, which deals with vibrational properties of the system under study. Although the analysis of vibrational spectra allows one to make some conclusions about changes of crystal structure upon compression, its indirect nature requires additional information to relate the observed spectrum and the underlying atomic structure. Therefore, density functional theory (DFT), which calculates both the atomic and electronic structures of the crystal upon compression from first principles, is a valuable tool to complement experimental studies by providing information that is difficult or sometimes impossible to obtain from experiment.

The goal of this work is to investigate the behavior of ammonium azide NH₄N₃ upon compression using first-principles density functional theory. This includes studies of crystal evolution upon compression, and the search for new polymorphs that may be obtained by subjecting NH₄N₃ crystal to high pressure and employing a simple atomic randomization algorithm. The possibility of new phases is envisioned due to the existence of multiple polymorphs in the case of metal azides such as LiN₃, KN₃, and NaN₃. Should other polymorphs of NH₄N₃ be found by experiment, a possibility then exists that one of these crystal phases may act as an intermediate for transition to hydro-nitrogen solid. In order to realize the existence of a proposed polymorph, however, it would be useful for experimentalists to have a priori knowledge of its structure at various pressures.
2. Computational Details

Plane-wave density functional theory calculations were performed using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [6] with norm-conserving pseudopotentials and the DFT-D2 van der Waals (vdW) correction of Grimme [7], as implemented in the Quantum Espresso package [8], to account for weak dispersive forces between molecules. The following parameters were carefully determined to give accurate forces and vibrational frequencies: an electronic kinetic energy cutoff of 100 Ry, Monkhorst-Pack [9] k-point sampling of the Brillouin zone with spacing 0.05 Å\(^{-1}\) along each reciprocal lattice vector, and a maximum force convergence criterion of \(10^{-7}\) Ry/\(a_0\). The equation of state (EOS) was calculated by first determining the equilibrium unit cell volume of Phase A-I, and then sequentially compressing and expanding hydrostatically at 0.02\(V_0^{\alpha+1}\) increments within the interval \(0.5V_0^{\alpha+1} < V < 1.1V_0^{\alpha+1}\). The geometry of each structure was optimized, followed by density functional perturbation theory calculation of the vibration spectrum. For comparison of the calculated equilibrium volume to that of experiment, as well as comparison of structural evolution through the Phase A-I to A-II transition, temperature and zero-point energy effects were incorporated into the EOS using the quasi-harmonic approximation, which was employed to calculate the free energy. The pressure contribution is calculated as the derivative of the free energy with respect to volume at 300 K. More details can be found in Ref. [10]. This contribution was then added to the cold pressure calculated by DFT. To investigate the possible existence of other \(\text{NH}_2\text{N}_3\) polymorphs, we utilize a simple atomic randomization scheme by which the crystal is sequentially compressed by 0.02\(V_0^{\alpha+1}\), atomic positions are randomly displaced by no more than 0.1 Å, and the atomic positions and cell parameters are then relaxed under constant volume constraint. Once reordering of the crystal is found, each structure is sequentially expanded back to zero pressure without randomization to determine the lowest pressure at which a new phase is retained. For compactness, phases A-I, A-II, and A-III are referred to as simply Phase A with the correct phase implied by the given pressure.

3. Results

The equilibrium volume for the \(\text{NH}_2\text{N}_3\) crystal was calculated by optimizing the experimental structure determined by Prince and Choi [11]. The comparison of calculated and experimental equilibrium volumes is shown in table 1. DFT alone over-predicts the equilibrium volume by 2.7%, whereas DFT with the D2 vdW correction by Grimme [7] under-predicts the volume by 6.5%, and DFT with vdW plus thermal correction at 300 K results in an equilibrium volume 3.3% below the experimental volume. The disagreement with experiment is likely due to an inadequate description of dispersive interactions, such as hydrogen bonding, despite the use of the DFT-D2 vdW correction. For completeness, the thermally corrected EOS is compared to the cold curve for \(\text{NH}_2\text{N}_3\) in figure 1.

Medvedev et al. [3] identified a phase transition from Phase A-I to A-II (Phase I to II in their work) at \(~3.3\) GPa based on abrupt changes in the Raman spectrum. They proposed that these changes were due to the rotation of azides causing the weakening of hydrogen bonds under compression [3]. To confirm this, hydrostatic compression calculations were performed using DFT, which subsequently showed the rotation of the azides along the c lattice vector within the c–b plane; see figure 2. The calculated structure at pressure 3.4 GPa reveals that the azides oriented along the c-lattice vector within the c–b plane make an angle of 14° with the c–a plane; though experiment suggests this angle should be closer to 20° [5]. The abrupt changes in Raman spectrum Medvedev et al. [3] had observed involved mode discontinuities and splitting with prominent red-shifting of the N-H stretch modes, all of which being attributed to the weakening of hydrogen bonding between the ammonium and azide ions. The red-shifting of the N-H stretch modes with pressure continued up to \(~10\) GPa, at which point these modes appear to begin blue-shifting with pressure [3]. Interestingly, our compression calculations show the azides flattening out along the c lattice vector and reversing orientation at 10.9 GPa. The calculations show that by 27.1 GPa the azides once again make a 14° angle with the c–a
plane, which may indicate a transition into a new Phase A-III as hydrogen bonding is expected to once again be enhanced by the azide orientation.

Table 1. Comparison of calculated and experimental equilibrium volumes for ammonium azide.

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<th>Volume (Å³)</th>
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<tr>
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Figure 1. EOS for Phase A of NH₄N₃ with and without thermal correction. Red line is Birch-Murnaghan fit of thermally corrected EOS with parameters V₀, B₀, and B'₀ shown.

Figure 2. Evolution of azides upon compression through Phase A-I to Phase A-II transition as seen from the c–b plane. 2x2x2 super cells are shown.

To determine the existence of novel NH₄N₃ polymorphs we employ the atomic randomization scheme explained above. At pressures above 64 GPa (T = 0 K) we find a new polymorph labeled Phase B, in which the azides are reoriented, see figure 5, and which is retained upon decompression to 0 GPa. The crystal structure evolution upon randomized compression and non-randomized decompression is shown in figure 3, which displays the relative enthalpy \( H = E^{\text{DFT}} + PV \) at zero temperature for each phase found, all referenced by that of Phase A. Following the randomization process, Phase A is retained until 50 GPa where the evolution of the “randomized” structure diverges.
from the horizontal reference line for Phase A. Decompression of any structure up to 64 GPa will result in full recovery of Phase A. Decompression of any structure at or above 64 GPa results in a path connecting the compressed point with the line corresponding to Phase B (one such segment is shown connecting the perturbed structure at 64 GPa to the Phase B line at 45 GPa. The decompression then follows the Phase B line back to 0 GPa. Finally, continued compression with randomization eventually results in the structure coinciding with Phase B above 80 GPa. Interestingly, the enthalpy of Phase B is lower than that of Phase A beyond ~5 GPa, indicating that Phase A should be metastable at high pressure. As the actual energy barrier for the transition from A to B is unknown it is difficult to make any conclusion on whether Phase B is accessed under conditions of diamond anvil cell experiments.

Figure 3. Relative enthalpy (T = 0 K) plots of Phases A, B, D, and transition from A to B via atomic randomizations referenced by Phase A. Phase C not shown as its range is limited to 1.5 GPa.

It is important to note that Phase B has a monoclinic crystal structure similar to that of \( \alpha\)-NaN\(_3\) [12]. One might expect that as seen with the \( \alpha \) to \( \beta \) transition in NaN\(_3\), induced by thermal expansion, Phase B should transition into another polymorph upon expansion. In fact, this is precisely what is seen for the EOSs in figure 4 as Phase B transitions to Phase C when expanded to a volume of \( \sim 287 \ \text{Å}^3 \) (1.04\( V_{\text{\( \alpha \)}} \)). However, Phase C does not have the same hexagonal symmetry as \( \beta \)-NaN\(_3\); rather it is orthorhombic and appears similar to AgN\(_3\) with azides arranged in a criss cross pattern offset by an angle of 155° when viewing the \( c-b \) projection; see figure 5. As Phase C is compressed, the azides push against each other along the \( c \) lattice vector up to \( \sim 1.5 \) GPa, at which point the crystal suddenly transforms into yet another polymorph, Phase D, resulting in reduction of the energy; see EOS in figure 4. This new, triclinic phase D has azide orientation similar to that of \( \alpha \)-NaN\(_3\) with all azides oriented in parallel. Surprisingly, the energy and pressure as functions of volume for Phase D are
almost indistinguishable from those of Phase B despite the different structures; see figure 5 for structure comparison. As a consequence, Phases B and D have nearly the same enthalpies as seen in figure 3. We believe it entirely possible that if Phase B were present at zero pressure, heated, and then compressed, a mixture of Phases B and D would be formed and retained at high pressures.

### Figure 5
Comparison of super-cell structures shown for projections of a-b, c-a, and c-b planes for Phases A-II, B, and D at 0.90 \( V_0^{\alpha^1} \), as well as for Phase C at 1.10 \( V_0^{\alpha^1} \) for completeness.

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### 4. Summary
Equations of state and enthalpies were calculated for the known phases of ammonium azide (A-I, II, and III) and three new phases (B, C, and D), which were found using a simple randomized atomic displacement algorithm applied upon static compression. We find that the transition from A-I to A-II reported by Medvedev et al. [3], and verified by Wu et al. [5] using x-ray diffraction, coincides with the rotation of azides within the \( b-c \) plane through less than a 14˚ angle with the \( c-a \) plane, thus weakening hydrogen bonding. We further classify a new Phase A-III as occurring near ~27 GPa, where the azides exceed a 14˚ angle with the \( c-a \) plane in reverse orientation along the \( c \) lattice vector. When randomized atomic displacements are included in the compression of Phase A-III, a new Phase B with symmetry similar to that of \( \alpha \)-NaN\(_3\) is retained. Upon expansion, a new Phase C is formed at...
1.04V₀, which appears similar to AgN₃. Compressing Phase C to ~1.5 GPa induces yet another transition into Phase D, which has an azide arrangement similar to that of α-NaN₃, and nearly the same enthalpy as Phase B. We predict that should Phase B ever be produced it should coexist with Phase D.

Acknowledgements
We would like to thank Su Peiris at DTRA and Jonathan Crowhurst at LLNL for invaluable discussions. Funding is provided by the Defense Threat Reduction Agency (DTRA). Calculations performed on XSEDE, USF Research Computing, and MSL computational facilities at USF.

References
Appendix 4: Ammonium Azide under High Pressure – a Combined Theoretical and Experimental Study

Publication Record

J. Crowhurst, J. Zaug, H. Radousky, B. A. Steele, A. C. Landerville, and I. I. Oleynik,

Contributions

Performed calculations of ammonium azide equation of state, and Raman spectra.

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Ammonium Azide under High Pressure – a combined Theoretical and Experimental Study

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ABSTRACT: Efforts to synthesize, characterize and recover novel polynitrogen energetic materials have driven attempts to subject high nitrogen content precursor materials (in particular metal and non-metal azides) to elevated pressures. Here we present a combined theoretical and experimental study of the high pressure behavior of ammonium azide (NH4N3). Using density functional theory we have considered the relative thermodynamic stability of the material with respect to two other crystal phases, namely trans-tetrazene (TTZ), and also a novel hydronitrogen solid (HNS) of the form (NH)4, that was recently predicted to become relatively stable under high pressure. Experimentally we have measured the Raman spectra of NH4N3 up to 71 GPa at room temperature. Our calculations demonstrate that the HNS becomes stable only at pressures much higher (89.4 GPa) than previously predicted (36 GPa). Our Raman spectra are consistent with earlier reports up to lower pressures, and at higher pressures, while some additional subtle behavior is observed (e.g. mode splitting) there is again no evidence of a phase transition to either TTZ or the HNS.
1. INTRODUCTION

Novel nitrogen compounds, $N_n$ with $n$ greater than three, have been of particular interest for the development of novel high energy density energetic materials with fast energy release\textsuperscript{1-6}. This is because these single and double bonded "polynitrogens" are expected to decompose into familiar triply-bonded diatomic nitrogen accompanied by the rapid release of enormous energy per unit mass. The origin of this energy is a substantial difference in strength of the N triple bond and that of single and double bonds, which are much weaker\textsuperscript{2}. Many such materials have been predicted on the basis of theoretical calculations, and include molecular (from $N_3$ up to $N_{60}$)\textsuperscript{7-15} and non-molecular polymeric “cubic gauche” (cg-N) forms\textsuperscript{16-21}. However, experimental progress in synthesizing novel pure nitrogen compounds has been slow. Recent examples include cg-N solid\textsuperscript{3}, as well as $N_5^-$ and $N_5^+$ ions\textsuperscript{2}. The exceptional properties of proposed polynitrogen energetic materials can be illustrated by comparing the predicted energy content of cg-N with a familiar explosive such as HMX (e.g. a 10-fold increase in detonation pressure. See the calculations by H. Östmark\textsuperscript{2}). However, such a comparison assumes that the density of cg-N, which was synthesized above 100 GPa and 2000 K, can be retained under ambient conditions. To date, the material has not been quenched and no tests of energetic performance have been possible. Nevertheless, attempts to synthesize new nitrogen compounds under high pressure and temperature continue both experimentally and theoretically. In particular various workers have investigated the possibility that high nitrogen content precursor molecules rather than pure nitrogen might offer pathways to new polynitrogen compounds that involve less extreme conditions and are therefore more practical. One potential precursor is that containing the $N_3^-$ anion, i.e. the azide\textsuperscript{4,5}. 
There has been growing interest in the behavior of ammonium azide NH$_4$N$_3$ some of which has been focused specifically on its behavior under high pressure. Ammonium azide is particularly relevant in the present context thanks to its high nitrogen content (more than 90% by weight) and, upon full decomposition, is expected to yield only environmentally benign products. Furthermore, it has been specifically predicted to undergo a transition at 36 GPa to a high energy density hydronitrogen solid (HNS) of the form (NH)$_4$. This prediction has motivated recent high pressure experimental efforts whose diagnostic was Raman scattering.

Medvedev et al. concluded that above 3 GPa and up to 55 GPa at room temperature ammonium azide is thermodynamically stable with no sign of a transition to the predicted hydronitrogen solid. Rather, their Raman spectra showed a polymorphic phase transition at 3 GPa. They named the phase “Phase II” to distinguish it from the lower pressure phase, “Phase I”, which is stable to ~ 3 GPa. Medvedev et al. provided an extensive summary of the Raman spectrum, its origins and its dependence on pressure. Wu et al. subsequently carefully analyzed the transition using a combination of x-ray diffraction and Raman spectroscopy. Our primary motivation here was to extend the earlier measurements to higher pressures to investigate the possibility that the transition predicted by Hu and Zhang might indeed occur. We also revisit theoretically the earlier prediction by carrying out density functional theory (DFT) calculations of the relative stability of the relevant phases.

2. THEORETICAL DETAILS

DFT calculations of the relative thermodynamic stability of ammonium azide, trans-tetrazene (TTZ), and the hydronitrogen solid (HNS). The phase transition to a hydronitrogen solid that was predicted by Hu and Zhang, would correspond to a radical chemical change, and if
it occurred would be expected to be clearly apparent in measured Raman spectra. Here we have reexamined the possibility of phase transitions of ammonium azide under high pressure by performing first-principles DFT calculations of the relative thermodynamic stability of ammonium azide, and the two other crystal phases, the HNS\textsuperscript{22} and trans-tetrazene\textsuperscript{28} (TTZ) considered by Hu and Zhang\textsuperscript{22} (Fig. 1). The DFT calculations employ the Perdew-Burke Ernzerhoff (PBE) generalized gradient approximation (GGA) functional to DFT and the empirical dispersive correction by Grimme\textsuperscript{29}, which takes into account long range van der Waals (vdW) interactions. The HNS contains infinite one-dimensional zig-zag nitrogen chains saturated by hydrogen, repeated (NH)\textsubscript{4} units being arranged in a monoclinic unit cell having P21/m space group\textsuperscript{22} symmetry (see Fig. 1). TTZ is a molecular crystal containing vdW-interacting (NH)\textsubscript{4} molecules arranged in a unit cell with triclinic P-1 space group symmetry\textsuperscript{1} (Fig. 1).

The relative enthalpies of TTZ, and the HNS referenced to the enthalpy of the NH\textsubscript{4}N\textsubscript{3} crystal are shown as a function of pressure (Fig. 2). Our calculations predict the following sequence of phase transitions: NH\textsubscript{4}N\textsubscript{3} to TTZ at 41.9 GPa (36 GPa\textsuperscript{22}) and TTZ to the HNS at 89.4 GPa (75 GPa\textsuperscript{22}). The values in parentheses are the transition pressures reported by Hu and Zhang\textsuperscript{22}, the differences being due to the inclusion of vdW interactions in our calculation. We also point out that the transition at 36 GPa that was predicted in the earlier work is actually the transition\textsuperscript{30} to TTZ and not the HNS. Therefore we do not expect to see evidence in our measured Raman spectra of a transition to the NHS since it should only occur at pressures substantially higher than reached in the experiment (71 GPa). Our spectra also show no evidence for a transition to TTZ (see below). In this case however the predicted pressure at which TTZ becomes relatively stable is substantially less than the highest experimental pressure; it would seem that in this case at least there is a large energetic barrier separating the two crystal phases.
3. EXPERIMENTAL DETAILS

Raman measurements were taken in a diamond anvil cell (DAC) equipped with “ultra-low” fluorescence diamonds (Almax) or Type II artificial diamonds (Sumitomo) of tip dimension 300 µm or 200 µm, respectively. The gasket material was rhenium; it was pre-indentated and then cut using electric arc discharge machining\textsuperscript{31} to form a sample cavity whose dimensions depended on the desired pressure range (around 100 µm diameter with a pre-indent to ~ 45 µm for the highest pressure experiments). The pressure medium was argon. The NH\textsubscript{4}N\textsubscript{3} sample in the form of a fine grain white polycrystalline powder and a small ruby chip were lightly compacted into the sample cavity under dry nitrogen gas. Over a period of approximately 5-10 minutes the solid ammonium azide sample would decompose into previously observed gas products such as presumably hydrazoic acid\textsuperscript{32} to the point where perhaps 20% of the sample cavity was filled with remaining solid NH\textsubscript{4}N\textsubscript{3} starting material. At this point the cavity was sealed. In one of the experimental runs the trapped material was subsequently characterized using FTIR spectroscopy – see below. The diamond cell was then placed in liquid argon. After approximately 10 minutes the cell was opened and then resealed in order to introduce and trap the argon. The small ruby chip (<10 µm) was used to determine pressure. Raman spectra from the azide were collected within 30-50 µm of the ruby chip.

The ammonium azide was prepared specifically for these experiments at LLNL. FTIR spectroscopy was conducted on the sample prior to loading argon into the DAC sample chamber. A detailed description of the FTIR instrument was previously reported\textsuperscript{33}. The 2 cm\textsuperscript{-1} resolution spectrum presented in Figure 3 confirms the presence of NH\textsubscript{4}N\textsubscript{3}; there is no indication of
contaminants. Peak positions below 2300 cm\(^{-1}\) were determined using Lorentz profile fits while those above were determined with an equally mixed Gaussian and Lorentz profile (Voigt profile) to achieve acceptable peak fits. Because of the sample thickness, the IR dynamic range of the instrument was reduced, thus resulting in a signal distortion of the most strongly absorbing peaks located in the internal N\(_3^+\) asymmetric stretch region; however, the more weakly absorbing peaks are more prominent in this spectrum. The measured values of the four \(v_2\) internal N\(_3^+\) bending modes are within 1-3 cm\(^{-1}\) of those measured at ambient temperature by Iqbal and Malhotra\(^{34}\). To our knowledge the peak at 642.1 cm\(^{-1}\) is present in all published infrared spectra but has not yet been assigned.

The Raman measurements were made using an excitation wavelength of 632.8 nm (1.96 eV). Laser power reaching the DAC was \(< 4\) mW or less. Spectra were recorded on a 300 lines/mm (“low resolution”) and an 1800 lines/mm (“high resolution”) grating. All quantitative results were obtained from high resolution spectra in the frequency range of \(\sim 100\) cm\(^{-1}\) to 3200 cm\(^{-1}\). The instrument was approximately calibrated using emission lines from a neon standard lamp. Instrumental nonlinearity across each spectral window was assumed to be small and we did not correct for either frequency or intensity. Measurement precision was expected to be \(1 \pm 2\) cm\(^{-1}\).

4. RESULTS

We carried out multiple experimental runs ranging in pressures from 1 to 71 GPa. Raman spectra obtained in different spectral regions and associated quantities are shown in the figures below: \(\sim 100\) to 700 cm\(^{-1}\) (Fig. 4), 1350 to 1550 cm\(^{-1}\) (Fig. 5), 1600 to 2250 cm\(^{-1}\) (Fig. 6), and 2800 to 3150 cm\(^{-1}\) (Fig. 7). Most of the data presented here were obtained from one run; data at 5.7 GPa and 20 GPa, and at 37.4 GPa were obtained in separate runs. Overall behavior did not
differ between runs, but frequencies and line widths for at least some features showed small but clear differences at similar nominal pressures.

We discuss our observations for each spectral window below. Medvedev et al. 2011\textsuperscript{23}, and Medvedev et al. 2012\textsuperscript{24} used Raman spectroscopy to study NH\textsubscript{4}N\textsubscript{3} at room temperature under high pressure in a silicone oil pressure medium. They provided quantitative results for some of the measured bands up to 10 GPa and 20 GPa respectively. We compare our results to theirs where possible.

\textbf{a. Spectral Region 100 – 700 cm\textsuperscript{-1} (lattice modes).} Figure 4a shows the evolution of the measured Raman spectra with pressure in the range of frequencies associated with lattice modes. We observe a profound, but expected, change in the spectrum between 1 GPa and 5.9 GPa and attribute this to the Phase I $\rightarrow$ Phase II transition reported by Medvedev et al\textsuperscript{23} and which occurs at approximately 3 GPa.

Above that pressure range the spectrum evolves smoothly up to the highest pressure achieved of 71 GPa, and there is no sign of a substantial physical or chemical transition. However, above approximately 35 GPa the most intense band, probably due to an ammonium ion translational mode (compare with the assignment given by Medvedev et al\textsuperscript{23} for Phase I), begins to broaden and then split. Above 60 GPa the band is clearly composed of (at least) two components. This behavior was reproducible as we observed it in three different runs. Medvedev et al\textsuperscript{23} show one spectrum in this range at 55 GPa; the mode in question does not appear split but might be relatively broadened.

Figures 4b and 4c shows measured frequencies vs pressure. Frequencies were obtained by assuming Lorentzian line shapes and linear backgrounds (Fig. 4d shows as an example the fit to the spectrum recorded at 70.2 GPa). In several cases, in both this spectral range and others, fits
were not definitive; some modes were clearly asymmetric and it was not obvious how many distinct bands were involved. Also, a few very weak bands were not fitted and their frequencies were merely estimated. The overall behavior was however quite clear. In the pressure range of overlap, we find good agreement between our results and those of Medvedev et al. There are a few small and we presume insignificant discrepancies. In Phase I we observe a small additional feature in the NH₄⁺ translational bands (at 239 cm⁻¹ at 1 GPa) not reported by Medvedev et al. This feature is not reported by Iqbal and Malhotra either in their 1-bar study although the mode they observed at 205 cm⁻¹ appears slightly asymmetric and may possibly contain a higher frequency component. In Phase II Medvedev et al report a weak mode with a frequency of ~ 155 cm⁻¹ at 3.5 GPa (circles in Fig. 4b). A weak band in this range is likely present in our low pressure spectra but we did not attempt to track it. Similarly, Medvedev report another weak mode that has a frequency of 355 cm⁻¹ at 21 GPa (up triangles).

b. Spectral Region 1350 – 1550 cm⁻¹ (azide symmetric stretch and ammonium ion bending modes). This spectral region is dominated by the ν₁ symmetric stretching mode of the N₃⁻ anion and the ν₄ HNH angle bending mode of the NH₄⁺ cation (Fig. 5). We observe that the former is split by about 5 cm⁻¹ due to the azide ion occupying non-equivalent crystal sites as noted by Medvedev et al. At low pressures additional bands are visible e.g. a shoulder at ~ between 1370 cm⁻¹ and 1380 cm⁻¹ (assigned to a combination of ν₁ and translational modes). We also note lower frequency bands in the range of 1250 – 1310 cm⁻¹ in our lowest pressure spectrum (1 GPa, Phase I), which are consistent with those measured by Medvedev et al. They were assigned to overtones of the azide bending modes, ν₂, with an intensity derived from ν₁ due to Fermi resonance. As pressure increased above 20.5 GPa we tracked only a single band due to the ν₄(NH₄⁺) mode.
Medvedev et al. discuss an interesting resonant coupling which occurs for the modes near 1400 cm\(^{-1}\), \(\nu_1(N_3^-)\) and \(\nu_4(NH_4^+)\), respectively. The modes appear to be crossing, but instead bend away from each other (Fig. 5b). At the same time the intensity of \(\nu_4\) grows while that of \(\nu_1\) shrinks. Once again we find that our data at 5.7 and 20 GPa are in good agreement with these lower pressure results, and we find a smooth extension of the \(\nu_4\) \((NH_4^+)\) frequency up to 71 GPa. We also note that the width of the band nominally associated with an \(NH_4^+\) bending mode shows a substantial increase in width at a similar pressure to that at which the splitting of the translational mode just discussed begins to occur.

c. Spectral Region 1700 – 1900 cm\(^{-1}\) (ammonium ion bending modes). In this frequency range the spectra are mostly much weaker than in the other ranges. Nevertheless a number of bands are observable (Fig. 6a). These are assigned to \(NH_4^+\) bending modes and combinations with torsional motion of the ammonium ion\(^{23}\). Above 20.5 GPa the spectrum is dominated by a band whose origin is assumed due to an \(\nu_2(NH_4^+)\) bond bending mode. After an initial rather sudden increase in frequency (presumably associated with the Phase I \(\rightarrow\) Phase II) the frequency dependence on pressure of the various bands is essentially monotonic (Fig. 6b). Figure 6c shows as an example the fit to the spectrum recorded at 20.5 GPa.

d. Spectral Region 2800 – 3150 cm\(^{-1}\) (N-H stretching modes). In this frequency range the spectrum is dominated by bands due to the symmetric and asymmetric N-H stretching modes, \(\nu_1(NH_4^+)\) and \(\nu_3(NH_4^+)\), respectively. There are however other contributions, e.g. due to an overtone of \(\nu_4(NH_4^+)\) apparently\(^{23}\). Generally, the evolution of the spectrum with pressure (Fig. 7a) is complicated and attempted fits assuming Lorentzian line shapes is once again not definitive. Nevertheless, a monotonic increase of the \(\nu_1(NH_4^+)\) frequency above 20.5 GPa is clear (Fig. 7b). As shown by Medvedev et al the frequency of this mode first increases up to the Phase
I→ Phase II transition before decreasing. On the basis of their results and ours the frequency passes through a minimum between 10 and 20 GPa. Figure 7c shows as an example the fit to the spectrum recorded at 51.4 GPa.

At the higher range of the pressures studied here the efficacy of the pressure medium needs to be considered. While argon is a relatively good (i.e. soft) medium at low pressures it becomes substantially harder at higher pressures. We found that in some cases measured frequencies and widths showed small but clear differences between runs at nominally similar pressures and attributed this to the different distribution of stresses obtained in each load. While experimentally more challenging a medium such as neon would be preferable. Therefore the role of the pressure medium in the observed splitting and broadening is currently unclear.

5. CONCLUSIONS
Raman spectra of ammonium azide have been measured up to 71 GPa. We observe previously unreported behavior including mode splitting and broadening. However, the transition to HNS predicted by Hu and Zhang to occur at moderate pressures above 36 GPa has not been detected in our experiments. Moreover, we reexamined the prediction by Hu and Zhang using density functional theory calculations and found that such a transition would happen at much higher pressures exceeding nearly 90 GPa.

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Calculations are performed using XSEDE, USF Research Computing cluster, and computational facilities at USF Materials Simulation Laboratory.

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REFERENCES

30. As is apparent from inspection of Figure 2 of Ref. 22, which may be compared with our corresponding figure (Fig. 2).
Figure 1

(a) Ammonium azide (NH₄N₃)  
(b) Trans-tetrazene (TTZ)  
(c) Hydronitrogen solid (HNS)

Figure 1 Crystal structures of (a) the molecular crystal ammonium azide (AA), (b) the molecular crystal trans-tetrazene (TTZ), and (c) the hydronitrogen solid (HNS).
Figure 2. The relative enthalpy of TTZ and HNS compared to ammonium azide (AA). The transition pressure between each pair of phases is displayed in the plot.
Figure 3. FTIR spectrum of polycrystalline NH$_4$N$_3$ in a sealed diamond anvil cell near 1 bar and at 295 K. The spectrum was obtained just prior to loading the cell with an argon pressure medium.
Figure 4a
Figure 4b
Figure 4c
Figure 4. (a) Raman spectra of NH$_4$N$_3$ measured in the frequency range of $\sim$ 100 cm$^{-1}$ to 700 cm$^{-1}$. External (lattice) mode region. Pressures range from $\sim$ 1 to 71 GPa and are indicated. Measured spectra are displaced vertically and scaled to permit comparison. The observed bands are assumed to have their origin in librational and translational modes consistent with the assignments of Medvedev et al$^{23}$. (b) and (c) Measured frequencies vs pressure of the bands shown in Fig. 4a. The vertical dashed line in (b) at 3 GPa delineates the approximate transition pressure$^{23}$ from Phase I to Phase II. Open symbols are data obtained by Medvedev et al$^{23,24}$. (d) An example fit to most of the bands observed at 71.2 GPa. The green lines are Lorentzian components and the red lines are their sum.
Figure 5a
Figure 5b

Figure 5. (a) Raman spectra of NH$_4$N$_3$ measured in the frequency range of $\sim$ 1350 cm$^{-1}$ to 1550 cm$^{-1}$. Pressures are indicated in GPa. Measured spectra are displaced vertically and scaled to permit comparison. Band origins are labeled according to the assignments of Medvedev$^{23}$. Inset: fit to bands due to the azide stretch and ammonium ion bending modes at 20.5 GPa. (b) Measured frequencies of most of the bands shown in Figure 5a. The vertical dashed line at 3 GPa delineates the approximate transition pressure$^{23}$ from Phase I to Phase II. Open symbols are data obtained by Medvedev et al$^{23,24}$. 

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Figure 6a
Figure 6b
Figure 6. (a) Raman spectra of NH$_4$N$_3$ measured in the frequency range of ~ 1600 cm$^{-1}$ to 2300 cm$^{-1}$. Pressures are indicated in GPa. Measured spectra are displaced vertically to permit comparison. Band origins are labeled according to the assignments of Medvedev. (b) Measured frequencies of the indicated bands of Figure 6a. The vertical dashed line at 3 GPa delineates the approximate transition pressure$^{23}$ from Phase I to Phase II. (c) Fits to the assumed $\nu_2$(NH$_4^+$) and $\nu_4$(NH$_4^+$) + R bands of the spectrum acquired at 20.5 GPa.
Figure 7a

![Raman shift spectrum](image)

- $2\nu(NH^+_2)$
- $\nu(NH^+_2)$
- $\gamma(NH^+_2)$

Intensity (a.u.)

Raman shift (cm$^{-1}$)

1.0 GPa
Figure 7b

![Graph showing frequency vs. pressure for different modes of ammonium ions](image-url)
Figure 7. (a) Raman spectra of NH$_4$N$_3$ measured in the frequency range of ~ 2800 cm$^{-1}$ to 3150 cm$^{-1}$. Pressures are indicated in GPa. Measured spectra are displaced vertically to permit comparison. Band origins are labeled according to the assignments of Medvedev. (b) Measured frequencies of the indicated bands of Figure 7a. The vertical dashed line at 3 GPa delineates the approximate transition pressure$^{23}$ from Phase I to Phase II. The dashed red lines are linear fits. The grey data are exactly twice the frequency of the $\nu_4$(NH$_4^+$) mode shown in Fig. 5b. (c) Fits to the spectrum acquired at 51.4 GPa.
Appendix 5: Reactive Molecular Dynamics of Hypervelocity Collisions of PETN Molecules

Publication Record

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Related Publications

Reactive Molecular Dynamics of Hypervelocity Collisions of PETN Molecules

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Born–Oppenheimer direct dynamics classical trajectory simulations of bimolecular collisions of PETN molecules have been performed to investigate the fundamental mechanisms of hypervelocity chemistry relevant to initiating reactions immediately behind the shock wavefront in energetic molecular crystals. The solid-state environment specifies the initial orientations of colliding molecules. The threshold velocities for initiating chemistry for a variety of crystallographic orientations were correlated with available experimental data on anisotropic shock sensitivity of PETN. Collisions normal to the planes (001) and (110) were found to be most sensitive with threshold velocities on the order of characteristic particle velocities in detonating PETN. The production of NO₂ is the dominant reaction pathway in most of the reactive cases. The simulations show that the reactive chemistry, driven by dynamics rather than temperature during hypervelocity collisions, can occur at a very short time scale (10⁻¹⁳ s) under highly nonequilibrium conditions.

1. Introduction

In spite of over a century of intensive experimental and theoretical investigations, an understanding of the mechanisms of detonation in explosives (or energetic materials (EMs)), including the shock-induced chemical reactions, still remains one of the challenging problems of chemical physics.1–3 The classic continuum theories of detonation were successful in predicting macroscopic properties, such as detonation speed and detonation pressure, using mostly hydrodynamic and thermodynamic descriptions with very little detailed input involving the chemistry of energetic materials.1–5 In particular, Chapman and Jouguet (C–J) assumed that the speed of detonation does not depend on the rate of the chemical reactions because they proceed so fast that the chemical transformation from reactants to detonation products occurs within the infinitesimally thin layer at the shock wavefront.6,8 The C–J model of detonation was later replaced by the Zeldovitch, von Neumann, and Doering (ZND) model9–12 which introduced a finite reaction rate and associated finite reaction zone. Despite these advancements in detonation theory, the detailed mechanisms of the chemical reaction dynamics were unnecessary.

As experimental studies progressed toward exploring ever smaller time and length scales, a detailed knowledge of the atomic-scale mechanisms of detonation became increasingly important for explaining the observed phenomena.13 The more important questions include how detonation is initiated and sustained and what mechanisms are responsible for shock-induced chemical reactions, including both the first endothermic steps and the following exothermic reactions toward detonation products. One way to include chemistry is to assume that there is a local thermal equilibrium characterized by a local temperature, and to use standard transition state theory (TST) to describe the reaction rates. Unfortunately, while such an approach has been highly successful for thermal decomposition studies,14–17 it ultimately ignores the highly nonequilibrium initial processes of the shock-wave mechanical energy transfer to the individual molecules when the notions of thermal equilibrium and temperature are ill-defined immediately behind the shock wavefront.

This problem attracted the attention of Henry Eyring, one of the founders of chemical reaction dynamics and transition state theory.18 In an attempt to explain the experimentally observed slow increase of the reaction rates with the shock temperature compared to that predicted by TST, he proposed a concept of starvation kinetics.19 The conventional view of endothermic bond breaking involves the concentration of a sufficient amount of energy along the reaction coordinate which is coupled with a thermal bath of surrounding molecular modes. This process is substantially less efficient when the reaction coordinate must draw its energy from a thermal bath that is in nonequilibrium with the translational degrees of freedom of the reacting molecule; e.g., molecular collisions cause deformations which lead to one part of the reacting molecule being in nonequilibrium with another part. This reduces the probability of concentration of the activation energy within the modes along the reaction coordinate.19–21

A further development of the theory of shock-induced chemical reactivity was the multiphonon up-pumping model.20–24 Assuming the standard notion of TST, i.e., the activation of a reactive vibrational normal mode, focus was placed on the mechanism of energy transfer from the shock wave to the high-frequency vibration modes of the molecules. According to this theory, the shock wave produces a bath of excited phonons of the molecular crystal which excite the low frequency doorway vibration modes (e.g., modes involving the entire molecule) due to anharmonic phonon–doorway mode coupling. This is followed by energy transfer into the high frequency modes (e.g., stretching modes) via multiphonon up-pumping and intramolecular vibration energy redistribution. Once the up-pumping is complete, within several tens of picoseconds, Arrhenius kinetics becomes valid. Both mechanisms of starvation kinetics and multiphonon up-pumping were incorporated in the nonequilibrium ZND theory of detonation developed by Tarver.25

Because of difficulties in real-time experimental investigations of shock-induced chemistry at the onset and during detonation,
experimental study of chemical reactivity in energetic materials has been limited to thermal decompositions of EMs at slow heating rates (cooloff).26–28 Although such studies are important for the evaluation of the thermal stability of explosives, it is not clear whether they are relevant for understanding the fast chemical processes of shock initiation, and the self-sustained propagation of detonation. Only recently, advances in experimental techniques have allowed direct investigation of the chemical reactivity behind the detonation front.13 For example, shock-induced decomposition chemistry of pentaerythritol tetranitrate (PETN), the EM to be discussed in this paper, was studied using optical transitions and light emission associated with PETN decomposition at the early stages of initiation.30

With tremendous advances in computational capabilities, it has become possible to perform computational experiments to study the reactive molecular dynamics at conditions similar to a detonation. One of the major challenges for theory/modeling is the disparate time and length scales associated with the various processes of detonation. For example, the initial shock compression takes place over picoseconds at the nanometer length scale,31 but the entire reaction zone width is at least several micrometers, while the corresponding time scale to complete chemical reactions is in excess of nanoseconds.

Previous modeling efforts were mostly concentrated on studying the gas-phase thermal decomposition of EMs such as RDX32 and HMX13 using transition state theory and density functional theory (DFT) based potential energy surfaces (PES). Classical trajectory simulations using model PES were also performed.14,15 Several studies of the condensed phase decomposition of EMs were concerned with the rapid heating from normal pressures and temperatures to the C–N point using DFT-based reactive molecular dynamics.36–39 Using continuum theory constraints introduced into reactive MD simulations, a quasi-metallic state was discovered in shocked nitromethane at detonation conditions.39 This observation is closely related to another proposal for the initiation of chemistry via electronic excitations of EMs; band gap lowering and excitations around crystal defects under high pressures and temperatures were considered as possible mechanisms of initiation.40–42

One promising approach to extend time and length scales of atomic-scale simulations of detonation chemistry is to develop reactive potentials that are capable of describing the fundamental chemistry of bond breaking and remaking.43–45 By devising reactive-empirical-bond-order (REBO) potentials for modeling a generic AB system, the first molecular dynamics simulations of a self-sustained detonation were performed45–47 with this model, leading to results consistent with a classic ZND detonation.46 Very recently, reactive force fields (ReaxFF) have been developed for organic energetic materials48 which enabled large-scale simulations of reactive shock wave propagation in EMs such as RDX49–51 and PETN.52 These simulations provided valuable insight into the reactive chemistry of EMs. However, extreme care should be exercised in making conclusions about the fundamental mechanisms of the detonation chemistry. This is because ReaxFF, although sophisticated, still provides a classical description of the intrinsically quantum mechanical processes of bond breaking and remaking via a complicated functional form and fitting (“or training”) of numerous ReaxFF parameters. We believe that, by understanding the mechanisms of chemistry in hypervelocity collisions of EM molecules, further refinement can be made to ReaxFF potentials which may ultimately lead to more accurate modeling of larger detonating systems.

The goal of this work is to investigate the first chemical events in detonating PETN initiated by the propagation of a strong shock wave. In contrast to the models of initiation of chemistry discussed above, which assume some sort of thermal equilibrium within specific groups of molecular degrees of freedom, as well as the existence of a corresponding temperature, special focus is placed on the highly nonequilibrium mechano-chemical regime of direct bond breaking due to hypervelocity molecular collisions initiated by the very fast uniaxial shock compression of a molecular crystal. Such a mechanism was first proposed in the works of Anatoly Dremin53 and Frank Walker.54,55 They both suggested that the kinetic energy of the shock wave is initially adsorbed by the translational molecular degrees of freedom which results in the direct endothermic breaking of the intramolecular chemical bonds. Because of the lack of equilibrium, the initiation of chemical reactions in the shock front is not a thermal process; i.e., it is not controlled by temperature which is ill-defined under such nonequilibrium conditions.

The computational studies reported in this paper were performed using quantum-mechanical descriptions of the interatomic interactions described by first-principles DFT. The object of these investigations, PETN, was chosen because of its known dependence of shock-induced initiation of detonation on the crystallographic direction of the shock propagation, as was discovered by Jerry Dick in his classic experiments.56–59 This property of anisotropic shock response implies a relationship between the high sensitivity of chemical reactivity to the initial mutual orientations of the colliding molecules specified by their relative geometry within the initial crystalline environment.

Although similar hypervelocity collision simulations have been attempted in the past,60–63 they were performed within a limited subset of initial conditions (fewer directions and velocities sampled) and mostly using the semiempirical electronic structure method PM3,64,65 which is known to give large errors in predicting heats of reaction and activation energies of organic molecules.61,66 Our goal is to use first-principles DFT to predict the dynamics of chemical transformation, including the reaction pathways and the associated time scales, as a function of the magnitude of the collision velocity and the initial mutual orientations of two colliding molecules specified by a given direction corresponding to the normal of the associated compression of planes within the molecular crystal. Special attention is paid to identifying the differences between the commonly used thermally activated reaction dynamics and the hypervelocity chemistry initiated by the fast uniaxial compression of the crystal behind the shock wavefront.

It is important to note that, while we assume molecular collisions to be the precursor to the initiation of chemical reactions at the detonation front, we have not simulated collisions involving more than two molecules due to computational expense. Such a study60 was performed by Decker et al. for nitromethane. They found that, while C–N bond scission was the main reaction pathway in both bimolecular and multimolecular collisions, only one of the higher energy multimolecular collision cases involved the transfer of a hydrogen atom from one molecule to another, a reaction which was not seen in any of the bimolecular cases. However, in general, multimolecular collisions imposed more steric constraint on the colliding molecules which resulted in a higher instance of C–N bond reformation; i.e., threshold velocities became higher than for bimolecular collisions.61 Still, in both bimolecular and multimolecular collisions of nitromethane simulated by Decker et al., essentially the same reaction pathway (C–N bond scission) was predominantly observed. Therefore,
II. Computational Details

The simulation of chemical reactions in the condensed phase is a challenging problem because it requires an accurate quantum mechanical description of interatomic interactions in a system consisting of a very large number of atoms. Because such simulations are currently unfeasible, we devised a simplified model system that contains a manageable number of atoms that are treated quantum-mechanically using first-principles density functional theory under the Born–Oppenheimer approximation, while preserving essential features of the chemistry induced by hypervelocity molecular collisions. Because the major focus is on chemical dynamics initiated by the shock wave, we assume that the initial steps involve the rapid approach and collisions of molecules within adjacent planes normal to the direction of shock compression. Therefore, molecular pairs were extracted from the EM crystal by preserving the local crystalline environment (relative position and orientation). Then, the bimolecular collisions are simulated by assigning the pair of selected molecules the relative velocity and following their collision dynamics.

Reactive MD of bimolecular collisions was studied by integrating the classical Newtonian equations of motion for each atom:

$$\frac{d^2 R_i}{dt^2} = -\frac{\partial V(R_i)}{\partial R_i}$$

(1)

where the potential energy $V(R_i)$ and the forces $-\partial V(R_i)/\partial R_i$ are evaluated on-the-fly by solving the Kohn–Sham DFT equations at each time step at fixed nuclear coordinates $R_i$ to obtain the total electronic energy $E_{\text{elDFT}}(R_i)$, which serves as a potential energy for nuclear dynamics: $V(R_i) = E_{\text{elDFT}}(R_i)$. Equation 1, together with the initial conditions (discussed below), completely specifies the dynamics of the bimolecular collisions.

The first-principles DFT calculations were performed using the linear combination of atomic orbitals (LCAO) code SIESTA. The effect of the core electrons is taken into account by employing norm-conserving pseudopotentials. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) density functional is used. The valence electronic states are expanded using the double-$\zeta$ plus polarization (DZP) basis set that we specifically optimized to achieve the highest level of accuracy in the description of the energies and forces as compared to the fully converged plane-wave calculations for several configurations of the colliding PETN molecules. A real space energy cutoff of 200 Ry was chosen to give reasonable accuracy without excessive computational expense.

The initial conditions for the reactive collision dynamics simulations were set up by constructing the two-molecule collision complex and specifying initial velocities for each atom of the complex. We are specifically interested in relating the bimolecular reactivity with observed orientation-dependent initiation pressures. Therefore, we investigated collisions caused by the compression of crystallographic planes, and consider all possible collisions along directions corresponding to the normals of the following crystallographic planes within the PETN unit cell: (001), (010), (011), (100), (101), (110), and (111). To simplify this selection procedure, each molecule in the crystal lattice was represented with a sphere of radius $R$ which is half the diameter of the molecule. Figure 1 shows this simplified model of the body centered tetragonal PETN crystal with each molecule indexed for the purpose of identifying a specific collision pair used in the simulations.

The inner spheres have a radius of $R/2$, and were used to define two different types of collisions—head-on and glancing. If the inner spheres of two molecules collide upon translation in a particular direction, then the collision is classified as head-on; if only the outer spheres collide, then the collision is labeled as glancing.

Once all possible collisions were found, the associated molecules were isolated in their crystallographic orientation with respect to one another and centered within an empty box. The molecules were then thermally equilibrated to 300 K. Next, one-half the desired collision velocity was applied to each molecule such that they collided in the center of the box, as depicted in Figure 2.

Collision velocities ranging from 3 to 7 km/s were sampled for 13 different orientations. Owing to the computational expense of DFT calculations, a statistical sampling was not performed. However, the statistics is indirectly sampled by running simulations with multiple collision orientations.

The trajectory data obtained from each simulation were analyzed to determine the onset of reaction, the reaction time scale, and the type of products. The lowest velocity at which reactions occurred for any particular direction and orientation was taken to be the threshold velocity for initiating chemistry for that particular case. All of the reactive cases at the threshold velocities share one important feature: the reaction products originate from one molecule, while its colliding counterpart remains chemically intact. At higher collision velocities, products were observed to be originating from both molecules. The investigation of the threshold velocities as a function of initial crystalline orientation allows us to make an important conclusion: the reactive initiation dynamics is orientation-
Assuming that $V$ and interaction region, Wu et al. involved molecules that were initially deformed to lower threshold velocities than those found in our study. This head-on collision cases, though glancing collisions showed much threshold velocities were found for the (001), (110), and (110) resolved shear stresses on slip systems of PETN. As is seen impose external conditions corresponding to the maximum energy surfaces (PES) are known. However, there is some can be answered if both the ground and excited state potential preciable electronic excitations. In principle, such a question is the system evolves from reactants to products at a time scale $\Delta E \sim 1$ eV. Although in the present work we cannot calculate the excited state PES using ordinary DFT, there are some indications that both the ground and excited states are well-separated. In particular, our DFT calculations of the PETN molecular crystal under both uniaxial and hydrostatic compressions show that the band gap is several eV at pressures up to 100 GPa. Taking into account that DFT systematically underestimates the band gaps, the real separation of ground and excited PES is expected to be even larger.

### III. Threshold Velocities to Initiate Chemical Reactions

We found a correlation between experimentally observed shock sensitivities reported by Dick and Yoo et al. and the threshold velocities for initiating chemistry; see Table 1. Essentially, the initiation pressures shown in the right column of Table 1 are a measure of the sensitivity for a given direction in bulk PETN. Known sensitive cases with lower initiation pressures have lower threshold velocities than the known insensitive cases with higher initiation pressures.

For example, two compression directions, normal to (001) and (110), were observed to be the most sensitive directions with initiation pressures of 12.1 and 4.2 GPa, respectively. And the threshold velocities 3.30 and 3.9 km/s for head-on (001) and (110) collisions are indeed among the lowest of all collision cases studied (no experimental data was available for shock compression normal to (011) which actually shows the greatest sensitivity for collisions). In contrast, the (100) case proved to have a high threshold velocity of 4.7 km/s which correlates with the high initiation pressure of 22.8 GPa determined by Yoo.

The (101) case also has high threshold velocities for all three glancing collisions—6.6, 4.6, and 4.4 km/s—which correlates with experiment in that initiation was not observed upon the application of shock normal to (101) for pressures less than the PETN Chapman–Jouguet pressure of 31 GPa. It is important to note that the correlation between detonation pressure and threshold velocity is merely suggestive, especially when comparing the pressures and velocities for the sensitive cases which include the so-called anomalous shock response of the (110) case (discussed below).

The number of products formed in reactive threshold cases shown in Table 1 can also serve as an indicator of the directional dependence of chemical initiation; see Figure 4. While one might expect more products to form with higher collision velocities, we observed some deviations from this trend. This is evident when comparing (010) mol. 1–2, (010) mol. 1–4, and (011) mol. 1–2, having threshold velocities of 4.7, 4.4, and 5.3 km/s, respectively, with (100), (101) mol. 1–2, and (101) mol. 1–3, having threshold velocities of 4.7, 6.6, and 4.6 km/s. The collisions in the first group all produce only one fragment, while the collisions of the second group all produce three fragments. In short, the number of products produced by a collision depends as much on the orientation as it does on the collision energy. Probing the issue of product formation deeper, one can look at the number of products formed for all collision velocities of any particular direction and see once again that product number does not necessarily scale with collision energy; see Figure 4.

Though the number of products increases with collision velocity in cases like (111) head-on and (110) glancing, other cases such as (100) head-on and (101) mol. 1–7 glancing show that the number of products can diminish at higher collision velocities. One interesting example of this is the (001) head-on case in which a single product is produced at 3.3 km/s, and no products are produced at 3.4 km/s. The reason for this is hidden
in the details of the dynamics of the simulations. In the 3.3 km/s case, which is discussed later in Figure 6, the reacting nitro group is imparted with translational kinetic energy as the connecting arm is thrown outward. As the associated O−NO₂ bond stretches in its oscillation, the connecting formaldehyde group snaps back toward its original configuration, leaving the NO₂ behind. In the 3.4 km/s case, the formaldehyde does not snap back quite as fast due to a twisting deformation in the center of the molecule. As a result, the O−NO₂ bond that was severed in the 3.3 km/s case is not severed in the 3.4 km/s case.

While this result may be due to the thermal fluctuations, the amplitudes of the O−NO₂, C−C, and C−O thermal vibrations are small (∼0.1 Å), making it unclear whether or not thermal effects are at play.

IV. Reaction Pathways

Several studies have addressed a correlation between bond dissociation energies (BDEs) and impact sensitivities of various colliding compounds.61−74 Wu et al. conducted such a study61 for PETN by calculating BDEs for PETN using DFT with the BPW91 GGA functional. They found that the dominant reaction pathway was the dissociation of the O−NO₂ single bond leading to the formation of NO₂. They found that the O−NO₂ single bond was indeed the weakest bond in PETN with a BDE of 157.8 kJ/mol.61 Another study74 by Fried et al. also found the single O−NO₂ bond to be weakest with a BDE of 167 kJ/mol.

We performed our own study of the BDEs for PETN including all bonds within the PETN molecular complex. Figure 5 shows these BDEs for the intact molecule, as well as the BDE of the C−C bond after the dissociation of the connecting NO₂.

In agreement with the study of Wu et al., we found NO₂ production to be the dominant chemical event in our simulations. Every reactive collision performed in this study began with the disassociation of the O−NO₂ bond leading to an NO₂ product, as seen in Table 1. This commonality can be at least partly attributed to the relative weakness of the O−NO₂ bond (182.69 kJ/mol) in the nonreacted PETN molecular complex, as seen in Figure 5. It is clear from the BDEs why we do not see the dissociation of other bonds within the molecule first. It should be pointed out that some studies28,77 have suggested that the O−NO₂ bond is not the first to break when PETN is exposed to high energy laser radiation, or high pressure; rather, they suggest that the C−C and C−O bonds are the first to break.

<table>
<thead>
<tr>
<th>hkl</th>
<th>type</th>
<th>mol.</th>
<th>vel (km/s)</th>
<th>N prod.</th>
<th>species</th>
<th>Rx time (fs)</th>
<th>exp. press. (GPa)</th>
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<tbody>
<tr>
<td>001</td>
<td>head-on</td>
<td>1−3</td>
<td>3.30</td>
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<td>NO₂</td>
<td>450</td>
<td>12.1</td>
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<td>glancing</td>
<td>1−2</td>
<td>4.70</td>
<td>1</td>
<td>NO₂</td>
<td>135</td>
<td>N/A</td>
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<tr>
<td></td>
<td>head-on</td>
<td>1−4</td>
<td>4.40</td>
<td>1</td>
<td>NO₂</td>
<td>410</td>
<td></td>
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<tr>
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<td>1−2</td>
<td>5.30</td>
<td>1</td>
<td>NO₂</td>
<td>110</td>
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<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>1</td>
<td>NO₂</td>
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<td></td>
<td></td>
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<td>1−6</td>
<td>4.70</td>
<td>3</td>
<td>NO₂, H₂CO, NO₂</td>
<td>130, 160, 420</td>
<td>22.8</td>
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<tr>
<td>101</td>
<td>glancing</td>
<td>1−2</td>
<td>6.60</td>
<td>4</td>
<td>NO₂, NO₂, H₂CO, NO₂</td>
<td>90, 245,316,480</td>
<td>no Rx⁵</td>
</tr>
<tr>
<td></td>
<td>1−3</td>
<td>4.60</td>
<td>3</td>
<td>NO₂, NO₂, H₂CO</td>
<td>90, 135, 160</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>1−7</td>
<td>4.40</td>
<td>2</td>
<td>NO₂, NO₂</td>
<td>155, 415</td>
<td></td>
<td>P &lt; 31</td>
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<tr>
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<td>1−2</td>
<td>4.50</td>
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<td>NO₂</td>
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<td>4.2</td>
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<tr>
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<td>4.20</td>
<td>2</td>
<td>NO₂, NO₂</td>
<td>140, 295</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*The molecular indices in column 3 match those labeling each molecule in Figure 1.⁵ PETN is believed to detonate at or above the Chapman−Jouguet pressure of 31 GPa for the (101) direction.*
Hypervelocity Collisions of PETN Molecules

![Figure 5](image)

The work\textsuperscript{72} by Zhurova et al., which cites the high electron density value of the O\textsuperscript{\textminus}NO\textsubscript{2} bond, we assert that it is the bond order, not the electron density, which determines the breaking of the bond. Also, in reference to the work\textsuperscript{28} by Ng et al., which finds no peak for NO\textsubscript{2} in a mass spectrometry study of laser decomposed PETN, we point out that the time resolution required to see the initial stages of chemical initiation is \(\sim 1\) ps, not \(\sim 100\) fs.

The next weakest bond in the PETN complex is the C\textendash C bond with a BDE of 250.48 kJ/mol. This particular bond scission occurred less frequently in threshold cases but was nonetheless prevalent, occurring only after or during the dissociation of the O\textsuperscript{\textminus}NO\textsubscript{2} bond in the reacting arm. We calculated the BDE for the C\textendash C bond after the dissociation of the accompanying O\textsuperscript{\textminus}NO\textsubscript{2} bond and found a drop in energy from 250.48 kJ/mol to only 77.07 kJ/mol. The lowering of the BDE for the C\textendash C bond may explain why H\textsubscript{2}CO forms instead of more NO\textsubscript{2} fragments; such a reaction pathway is actually favored by the low value of BDE. From Table 1, it is evident that some threshold cases produced multiple NO\textsubscript{2} fragments without producing H\textsubscript{2}CO. In both such cases for glancing collisions in the (101) direction, the only outer nitro groups of the colliding PETN molecules interacted, leaving the interiors relatively intact. Likewise, the (111) head-on threshold collision was oriented such that the nitro groups in multiple arms took the brunt of the collision simultaneously, allowing no close approach to the interior of either molecule. In other collisions in which multiple fragment types were formed, close approaches affecting the interiors of the reacting molecule were prevalent. It therefore must be concluded that, while BDEs can account for part of the chemical phenomena seen in our simulations, the actual dynamics of the collisions must also be considered for a more complete picture of the initiation of chemistry to emerge.

V. Reaction Dynamics

Apart from the BDEs of the various bonds in the PETN molecular complex, a study of the dynamic factors of collisions is necessary to understand the localized transfer of energy leading to the rapid reactions seen in our simulations. As a starting point, we looked at the simple dissociation of the O\textsuperscript{\textminus}NO\textsubscript{2} bond in single product threshold cases such as the (001) head-on collision. The depiction in Figure 6 shows various important stages leading to the formation of NO\textsubscript{2} for the (001) collision.\textsuperscript{28} Upon collision, the approaching arms in the left molecule are thrown outward; see Figure 6b and c. The nitro group at the top of the left molecule continues to move to the left as the connecting formaldehyde group recoils back to the right (Figure 6d and e). Because of this opposing motion, the O\textsuperscript{\textminus}NO\textsubscript{2} bond connecting the nitro group to the formaldehyde group is stretched to the breaking point (Figure 6f). Essentially, the entire arm was moved out of its equilibrium position, and like a loaded spring tended to return to its original state. However, while the inner part (the formaldehyde group) recoiled back toward its equilibrium position, the nitro group was prevented from doing so by its momentum. Figure 6g shows a plot of the bond lengths for the O\textsuperscript{\textminus}NO\textsubscript{2}, C\textendash C, and C\textendash O bonds within the reacting arm. The C\textendash C and C\textendash O bonds remain out of phase during the stretching periods of the O\textsuperscript{\textminus}NO\textsubscript{2} bond—the carbon atom within the arm is moving between the connecting oxygen and center carbon. When the C\textendash C and C\textendash O bonds finally come into phase, the oxygen atom is pushed to the right as both bonds stretch, severing the O\textsuperscript{\textminus}NO\textsubscript{2} bond. Then, the carbon atom is pulled back down as both the C\textendash C and C\textendash O bonds contract, making the O\textsuperscript{\textminus}NO\textsubscript{2} scission permanent.

In general, the loading of the bonds in the reacting molecule is mainly localized to only those parts immediately affected by the collision. A prime example of this is the (100) head-on threshold case, shown in Figure 7, in which an O\textsuperscript{\textminus}NO\textsubscript{2} bond is immediately broken as a nitro group from the right molecule strikes the reacting nitro group in the left molecule almost laterally.\textsuperscript{72} The O\textsuperscript{\textminus}NO\textsubscript{2} bond scission is immediately followed by a C\textendash C bond scission and subsequently by another O\textsuperscript{\textminus}NO\textsubscript{2} bond.

The O\textsuperscript{\textminus}NO\textsubscript{2} bond scission happens fast, occurring before any massive deformation to the rest of the reacting molecule (Figure 7a–c). The stretching mode of the O\textsuperscript{\textminus}NO\textsubscript{2} bond in the nonreacting molecule on the right is loaded as it pushes against the first reacting nitro group on the left. As seen in Figure 7g, the amplitude of the O\textsuperscript{\textminus}NO\textsubscript{2} stretching mode in the nonreacting molecule increases once the O\textsuperscript{\textminus}NO\textsubscript{2} bond in the reacting molecule is cleaved. With the majority of the collision energy localized in the reacting arm, the connecting formaldehyde group is pulled down, stretching the associated C\textendash C bond to its breaking point (Figure 7d). As discussed earlier, the BDE for the O\textsuperscript{\textminus}NO\textsubscript{2} bond is initially the lowest (182.69 kJ/mol) in the molecular complex; however, once the O\textsuperscript{\textminus}NO\textsubscript{2} bond breaks, the BDE for the associated C\textendash C bond drops significantly to become the lowest (from 250.48 kJ/mol down to 77.07 kJ/mol) which can in part account for the reaction pathway seen here. In Figure 7e, the upper arm of the reacting molecule begins a downward swing, bending sharply between the central carbon atom and the formaldehyde group. The bend is so sharp that the oxygen atom in the formaldehyde group bonds with the central carbon atom while the downward motion of the nitro group and the stretching of the associated O\textsuperscript{\textminus}NO\textsubscript{2} bond leads to the formation of another NO\textsubscript{2} (Figure 7f). The fact that this reaction pathway occurred as described offers supporting evidence that the chemical initiation due to a hypervelocity collision is not thermal. If the reactions were thermal, then the formation of NO\textsubscript{2} and H\textsubscript{2}CO would not have been immediate.

At the very least, they would have had to occur only after some number of oscillations of their associated modes of vibration. It is also important to note that between frames d and f in Figure 7, some of the nitro groups in the nonreacting molecule seemed to dissociate temporarily, as seen in Figure 7f. If these apparent dissociations, which were identified by extremely large bond lengths, can indeed be considered reactions, then these nitro groups reform as they travel along trajectories similar to their parent molecule.

The rarest reaction pathway observed in the threshold collision cases involves C\textendash H bond scissions at a rather low collision
velocity. In the (110) head-on threshold case, NO$_2$ is formed in much the same manner as in the (001) threshold case. H$_2$CO forms almost immediately after the formation of NO$_2$ in a manner similar to that of the (100) threshold case. These products form almost simultaneously and have rotations imparted to them. As a result, the hydrogen atoms in the H$_2$CO come within bonding distance of both the central carbon atom of the reacting molecule, and an oxygen atom in the NO$_2$ causing the C–H bond scissions, as depicted in Figure 8a–d,72

The C–H reaction events can be seen in Figure 8e where the plots of the bond lengths of the reactants cross those of the resulting products. The thermal behavior of the hydrogen bonds is evident before and after the reaction events. It is interesting to point out that a study$^{67}$ done by Dick, which reported an anomalous shock response normal to (110) at 4.2 GPa, also reported Raman spectra data that suggested the formation and decomposition of HONO. Another interesting study$^{39}$ by Wu et al. suggested the importance of HONO as an intermediate in water catalysis which was shown to speed up the thermal decomposition of EMs. It is possible that the early formation of HONO at such a low threshold velocity as seen in our collision simulation of (110) may be responsible for the anomalous shock response$^{67}$ observed by Dick, especially since the (110) head-on collisions were the only set of collisions that produced HONO with collision velocities below 5 km/s, with the (111) head-on collisions being the only other set to produce

Figure 6. Case of (001), head-on, mol. 1–3, 3.3 km/s collision: (a–f) collision dynamics leading to an O–NO$_2$ bond scission; (g) bond lengths plotted against time. The vertical lines show the frames depicted in parts a–f.
HONO below 6 km/s (though (111) was not included in the experimental studies of Dick et al.). Because C–H thermal vibrations were at play in the formation of CO and HONO, and because of the unique reaction dynamics, we performed another simulation of the (110) head-on collision at the same threshold velocity of 3.9 km/s. In this simulation, we equilibrated the bimolecular complex to 310 K to investigate the possibility that the reaction pathway we observed in the first simulation might have been a statistical aberration. We found that the sequence of chemical events in the 310 K case was nearly identical to that in the 300 K case, differing only in that the events occurred about 15 fs earlier in the later simulation. This suggests that thermal factors leading up to the reaction within a comparable temperature range do not affect the reaction pathway in this case—the formation of HONO and CO is an intrinsic property of the (110) head-on collision case at the threshold velocity. The C–H scissions occurred due to a combination of the relatively slow rotation of the H$_2$CO, the fast thermal vibrations of the C–H bonds, and the proximity of the H$_2$CO to the NO$_2$ and parent molecule. When we looked at similar reactions involving C–H scissions in some of the high energy collisions, we found the reaction mechanism to be

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Figure 7. Case of (100), head-on, mol. 1–6, 4.7 km/s collision: (a–f) collision dynamics leading to O–NO$_2$, C–C, and O–NO$_2$ bond scissions; (g) bond lengths plotted against time. The vertical lines show the frames depicted in parts a–f; the bond length of the constrained, nonreacting N=O bond responsible for the first reaction is represented by a dashed line.
VI. Nonequilibrium Chemistry

We found from our simulations that the hypervelocity reactions of colliding molecules in PETN are due to a combination of mechanical deformation, steric proximity, and localized vibrations (excited or thermal in the case of hydrogen). Obviously, due to the very short time scale of the reactions (on the order of 100 fs), thermal equilibrium does not exist. Therefore, classical transition state theory (which implies thermal equilibrium within reactant and product subsystems, and between those subsystems and the activated complex) does not apply to the case of hypervelocity collision reactions, which we assume to be the cause of initiation of chemical reaction behind a detonation front. In Table 1, we see that reactions occur between 100 and 500 fs which puts the reaction time scale at $\sim 10^{-11}$ s, exactly what was suggested by Walker et al.\textsuperscript{44,55} If one were to assume that there is such thermal equilibrium, then there are problems that must be confronted. For instance, assuming that the entire kinetic energy of the translational degrees of freedom within the colliding PETN molecules for a 4 km/s collision is distributed throughout all of the internal degrees of freedom within the binary collision complex, the system would have a temperature of 2000 K. This thermal equilibration should take place during tens of picoseconds ($\sim 10^{-11}$ s).\textsuperscript{11} Then, according to TST, the reaction rate of the O–NO$_2$ bond scission which produces the NO$_2$ products can be estimated as

$$k_r = f \exp\left(-\frac{E_b}{k_B T}\right)$$

where the N–O stretching mode frequency is $f = 10^{13}$ s$^{-1}$ and the O–NO$_2$ bond dissociation energy is $E_b = 183$ kJ mol$^{-1}$. The rate of reaction would then be $k_r \approx 10^8$ s$^{-1}$, or one reaction every $t = 10$ ns which is 3 orders of magnitude larger than the time required to establish thermal equilibrium ($\sim 10^{-11}$ s). This seems much too slow for the chemical events sustaining a detonation. For example, if we assume a reactive zone of thickness $1 \mu$m behind a shock front traveling with detonation speed $v_d = 7$ km/s, then the time of the passage of the reactive zone would be $t \approx 0.1$ ns. Thus, little, if any, reaction would occur between the von Neumann spike and the C–J point of the detonation wave. In addition, this TST reaction time scale

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Case of (110), head-on, mol. 1–8, 3.9 km/s collision: (a–d) collision dynamics leading to C–H reaction events; (e) bond lengths of both reactants and products plotted over the entire time of simulation.}
\end{figure}
is several orders of magnitude larger than those seen in simulation. Finally, the orientation dependence of these collisions strongly suggests that thermal processes are not all that is at work here. If the reactions were temperature driven, then energy would be evenly distributed throughout the colliding molecules; thus, any difference in threshold velocities for all possible collision orientations would be statistical in nature. However, the correlation between threshold velocities and detonation pressures suggests that the orientation dependence is real and not a statistical aberration. From this, it must be concluded that these initial chemical events are not temperature driven. Rather, they are driven directly by the dynamics of the collisions and exhibit explicit orientation dependence in a hypervelocity chemical regime.

VII. Conclusions

First-principles reactive molecular dynamics simulations of hypervelocity bimolecular PETN collisions revealed that the threshold velocities for initiating chemistry along directions corresponding to the compression of specific crystallographic planes correlate to the experimental anisotropic sensitivities determined for bulk crystalline PETN. Collisions in the (001), (011), and (110) directions are most sensitive with lowest threshold velocities of 3.3, 3.2, and 3.9 km/s, respectively, while collisions normal to the (010), (101), and (100) planes are most insensitive with threshold velocities of 4.4, 4.4, and 4.7 km/s, respectively. The (111) collision case is at the middle of the spectrum with an intermediate threshold velocity of 4.2 km/s. The reactive case simulations show the formation of NO2 as the dominant reaction pathway in all cases, with H2CO formation for cases in which a large amount of collision energy is localized in a particular arm of the molecule. In such cases where H2CO is formed, we find that the bond dissociation energy for the C–C bond drops after the connecting NO2 group dissociates. An exception was found for the sensitive (110) mol. 1–8 threshold case in which HONO and CO were ultimately produced as a result of atomic proximity and C–H thermal vibrations. A relationship between the steric orientation of the colliding molecules and chemical enhancement is evidenced by both threshold velocities for initiating chemistry and product formation. Reactive cases yielded product formation on time scales of the same order of magnitude as the oscillation periods of the various modes of vibration within the PETN molecule, $10^{-13}$ s. These reaction time scales are much too short for thermal processes to drive the reactions, leading us to conclude that the direct physical dynamics of the collisions is paramount in sustaining and perhaps initiating a detonation. More specifically, reactions are driven by dynamics that involve mechanical deformation, steric proximity, thermal vibrations (in the case of C–H scission), and localized excitations in vibration modes rather than temperature.

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References and Notes

Appendix 6: Reactive Molecular Dynamics of Hypervelocity Collisions of Si-PETN Molecules

Publication Record


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Reactive Molecular Dynamics of Hypervelocity Collisions of Si-PETN Molecules

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Abstract

First-principles density functional theory classical trajectory simulations of hypervelocity bimolecular collisions of sila-pentaerythritol tetranitrate (Si-PETN) molecules have been performed to investigate the cause of its high sensitivity of detonation initiation to mechanical stimulus. The solid-state environment of Si-PETN, specifies the initial orientations of colliding molecules. The threshold velocities for initiating chemistry for a variety of crystallographic orientations have been found to be similar to those of a previous study involving PETN. However, hypervelocity reaction pathways of Si-PETN differ from those of PETN due to the propensity of the central Si atom to form a five-atom bonding state that leads to both bimolecular reactions between colliding molecules, as well as the destabilization of functional groups causing homolytic reactions. New reaction pathways are identified, and their heats of reaction are calculated.

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Sila-pentaerythritol tetranitrate (Si-PETN) is a synthesized \(^1\) silicon analogue of the widely used energetic material (EM) pentaerythritol tetranitrate (PETN) in which the central carbon atom has been replaced by a silicon atom. While its molecular geometry is very close to that of PETN, Si-PETN has demonstrated extremely high sensitivity to relatively weak mechanical stimulus such as simply touching a crystalline sample with a spatula. \(^1\) A computational transition state theory (TST) study by Liu et al. \(^2\) of Si-PETN attempted to find the causes responsible for its high instability. It was found that while the activation energies for various homolytic reactions were slightly lower in Si-PETN, as compared to PETN, the differences were scarcely enough to account for the extreme differences in mechanical sensitivity. \(^2\) However, one reaction stood out in the study — the so called oxygen attack seen in Figure 1 (a). \(^2\) According to Liu et al., \(^2\) the barrier for this reaction in Si-PETN is half that of the same reaction in PETN (134 kJ/mol for Si-PETN compared to 335 kJ/mol for PETN), and results in substantial exothermic release after completion (186 kJ/mol for Si-PETN compared to 56 kJ/mol for PETN) that facilitates further decomposition.

A more recent study by An et al. \(^3\) focused on the investigation of mechanisms of hot-spot formation and reaction initiation involved reactive molecular dynamics (MD) shock simulations of both PETN and Si-PETN using reactive force field (ReaxFF) applied to large systems consisting of 2.7 million atoms. They found that initiation chemistry of PETN proceeded through mostly of NO\(_2\) homolytic reactions, while for Si-PETN, the initial reaction step is the rearrangement of the O and C atoms of the formaldehyde group involving the virtual five-atom bonding state. The rearrangement of the formaldehyde group in Si-PETN provides more energy release, and thus leads to complete decomposition.

The difficulties associated with its handling \(^1\) make unclear whether the high reactivity of Si-PETN is due to thermal and/or mechanical induction; however, to date, mostly the thermal mechanisms have been investigated, \(^2,4\) with exception of one shock study which was limited to one set of initial conditions. \(^3\) Therefore, the goal of this work is to elucidate potential mechano-chemical reaction pathways responsible for its extreme sensitivity.
Figure 1: Oxygen attack reaction observed in Ref.\textsuperscript{2,4}; $\Delta E$ is the heat of reaction, from the unreacted Si-PETN molecule (left) to the resulting isomer (right). Virtual 5-atom bonding state connecting O atom to Si atom is shown in the middle panel.

by investigating differences in the collision dynamics and resulting initiation chemistry between Si-PETN and PETN using first-principles molecular dynamics. The first-principles simulations are performed under conditions similar to that of our previous work to allow for a detailed comparison between these two systems. The simulations are performed under the adiabatic approximation, assuming that no appreciable electronic excitation can occur within the range of collision speeds used in this study. This assumption is based on the fact that the band gap for organic molecules typically used as EMs is greater than 1 eV at pressures approaching the detonation pressure. A more detailed discussion of the validity of the adiabatic approximation for hypervelocity molecular collisions can be found in\textsuperscript{5}.

To maintain direct correspondence between Si-PETN and PETN, we simulate bimolecular collisions of Si-PETN with initial positions and orientations taken from the crystalline environment, as was done for PETN;\textsuperscript{5} see Figure 2. We considered all possible orientations for collisions normal to the (001), (010), (011), (100), (101), (110), and (111) crystallographic planes. For each orientation, the system was equilibrated to 300 K, and separate runs were generated for the desired collision velocities within the range of 3–7 km/s. MD was run under the NVE ensemble (constant number, volume, and energy) by integrating the classical Newton’s equations of motion for each atom: $M_i (d\mathbf{R}_i/dt^2) = -(\partial V \{ \mathbf{R}_i \} / \partial \mathbf{R}_i)$. Interatomic interactions were evaluated using density functional theory (DFT) with PBE (Perdew, Burke, and Erzhanoff) generalized gradient approximation functional\textsuperscript{6}, optimized
double zeta polarized basis sets, and a real-space energy cutoff of 200 Ry within the framework of the Siesta DFT package.\textsuperscript{7}

Figure 2: Simplified representation of Si-PETN (and PETN) crystal with molecules shown as concentric spheres of molecular radii \( R \) and \( R/2 \). Bi-molecular collisions of outer spheres only are considered glancing collisions, while collisions of inner spheres are considered head-on collisions. Numbers indexing spheres match molecular index in column 3 of Table 1.

The trajectory data of each collision case are analyzed to determine threshold collision velocities for initiation of chemical reactions; subsequent reaction pathways are then investigated. Threshold velocities for Si-PETN are compared to those of PETN in Table 1. The differences in threshold velocities of Si-PETN and PETN are within 1 km/s, and show the same trend in directional dependence, indicating that collision sensitivity is predominantly due to geometry. However, threshold velocities for Si-PETN tend to be consistently lower, hinting at differences in chemical initiation as evidenced by the markedly different reaction pathways.

Table 1 lists the threshold velocities and corresponding products that are present after 0.5 ps of simulation together with the net heats of reaction \( \Delta E_{Path} \) from the initial pair of Si-PETN molecules to the products listed. Table 2 gives additional information for product species that are contained in both threshold cases, and corresponding cases with collision velocities that are higher, showing the cases with the lowest collision velocity to produce the listed products. Some products in Tables 1 and 2 are referenced by their locations
in Figures 4 and 5. The threshold velocities listed in Table 1 are related to the amount of kinetic energy required to facilitate the mechano-chemistry of initiation when the interacting molecules are in some predetermined orientation. It is also worth pointing out that this study has not attempted a complete sampling of the initial vibrational phase, as was done in a previous study on PETN collisions by Schweigert and Dunlap. In fact, Schweigert and Dunlap found a 800 kJ/mol spread in collision energy (~1.6 km/s spread in velocity) to initiate reactions for PETN molecules in the (000) and (100) locations (molecules 1 and 6 in Figure 2). Although the threshold collision velocities of reaction initiation for Si-PETN are slightly smaller than those for colliding PETN molecules, their differences cannot account for the great disparity in mechanical sensitivity observed for Si-PETN and PETN, as seen in experiments. Therefore, the extreme sensitivity of Si-PETN should be related to the differences in the reaction pathways upon hypervelocity collisions of Si-PETN and PETN molecules.

For PETN, bimolecular collisions generally result in massive deformation and direct bond shearing that leads to NO₂ homolysis, which weakens the C–C bond in the reacting arm, occasionally causing CH₂O homolysis. While this same behavior is also observed in simulations of colliding Si-PETN, the reaction pathways are far more complex due to the presence of the central Si atom. This leads to a greater number and diversity of products, which is attributed to the formation of the virtual five-atom bonding state of the central Si atom. This five-atom bonding state is not easily formed in the case of the central C atom in PETN molecules. Although this virtual five-atom bonding state seen in collision simulations resembles the transition state reported by Liu et al., and is more or less commensurate with the formaldehyde rearrangement reported by Murray et al., the mechanism of its formation during the close approach of two colliding Si-PETN molecules is different and involves rapid, nonuniform excitation of many modes as energy is transferred from the translational kinetic energy of rapidly approaching molecules directly into the bonds by inducing mechanical deformation.
Table 1: Threshold collision velocities ($V_{thr}$ in km/s) for chemical reaction initiation in both Si-PETN and PETN. Collisions are normal to planes given by $hkl$ in column 1, head-on or glancing as indicated in column 2, and molecular indices in column 3 match those labeling each molecule in Figure 2. Products for Si-PETN are shown in column 6 with corresponding heats of reaction ($\Delta E$) from initial unreacted to final states in column 7. Some species in column 6 are represented by their locations in Figures 4 and 5.

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>Type</th>
<th>Mol.</th>
<th>PETN $V_{thr}$</th>
<th>Si-PETN $V_{thr}$</th>
<th>Products</th>
<th>$\Delta E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>001 h</td>
<td>1 - 3</td>
<td>3.30</td>
<td>3.10</td>
<td>5-d, 2NO₂, 2CH₂O</td>
<td>+132.8</td>
<td></td>
</tr>
<tr>
<td>010 g</td>
<td>1 - 2</td>
<td>4.70</td>
<td>4.40</td>
<td>4-a, 4-c, 2NO₂, CH₂O</td>
<td>+175.8</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>1 - 4</td>
<td>4.40</td>
<td>4.00</td>
<td>4-a, 4-d, NO₂, CH₂O</td>
<td>+239.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 - 2</td>
<td>5.30</td>
<td>5.80</td>
<td>4-a, 4-c, 2NO₂, CH₂O</td>
<td>+175.8</td>
<td></td>
</tr>
<tr>
<td>011 g</td>
<td>1 - 3</td>
<td>3.40</td>
<td>3.50</td>
<td>5-c, 2NO₂, CH₂O</td>
<td>+132.8</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>1 - 5</td>
<td>3.20</td>
<td>3.10</td>
<td>4-a, 4-d, NO₂, HCO</td>
<td>+237.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 - 6</td>
<td>4.70</td>
<td>4.10</td>
<td>5-d, 3NO₂, 3CH₂O</td>
<td>+358.0</td>
<td></td>
</tr>
<tr>
<td>100 h</td>
<td>1 - 2</td>
<td>6.60</td>
<td>5.10</td>
<td>4-a, 4-c, 2NO₂, CH₂O</td>
<td>+175.8</td>
<td></td>
</tr>
<tr>
<td>101 g</td>
<td>1 - 3</td>
<td>4.60</td>
<td>3.50</td>
<td>5-c, 2NO₂, CH₂O</td>
<td>+4.8</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>1 - 7</td>
<td>4.40</td>
<td>3.50</td>
<td>4-a, 4-d, NO₂</td>
<td>+157.8</td>
<td></td>
</tr>
<tr>
<td>110 g</td>
<td>1 - 2</td>
<td>4.50</td>
<td>4.40</td>
<td>4-a, 4-c, 2NO₂, CH₂O</td>
<td>+395.5</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>2 - 3</td>
<td>-</td>
<td>4.50</td>
<td>4-b, 2NO₂</td>
<td>-55.7</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>1 - 8</td>
<td>3.90</td>
<td>3.00</td>
<td>5-c, 2NO₂, CH₂O</td>
<td>+4.8</td>
<td></td>
</tr>
<tr>
<td>111 h</td>
<td>1 - 2</td>
<td>4.20</td>
<td>4.10</td>
<td>4-c, 3NO₂, 2CH₂O</td>
<td>+389.5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3: Bond dissociation energies of Si-PETN compared to those of PETN.
Table 2: List of various products seen in Si-PETN collision simulations with net heats of reaction $\Delta E_{Path}$ and minimum collision velocities $V_{min}$ at which products occur. Corresponding cases are also shown. Some products are referenced by their locations in Figures 4 and 5.

<table>
<thead>
<tr>
<th>Products</th>
<th>$\Delta E_{Path}$ (kJ/mol)</th>
<th>$V_{min}$ (km/s)</th>
<th>Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-a.2, NO$_2$</td>
<td>+157.8</td>
<td>3.0</td>
<td>(110) mol. 1–8</td>
</tr>
<tr>
<td>4-a.4, 2NO$_2$, CH$_2$O</td>
<td>+395.5</td>
<td>4.4</td>
<td>(110) mol. 1–2</td>
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<td>4-b.2, NO$_2$</td>
<td>+92.0</td>
<td>4.5</td>
<td>(110) mol. 2–3</td>
</tr>
<tr>
<td>4-b.3, 2NO$_2$</td>
<td>+260.3</td>
<td>4.5</td>
<td>(110) mol. 2–3</td>
</tr>
<tr>
<td>4-b.4, 2NO$_2$</td>
<td>-55.7</td>
<td>4.5</td>
<td>(110) mol. 2–3</td>
</tr>
<tr>
<td>4-c.3, 2NO$_2$, CH$_2$O</td>
<td>+175.8</td>
<td>4.4</td>
<td>(101) mol. 4–2</td>
</tr>
<tr>
<td>4-d.2, NO$_2$, CH$_2$O</td>
<td>+239.2</td>
<td>3.1</td>
<td>(011) mol. 1–5</td>
</tr>
<tr>
<td>4-d.3, NO$_2$, HCO</td>
<td>+237.2</td>
<td>3.1</td>
<td>(011) mol. 1–5</td>
</tr>
<tr>
<td>4-e.2, 2NO$_2$, 2CH$_2$O</td>
<td>+384.9</td>
<td>4.1</td>
<td>(111) mol. 1–2</td>
</tr>
<tr>
<td>4-e.3, 3NO$_2$, CH$_2$O</td>
<td>+389.5</td>
<td>4.1</td>
<td>(111) mol. 1–2</td>
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<tr>
<td>5-b.3, 4-a.2, NO$_2$, CH$_2$O</td>
<td>+83.6</td>
<td>3.3</td>
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<tr>
<td>5-c.3, 2NO$_2$, CH$_2$O</td>
<td>+4.8</td>
<td>3.0</td>
<td>(110) mol. 1–8</td>
</tr>
<tr>
<td>5-d.2, 2NO$_2$, 2CH$_2$O</td>
<td>+132.8</td>
<td>3.1</td>
<td>(001) mol. 1–3</td>
</tr>
<tr>
<td>5-d.3, 3NO$_2$, 3CH$_2$O</td>
<td>+358.0</td>
<td>4.1</td>
<td>(100) mol. 1–6</td>
</tr>
</tbody>
</table>
We calculated bond dissociation energies (BDEs) or heats of reactions ($\Delta E$) within geometrically optimized reactant and product molecules as a means of quantifying mechanisms of reactions that take place along a particular pathway. As seen in Figure 3, the O–NO$_2$ and C/Si–CH$_2$O BDEs for PETN and Si-PETN are found to be similar. Additionally, the C/Si–CH$_2$O BDEs in both molecules are found to drop by approximately the same amount upon NO$_2$ homolysis.

The principal difference in reaction pathways seen for Si-PETN collision simulations, as compared to those for PETN, is the virtual five-atom bonding state, which is rarely observed in collision simulations of PETN. The reaction pathways that evolve from this bonding state depend greatly on the relative orientations of the colliding molecules, and result from molecular deformation upon collision. The most common pathways are initiated by the oxygen attack reaction seen in the first two steps of Figure 1. When oxygen attack occurs, reactions progress along one of three possible pathways. In one such pathway shown in Figure 4 (a), the approaching oxygen atom comes within the Si coordination sphere, immediately resulting in NO$_2$ homolysis, after which the O atom moves back out of the Si coordination sphere, and the molecule relaxes back to a Si-PETN molecule with a dissociated NO$_2$ group. Essentially NO$_2$ homolysis with and without oxygen attack has the same net change in energy, +157.8 kJ/mol, which agrees with +163.8 kJ/mol calculated by Liu et al.; but little can be said for whether or not the virtual five-atom bonding state facilitates the NO$_2$ homolytic reaction. For some cases in which NO$_2$ homolysis occurred, CH$_2$O homolysis resulted due to the drop in BDE for the Si–CH$_2$O bond from +233.0 to +81.4 kJ/mol, as seen in Figure 3, or +80.5 kJ/mol after a second NO$_2$ homolysis with BDE of +157.2 kJ/mol; seen in Figure 4 (a).

The second reaction pathway initiated by oxygen attack is similar to the first with the exception that after NO$_2$ homolysis, the formaldehyde group flips as seen in Figure 4 (b), in agreement with An et al., resulting in an exothermic heat of reaction $\Delta E = -65.8$ kJ/mol. Though rare in our MD simulations, this pathway may lead to a reaction of the type seen for the (110) mol. 2–3, 4.5 km/s collision case in which the flipped CH$_2$O group forms a ring

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with a neighboring CH$_2$O group after a second NO$_2$ homolytic reaction; see Figure 4 (b). The second NO$_2$ homolysis has a BDE of +168.3 kJ/mol; however, the bonding of the two CH$_2$O groups results in $\Delta E = -316.0$ kJ/mol, as well as $\Delta E_{path} = -55.7$ kJ/mol from the unreacted to final states of the molecular complex.

In the third pathway, seen in Figure 4 (c), oxygen attack coincides with the destabilization of an adjacent CH$_2$ONO$_2$ arm causing additional NO$_2$ and CH$_2$O homolytic reactions, while the Si–O and the Si–C bonds from the same formaldehyde group remain stable. The net energy change from unreacted to final states for this reaction, despite three homolytic reactions, is $\Delta E_{path} = +175.8$ kJ/mol, with $\Delta E = +395.6$ kJ/mol for all three homolytic reactions (two NO$_2$ and one CH$_2$O), and $\Delta E = -219.7$ kJ/mol for Si–O bond formation. Additionally, the pathway in Figure 4 (c) is the most commonly observed in our collision simulations for Si-PETN. Such a reaction is seen for PETN$^5$ in the (100) mol. 1–6, 4.7 km/s collision case, but the bonding of the O atom with the central C atom only occurs after a nitro and formaldehyde group from the same arm both dissociate.

Like PETN, some Si-PETN showed simple NO$_2$ and CH$_2$O dissociation reactions without an O atom passing within the coordination sphere of the central Si atom. As seen in Figure 4 (d), NO$_2$ dissociation is followed by CH$_2$O dissociation; however, the CH$_2$O fragment immediately gives up one of its H atoms to the central Si atom of the reacting Si-PETN molecule to form CHO with $\Delta E = -2.0$ kJ/mol, which is seen in the (011) mol. 1–5, 3.1 km/s case. Figure 4 (e) shows multiple dissociations of NO$_2$ and CH$_2$O from a single Si-PETN molecule without the virtual five-atom bonding state, as is observed for the (111) mol.1–2, 4.1 km/s case. One of the CH$_2$ONO$_2$ arms dissociate in a concerted fashion, followed by another NO$_2$ homolytic reaction. A second formaldehyde group dissociates, which, interestingly, is exothermic with $\Delta E = -10.6$ kJ/mol. Afterward, NO$_2$ homolysis occurs as the O atom of the remaining formaldehyde group moves within the Si coordination sphere, thus forming a third bond with the Si atom, with $\Delta E = +4.5$ kJ/mol.

Oxygen attack is not the only observed reaction involving a virtual five-atom bonding
Figure 4: Unimolecular reactions of Si-PETN with heats of reaction between steps. $\Delta E_{\text{Path}}$ gives the heat of reaction for the entire pathway shown from the initial, unreacted Si-PETN molecule. Narrow, curved arrows show where species will go; dashed lines show from where species came, dashed circles show what chemical groups will react next.
Figure 5: Bi-molecular reactions for Si-PETN involving the five-atom bonding state: a) apparent destabilization of CH$_2$ONO$_2$ arm due to five-atom bonding state with O atom from nitro group of second molecule; b) formation of intermolecular formaldehyde bridge; c) Intermolecular Si–Si bonding. Values above arrows are heats of reaction in kJ/mol. Net heats of reaction ($\Delta E_{Path}$) from initial bimolecular complex are given in bottom right of each panel.
The breakdown of H$_2$O involves bimolecular head-on collisions bringing the silicon bond; see Figure 3 (d). The (100), (010), and (110) head-on collisions bring the formation within the bridge (4) yields $\Delta V = -3.97$ kcal/mol. The breaking of Si-O bond best describes the initial formation of Si-O bonds. However, the homolytic reaction with the formylpyridine molecule immediately follows by NO$_2$ homolysis. Next, the O atom within the formylpyridine group bonds with the central Si atom of the second Si-PETN molecule as NO$_2$ and CH$_2$O groups immediately follow the NO$_2$ homolysis. The reaction proceeds from the initial P$2$H$_2$O decomposition state to the initial head-on collisions, as shown in Figure 3 (e) and seen for the (010) mod. 1-3, and (110) mod. 1-3). This results in the formation of the second molecule, a stable formylpyridine bridge between the centers of the two molecules, as shown in Figure 3 (e). Once again, some head-on and E$^\text{high}$ collisions bring an O atom from a formylpyridine group in one second molecule bonds to the Si atom of the first as the corresponding nitro group dissociates CH$_2$ONO$_2$ from the first molecule. The O atom from the intermediate nitro group of the Si atom in the first molecule is instead of merely colliding with the decomposition of a Si atom of a nitro group on the second molecule, enters the coordination sphere of the O atom of a nitro group on the second molecule as shown in Figure 3 (q). Once again, similar to that of the previous bimolecular case occurs as shown in Figure 3 (q). For the (011) mod. 1-2, 3-3 km/s and 3-4 km/s cases, a virtual head-on bonding state would result in molecules decolating from one another, so such pathway is observed for any of the transitions described. For E$^\text{high}$ collisions, several bimolecular reactions are observed that depend greatly on col-
central Si atoms of both molecules into close proximity, leading to a Si–Si bond that seems to destabilize one CH$_2$ONO$_2$ arm from each molecule as the central Si atoms bond to one another. The net change in energy for the four homolytic reactions is $\Delta E = +478.4$ kJ/mol; however, the formation of the Si–Si bond is exothermic with $\Delta E = -345.6$ kJ/mol, giving $\Delta E_{\text{Path}} = +132.8$ kJ/mol. Only the (001) and (100) cases produce stabilized Si–Si bonds for threshold cases after homolytic reactions. The Si–Si bond in the (010) threshold case seems temporary since in this orientation three pairs of functional CH$_2$ONO$_2$ arms are aligned to collide first, and thus push the temporarily bonded Si atoms apart as they relax to a lower energy configuration. Still, the temporary Si–Si bond coincides with the destabilization of at least one molecule in the (010) threshold case, leading to NO$_2$ and CH$_2$O homolytic reactions. For collision energies higher than those of the corresponding threshold case, stabilized Si–Si bonding occurs for the (010) collision geometry after homolytic reactions occur on both molecules. For the (100) threshold case, an additional arm dissociates as seen in the third step of Figure 5 (d) with $\Delta E = +225.2$ kJ/mol and $\Delta E_{\text{Path}} = +358.0$ kJ/mol.

In summary, bimolecular collisions of Si-PETN show similar trends in threshold velocities to initiate chemical reactions as those of PETN; however, Si-PETN collisions produce a greater number of products, and more complex initial reaction pathways with higher exothermicity due to the ability of the central Si atom to form a virtual five-atom bonding state. Additionally, further decomposition of the Si-PETN molecule involving dissociation of nitro and formaldehyde groups seem to become increasingly exothermic as the central Si atom tends to attract the O atom of remaining formaldehyde groups to form Si–O bonds that lower the energy of the reacting complex. This result seems consistent with the notion that the exothermicity of further Si-PETN decomposition is much greater than that of PETN in agreement with An et al.$^3$ The fact that the threshold collision velocities to initiate chemical reactions are very similar in both Si-PETN and PETN, despite the fact that Si-PETN is so much more sensitive to mechanical stimulus, suggests that these threshold collision velocities can not be directly correlated to sensitivity to mechanical stimulus; rather they serve
as an indicator of how much locally deposited kinetic energy is required to initiate chemical reactions for a specific bimolecular orientation.

While BDEs of the Si-PETN and PETN molecular complexes are similar, the virtual five-atom bonding state of the Si atom often results in the destabilization of functional arms, and plays an important role in bimolecular reactions. Within the hypervelocity bimolecular collisions of this work, several new reaction pathways beyond the oxygen attack reaction discussed in the works of Lui et al.\textsuperscript{2}, Murray et al.\textsuperscript{4}, and An et al.\textsuperscript{3} that involve the virtual five-atom bonding state are identified. These new pathways demonstrate differences between thermally and mechanically activated chemistry, while providing a broader view of the reaction pathways that are possible upon mechanical initiation of detonation in highly-sensitive Si-PETN.

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Appendix 7: Reactive Molecular Dynamics of Hypervelocity Bi-molecular Collisions of Ringed Energetic Materials: RDX, HMX, TATB

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Hypervelocity Chemistry of Ringed Energetic Materials: RDX, HMX, TATB

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Abstract

First-principles reactive molecular dynamics of hypervelocity bimolecular collisions of RDX, HMX, and TATB molecules has been performed to elucidate the initiation chemistry that occurs at a shock wave front upon initiation of detonation. Collision velocities ranged from 2 km/s to 7 km/s for RDX and HMX, and 2 km/s to 10 km/s for TATB, along directions normal to the (001), (010), (011), (100), (101), (110), and (111) crystallographic planes with initial positions corresponding to those of the associated crystal lattice. Reaction dynamics for each case show that NO₂ homolysis is the dominant first reaction for most cases, while more exotic reactions, not seen in cookoff studies, are observed, many involving ring reconformations. Net changes in energy for each reaction are calculated and show qualitative correspondence to the order in which reactions progress.

Introduction

The initiation of a detonation in an energetic material (EM) is a process that involves the rapid chemical decomposition of EM molecules as a result of a passing shock wave. It is

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assumed that the passage of the shock wave front induces hypervelocity (\(> 1 \text{ km/s}\)) intermolecular collisions that feed energy into chemical bonds at rates faster than those described by classical chemical kinetics.\(^1\)\(^,\)\(^2\) Indeed, such rapid decomposition was demonstrated in previous bimolecular hypervelocity collision simulations of PETN,\(^3\) with initial positions and orientations corresponding to the crystalline environment, in which chemical events occurred at the time scale \(\sim 10^{-13} \text{ s}\). In contrast, the processes of redistribution of the translational kinetic energy of collision to all of the degrees of freedom within an EM molecule, including the reaction coordinate, are much slower and occur on the time scale \(\sim 10^{-11} \text{ s}\).\(^4\) This implies that while transition state theory (TST) and cookoff studies are no doubt useful in elucidating various chemical decomposition pathways for EMs under thermal stimuli, they essentially fall short of describing many chemical pathways possible within non-equilibrium conditions in a shock wave front, where the concepts of temperature and reaction coordinates are ill-defined. The reason for this is obvious since many reaction pathways that are considered highly unfavorable under thermal equilibrium conditions may readily become available for colliding molecules due to the rapid localization of mechanical strain and abundance of energy. The kinetic energy of colliding molecules is quickly converted into potential energy of specific bonds first in only those parts of the colliding molecules that initially interact, leading to severe deformation and, potentially, mechanical bond breaking.

It has been known for some time that reaction rates can be greatly enhanced by the presence of stress on a system. In fact, increase of reaction rates in stress-loaded systems has been put forward by Zhurkov.\(^5\) However, explicit exclusion of stress in simulations of complex reactive environments is quite a challenging task. Therefore, direct molecular dynamics (MD) simulation of mechano-chemical decomposition seems to be a useful approach to investigate the chemical pathways leading to detonation initiation. Though the flow of energy during such collisions is difficult to track, the numerous initial endothermic chemical steps of initiation that involve the breaking of the weakest bonds can be predicted based on bond dissociation energies (BDEs), while heats of reaction for highly exothermic chem-
ical steps occurring later in the collision simulations offers evidence of the rapid chemical decomposition possible within the first pico-second of initiation.\textsuperscript{3}

As this work discusses novel reaction pathways observed in hypervelocity collisions of the ringed nitro compound EMs, a review of the reaction pathways known to occur upon thermal stimuli is warranted. The reaction chemistry of RDX, for instance, has been studied extensively.\textsuperscript{13–20} In an experimental study by Zhao et al.,\textsuperscript{13} involving infrared multi-photon dissociation of RDX molecules in a molecular beam, several distinct chemical pathways were discerned. Among these were successive NO\textsubscript{2} homolytic reactions, successive HONO elimination, NO\textsubscript{2} homolysis followed by HONO elimination, ring cleavage with CH\textsubscript{2}NNO\textsubscript{2} dissociation, and concerted ring depolymerization, in which the RDX molecule simultaneously decomposes into 3(CH\textsubscript{2}NNO\textsubscript{2}). Concerted ring depolymerization was found to be dominant and produced the highest quantity of products, despite the fact that the barrier for this reaction was higher than those for NO\textsubscript{2} homolysis.\textsuperscript{13}

Wight and Botcher\textsuperscript{14} performed a similar study on solid phase RDX and found no evidence of concerted ring depolymerization, but only pathways involving N–N bond scission; they speculated that the condensed phase strongly inhibits the concerted depolymerization pathway due to the presence of neighboring molecules. Subsequently, several computational studies\textsuperscript{15,17,18} investigated thermal decomposition pathways and found that while homolytic NO\textsubscript{2} reactions were favored energetically, HONO elimination was likely to be the pathway leading to initiation chemistry in RDX due to its exothermic nature, as opposed to only endothermic NO\textsubscript{2} homolysis. Essentially, HONO elimination produces more subsequent reactions, whereas NO\textsubscript{2} homolysis actually slows down decomposition.\textsuperscript{19}

Chemical reactions in thermally excited RDX are thought to be similar to HMX. Lewis \textit{et al.}\textsuperscript{22} performed a TST study of HMX and proposed that while N–NO\textsubscript{2} scission is most favorable, HONO elimination and C–N ring cleavage would occur most likely in the condensed phase since the latter two have comparable barriers to nitro group dissociation, while being less hindered by steric constraints introduced by surrounding molecules. Additionally,
concerted depolymerization was found to be unfavorable. Later TST studies of HMX\textsuperscript{16,17} did in fact reveal some similarities to RDX reactivity: while NO\textsubscript{2} homolysis was favored, it led to fewer subsequent reactions; exothermic HONO elimination was favored leading to more products; ring cleavage resulted in the formation of H\textsubscript{2}CNNO\textsubscript{2} and an open-ring RDX molecule, which in turn led to associated RDX reaction pathways such as H\textsubscript{2}CO and N\textsubscript{2}O formation from both open-ring RDX and H\textsubscript{2}CNNO\textsubscript{2}. In contrast to RDX, HMX exhibited no concerted ring depolymerization pathways.\textsuperscript{16,17}

TATB is yet another ringed nitro compound EM, but with an aromatic all-carbon ring and alternating ammonia and nitro groups. It is generally considered to be highly insensitive, as compared to nitramine EMs, likely due to the fact that all proposed decomposition pathways are endothermic with higher barriers for homolytic reactions than RDX and HMX, in addition to the high stability of the all-carbon ring. A TST study by Wu and Fried\textsuperscript{23} found that the most favorable pathway is ring closure to form benzofurazan, with a barrier comparable to those of homolytic NO\textsubscript{2} reactions in RDX and HMX. This ring closure reaction occurs when an H atom transfers from an ammonia group to bond with an O atom in a neighboring nitro group, generating HONO, and subsequently leading to the formation of a water molecule. While this reaction can also occur in the form of intermolecular H transfer, the barrier for the intramolecular ring closure reaction is \textasciitilde 12 kcal/mol lower. However, as cautioned by Wu and Fried, it may be that intermolecular H transfer would have a lower barrier than intramolecular ring closure under high pressure conditions in a shock front.\textsuperscript{23}

Interestingly, a recent experimental study performed by Glascoe \textit{et al.}\textsuperscript{24} on photo-induced decomposition of TATB at ambient pressures did not reveal the presence of water within the decomposition process, indicating that NO\textsubscript{2} homolysis was the dominant pathway. However, decomposition experiments at 8 GPa did show the presence of water, indicating that H transfer was favored at high pressure. Glascoe \textit{et al.}\textsuperscript{24} also found that the intensity of the absorption spectrum associated with the carbon ring decreased early on without an appreciable decrease in spectra associated with the nitro and ammonia groups during decomposition.
This seemed to suggest that ring cleavage, though highly unlikely, was a primary pathway for photo-induced decomposition. Due to the stability of the carbon ring determined in previous decomposition studies of TATB, Glascoe et al.\textsuperscript{24} proposed a more likely scenario that the ring was “sufficiently distorted” such that its vibrational frequencies were shifted out of the range of their spectral probe at 1433 cm\textsuperscript{-1}.

The goal of this work is to investigation chemical reaction pathways leading to the initiation of detonation processes in the ringed nitramine EMs RDX (1,3,5-Trinitroperhydro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), as well as the aromatic EM TATB (1,3,5-triamino-2,4,6-trinitrobenzene) by first-principles density functional theory (DFT) molecular dynamics (MD), which is used to simulate hypervelocity collisions of molecules under shock-wave conditions. Many of the pathways proposed in this work are not discussed in the previous literature, likely due to their high improbability in previously performed TST and cookoff studies. We perform simulations of hypervelocity bimolecular collisions in the range of 2-7 km/s for RDX and HMX, and 2-10 km/s for TATB, using DFT under the adiabatic approximation. It is assume that no appreciable electronic excitation within the range of collision velocities occurs as the bandgap for most nitro compound EMs under compression is greater than 1 eV.\textsuperscript{[3]} Though it has been suggested that metallization at high pressure plays a major role in initiation for TATB,\textsuperscript{25-26} Wu and Fried\textsuperscript{23} found that bandgap closure occurs at very high uniaxial compression \textasciitilde47% along directions involving the \textit{c}-lattice vector, which corresponds to a pressure of \textasciitilde120 GPa, thus contradicting the metallization hypothesis. A recent DFT study,\textsuperscript{27} which incorporated van der Waals interactions, showed a decrease in bandgap as a function of uniaxial compression up to 70% that agreed with the results of Wu and Fried; at 70% compression along directions involving the \textit{c}-lattice vector, the bandgap for TATB was \textasciitilde1 eV. Therefore, even 10 km/s collision simulations of TATB should be qualitatively correct under the adiabatic approximation.
Computational Details

Bimolecular collision simulations are performed with molecules and atomic positions corresponding to those of the solid state environment for directions normal to the (001), (010), (011), (100), (101), (110), and (111) crystallographic planes. For a given direction, all possible molecular collisions are identified, and the corresponding molecules are isolated and centered within a simulation box sufficiently large to contain all post reaction fragments over the simulation timescale of 0.5 ps. An equilibration at temperature 300 K is then applied to the isolated molecules, after which one half the desired collision velocity is added to the thermal velocities of each atom in each molecule such that the molecules collide in the center of the simulation box. In this work, each collision is described by the crystallographic plane normal to the direction of the collision, the molecules participating in the collision as indexed in Figure 1, as well as the collision velocity; e.g. a collision between molecule 1 and molecule 2 normal to the (100) plane with a collision speed of 3.0 km/s is described as (100) mol. 1–2 3.0 km/s.

Under the NVE (constant number, volume, and energy) ensemble, first-principles MD is performed by integrating the Newtonian equations of motion for each atom: $M_i \left( d\mathbf{R}_i^2 / dt^2 \right) = - \left( \partial V \{ \mathbf{R}_1 \} / \partial \mathbf{R}_i \right)$. Interactions between atoms are calculated using DFT such that $V(\{ \mathbf{R}_1 \}) = E_{\text{DFT}}\{ \mathbf{R}_1 \}$, where $E_{\text{DFT}}$ is the total energy of the system at fixed atomic positions $\{ \mathbf{R}_1 \}$. The electronic structure calculations employ the PBE (Perdew, Burke, and Erzhanhoff) generalized gradient approximation (GGA) functional, optimized double zeta polarized basis sets, and a real-space energy cutoff of 200 Ry within the framework of the Siesta DFT package. The trajectories for each atom are traced, and reaction pathways are determined for each collision case.

Bond dissociation energies (BDEs) and heats of reactions ($\Delta E_{\text{Rxn}}$) are calculated by simply subtracting the total energy of reactants from that of products obtained by DFT. Energies for the various chemical species of interest are calculated after geometric optimization with a force tolerance of no more than 0.02 eV/Å.
Figure 1: Crystallographic orientations of molecules within supercell for bimolecular collisions of RDX (left), HMX (center), and TATB (right). Spheres represent molecular centers, and are indexed for identification in collisions naming scheme.

RDX Collisions

Simulations of colliding RDX molecules display the NO₂ homolytic reaction, with BDE \( \Delta E_{Rxn} = +192.8 \text{kJ/mol} \) as seen in the first step in Figure 2 (a), to be the dominant first step, particularly for threshold cases, for which the collision velocity was at the minimum required for inducing chemical reactions. In a couple of these threshold cases, ((010) mol. 4–8 4.2 km/s and (111) mol. 1–8 6.9 km/s), a dissociated NO₂ pulls a hydrogen atom from the parent molecule to generate hydronitrite, or HNO₂ (not HONO) as seen in Figure 2 (b). At velocities higher than those of the threshold cases, several more exotic reaction pathways were observed. While HONO formation did occur in a few of these cases, ((100) mol. 2–5 6.0 km/s, (101) mol. 1–2 7.0 km/s, and (110) mol. 4–5 6.0 km/s), as shown in the last step in Figure 2 (a), the NO₂ involved in its formation had already dissociated in every case. The calculated BDE for the N–NO₂ bond is \( \Delta E_{Rxn} = +192.8 \text{kJ/mol} \), while the heat of reaction for the process in which NO₂ pulls a hydrogen atom from the parent molecule to form HONO is \( \Delta E_{Rxn} = -191.8 \text{kJ/mol} \), giving a net \( \Delta E_{Path} \) for the entire pathway of +1.0 kJ/mol, as shown in Figure 2 (a). While the kinetics of this pathway don’t exactly agree with the notion of HONO elimination laid out in TST studies,\(^{15-18} \) the energetics and end result (HONO formation) do. Further, HONO formation only occurs at high collision velocities, which is in agreement with shock simulations of solid RDX.\(^{20} \) Finally, the formation of HONO occurs within 300 fs of the start of the collision simulation. In the case where HNO₂ is formed, the
calculated heat of reaction is $\Delta E_{Rxn} = -168.3 \text{kJ/mol}$, resulting in $\Delta E_{Path} = +24.5 \text{kJ/mol}$, and suggesting that HONO formation is the energetically preferred pathway.

In some (100) collision cases in which double NO$_2$ homolysis occurs, such as (100) mol. 1–6 7.0 km/s and mol. 2–5 5.00 km/s, an H atom is transferred from the C atom across the ring from the remaining nitro group to an N atom located on the ring as seen in Figure 2 (c). The first and second NO$_2$ homolytic reactions have BDEs of $\Delta E_{Rxn} = +192.8 \text{kJ/mol}$ and $\Delta E_{Rxn} = +205.0 \text{kJ/mol}$ respectively, while the H transfer from the C atom to N atom has $\Delta E_{Rxn} = -314.0 \text{kJ/mol}$, resulting in $\Delta E_{Path} = +83.8 \text{kJ/mol}$. Another H transfer reaction, seen in the (110) mol. 4–5 7.0 km/s case, has a heat of reaction $\Delta E_{Rxn} = -290.6 \text{kJ/mol}$ and occurs after final NO$_2$ homolysis, with a BDE of $+200.6 \text{kJ/mol}$; see Figure 2 (d).

Clearly, these intramolecular H transfer reactions release more energy than either of the previously mentioned NO$_2$ H-elimination reactions; however, the ring still remains intact. This is not the case for the H transfer reaction seen in Figure 2 (e), originally observed in the (100) mol. 2–5 6.0 km/s collision case. This particular pathway involves H transfer from a C atom adjacent to the remaining NO$_2$ group to a neighboring N atom on the ring, which ends in exothermic ring cleavage with $\Delta E_{Rxn} = -142.4 \text{kJ/mol}$. The resulting H–N bond is quite strong with a BDE of 345.6 kJ/mol, and is very resistant to H-elimination reactions as $\Delta E_{Rxn}$ for an NO$_2$ to pull it away to form HONO is $+84.6 \text{kJ/mol}$. Interestingly, ring cleavage from the same bond without H transfer has $\Delta E_{Rxn}$ of $+84.4 \text{kJ/mol}$ compared to -142.4 kJ/mol with H transfer, indicating that this particular mode of H transfer can offer a far more energetically favorable pathway to ring cleavage.

Other ring cleavage pathways not involving intramolecular H transfer were observed for cases with collision velocities higher than those of the corresponding threshold cases, but the traditional sense of ring cleavage – a bond in the ring breaks and the ring opens – is seen only in three collision cases: after NO$_2$ homolysis in (100) mol. 1–6 6.0 km/s, and before NO$_2$ homolysis in both (100) mol. 2–5 6.0 km/s and (110) mol. 1–8 6.0 km/s. For the case in which ring cleavage occurs after NO$_2$ homolysis, shown in Figure 2 (f), $\Delta E_{Rxn}$ for ring cleavage was
only +90.6 kJ/mol after the first homolytic reaction of a nitro group. The ring was found to be weakest in either of the C–N bonds closest to the N atom from which the NO₂ dissociated. For the cases in which ring cleavage occurs before NO₂ homolysis, the open ring was found to be unstable, thus leading to immediate NO₂ homolysis with \( \Delta E_{Rxn} = +283.4 \text{ kJ/mol} \), as well as suggesting that ring cleavage with the first NO₂ homolytic reaction is a concerted event; see second step in Figure 2 (g). The resulting open ring configurations matched that of the case in which cleavage occurred after NO₂ homolysis; however, in both prehomolytic cases reactions continued such that the dissociated NO₂ bonds to another ring nitrogen atom already bonded to an NO₂ leading to the 'double headed' configuration seen in the third step of Figure 2 (g), with \( \Delta E_{Rxn} = -135.5 \text{ kJ/mol} \) and \( \Delta E_{Path} = +147.9 \text{ kJ/mol} \). For the (110) mol. 1–8 6.0 km/s case, however, ring cleavage occurred for both colliding molecules such that one molecule followed the previously described pathway for the (100) mol. 2–5 6.0 km/s case shown in Figure 2 (g), while the other followed a pathway involving a '3/5' ring conformation described below, and shown in Figure 2 (h).

For several cases ((101) mol. 1–2 6.0 km/s, (110) mol. 1–8 6.0 & 7.0 km/s, (110) mol. 4–5 6.0 km/s, and (111) mol. 1–2 7.0 km/s), a '3/5' ring conformation pathway was seen in which the affected RDX molecule underwent two consecutive NO₂ homolytic reactions with \( \Delta E_{Rxn} = +397.8 \text{ kJ/mol} \), followed by the intra-ring bonding of the two nitrogen atoms from which nitro groups dissociated, thus yielding a '3/5' ring conformation isomer of \((\text{H}_2\text{CNNO}_2)\text{(H}_2\text{CN})_2\) and \( \Delta E_{Rxn} = -107.9 \text{ kJ/mol} \); see Figure 2 (h). This '3/5' ring conformation is only stable so long as it either remains bonded to a nitro group opposite the intra-ring N–N bond, or if an H-elimination reaction occurs on the ring before or during its formation. In the (110) mol. 1–8 7.0 km/s case, just such a ring conformation appears; however, the remaining nitro group dissociates causing the '3/5' ring to break as seen in Figure 2 (h). The heat of reaction for the breaking of the 5 member ring after NO₂ homolysis is \( \Delta E_{Rxn} = +270.5 \text{ kJ/mol} \). Though not seen in any of the simulations, the diazirine (3 member ring) should inevitably break away from the H₂CNNCH chain as the BDE for the
Figure 2: Unimolecular reactions of RDX with heats of reaction in kJ/mol between steps. Values near bonds or H₂ are BDEs or heats for H elimination reactions involving NO₂ to produce HONO respectively, both in kJ/mol. \( \Delta E_{Path} \) is the net heat of reaction from unreacted RDX molecules to the step shown. Hashed lines show from where species originate; thin, solid arrows show where species will go after reacting.
C–N bond is only $\Delta E_{Rxn} = +5.4 \text{ kJ/mol}$.

Within the set of RDX hypervelocity collisions studied, only two actually produced bimolecular reactions: (110) mol. 4–5 6.0 km/s and (100) mol. 2–5 7.0 km/s. For the (110) mol. 4–5 6.0 km/s case shown in Figure 3 (a), five NO$_2$ molecules dissociate, having a net heat of reaction of $\Delta E_{Rxn} = +996.2 \text{ kJ/mol}$ (step 2 in Figure 3 (a)), followed by H-elimination from a resulting triazine to produce HONO with $\Delta E_{Rxn} = -224.6 \text{ kJ/mol}$ (step 3 in Figure 3 (a)). The HONO radical then pulls an H atom from the second reacting ring, producing NO and H$_2$O only 90 fs later, with $\Delta E_{Rxn} = -126.6 \text{ kJ/mol}$ (step 4 in Figure 3 (a)). At the same time, the H deficient triazine, being under high stress from the transfer of collision energy, reforms into a stable ’3/5’ ring conformation with $\Delta E_{Rxn} = -80.0 \text{ kJ/mol}$ (step 5 in Figure 3 (a)). Taking into account the entire set of reactions occurring within the 0.5 ps time frame, the energy change for the entire path is $\Delta E_{Path} = +565.0 \text{ kJ/mol}$, which produces the ’3/5’ conformation with a missing H atom, three NO$_2$ molecules, an NO molecule, and an H$_2$O molecule. The abundance of products in such a short period of time is commensurate with the concept of shattering dissociation, as coined by Schweigert et al.,$^{29}$ under the extreme conditions of initiation at the detonation front. Additionally, the production of a water molecule in such a short period of time indicates the likelihood of further decomposition by water catalysis proposed by Wu et al.$^{28}$

Within the second bimolecular collision case, (100) mol. 2–5 7.0 km/s shown in Figure 3 (b), an O atom within a nitro group of one RDX molecule interacts with a C atom on the ring of the second, which causes ring cleavage as seen in the second step of Figure 3 (b). The nitro group then takes an H atom from another C atom on the ring, while leaving behind an O atom bonded to the original C atom (step 3 of Figure 3 (b)). Finally, the H atom is quickly transferred to the O atom left on the ring, as the remaining NO group dissociates (step 4 of Figure 3 (b)). The entire process involves unstable intermediates, prohibiting the calculation of heats of reaction, but is completed within 90 fs from the initial approach of the molecules with a net energy change of $\Delta E_{Rxn} = +206.0 \text{ kJ/mol}$. 
Figure 3: Bimolecular reactions involving oxygen attack from the (100) mol. 2–5 7.0 km/s case. Details of reaction evolution are shown in (a), while a reaction summary is shown in (b). Heats of reaction for (a) are not calculated due to unstable nature of intermediates. Hashed lines show from where reacting atoms came, while thin, solid arrows show where atoms will go after reacting.
HMX Collisions

Being that HMX consists of the same H₂CNNO₂ building blocks that constitute RDX, it stands to reason that many reaction pathways for HMX must be similar to those for RDX. This is more or less true for NO₂ homolytic reactions, as well as reactions occurring after ring breaking. In fact, one surprising outcome is the occurrence of a concerted ring depolymerization reaction for HMX that produces 4 (H₂CNNO₂), similar to that for RDX described by Zhao et al., which is observed in the (111) mol. 2–5 7.0 km/s case; see Figure 4 (a). To our knowledge, this pathway, with ΔE_{Path} = +400.8 kJ/mol, has not been reported in previous work, and is especially surprising considering that such a reaction was not observed for RDX in any of our collision simulations.

As for other similarities, HMX, like RDX, has NO₂ homolysis with ΔE_{Rxn} = +191.2 kJ/m as the dominant first reaction in almost all threshold cases; see Figure 4 (b). It is also worth noting that from a collision standpoint, HMX appears less sensitive than RDX given that the majority of threshold cases occur at collision speeds in excess of 5 km/s, whereas the majority of RDX threshold cases occur under 5 km/s. Though it is not entirely clear why HMX should be less chemically sensitive to collisions than RDX, given their similarities, it seems feasible that the difference between the two simply involves the higher degrees of freedom that result from the greater number of atoms in HMX – essentially, a larger molecular complex over which collision energy may be deposited.

At high collision velocity, multiple NO₂ homolytic reactions can be observed while the ring still remains intact. For the second NO₂ homolysis, there are two possibilities: the second reaction can occur across from the first N atom from which the nitro group dissociated, resulting in the structure shown in Figure 4 (g), or adjacent to this N atom resulting in the structure shown in in Figure 4 (h). Though the former has a lower ΔE_{Rxn} (+192.3 kJ/mol versus +206.3 kJ/mol), the latter is seen more frequently, likely due to the fact that the energy in most collisions is localized, initially, on only one side of each molecule.

Typically, by the time two nitro groups dissociate from a single HMX ring, the ring
either deforms or breaks; however, a third NO$_2$ homolytic reaction from an unbroken ring is observed in the (101) mol. 1–8 7.0 km/s case, with $\Delta E_{Rxn} = +208.8$ kJ/mol, which can be seen in Figure 4 (j). The third NO$_2$ homolytic reaction, therefore, is only observed for a case in which the two remaining nitro groups are adjacent. This may be due to the fact that when the remaining nitro groups are opposite each other, the next homolytic reaction has a higher BDE (+222.8 kJ/mol); though it is important to point out that by this point, ring breaking requires less energy, and other ring reactions may be preferable. In fact, after the third NO$_2$ homolytic reaction in the (101) mol. 1–8 7.0 km/s case, some ring reconfiguration reactions (discussed below) occur; therefore, a fourth NO$_2$ dissociation, as shown in Figure 4 (n) with $\Delta E_{Path} = +220.0$ kJ/mol, is not observed in our collision simulations.

Like RDX, only a few of the threshold cases result in reactions other than single NO$_2$ homolysis within the 0.5 fs time frame of the simulations. Among these are the (001) mol. 1–6 6.6 km/s, (101) mol. 1–8 5.9 km/s, and (111) mol. 2–10 6.8 km/s cases, in which ring cleavage occurs either during or immediately before NO$_2$ homolysis. In fact, geometry optimizations of an open-ring HMX molecule suggested that NO$_2$ homolysis must occur as the terminating C atom within the chain acquires a double bond with its adjacent N atom, causing one of the NO$_2$ groups within the middle of the chain to dissociate as shown in Figures 4 (c) and (l).

In both MD simulations and geometry relaxations, it is observed that ring cleavage results in homolytic reactions for the NO$_2$ group adjacent to the terminal C atom, as well as for one of the NO$_2$ groups located in the middle of the chain with no preference for the order in which reactions occur, making them concerted with $\Delta E_{Rxn} = +510.0$ kJ/mol for the product shown in Figure 4 (c), and $\Delta E_{Rxn} = +466.6$ kJ/mol for the intermediate shown in Figure 4 (l).

The (111) mol. 1–2 5.2 km/s case is another example of ring cleavage, resulting in the structure shown in Figure 4 (d), but is different in that after NO$_2$ homolysis, H$_2$CNO$_2$ dissociation occurs with $\Delta E_{Rxn} = +396.8$ kJ/mol. Other cases, such as the (010) mol.
1–7 4.8 km/s case, unimolecularly produce HONO after NO₂ homolysis with \( \Delta E_{\text{Rxn}} = -164.9 \text{ kJ/mol} \); see Figure 4 (e). Interestingly, H-elimination never involves H atoms between two adjacent nitro groups. This is likely due to the fact that the surrounding NO₂ groups may prevent a free NO₂ molecule from approaching close enough to grab the H atom, as well as the fact that the heat of reaction for this type of HONO production is endothermic with \( \Delta E_{\text{Rxn}} = +68.6 \text{ kJ/mol} \). Additionally, as with RDX, HNO₂ is produced for the high collision velocity cases (011) mol. 4–7 6.0 and 7.0 km/s in a similar fashion as seen for HONO with \( \Delta E_{\text{Rxn}} = -141.3 \text{ kJ/mol} \); see Figure 4 (f).

HONO producing reactions are not the only form of unimolecular hydrogen elimination; H atom transfer from a C atom to a vacant N atom on the ring were observed for the HMX (010) mol. 4–7 7.0 km/s and (001) mol. 1–6 6.9 km/s cases. For the former case, seen in Figure 4 (i), the HMX molecule has already undergone the homolysis of two adjacent nitro groups before an H atom jumps from the C atom between the two empty N atom sites to an adjacent N atom with a heat of reaction \( \Delta E_{\text{Rxn}} = -296.2 \text{ kJ/mol} \). For the latter case, seen in Figure 4 (m), the HMX molecule has lost two nitro groups on opposite sides. Due to deformation of the ring, an H atom is able to jump from a C atom to an N atom across the ring with \( \Delta E_{\text{Rxn}} = -256.8 \text{ kJ/mol} \).

As mentioned earlier, observing three NO₂ homolytic reactions from a single HMX molecule without some form of ring breaking or reconformation is rare. In fact, we observe several instances of unimolecular ring reconformation for many collision cases above their associated threshold velocities to initiate chemistry. The most common type of ring deformation we observed is the ’3/7’ conformation seen in the (010) mol. 1–7 7.0 km/s, (011) mol. 2–8 7.0 km/s, (101) mol. 1–8 6.0 km/s and 7.0 km/s, and (111) mol. 1–8 7.0 km/s cases; and shown in Figure 4 (k). The reason the ’3/7’ conformation is the most commonly observed ring reconformation is likely due to the fact that it forms from an HMX ring with only two adjacent nitro groups remaining, which appears more commonly than that with two nitro groups at opposite ends. The ’3/7’ conformation, being similar to the ’3/5’
confirmation seen for RDX, forms when the two adjacent N atoms on the ring without nitro groups come close together due to ring deformation. The N atoms bond to one another with a heat of reaction $\Delta E_{\text{Rxn}} = -131.8 \text{ kJ/mol}$.

In some cases, such as (101) mol. 1–8 7.0 km/s, the '3/7' conformation breaks at the C–N bond where the 3 member and 5 member rings meet, while the nitro group closest to the breaking C–N bond dissociates simultaneously; the heat of reaction being $\Delta E_{\text{Rxn}} = +226.0 \text{ kJ/mol}$ as also seen in Figure 4 (k). The resulting chain with a 3 member ring is not an exclusive product of the ring breaking reaction of the '3/7' conformation; rather, it is also produced after ring breaking occurs for an HMX molecule with two nitro groups opposite one another as seen in 4 (l), which is observed for the (001) mol. 1–6 6.7 km/s case. For this pathway, the ring breaks at an N atom that is bonded to a nitro group with $\Delta E_{\text{Rxn}} = +83.1 \text{ kJ/mol}$. Then, due to deformation of the chain, this same N atom bonds to an adjacent N atom about 30 fs after ring cleavage with $\Delta E_{\text{Rxn}} = -110.6 \text{ kJ/mol}$. Finally, the nitro group bonded to the 3 member ring dissociates with a BDE that has been lowered from +179.8 kJ/mol to +135.7 kJ/mol.

Another ring reconformation, we refer to as the 'Mask' conformation, and which is seen in the (001) mol. 1–6 7 km/s, (110) mol. 1–7 7.0 km/s, and (111) mol. 2–5 7.0 km/s cases, is composed of two 5 member rings with nitro groups on opposing sides, and occurs when an HMX molecule that has lost two nitro groups opposite from one another has been deformed enough to bring the non-bonded N atoms on opposite sides of the ring close enough to form a bond; see Figure 4 (o). The heat of reaction associated with the formation of this bond is $\Delta E_{\text{Rxn}} = -110.1 \text{ kJ/mol}$. Further decomposition for the 'Mask' conformation seems only to involve NO$_2$ homolysis with lowered barriers ($+150.7 \text{ kJ/mol}$ for the first homolytic reaction, and $+169.4 \text{ kJ/mol}$ for the second), and is not observed to be a precursor for any ring breaking reactions in our collision simulations.

In addition to the unimolecular pathways discussed above, several bimolecular pathways are identified, including intermolecular H transfer, as well as inter-ring bonding of two HMX
Figure 4: Unimolecular reactions of HMX with heats of reaction in kJ/mol between steps. Values near bonds or H₂ are BDEs or heats for H elimination reactions involving NO₂ to produce HONO respectively, both in kJ/mol. \( \Delta E_{\text{Path}} \) is the net heat of reaction from unreacted HMX molecules to the step shown. Hashed lines show from where species originate; thin, solid arrows show where species will go after reacting.
molecules. Figure 5 (a) shows the transfer of an H atom from one HMX molecule to an empty N atom site on the ring of the other after both molecules undergo single NO2 homolysis. The heat of reaction for the H transfer is $\Delta E_{Rxn} = -279.1 \text{ kJ/mol}$, with a net change in energy for the pathway $\Delta E_{Path} = +103.3 \text{ kJ/mol}$, which includes NO2 homolytic reactions. The intermolecular H transfer pathway is observed in only three cases tested, all with the same geometry: (110) mol. 2–10 5.0 km/s, 6.0 km/s, and 7.0 km/s.

Inter-ring bonding reactions are shown in Figure 5 (b), (c), and (d), which occur after NO2 homolytic reactions brought on by the direct collision of the nitro groups involved. The only geometries that seem to facilitate this are seen for the (010) mol. 1–4 and mol. 3–5 head-on collision cases, as well as the (110) mol. 1–7 7.0 km/s glancing collision case. For the latter, the intermolecular N–N bond forms after the reacting nitro groups shear each other away from their respective rings within the first 80 fs of the collision simulation; however this N–N bond lasts only for ~50 fs as the momentum of the glancing molecules tear it apart. In contrast, the former cases, being head-on collisions, result in an intermolecular N–N bond that persists, and in some cases completely breaks down the molecular complex. Figure 5 (b) shows a bimolecular bonding pathway in which NO2 homolysis and the ’Mask’ ring conformation occur, which is observed for the (010) mol. 1–4 5.4 km/s case. The BDE for each initial NO2 homolytic reaction is $\Delta E_{Rxn} = +191.2 \text{ kJ/mol}$, followed by intermolecular N–N bond formation with heat of reaction $\Delta E_{Rxn} = -170.2 \text{ kJ/mol}$. After the N–N bond forms, NO2 homolysis from the second ring occurs with BDE $\Delta E_{Rxn} = +203.8 \text{ kJ/mol}$, followed by a second NO2 homolysis from the same ring with BDE $\Delta E_{Rxn} = +200.3 \text{ kJ/mol}$, and finally ring reconfirmation into the ’Mask’ conformation with a heat of reaction $\Delta E_{Rxn} = -182.8 \text{ kJ/mol}$. The total heat of reaction for this pathway from the unreacted bimolecular complex is $\Delta E_{Path} = +433.5 \text{ kJ/mol}$.

Figure 5 (c) offers yet another example involving intermolecular N–N bonding of the HMX rings in which ring cleavage, rather than ring reconfirmation, occurs. For the (010) mol. 1–4 5.5 km/s and (010) mol. 3–5 5.4 km/s case, one of the rings breaks at the N–N
intermolecular bond, as seen in the second step of Figure 5 (c), which simultaneously causes a homolytic reaction of the nitro group closest to the broken ring bond as a double bond forms at the end of the chain. The heat of reaction for the concerted ring cleavage and NO₂ homolysis is \( \Delta E_{Rxn} = +133.2 \text{ kJ/mol} \). In the (010) mol. 1–4 and mol. 3–5 cases at both 6.0 km/s and 7.0 km/s, the reactions proceed through all steps shown in Figure 5 (c) such that the first ring cleavage is repeated on the same ring but on the other side of the N–N bond producing a chain molecule and an HMX molecule with an N atom in the place of a nitro group, for which \( \Delta E_{Rxn} = +260.2 \text{ kJ/mol} \) shown in the third step. Then, the pathway proceeds to the fourth step in Figure 5 (c), in which the ring of the second HMX molecule breaks on either side of the N–N bond simultaneously while causing double NO₂ homolysis with \( \Delta E_{Rxn} = -124.6 \text{ kJ/mol} \). The fact that this particular step is exothermic despite ring cleavage and NO₂ homolytic reactions is due to the formation of triply bonded N₂ left at the center of the reacting molecular complex. The total heat of reaction for the entire pathway from the unreacted bimolecular complex is \( \Delta E_{Path} = +481.0 \text{ kJ/mol} \), which includes six homolytic reactions for the nitro groups, ring cleavage on both rings, and the formation of N₂. Finally, Figure 5 (d) shows the further decomposition of the chain, which is observed in only the (010) mol. 1–4 7.0 km/s case. The chain breaks between a C atom and the N atom bonded to a nitro group with \( \Delta E_{Rxn} = +356.1 \text{ kJ/mol} \). The high heat of reaction for this step is likely the reason it is only seen for the one case at 7.0 km/s.

**TATB Collisions**

TATB collisions initiate reactions at much higher collision velocities. In fact, the most sensitive case for TATB was the (100) mol. 1–8 5.8 km/s. This is in agreement with the fact that TATB has proven to be highly insensitive to shock. However, the planar structure of TATB causes some difficulties with the collision simulations stemming from the fact that the colliding molecules are not constrained in the crystalline environment, and are free to
Figure 5: Bimolecular reactions of HMX with heats of reaction in kJ/mol between steps. Values near bonds or H2 are BDEs or heats for H elimination reactions involving NO2 to produce HONO respectively, both in kJ/mol. ΔE_{Path} is the net heat of reaction from unreacted HMX molecules to the step shown. Hashed lines show from where species originate; thin, solid arrows show where species will go after reacting.
glance off one another and separate before reacting. Nonetheless, several interesting reaction pathways are discerned that may have important implications; though the majority were highly endothermic, with a few notable exothermic reactions discussed below.

As with RDX and HMX, NO₂ homolysis is the primary first-step for almost all reaction pathways for TATB. The BDE for the C–NO₂ bond in TATB is found to be much higher than that of the N–NO₂ bond for both RDX and HMX: ~350 kJ/mol for TATB versus ~200 kJ/mol for both RDX and HMX. Nonetheless, our TATB collision simulations present several pathways, not considered before, that include nitro group flipping and intermolecular swapping, intra- and inter-molecular H transfer, ring cleavage, ring reconformation, and even ring reduction from six atoms down to four.

By far, the most common initial step in our TATB collision simulations is NO₂ homolysis with BDE $\Delta E_{Rxn} = +341.1$ kJ/mol, as seen in Figure 6 (a). The second and third homolytic reactions have BDEs of +346.5 and +346.8 kJ/mol respectively. Also seen in Figure 6 (a) are BDEs for NH₂ homolysis, which drop from ~ 510 kJ/mol to ~ 375 kJ/mol when an adjacent NO₂ dissociates, as well as heats of reaction for potential H elimination reactions to form HONO, the majority of which tend to be endothermic.

Figure 6 (b) shows another decomposition pathway involving a ring reconformation that occurs after the first NO₂ homolytic reaction, which was present in the (110) mol. 1–4 7.0 km/s and (111) mol. 1–2 from 7.0 up to 10 km/s cases. This stable ring reconformation comes in the form of a '3/5' ring conformation that may explain the disappearance of the IR spectrum around 1433 cm⁻¹ for the carbon ring reported by Glascoe et. al. 24 To test whether this conformation would be undetectable by the 1433 cm⁻¹ spectral probe of Glascoe et. al. 24, we calculated its vibration spectrum, shown in Figure 7. Since we have calculated the vibration spectrum for the gas phase molecule, we find the associated ring mode for TATB to be slightly higher at 1495 cm⁻¹. Additionally, modes associated with the '3/5' ring conformation are shifted away from that of the original hexagonal TATB ring, lending to the notion that a '3/5' ring conformation would create a sizable enough shift to cause the
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<td>f</td>
<td>$\text{H}_2\text{N}^+\text{N}_2\text{O}^-$ → $\text{H}_2\text{N}^+\text{N}_2\text{O}^-$ + NO₂</td>
<td>+152.7 kJ/mol</td>
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Figure 6: Unimolecular reactions of TATB with heats of reaction in kJ/mol between steps. Values near bonds or H₂ are BDEs or heats for H elimination reactions involving NO₂ to produce HONO respectively, both in kJ/mol. ΔE<sub>Path</sub> is the net heat of reaction from unreacted TATB molecules to the step shown. Hashed lines show from where species originate; thin, solid arrows show where species will go after reacting.
TATB ring peak to disappear after the first NO₂ homolytic reaction.

The ‘3/5’ ring conformation reaction channel shown in 6 (b) appears to be energetically favorable compared to the pathway in Figure 6 (a), while also leading to triple NO₂ homolysis with ring cleavage, as seen in the (101) mol. 1-2 10 km/s case. If one assumes that NO₂ homolytic reactions occur without the '3/5' ring conformation, then the first dissociation of NO₂ has a BDE of +341.1 kJ/mol, the second +346.5 kJ/mol, and the last +346.8 kJ/mol, resulting in a net change in energy for the path $\Delta E_{Path} = +1034.4 \text{ kJ/mol}$. But if one allows for the '3/5' ring conformation after the first homolytic reaction, then the ring reaction has $\Delta E_{Rxn} = +191.2 \text{ kJ/mol}$, the second NO₂ homolytic reaction is much lower with $\Delta E_{Rxn} = +103.3 \text{ kJ/mol}$, and the final homolytic reaction with concerted ring cleavage having $\Delta E_{Rxn} = +397.2 \text{ kJ/mol}$. The net heat of reaction for the entire pathway is $\Delta E_{Path} = +1032.8 \text{ kJ/mol}$, demonstrating that the '3/5' ring conformation pathway offers an intermediate step that reduces the BDE of one NO₂ homolytic reaction while also leading to ring cleavage with a net energy change for the pathway that is about 2.4 kJ/mol less than triple NO₂ homolysis without the '3/5' ring conformation. Interestingly, we calculate that the heat of reaction to form the '3/5' conformation after the second NO₂ homolytic reaction to be $\Delta E_{Rxn} = -52.0 \text{ kJ/mol}$, as seen by the arrow connecting the third species in Figure 6 (a) and (b); but, this reaction was never observed in our collision simulations.

While Figure 6 (b) represents the typical order in which NO₂ homolysis occurs – that being with the last NO₂ group attached opposite to the three-member ring of the '3/5' conformation– the (111) mol. 1-2 7.5 km/s case displayed in Figure 6 (c) shows a different ordering of NO₂ homolysis such that the last remaining NO₂ group is attached to both the three and five member rings. This particular ordering of homolytic reactions was seen in only the one case, likely because the NO₂ group bonded to the five member ring is bound more strongly with a BDE of +263.0 kJ/mol versus the BDE of +103.3 kJ/mol for the NO₂ group bound to both the three and five member ring. Though not seen in our simulations, the final NO₂ homolysis for the case seen in Figure 6 (c) was calculated to be +237.5 kJ/mol,
and should result in the same product seen in Figure 6 (b). Finally, Figure 6 (d) shows the (100) mol. 1–8.9 km/s case in which H elimination to form HONO occurs instead of a second NO₂ homolytic reaction with a heat of reaction \( \Delta E_{Rxn} = -46.3 \text{ kJ/mol} \).

![Graph showing vibrational spectrum for gas phase TATB](image)

**Figure 7:** (Color online) Calculated vibration spectrum for gas phase TATB. Ring mode for unreacted TATB at 1495 cm⁻¹ shown in black. All other peaks shown are modes related to the ‘3/5’ ring conformation.

Figure 6 (e) shows the ring closure reaction proposed by Wu and Fried²³, which was present in the (010) mol. 1–5 8.5 km/s case, having \( \Delta E_{Rxn} = +167.9 \text{ kJ/mol} \). Because these reactions occurred late in the simulations (≈0.5 ps), we saw no instances of HONO homolytic reactions within the time span of our simulations; but since such a reaction has \( \Delta E_{Rxn} = +282.8 \text{ kJ/mol} \), HONO homolysis should be inevitable due to the amount of collision energy available within the system. Additionally, another isomer reaction was observed in the 100 mol. 1–8 9.5 km/s case, which involves the flipping of a nitro group as shown in Figure 6 (f). While the homolytic barrier to break the C–NO₂ bond is +341.1 kJ/mol, the isomer reaction reaction has \( \Delta E_{P_{att}} = +29.2 \text{ kJ/mol} \), and thus the BDE for this new C–ONO bond is consequently \( \Delta E_{Rxn} = +311.9 \text{ kJ/mol} \). However, the BDE for the O–NO bond with the flipped nitro group is only +34.1 kJ/mol suggesting that the formation of NO is extremely likely.

Bimolecular reaction pathways for TATB include NO₂ transfer, H transfer, ring cleavage,
and ring reduction, which are all shown in Figure 8. Compared to the unimolecular reaction pathways discussed above, the bimolecular reactions tend to have more exothermic steps. Figure 8 (a) shows a pathway that was observed for the (100) mol. 1–8 8 km/s and 8.5 km/s cases in which an O atom of a nitro group from one molecule bonds to a C atom on the second molecule that is already bonded to an amino group. The reaction is endothermic with \( \Delta E_{Rxn} = +439.1 \text{kJ/mol} \). Since the homolytic reaction of the first molecule has an associated BDE of +341.1 kJ/mol, the BDE for the newly formed C–O bond is -98.0 kJ/mol, and is in fact a stable structure when structurally relaxed; however, because of the trajectory of the NO\(_2\) group and the fact that the reacting O atom is at the peak of its oscillation from the N atom, the N–O bond of the nitro group breaks about 7 fs later leading to NO homolysis with \( \Delta E_{Rxn} = +163.6 \text{kJ/mol} \). The next and final step in the reaction pathway shown in Figure 8 (a) involves the simultaneous transfer of an H atom from an amino group of the second molecule to an open C atom site on the ring of the first, and the collapse of the ring of the second molecule from six members to five, with one member bonded to an isocyanic acid group. Together, these two reactions result in \( \Delta E_{Rxn} = -509.7 \text{kJ/mol} \). At this point, the total heat of reaction for the entire path is \( \Delta E_{Path} = +93.0 \text{kJ/mol} \); however the pathway does not stop here; rather it continues as shown in Figure 8 (b) for the 8 km/s case, and as seen in Figure 8 (c) for the 8.5 km/s case. For the 8 km/s case shown in Figure 8 (b), the isocyanic acid, with a BDE of +86.3 kJ/mol, dissociates from the five member ring resulting in a net heat of reaction for the path \( \Delta E_{Path} = +179.3 \text{kJ/mol} \). For the 8.5 km/s case, shown in Figure 8 (d), the O atom within the isocyanic acid group moves close enough to the C atom within the five member ring to form a bond with \( \Delta E_{Rxn} = -27.2 \text{kJ/mol} \). Unimolecular reactions then continue for the second molecule that result in the breaking of the C–O bond within the isocyanic acid group, as well as the cleavage of the five member ring with \( \Delta E_{Rxn} = +339.5 \text{kJ/mol} \). Next, carbon monoxide and nitroxy form with \( \Delta E_{Rxn} = +284.6 \text{kJ/mol} \), followed by the exothermic formation of a four member ring with \( \Delta E_{Rxn} = -303.1 \text{kJ/mol} \). The net heat of reaction for the entire pathway, which
results in the formation of nitric oxide, carbon monoxide, nitroxyln, and a four member ring
with two nitro and amino groups, is $\Delta E_{Path} = +386.8 \text{kJ/mol}$.

As already seen in Figure 6 (f) for the (100) mol. 1–8 9.5 km/s case, a nitro group
flips, breaking its C-N bond to form a C-O bond with $\Delta E_{Rxn} = +29.2 \text{kJ/mol}$. Figure 8 (d)
shows the continuation of initiation chemistry for this case, which involves NO homolysis from
the flipped nitro group on the second molecule ($\Delta E_{Rxn} = +34.1 \text{kJ/mol}$), NO$_2$ ($\Delta E_{Rxn} =
+341.1 \text{kJ/mol}$) and NH$_2$ ($\Delta E_{Rxn} = +375.5 \text{kJ/mol}$) homolysis from the first molecule, H
transfer from the second molecule to the NO$_2$ formerly of the first molecule to form HONO
($\Delta E_{Rxn} = +63.6 \text{kJ/mol}$), and the bonding of the NO from the second molecule to the C
atom of the first molecule, formerly bonded to the dissociated NH$_2$ ($\Delta E_{Rxn} = +94.2 \text{kJ/mol}$);
hence, the net heat of reaction for the first step in Figure 8 (d) is $\Delta E_{Rxn} = +720.1 \text{kJ/mol}$.
The next step involves ring cleavage on the second molecule as the C atom bonded to
the O atom and the C atom bonded to the NH dissociate with $\Delta E_{Rxn} = +263.3 \text{kJ/mol}$.
Finally, NO homolysis occurs on the same molecule ($\Delta E_{Rxn} = +94.2 \text{kJ/mol}$), followed by
the reformation of the C-NH$_2$ bond on the same C atom site ($\Delta E_{Rxn} = -375.5 \text{kJ/mol}$),
while the empty C atom on the ring of the first molecule pulls the H atom from the HONO
molecule ($\Delta E_{Rxn} = -172.7 \text{kJ/mol}$); the net heat of reaction for this step being $\Delta E_{Rxn} =
-454.0 \text{kJ/mol}$. The net heat of reaction for the entire pathway shown in Figure 8 (d), along
with the reaction shown in Figure 6 (f), is $\Delta E_{Path} = +558.6 \text{kJ/mol}$; however, reactions for
the second molecule with the broken ring continue unimolecularly as shown in Figure 8 (e).

The ring cleavage reaction from the (100) mol. 1–8 9.5 km/s case shown in Figure 8
(e) results in the formation of a 3 member ring and double NO$_2$ homolysis. Starting from
the unbroken ring with an NH and an O atom bonded to adjacent C atoms, the ring breaks
between these two C atoms with $\Delta E_{Rxn} = +263.3 \text{kJ/mol}$. This reduces the BDEs of the two
remaining C-NO$_2$ bonds to +175.0 kJ/mol and +151.1 kJ/mol. The first nitro group with
the BDE of +175.0 kJ/mol dissociates as two C atoms across from this nitro group come close
together. Then, these two C atoms bond to form a 3 member ring, which simultaneously
Figure 8: Bimolecular reactions of TATB with heats of reaction in kJ/mol between steps. Values near bonds or H₂ are BDEs or heats for H elimination reactions involving NO₂ to produce HONO respectively, both in kJ/mol. ΔEₚₑᵗₙ is the net heat of reaction from unreacted TATB molecules to the step shown. Hashed lines show from where species originate; thin, solid arrows show where species will go after reacting.
results in the dissociation of the second nitro group with $\Delta E_{Rxn} = +215.6 \text{ kJ/mol}$. The total net heat of reaction for the entire pathway is $\Delta E_{Path} = +949.2 \text{ kJ/mol}$.

**Discussion and Conclusions**

While it seems true that NO$_2$ homolysis is the dominant first reaction step towards initiation of chemical reactivity in detonating EMs, there is actually more to the picture than this one reaction, especially in the case of the ringed nitro compounds RDX, HMX, and TATB. Certainly, the exothermic H elimination reactions resulting in the formation of HONO play a major role towards further deconstruction of EM molecules after or in concert with the first NO$_2$ homolytic reaction. However, this work investigates the role of several other reactions, including intra- and inter-molecular H transfer, ring reconformations, ring member reductions, as well as ring breaking. Additionally, the calculation of heats of formation for both individual steps and entire pathways, while only quantitatively applicable to molecules at equilibrium with no strain imposed, offers a qualitative understanding of the dynamics of each pathway when combined with steric considerations involving proximity of reacting atoms and collision geometry.

Because the kinetic energy of the colliding molecules tends to be initially localized on the atoms that directly experience the collision, high strain is observed within the molecules. Hence the activation barriers for the possible chemical reactions are believed to become much lower. Therefore, reactions with the lowest calculated heats tend to originate from these sites or from sites elsewhere on the molecule that are greatly deformed due to recoil from high strain. All this, however, is based on the assumption that reactions, such as H elimination and ring reconformations, that would have a somewhat substantial barrier under normal conditions of thermal excitation, should have reduced barriers due to localized strain that can be more easily surmounted given the abundance of energy locally deposited by the collision. Therefore, the low or negative heats of reactions calculated using structurally optimized
reactants and products can be correlated with the direction of the chemical transformation. This is of course a qualitative approach as it is difficult to quantify the reduction of the reaction barriers due to local stress in a dynamically changing environment. Such challenges make, for the time being, MD simulations essential for observing specific channels of chemical transformations in the energetic materials under detonating conditions.

Good examples of using heats of reaction to understand how reaction dynamics progress through various pathways may be the investigation of both H-elimination and ring reconformation reactions. In the previous work for PETN\textsuperscript{3} H-elimination reactions were shown to be very important for sending the pathway downhill in energy as these are typically exothermic. This notion was examined in more detail by Wu et al.,\textsuperscript{28} and shown to be critical for water catalysis to promote total, rapid decomposition of the EM molecules. However, in some instances H elimination reactions may become endothermic depending on what pathway is taken. In RDX and HMX cases, for example, ring breaking causes heats of reaction for H elimination on particular parts of the chain to become endothermic as seen in Figures 2 (f) and 4 (c) and (l), ; When nitro groups dissociate from an N atom on the ring, however, often a dangling bond is left that would form a double bond with a neighboring C atom if that C atom were to lose one of its H atoms. In such a case H-elimination from that C atom becomes highly exothermic since the formation of a double N–C bond generally lowers the total energy.

Similarly, ring reconformations may cause commensurate behavior. As seen in Figure 4 (h) and (l), H-elimination reactions adjacent to vacant N atoms on the ring are highly exothermic; however, ring reconformations, as seen in Figure 4 (h) and (l) create bonds between two vacant N atoms that eliminates dangling bonds, , and results in H-elimination reactions becoming endothermic. As seen in Figure 4 (o), subsequent NO\textsubscript{2} homolytic reactions leave dangling bonds on the N atoms such that the energy should drop as a result of further H elimination reactions as C–N double bonds will form. TATB also exhibits such behavior in that H elimination only becomes exothermic when the N atom within the asso-
ciated amino group can form a double bond with the adjacent C atom upon H-elimination. This can be deduced from Figure 6 (a) and (b) by redrawing the Lewis structures after removing a single H atom. For instance, removing any H atom from the second structure in Figure 6 (b) will result in a double bond between the adjacent N and C atoms, as well as removing the dangling bond on the lower left C atom, hence the energy will be lowered. Basically, reactions pathways are identified using reactive MD, while heats of reaction combined with Lewis structures provide explanation why the reactions occurred. Of course, it is also important to recognize that H-elimination reactions to form HONO are not the only exothermic reactions available. In fact, ring reconformations are themselves exothermic, and are as common as H elimination reactions in initiation chemistry. The main ingredient for ring reconformations, however, is localized strain to bring ring vacant ring members close enough to bond.

The mostly exothermic ring reconformation reactions, in addition to being important steps towards complete decomposition of EM molecules, offer compelling evidence for the role of high localized strain in initiation chemistry. However, despite their exothermicity in RDX and HMX, or low endothermicity in the case of TATB, these reactions have yet to be seen in cookoff studies since significant ring deformation seems a necessary prerequisite to induce such chemistry. The extreme example of this is the reconformation of the HMX ring into the 'Mask' conformation, having $\Delta E_{\text{Rxn}} = -110.1 \text{kJ/mol}$. Nitro groups on opposite ends of the ring must first dissociate; then the associated N atoms on the ring must be pushed together.

To estimate the barrier heights for these ring reconformation reactions without performing lengthy transition state searches, we performed static relaxation calculations in which the ring atoms to participate in bonding under reconformation are sequentially pushed together, effectively treating these atoms as a rigid pair at a fixed interatomic distance while the rest of the molecule is allowed to relax. The results for each ring reconformation are shown in Figure 9. The RDX '3/5' conformation seen in Figure 2 (h) has a barrier estimated at
+63.1 kJ/mol; while that of the HMX ’3/7’ conformation seen in Figure 4 (k) is similar in magnitude, being +61.8 kJ/mol. The HMX ’Mask’ conformation seen in Figure 4 (o) has the highest barrier at +206.4 kJ/mol. Finally, the TATB ’3/5’ conformation seen in Figure 6 (b) has a barrier height just under that of the HMX ’Mask’ conformation at +199.3 kJ/mol. All but the TATB reconformation have energies lower than those for the reactant structures; and interestingly, the TATB reconformation appears almost monotonic, as in homolytic reactions, with the energy dropping only -8.3 kJ/mol from the top of the barrier.

These estimates of barrier height are only relevant for thermally activated reactions, and are expected to be lower within the colliding molecular complex due to increased local strain. Nonetheless, the barriers for these reactions are in fact lower than homolytic NO₂ dissociation, but still require at least two NO₂ homolytic reactions to occur first so that members on the ring are able to bond. But this still begs the question on why these ring reconformations have not been seen in cookoff studies. One reason may be that since all modes are equally populated in a cookoff, ring breaking followed by NO₂ homolysis and H elimination dominate; while localized mechanical deformations become important under detonation initiation conditions. Another reason may be that these species are in fact intermediates in a cookoff, but are extremely rare and short-lived due to the fact that ring reconformations are driven by a very particular ring mode while, once again, equipartition requires all modes to be populated equally. Finally, it may be that these ring reconformations are inhibited by surrounding molecules, which is not addressed in this study.

Provided that the reactions predicted within this study are observed in experiments on the initiation chemistry of RDX, HMX, and TATB, the use of cookoff studies as representative of reaction chemistry for detonating EMs will need to be reconsidered. The pathways observed in our hypervelocity collision simulations may well redefine how the initiation chemistry at a detonation front is modeled, and how potentials are trained for these models. Though ring reconformations and breaking are not common in lower velocity collisions, which produce predominantly NO₂, this may be simply explained. First, there is a the need for more
than one NO₂ homolytic reaction to prime the remaining molecule for more exotic chemical pathways. Secondly, there exists the necessity to deposit ample potential energy into the nitro groups, and amino groups in the case of TATB, to sufficiently load the inner ring to react. The requirement for geometric distortion and high localized strain within reacting molecules at the detonation front cannot be understated in initiation chemistry.

It is important to realize that many of these pathways, while offering perhaps more energetically favorable initial steps, introduce bottlenecks towards complete chemical decomposition. However, by passing through these bottlenecks in some cases, a variety of highly exothermic reactions may become available. In a true detonating system, many, if not all, of the aforementioned pathways suggested for a particular molecule could occur simultaneously, provided steric constraints and bulk compression of the crystalline environment, which are not addressed within this study, permitted such pathways. Nonetheless, the information herein provides some evidence that detonation chemistry for crystalline EMs likely involves many simultaneous reaction channels that go beyond what can be seen in cookoff studies, with differing rates and barriers that are mitigated by local strain induced by collisions. This prospect deserves careful consideration by those intending to perform large-scale modeling.
of the chemical events that lead to initiation in detonating systems.

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References


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