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Ultrafast detonation of hydrazoic acid (HN_3)

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The fastest self-sustained chemical reactions in nature occur during detonation of energetic materials where reactions are thought to occur on nanosecond or longer timescales in carbon-containing materials. Here we perform the first atomistic simulation of an azide energetic material, HN_3, from the beginning to the end of the chemical evolution and find that the timescale for complete decomposition is a mere 10 picoseconds, orders of magnitude shorter than that of secondary explosives and approaching the fundamental limiting timescale for chemistry, i.e. vibrational timescale. We study several consequences of the short timescale including a state of vibrational disequilibrium induced by the fast transformations.

Little is known about the chemical evolution and states of matter found within an energetic material undergoing detonation. The short timescales of the chemical reactions (microseconds and less) and inherent danger of experimental work have been a major obstacle to understanding their microscopic nature. Recently, molecular dynamics simulations have been effectively utilized to shed light on the initial steps during detonation in *secondary* explosives, the less sensitive class of energetic materials. [1–3] However, significantly less is known about detonation in *primary* explosives, those which are most easily detonated by external stimuli and are most dangerous to work with. Detonation has been studied using molecular dynamics calculations employing reactive bond-order (REBO) energy models for simple chemical systems,[4, 5] including ozone (O_3) in 2D.[6] The reaction zones in these calculations exhibit much faster timescales than secondary explosives, suggesting the potential for ultrafast chemical dynamics during detonation in a wider variety of simple chemical systems. [4] Here we perform the first molecular dynamics simulation of a detonation wave in an azide explosive, hydrazoic acid, HN_3. Hydrazoic acid is a highly sensitive liquid azide that is a chemically simpler analog of commonly utilized azides like lead azide and sodium azide; the latter has been used in automobile air bags. We discover that chemical decomposition to stable products is complete in approximately 10 picoseconds, in stark contrast to secondary explosives which exhibit orders of magnitude longer reaction zones. Our simulations provide the the first quantum molecular dynamics prediction of detonation velocity in an explosive and the first microscopic picture of the chemical evolution from the initial state to the completely reacted state (Chapman-Jouguet state) for an azide explosive. The present simulations show the evolution of chemistry from beginning to final, stable products.

Primary explosives are used for a variety of purposes including blasting caps, inflatable escape slides on jet aircraft, and toy store noisemaking novelties. While little understanding about the detonation process exists, some hypotheses regarding the chemistry that occurs during detonation have been proposed. [7, 8] These include ordinary thermal decomposition processes and exotic electronic non-equilibrium processes. The pathway and products of chemical decomposition of HN_3 gas are known to depend on the mode of decomposition, of which at least three have been observed. [9] In this work, we focus on the liquid state where the decomposition pathways and kinetics of detonation are unknown. [10]

The simulations here utilize the self-consistent charge density functional tight binding (SCC-DFTB) method. [11] SCC-DFTB has been found to provide reasonable agreement with density-functional theory calculations of nitromethane under pressure. [12, 13] We utilize the DFTB+ code [14] in conjunction with the multi-scale shock simulation technique (MSST) [15–19] including an approximate treatment of electron-ion energy coupling. [19] Instead of simulating a shock wave within a large computational cell with many atoms (the direct approach), the computational cell of MSST follows a Lagrangian material element through a shock wave at a specified shock speed, enabling simulation of the shock wave with significantly fewer atoms and lower computational cost. The MSST has been demonstrated to accurately reproduce the sequence of thermodynamic states throughout the reaction zone of explosives with analytical equations of state, shock waves in amorphous Lennard-Jones and amorphous Tersoff carbon. [17, 18] Simulations in this work utilized an orthorhombic computational cell containing 64 molecules and employed periodic boundary conditions. The Supporting Information section contains additional details.

Results and Discussion. Figure 1 shows temperature, stress, and volume versus time behind the shock front for shocks of various speeds propagating through HN_3. In all cases, the volume decreases rapidly during the initial compression before chemical reactions occur. Initial compression is followed by a slower volume increase as chemistry occurs. The slower expansion is accompanied by a temperature increase as heat is evolved from the reaction.

Our previous work on the MSST has shown that the ideal detonation velocity (for an infinite charge diameter) can be determined from first principles. [17] This velocity is the natural propagation speed of the detonation shock wave, an intrinsic property of the material. The MSST exhibits a volume divergence (computational cell volume rapidly increases to infinity) when the mechanical stability conditions for a shock wave are not met, indicating there are no steady shock solutions at the chosen shock speed. The ideal detonation velocity of an explosive was shown to be bounded by the shock speed of a simulation that exhibits divergence and the shock speed of a simulation that does not when all chemical reactions have been completed. The final state of the lowest shock speed simulation that does not diverge before chemistry completion corresponds to the Chapman-Jouguet (CJ) state. In Figure 1, the smallest shock speed that does not exhibit the volume divergence is 6 km/s. Figure 2 shows that the chemical species populations in this simulation have achieved constant values by the end of the simulation, indicating 6 km/s is near the ideal detonation velocity. Our calculated initial shock pressure and temperature (or Zeldovich-von Neumann-Doering (ZND) theory spike conditions) are approximately 20 GPa and 2300 K, respectively. The calculated CJ state pressure and temperature are approximately 11 GPa and 4400 K, respectively. Non-equilibrium molecular dynamics calculations of detonation in condensed phase model systems have been found to yield detonation velocities and CJ conditions within a few percent of those predicted by 1D continuum theory utilized here. [4, 20]

While experimental results on HN_3 are sparse, the detonation velocity has been reported to range from 7.1-7.6 km/s. [21, 22] The detonation velocity is determined largely by the magnitude of energy released by reactions and by the composition and equation of state of the final reaction products. It is likely that the DFTB representations of both of these play some role in the difference between our calculated detonation velocity and experiments. The energy of formation (without zero-point energy) using the DFTB scheme is 0.083 E_h, slightly less than the value of 0.092 E_h calculated using DFT at the B3LYP/6-31G* level and 0.114 calculated at the QCISD/cc-PVTZ level (quadratic configuration interaction with single and double substitutions, Ref. [23]).

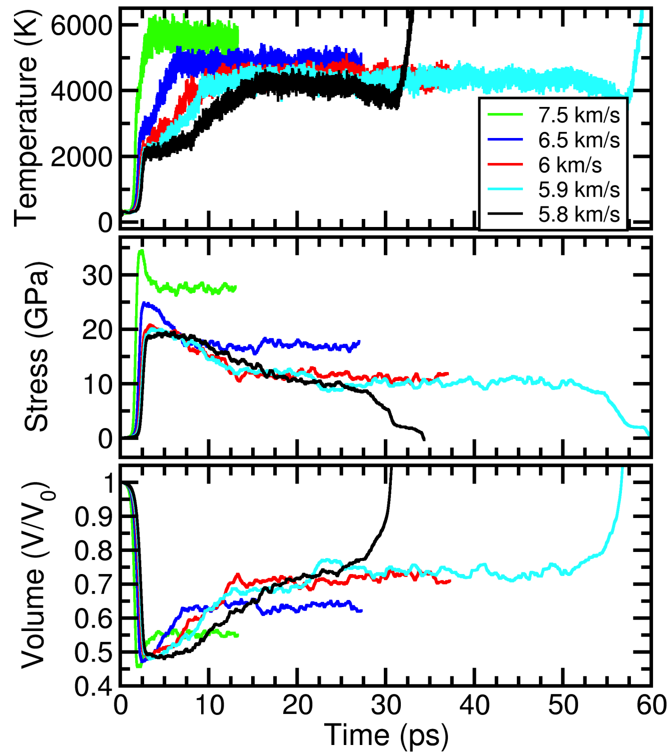

FIG. 1. Temperature, stress (shock propagation direction component), and volume versus time behind the shock front for shocks of various speeds propagating through HN_3. A volume divergence observed at the lowest shock speeds indicates that these speeds are below the Chapman-Jouguet (CJ) detonation velocity. The smallest shock speed that does not exhibit the volume divergence before completion of chemistry is 6 km/s, indicating this is near the CJ detonation velocity (see text for details).

These deviations are consistent with a simulated shock speed being lower than experimental values. The Supporting Information section contains additional detail.

Figure 2 shows the time-dependence of the population of most prevalent molecules for a 6 km/s shock, near detonation speed. HN_3 molecules react to form N_2, NH_3, and a small amount of H and H_2 as final products. The overall reaction can be approximately written,

$$64HN_3 \rightarrow 86N_2 + 20NH_3 + H_2 + 2H. \qquad (1)$$

N_3 is formed as the most dominant intermediate. Charged species include $N_3^{-0.3}$, $H_2N_3^{+0.4}$ and a small amount of $NH_4^{+0.8}$ formed from the ammonia. The atomic hydrogen charge is found to be neutral. Several intermediate reactions are given in the Supporting Information.

Figure 2 shows that the time required for completion of the reaction is approximately 10 ps. This short timescale corresponds to a reaction zone extending a distance of approximately 40 nm in space behind the shock front.

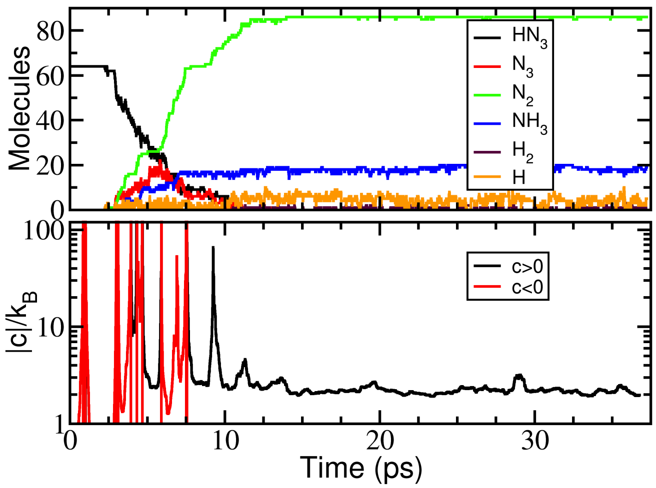

FIG. 2. Top panel shows time-dependence of the population of most prevalent molecules for a 6 km/s shock, near detonation speed. The time required for completion of the reaction is approximately 10 ps, substantially shorter than the nanosecond and greater timescales of secondary explosives. Bottom panel shows deviation from vibrational equilibrium given by time-dependent temperature fluctuations expressed as time-dependent heat capacity for the 6 km/s shock. The feature at 2 ps corresponds to shock compression, subsequent excursions are associated with chemical reactions, and fluctuations occur around a constant value after chemistry is complete.

It is interesting to note that this reaction is likely one of the fastest naturally occurring chemical reactions in nature. Only ultrafast photon-induced reactions are faster because excitations into vibrationally unstable states can be achieved on subpicosecond timescales. In the case of detonating HN_3, the timescale is an intrinsic material property (as is the case for all explosives) and is not determined by the timescale of an external impulse. The picosecond timescale response of shocked materials is potentially observable using existing experimental techniques. [24, 25]

A crude Arrhenius estimate of the variation of kinetic rates with DFTB representation of reaction barriers gives a reaction zone timescale of 100 ps (factor of 10 slower than observed in simulations) for a DFTB reaction barrier 0.8eV lower than actual, and a reaction zone timescale of 1ns for a DFTB reaction barrier 1.6 eV lower than actual. The calculated DFTB barrier for dissociation of a gas phase HN_3 molecule into N_2 and HN (one of the initial reactions, see Supporting Information) is 0.6eV higher than QCISD/cc-PVTZ calculations, suggesting that Arrhenius kinetics are slower in the DFTB case.

The anomalously fast reaction times might be partially understood in terms of the lack of significant chemical diffusion. Carbon containing explosives, like nitromethane (CH_3NO_2) and TATB ($C_6N_6O_6H_6$) are thought to initially form small molecules like CO_2, N_2, H_2O, etc. followed by carbon clusters on longer timescales. [3] Formation of such clusters requires the diffusion and accumulation of carbon atoms, a process that has a timescale slower than reactions that do not require any atomic diffusion. The reaction zone length is reported to be on the order of tens of microns in nitromethane and on the order of 1 mm in TATB, [26] much longer than the 40 nm length of HN_3. Hydrazoic acid lacks carbon and therefore might be expected to have a faster decomposition timescale.

Another condition for fast chemistry is that the temperature at the shock front is sufficiently high to yield fast kinetics. The temperature at the shock front is determined by the equation of state of the material and the magnitude of energy release during detonation, both parameters that are unrelated to the activation barrier magnitudes in the system.

The timescale for chemistry here is sufficiently fast that reacting intermediates could be out of vibrational equilibrium. It has been proposed that vibrational disequilibrium might play an important role in shock-induced chemistry. [27–29] While vibrational equilibrium in molecular solids is established on timescales longer than 1 ps, [30] the reaction intermediates observed here have lifetimes that are much shorter. The primary intermediate N_3 has an average lifetime of 330 fs. Some direct evidence for vibrational disequilibrium can be observed in the magnitude of kinetic energy fluctuations, or instantaneous temperature fluctuations. In analog with the NPH ensemble where temperature fluctuations are related to the heat capacity at constant pressure, [31] the MSST temperature fluctuations at equilibrium are expected to be related to a heat capacity at constant shock speed, $\frac{\langle T(t)^2\rangle - \langle T(t)\rangle^2}{\langle T(t)\rangle^2} = \frac{2}{3N}\left(1 - \frac{3k_B}{2c}\right)$. For a fixed heat capacity c and number of atoms N, the magnitude of fluctuations are expected to be time-independent at equilibrium. Significant deviations from a constant value can occur if the system is not in vibrational equilibrium. The bottom panel in Figure 2 shows that the the magnitude of c deviates from equilibrium values by more than an order of magnitude while chemistry occurs, indicating that vibrational equilibrium is not established during this period. Supplementary detail can be found in the Supporting Information. Detonating HN_3 is an unusual state of matter where statistical mechanics-based approaches to kinetic descriptions (e.g. transition state theory) are questionable.

Figure 3 shows the time-dependence of electronic density of states in HN_3 with a shock speed of 6 km/s, near detonation speed. The Fermi-energy is depicted by the white line. The bandgap of the material decreases upon shock compression and states can be observed within the gap during the region of peak chemical reactions from 2-

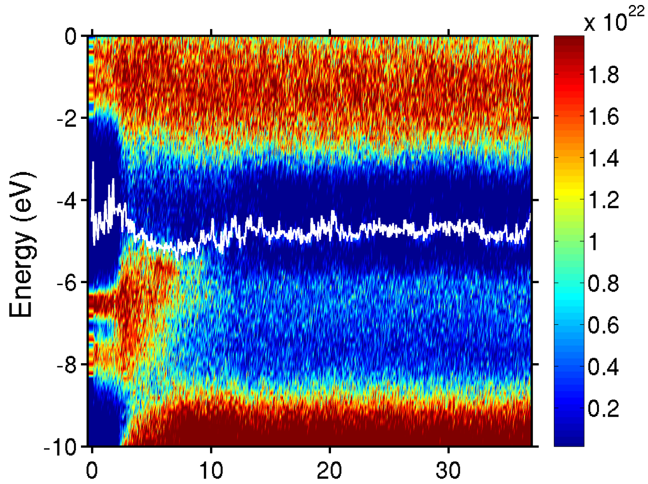

FIG. 3. Time-dependence of electronic density of states in shocked HN_3 (near detonation conditions). The Fermi-energy is depicted by the white line. The bandgap of the material decreases upon shock compression and states can be observed within the gap during the region of peak chemical reactions from 2-10 ps.

10 ps. Similar behavior was observed on longer timescales in earlier studies of detonation in nitromethane. [2]

The ultrafast kinetics of HN_3 detonation may play a role in the extreme sensitivity of this material to mechanical perturbations. The initiation of detonation is thought to occur through localized hot regions in the material (hot spots) that react and release energy before the heat can diffuse away from the hot spot. [32] The critical hot spot size decreases with increasing reaction kinetics, leading to a material more sensitive to mechanical and other perturbations. It is possible to speculate that the ultrafast chemistry of this nitrogen compound may also play a role in other polynitrogen compounds that have been long sought as ultra-high energy density materials like N_4, N_5 ions, and polynitrogen. [33, 34] The relationship of the present results to the kinetics of metal-azides is less clear since the metal chemistry may be quite different than that of hydrogen.

Conclusions. We have performed molecular dynamics simulations of detonating HN_3 from the shock front to the final, Chapman-Jouguet state. These are the first simulations of detonation in an azide material from beginning to end. The simulations show that the material decomposes into stable products in about 10 picoseconds. Deviations from vibrational equilibrium occur during chemistry, a feature associated with the fast kinetics of this material.

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