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## Catalytic Behavior of Dense Hot Water

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### Abstract

**Water is known to exhibit fascinating physical properties at high pressures and temperatures. Its remarkable structural and phase complexity suggest the possibility of exotic chemical reactivity under extreme conditions, though this remains largely unstudied. Detonations of high explosives containing oxygen and hydrogen produce water at thousands of K and tens of GPa, similar to conditions of giant planetary interiors. These systems thus provide a unique means to elucidate the chemistry of "extreme water." Here we show that water plays an unexpected role in catalyzing complex explosive reactions—contrary to the current view that it is simply a stable detonation product. Using first-principles atomistic simulations of the detonation of high explosive pentaerythritol tetranitrate (PETN), we discovered that H<sub>2</sub>O (source), H (reducer) and OH (oxidizer) act as a dynamic team that transports oxygen between reaction centers. Our finding suggests that water may catalyze reactions in other explosives and in planetary interiors.**

Water, one of the most abundant materials in the Earth's surface and the interiors of Uranus and Neptune<sup>1</sup>, is famous for its complexity and abnormal behaviors<sup>2-9</sup>. At ambient conditions, many of water's abnormalities, such as its unusually large heat capacity, melting temperature, and dielectric constant, are known to be the result of pronounced hydrogen bonding between water molecules. At pressures above 26 GPa, other exotic behaviors are found as hydrogen bonding is lost<sup>8</sup> and covalent interactions

are substantially weakened. For instance, based on quantum simulations, Cavazzoni *et al.* have predicted that water becomes a superionic solid above 22 GPa and 1500 K, dissociates into an ionic liquid above 3500 K, and transforms into a metallic phase above 7000 K<sup>2</sup>. Recently, diamond anvil cell experiments<sup>5</sup> and quantum molecular dynamics (MD) simulations<sup>6</sup> have confirmed the presence of a superionic solid at elevated conditions (ca. 47 GPa, 1500 K). This phase is characterized by fast H diffusion through a body-centered-cubic oxygen network. Given the dramatic alterations of water's structure and bonding characteristics that occur under extreme conditions, it is possible that these exotic water phases would exhibit unique chemical behavior.

To probe the chemical properties of extreme water, one needs to go beyond pure water. Water more commonly acts as a solvent or a reactant (e.g., supercritical water<sup>10</sup>). In addition, water has been found to act as a “physical” catalyst<sup>11-13</sup> in a couple of reactions, in which water's catalytic ability is associated with its physical interactions with reactants. For instance, water increases rates of solvolytic reactions due to its enhancement of charge screening as an effective dielectric medium<sup>11</sup>. Recently, Vohringer-Martinez<sup>12, 13</sup> *et al.* have reported that water accelerates the reaction between hydroxyl radicals and acetaldehyde because of its ability to form hydrogen bonding with acetaldehyde, analogous to a substrate in heterogeneous catalysis. Here, we report a novel “chemical” catalytic behavior of water as oxygen transportation in the Chapman–Jouguet (CJ) state. The CJ state is the sonic point behind a shock front at which the energy of the detonation wave has been completely released<sup>14, 15</sup>. The thermodynamic condition of CJ state achieved at chemical equilibrium determines the propagation rate and pressure of a detonation wave<sup>14, 15</sup>. Using density functional theory (DFT) MD simulations for a time of 11 ps, we discovered that the team of H<sub>2</sub>O, H, and OH transports oxygen from nitrogen storage to carbon fuel during PETN decomposition

reactions at the estimated CJ detonation condition<sup>15</sup> ( $\rho = 2.38$  g/cc,  $T = 4200$  K), and also at somewhat lower temperature ( $\rho = 2.38$  g/cc,  $T = 3000$  K). Under both temperature conditions, “extreme water” serves both as an end product and as a key chemical catalyst.

The observed catalytic behavior of water in PETN reactions challenges the traditional view of water in high explosive chemistry<sup>16-24</sup>. For a molecular high explosive that consists of carbon, nitrogen, oxygen and hydrogen (e.g., PETN), water, carbon dioxide and molecular nitrogen are known as the three major gaseous products<sup>14, 15</sup>. However, the chemical processes leading to these stable compounds are not well understood<sup>16-24</sup>. Currently, these products are assumed to form a molecular mixture at the CJ state<sup>14</sup>. In contradiction, we find that water forms much faster than carbon dioxide and molecular nitrogen during PETN thermal decomposition. Subsequently, water substantially accelerates the formation of carbon dioxide and molecular nitrogen. Further, we find that under the CJ condition, the lifetime of a molecule is so short that it is comparable to that of a molecular vibration, which calls the very concept of a molecule into question<sup>25</sup>. As a result, the traditional approach based on molecular reactions that is commonly applied in gas-phase combustion chemistry, is no longer adequate for describing chemical reactions under extreme conditions. In this context, we suggest that the progress of condensed-phase explosive reactions may be treated as an oxygen transport problem.

## **Results and Discussion**

Details of the simulation method and analysis are provided in the Methods section. Figure 1a shows the initial simulation cell containing four PETN molecules before decomposition. Chemical reactions started when the system was heated to the desired

temperature. MD snapshots were saved at every 6 fs for post-simulation analysis. To analyze reactions, we have developed a molecular analyzer code that determines the chemical species, lifetimes, reaction events and rates based on simulation trajectories. To demonstrate visually how chemical reactions are traced from simulation trajectories, we display two MD snapshots in Fig. 1b and 1c that show the hydrogen, oxygen and nitrogen atoms before and after a reaction. The reaction shown creates molecular nitrogen in a background of dense atomic fluid, a key step of energy release. Due to the dense and highly reactive environment, it is difficult to learn key chemical kinetics based on the connectivity of bonding alone. For instance, at 4200 K, we have determined over 3000 unique reactions, 78% of which only occur once in the simulation. By painstakingly tracing key reactions among snapshots, we found that many reactions occur locally. Specifically, the same type of functional group transformation (i.e., a local reaction) may occur for reactions involving different molecules.

### **Observations of Water's Catalytic Behavior**

In a PETN crystal, oxygen is stored as  $\text{NO}_2$  groups. The progression of the PETN reaction can be viewed as the flow of oxygen from storage sites ( $\text{NO}$  or  $\text{NO}_2$ ) to fuel sites such as carbon (forming  $\text{CO}$  or  $\text{CO}_2$ ) or hydrogen (forming  $\text{H}_2\text{O}$ ). When we analyzed the key local reactions that lead to formation of carbon dioxide and molecular nitrogen, we observed an intriguing catalytic function of  $\text{H}_2\text{O}$ ,  $\text{OH}$ , and  $\text{H}$ . The catalysis can be visualized by considering local reaction centers. First, we found that nitrogen loses its oxygen mostly to hydrogen, not to carbon, even after the concentration of water reaches equilibrium. Second, we observed that carbon atoms capture oxygen mostly from  $\text{OH}$ , rather than directly from  $\text{NO}$  or  $\text{NO}_2$ . Meanwhile,  $\text{H}_2\text{O}$  dissociates and recombines with  $\text{H}$  and  $\text{OH}$  frequently, thus a steady concentration of  $\text{H}$  and  $\text{OH}$  is maintained.

A schematic of this catalytic cycle is outlined in the reaction flowchart in Fig. 2a, which demonstrates how H and OH catalytically transport oxygen from NO<sub>2</sub> to CO to form CO<sub>2</sub>. First, dissociating H<sub>2</sub>O provides both oxidizing OH species and reducing H atoms. In the reduction cycle, H and ONO form an intermediate species of HONO (H + ONO → HONO). Then, HONO dissociates into OH and NO. In essence, hydrogen acts as a reducer and removes oxygen from nitro-groups. In contrast, OH acts as an oxygen donor to carbon compounds that are not fully oxidized. For instance, in the oxidation cycle, OH reacts with CO to form HOCO, which then becomes H and CO<sub>2</sub> (OH + CO → HOCO → H + CO<sub>2</sub>). The net result of this oxidation process is the transport of oxygen (shown in red) from OH to CO, thus producing CO<sub>2</sub>. Recombining OH and H produces H<sub>2</sub>O again. In comparison, the process of OH + CO → H + CO<sub>2</sub> also plays an important role in hydrocarbon combustion, where OH is a key free radical and H<sub>2</sub>O<sub>2</sub> is the source<sup>26</sup>.<sup>27</sup> During PETN reactions, H<sub>2</sub>O (with OH) acts as an oxidizer only when it reacts with carbon. When H<sub>2</sub>O (with H) reacts with nitro-groups, it acts as a reducer.

Catalysts are reagents, which accelerate chemical reactions without being consumed. The above example shows that H<sub>2</sub>O, with H and OH, participates in the overall reaction CO + NO<sub>2</sub> → CO<sub>2</sub> + NO, without being consumed. We have produced a time history of the bonding of oxygen during the overall reaction, which sheds additional light on how this catalysis accelerates oxygen transport. In Fig. 2b, the number of oxygen atoms bonded with nitrogen (red curve) decreases, while the number of oxygen atoms captured by carbon as species of CO and CO<sub>2</sub> grows with time (blue curve) as the reaction progresses. Note that after the initial production of water, the oxygen content associated with H (such as OH and H<sub>2</sub>O) oscillates around a relatively constant average (green curve), at the same time that oxygen atoms are transported from nitrogen to

carbon. The individual concentrations of H and OH also achieve nearly constant values during this time period (not shown), indicating a typical catalytic behavior.

The overwhelming participation of H and OH in the chemical reactions of PETN is further illustrated in Fig. 3, in which each column represents one unique elementary reaction identified by our molecular analyzer based on the entire MD trajectory. For instance, the first column represents the reaction of  $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ . Only the 176 most frequent reaction types are shown on the plot. Correspondingly, the slowest reaction shown on this plot has a rate of roughly once every 10 ps per PETN. Among the top 176, 118 reactions involve H, 25 involve OH, and 9 involve both H and OH. Only 24 reactions did not involve H or OH. Among all 3000 unique reaction events identified from the simulation at 4200 K, more than 76% involve H atoms.

### **Factors Governing the Catalytic Cycle**

Three factors are crucial contributors for this catalytic cycle: (1) fast formation of water prior to production of carbon dioxide and molecular nitrogen, making it an available catalyst; (2) rapid dissociation of  $\text{H}_2\text{O}$  to generate the oxidizer OH and the reducer H; and (3) accelerated hydrogen mobility that enables fast transport of oxygen between species. The first factor is largely due to PETN's unique molecular structure and composition. In comparison, the latter two factors are associated with extreme conditions.

The formation of water is extremely fast—it appears after only 18 fs at 4200K—and is produced more than an order of magnitude faster than carbon dioxide or molecular nitrogen. The time sequence can be explained largely by the relative proximity of hydrogen to oxygen in comparison to other atoms in a PETN molecule (shown in Fig. 1a). The closer the reactants, the shorter time it takes to form products. Upon heating,

PETN dissociates, producing mobile H and NO<sub>2</sub> groups. The short distance between the H atoms and the NO<sub>2</sub> in PETN provides an environment for the fast reaction of 2H + NO<sub>2</sub> → HONO + H → H<sub>2</sub>O + NO. Further reduction of NO to N<sub>2</sub> is a much slower process because nitrogen atoms are far from each other in the un-reacted PETN molecule and atomic nitrogen is much less mobile and has a lower concentration than atomic hydrogen. In fact at 4200 K, the first N<sub>2</sub> molecule is formed from an intermediate species, NNO after 1 ps. Reduction of NNO to N<sub>2</sub> is also carried out by two H atoms, first to HONN (Fig. 1b) and then to H<sub>2</sub>O and N<sub>2</sub> (Fig. 1c) via H + HONN. Notice that the key process leading to formation of molecular nitrogen is the transport of oxygen from nitro-groups to hydrogen.

At extreme conditions, the dissociation of water occurs at a much faster rate and by a different mechanism than at ambient conditions. On average, water molecules do not live very long. As Fig. 3 shows, H<sub>2</sub>O → H + OH is the most frequent event, at about 14 events/ps per PETN molecule, while its reverse reaction ranks second. In contrast, at ambient conditions, water dissociates predominantly by a bimolecular reaction of 2H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + OH<sup>-</sup><sup>28</sup>. At the CJ condition, the bimolecular water dissociation pathway occurs at a much lower frequency (about 1.6 events/ps per PETN). Our observation of the unimolecular dissociation mechanism is consistent with previous experiments. For instance, Holmes *et al.*<sup>8</sup> reported that the Raman spectra of H<sub>3</sub>O<sup>+</sup> associated with the intermolecular hydrogen bonds vanish at 26 GPa, which led them to support the unimolecular mechanism. In contrast, Schwegler *et al.*<sup>9</sup> reported that water dissociates via the bimolecular mechanism, based on quantum simulations of pure water at 2000 K. The discrepancy between our result and that of Schwegler *et al.*<sup>9</sup> is likely due to the difference in simulation temperatures (2000 K<sup>9</sup> vs. 3000–4200 K) and water

concentration (pure vs. mixture). The bimolecular dissociation mechanism is expected to be favored at lower temperature and higher water concentration. The rapid dissociation of water enables it to be a continuous source of oxidizing (OH) and reducing (H) agents, a property that is unique for “extreme water.” It also implies that bonds containing hydrogen are inherently non-molecular, and thus the CJ state should not be treated as a mixture of conventional molecules, as currently assumed<sup>14</sup>. This observation is consistent with a recent quantum MD study of shocked nitromethane by Reed *et al.*<sup>25</sup>

The mobility of hydrogen in these mixed fluids is far greater than that of the heavier elements. Figure 4a shows a snapshot of hydrogen atoms (white) and oxygen atoms (red) after 8.98 ps at 4200 K. In order to show atomic mobility with traveled distances, the atomic positions are shown with the periodic boundary conditions removed. Obviously, hydrogen atoms have traveled much farther than oxygen atoms from their initial positions inside the simulation cell. Similar hydrogen behavior was previously found for pure water<sup>9</sup>. Figure 4b illustrates the diffusion constants of hydrogen, carbon, nitrogen and oxygen atoms at 3000 K (black dotted line) and 4200 K (red dotted line). At 4200 K, hydrogen atoms diffuse at a rapid rate of  $1.83 \times 10^{-3} \text{ cm}^2/\text{s}$ . As a comparison, hydrogen diffuses at a slower rate of  $3 \times 10^{-4} \text{ cm}^2/\text{s}$  in the superionic phase of water ( $\rho = 2.6 \text{ g/cc}$ ,  $T = 2000 \text{ K}$ )<sup>6</sup>. To better understand the mechanism of hydrogen transport, we performed a simulation where the motions of elements other than hydrogen were frozen at the positions obtained from the 4200 K simulation at 6 ps. We found that the hydrogen diffusion constant increased to  $4.3 \times 10^{-3} \text{ cm}^2/\text{s}$ , indicating that hydrogen transport can be thought of as random diffusion through a slowly evolving matrix of heavy atoms, an approximation applied to our conductivity calculation (shown later). Furthermore, we found that hydrogen mobility is thermally activated. As we decreased

the temperature to 3000 K, the hydrogen diffusion constant decreased to  $8.5 \times 10^{-4}$  cm<sup>2</sup>/s.

### **Charge Characteristics and Electrical Conductivity**

So far, we have not addressed the electronic characters of H, OH and major products. In particular, are the species best described as ions (e.g., in solution chemistry) or as radicals (e.g., in combustion)? Fig. 5 shows charge histograms of carbon, nitrogen, hydrogen and oxygen atoms at the end of simulation at 4200 K. Notice that carbon and nitrogen charge distributions are approximately centered around neutrality (Fig. 5a, 5b), This is consistent with the charge neutrality found for CO, CO<sub>2</sub> and N<sub>2</sub>. In comparison, hydrogen and oxygen have noticeable net charges [e.g., H (+0.3 e), and OH (-0.16e)] on average. As a result, oxygen has a bimodal distribution depending on whether it bonds to hydrogen or carbon. Interestingly, the overall fluid has a root-mean-square charge separation ( $\langle q^2 \rangle^{1/2}$ ) of 0.3e, the same as the average charge on hydrogen. The average atomic charges correlate with the Pauling electronegativity<sup>29</sup>. Hydrogen, the element with the lowest electronegativity of 2.1, has net positive charge, while oxygen, the element with the highest electronegativity of 3.5, has net negative charge. Carbon and nitrogen with intermediate electronegativity, have no net charge.

Estimating the background dielectric constant of a CJ fluid experienced by the mobile ions provides important information about dielectric screening, a key factor in determining the relative stability between a radical and an ion. We have estimated an upper bound of the dielectric constant of the CJ mixture based on another method, which was calculated using the concentrations of neutral species predicted by the thermal chemistry code Cheetah<sup>15</sup> at the CJ condition. In this case, a simple extension to mixtures of the method applied in a previous study<sup>30</sup> of supercritical water yields a

dielectric constant  $\epsilon$  of approximately 2. This suggests that the behavior of a hot, dense fluid at the CJ condition is more similar to a molten salt<sup>31, 32</sup> or a polymer (e.g. Teflon<sup>33</sup>,  $\epsilon \approx 2$ ) than a standard ionic solution ( $\epsilon \approx 100$ ) or gas phase mixtures ( $\epsilon \approx 1$ ).

Making a comparison to the experimental DC electrical conductivity<sup>34</sup> provides an important verification of our MD results on the charge characteristics of the CJ fluid. From analyzing the time-dependent electronic structure of the simulations, we learned that the fluid near chemical equilibrium is an electronic insulator, although temporary metallization was observed near the height of chemical reactivity [see Supplementary Information (SI)]. Thus, an ionic conduction mechanism determines the electrical conductivity of the system,  $\sigma$ . To calculate the ionic conductivity of the CJ fluid, we assumed that hydrogen atoms (+0.3 e) move in a background of slowly evolving heavy atoms of average charge  $-0.3e$ . Using the Nerst-Einstein<sup>35</sup>, averaged charges and diffusion constants of fast and slow populations, we estimated  $\sigma$  to be about  $70 \Omega^{-1}\text{m}^{-1}$  (see Methods). This value agrees excellently with the experimental value of  $60 \Omega^{-1}\text{m}^{-1}$ , measured for PETN at the CJ condition<sup>34</sup>.

## Conclusions

This novel catalytic mechanism is completely different from previously proposed decomposition mechanisms for PETN<sup>16-20</sup> or for similar explosives<sup>21-25</sup>, in which water is just an end product. It shares certain similarity with hydrocarbon combustion, in that OH plays an important role in converting CO to CO<sub>2</sub><sup>26, 27</sup>, although they are substantially different. For instance, H<sub>2</sub>O is the source for OH instead of H<sub>2</sub>O<sub>2</sub><sup>26, 27</sup> in combustion. In addition, OH and H of a dense hot fluid are partially charged, not neutral, and their concentrations remain nearly unchanged after initial formation. In contrast, radical population grows in combustion and vanishes after burning. Given the active role played

by H<sub>2</sub>O, H and OH in detonation chemistry, it is conceivable that the kinetics of water formation may also contribute to high explosive sensitivity (ease of initiating a violent reaction). Furthermore, the chemistry of “extreme water” also has important implications for planetary science. The conditions of high explosive detonation are similar to those of the interiors of giant planets such as Uranus and Neptune<sup>1</sup>. The interiors of these planets are expected to be composed primarily of hydrogen, carbon, nitrogen and oxygen, as is PETN. Our results show that hydrogen atoms retain the high mobility at extreme conditions found in previous work on pure H<sub>2</sub>O<sup>2,6,9</sup> and NH<sub>3</sub><sup>2</sup>, even when mixed with substantial quantities of carbon. The catalytic activity of water found here suggests that the chemistry of these planetary interiors may be very fast, maintaining chemical equilibrium even in the presence of very non-reactive species such as diamond.

## Methods

### DFT/MD Simulations

At ambient conditions, the most stable form of PETN is a molecular crystal of  $P\bar{4}2_1c$  space group<sup>36, 37</sup>, which consists of two molecules per unit cell. We started with an uncompressed cell containing 4 PETN molecules/116 atoms (shown in Fig. 1a) based on 1x1x2 super-lattice under experimental geometry of 9.38Å x 9.38Å x 13.418Å. We then uniformly scaled the crystal axes in several steps until the estimated CJ density of 2.38 g/cc was achieved. At each step we minimized the energy of the configuration.

We used a code developed by one of the authors, L. H. Yang, to perform DFT/MD simulations under constant particle number, volume, and temperature (NVT) ensembles<sup>38</sup>. The code uses a pseudopotential treatment of core electrons and a plane-wave basis set<sup>38</sup>. Dynamics are based on the Born–Oppenheimer approximation.

The code is specifically designed to take advantage of the massive parallel architecture of teraflop computer Blue Gene/L at Lawrence Livermore National Laboratory. Three-dimensional periodic boundary conditions were applied to mimic a solid environment. The NVT condition is comparable to those produced by heated diamond anvil cells or thermal ignition experiments, which are different from detonations that experience a wider range of densities and temperatures. We believe the chemical kinetics at a well-defined NVT condition are likely to shed light on other extreme conditions, such as shock (for more discussions of a similarity between reactions under shock and constant volume, see SI).

We employed the Perdew–Burke–Ernzerhof (PBE<sup>39</sup>) exchange–correlation function and single k-point. Core electrons were represented by Troullier–Martins pseudopotentials<sup>40</sup>, with a kinetic-energy cutoff of 80 Ry<sup>6</sup>. The electron temperature was set to be the same as ions using Fermi–Dirac smearing. A time step of 1.2 fs was used in time integration. The NVT<sup>41</sup> simulations were performed at 4200 K and 3000 K. Snapshots were collected at every 6 fs for post-simulation analysis. Chemical reactions were traced and analyzed for the total simulation time of 11 ps.

We investigated system size effects using the computationally efficient density functional tight binding (DFTB<sup>42</sup>) technique with self-consistent charges on a larger simulation cell of  $2 \times 1 \times 2$  supercell. The concentration histories of major species discussed here were investigated for possible size dependence. The concentration fluctuations in the larger simulations were less than those in the smaller simulations, but concentration trends were very similar. This is consistent with our observations that PETN decomposition is unimolecular and that the majority of reactions are localized events. Smaller time steps were also investigated with DFTB. We found concentration histories with a 0.5 fs time step to be similar to those determined with a 1.2 fs time step.

## Post-Simulation Analysis

To analyze the MD snapshots, we defined chemical species based on a set of bond distances (obtained from radial distribution function) and a minimum bond lifetime criterion<sup>20</sup>, which is used to distinguish between transient configurations and stable chemical species. Two atoms were not considered bonded unless they stayed continuously within the bond-distance criterion during the chosen minimum bond lifetime of 12 fs. Shorter or longer bond-lifetime criteria (6-30 fs) have also been tested. Although the concentrations of species quantitatively depend on the specific choice of bond criteria, no impact was found for the qualitative conclusions reached by this work. Reaction events were then traced between snapshots, with rate constants determined by the traced elementary rate equation and concentrations of the species. In order to estimate Mulliken charges, the mixed basis set CP2K<sup>44</sup> code was used with a cutoff of 30 Ry and a double-zeta basis set (dzvp)<sup>45</sup>.

We employed the Nerst–Einstein<sup>35</sup> relation to calculate the ionic conductivity:

$$\sigma = \frac{1}{k_B T} \sum_i n_i q_i^2 D_i (1 - \Delta),$$
 where  $n_i$ ,  $q_i$  and  $D_i$  are the number density, charge, and self-

diffusion constant of species  $i$ , respectively.  $\Delta$  is a deviation parameter due to transient cross-correlations between the velocities of different ions.<sup>32</sup> Since the atomic self-diffusion constants suggest that the mobility of the H population is much faster than that of the other species, we assumed that the slow-moving population in which H travels can be described by a single self-diffusion constant  $D_{slow}$ , which we approximate by the average of the carbon, nitrogen, and oxygen values. The ionic conductivity can then be

written as 
$$\sigma = \frac{n_H q_H^2}{k_B T} \left[ D_H + D_{slow} \left( \frac{\langle q^2 \rangle}{x_H q_H^2} - 1 \right) \right] (1 - \Delta),$$
 where  $x_H = n_H/n_{total}$ . Since the

dielectric constant in reacting PETN is close to that of a molten salt, we approximated its

value of  $\Delta$  using the averaged value of 0.26 for molten salts (approximate range of 0.08–0.43) published by a previous study<sup>34</sup>. Namely, we have assumed that 26% of the mobile H atoms form transient dynamic complexes with the heavier background ions, which contribute to diffusive motion but do not contribute to electrical current. This assumption is based on our previous observation that the dielectric properties of the system are very similar to those of molten salts.

### Figure Captions:

1. **Initial MD configuration and example simulation snapshots:** **a**, Simulation cell containing four un-reacted PETN molecules. **b** and **c** are two configurations at 4200 K showing the left and right sides of the reaction  $\text{H} + \text{HONN} \rightarrow \text{H}_2\text{O} + \text{N}_2$ . This demonstrates that H and OH play major roles in catalyzing  $\text{N}_2$  formation. For clarity, other atoms in the simulation cell are rendered with transparency. Nitrogen, oxygen, carbon, and hydrogen are colored blue, red, gray, and white, respectively.
2. **Typically observed catalytic cycle on local reaction centers and oxygen transportation from nitrogen to carbon and hydrogen.** **a**, Schematic drawing of a typical set of reactions where oxygen (red) flows from nitrogen to carbon. **b**, Time dependence of oxygen concentrations bonded with hydrogen (e.g. OH and  $\text{H}_2\text{O}$ , green), nitrogen (e.g.  $\text{NO}_3$ ,  $\text{NO}_2$  and NO, red) and carbon (e.g. CO and  $\text{CO}_2$ , blue) at 3000 K. Formations of C–O and N–O bonds increase and decrease with time, respectively, while the H–O bond number remains roughly constant after initial formation. This suggests catalysis mediated by OH. The smooth dashed lines are analytic fits of solid lines to reflect the overall trend.

3. **Overwhelming participation of hydrogen observed in majority of reactions.**  
Frequencies (event/ps per PETN molecule) of the 176 most frequent reactions obtained at  $T = 4200$  K.
4. **Hydrogen is much more mobile than other heavier atoms. a**, Snapshot of hydrogen (white) and oxygen (red) positions at 8.95 ps,  $T = 4200$ K, with periodic boundary conditions removed to track their distances traveled. The simulation cell (yellow box) indicates the initial boundary of hydrogen and oxygen atomic positions at  $t = 0$ . **b**, Diffusion constants of hydrogen, carbon, nitrogen and oxygen atoms obtained at  $T = 3000$  K (black dotted line) and  $T = 4200$  K (red dotted line) at  $\rho = 2.38$  g/cc.
5. **Atomic charge distributions obtained at the CJ condition.** Charge histograms of **a**, carbon, **b**, nitrogen, **c**, hydrogen and **d**, oxygen atoms obtained from Mulliken population analysis on 30 consecutive configurations near the end of the 4200 K simulation.

## References

1. Hubbard, W.B. *Science* **275**, 1279 (1997).
2. Cavazzoni, C. *et al.* Superionic and metallic states of water and ammonia at giant planet conditions. *Science* **283**, 44–46 (1999).
3. Hemley, R.J. *et al.* Static compression of H<sub>2</sub>O-ice to 128 GPa (1.28 Mbar). *Nature* **330**, 737–740 (1987).
4. Goncharov, A.F., Struzhkin, V.V., Somayazulu, M.S., Hemley, R.J. & Mao, H.K. Compression of ice to 210 gigapascals: Infrared evidence for a symmetric hydrogen-bonded phase. *Science* **273**, 218–220 (1996).

5. Goncharov, A.F. *et al.* Dynamic ionization of water under extreme conditions. *Phys. Rev. Lett.* **94**, 125508 (2005).
6. Goldman, N., Fried, L.E., Kuo, I. F.W. & Mundy, C.J. Bonding in the superionic phase of water. *Phys. Rev. Lett.* **94**, 217801 (2005).
7. Lin, J.F. *et al.* Melting behavior of H<sub>2</sub>O at high pressures and temperatures. *Geophys. Res. Lett.* **32**, L11306 (2005).
8. Holmes, N.C., Nellis, W.J., Graham, W.B., & Walrafen, G.E. Spontaneous Raman scattering from shocked water. *Phys. Rev. Lett.* **55**, 2433–2436 (1985).
9. Schwegler, E., Galli, G., Gygi, F. & Hood, R.Q. Dissociation of water under pressure. *Phys. Rev. Lett.* **87**, 265501 (2001).
10. Ding, Z.Y., Frisch, M.A., Li, L., Gloyna, E.F. Catalytic oxidation in supercritical water. *Ind. Eng. Chem. Res.* **35**, 3257–3279 (1996).
11. Farinacci, N.T. & Hammett, L.P. Polymolecular solvolytic reactions: Water catalysis in the alcoholysis of benzhydryl chloride. *J. Am. Chem. Soc.* **59**, 2542–2546 (1937).
12. Vohringer-Martinez, E. *et al.* Water catalysis of a radical-molecule gas-phase reaction. *Science* **315**, 497–501 (2007).
13. Smith, I. *Science* **315**, 470–471 (2007).
14. Ree, F.H. A statistical mechanical theory of chemically reacting multiphase mixtures: Application to the detonation properties of PETN. *J. Chem. Phys.* **81**, 1251–1263 (1984).
15. Fried, L.E. & Howard, W.M. An accurate equation of state for the exponential-6 fluid applied to dense nitrogen. *J. Chem. Phys.* **109**, 7338–7348 (1998).
16. Ng, W.L., Field, J.E. & Hauser, H.M. Thermal, fracture, and laser-induced decomposition of pentaerythritol tetranitrate. *J. Appl. Phys.* **59**, 3945–3952 (1986).

17. Gruzdkov, Y.A. & Gupta, Y.M. Shock wave initiation of pentaerythritol tetranitrate crystals: Mechanism of anisotropic sensitivity. *J. Phys. Chem. A* **104**, 11169–11176 (2000).
18. Yoo, C.S. *et al.* Anisotropic shock sensitivity and detonation temperature of pentaerythritol tetranitrate single crystal. *J. Appl. Phys.* **88**, 70–75 (2000).
19. Tarver, C.M., Tran, T.D. & Whipple, R.E. Thermal decomposition of pentaerythritol tetranitrate. *Propell., Explos. Pyrot.* **28** 189–193 (2003).
20. Wu, C.J., Manaa, M.R. & Fried L.E. Tight binding molecular dynamic simulation of PETN decomposition at an extreme condition. *Proc. Mater. Res. Soc.*, **987**, 139–144 (2007).
21. Manaa, M.R., Fried, L.E., Melius, C.F., Elstner, M., & Frauenheim, T. Decomposition of HMX at extreme conditions: A molecular dynamics simulation, *J. Phys. Chem. A*, **106**, 9024–9029 (2002).
22. Strachan, A., van Duin, A.C.T., Chakraborty, D., Dasgupta, S. & Goddard, W. A. III Shock waves in high-energy materials: The initial chemical events in nitramine RDX. *Phys. Rev. Lett.* **91**, 098301 (2003).
23. Strachan, A., Kober, E.M., van Duin, A.C.T., Oxgaard, J. & Goddard, W. A. III Thermal decomposition of RDX from reactive molecular dynamics. *J. Chem. Phys.* **122**, 054502 (2005).
24. Nomura, K. *et al.* Dynamic transition in the structure of an energetic crystal during chemical reactions at shock front prior to detonation. *Phys. Rev. Lett.* **99**, 148303 (2007).
25. Reed, E.J., Manna, M.R., Fried, L.E., Glaesemann, K.R. & Joannopoulos, J.D.A transient semimetallic layer in detonating nitromethane. *Nat. Phys.* **4**, 72–76 (2008).

26. Westbrook, C.K. & Dryer, F.L. Chemical kinetic modeling of hydrocarbon combustion. *Prog. Energy Combust.* **10**, 1–57, (1984).
27. Westbrook, C.K. Chemical kinetics of hydrocarbon ignition in practical combustion systems. *Proc. Comb. Inst.*, **28** 1563–1577 (2000).
28. Giguere, P.A. Great fallacy of the H<sup>+</sup> ion and the true nature of H<sub>3</sub>O<sup>+</sup>. *J. Chem. Educ.* **56**, 571–575 (1979).
29. Pauling, L. *The Nature of the chemical bond*. Cornell University Press. (1960), p. 90.
30. Bastea, S., L.E. Fried. Exp6-polar thermodynamics of dense supercritical water, *J. Chem. Phys.* **128**, 174502 (2008).
31. Hansen, J.P. & McDonald, I.R. Statistical mechanics of dense ionized matter. IV. Density and charge fluctuations in a simple molten salt. *Phys. Rev. A* **11**, 2111–2123, (1975).
32. Wilke, S.D., Chen, H.C. & Bosse, J. Dielectric and transport properties of a supercooled symmetrical molten salt. *Phys. Rev. E.* **60**, 3136–3149 (1999).
33. [http://clippercontrols.com/info/dielectric\\_constants.html](http://clippercontrols.com/info/dielectric_constants.html), (2007) Clipper Controls.
34. Hayes, B. On electrical conductivity in detonation products. *Proc 4th Symp. Intl. Det.*, White Oak, MD, October 1965 (Office of Naval Research, Department of the Navy), pp. 595–601.
35. Weinert, U. & Mason, E.A. Generalized Nernst-Einstein relations for nonlinear transport coefficients. *Phys. Rev. A* **21**, 681–690 (1980).
36. Booth, A.D. & Llewellyn, F.J. The crystal structure of pentaerythritol tetranitrate. *J. Chem. Soc.* 837–846 (1947).
37. Trotter, J. Bond lengths and angles in pentaerythritol tetranitrate. *Acta Cryst.* **16**, 698–699 (1963).

38. Yang, L.H., Hood, R.Q., Pask, J.E. & Klepeis, J.E. Large-scale quantum mechanical simulations of high-Z metals. *J. Computer-aided Mater. Design* **14**, 337–347 (2007).
39. Perdew, J.P., Burke, K., & Ernzerhof, M., Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
40. Troullier, N. & Martins, J.L. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B* **43**, 1993–2006 (1991).
41. Brown, D. & Clarke, J.H.R. A comparison of constant energy, constant temperature and constant pressure ensembles in molecular-dynamics simulations of atomic liquids. *Mol. Phys.* **51**, 1243–1254 (1999).
42. Frauenheim, T. *et al.* A self-consistent charge density-functional based tight-binding method for predictive materials simulations in physics, chemistry and biology. *Phys. Status Solidi. B* **217**, 41–62 (2000).
43. Mulliken, R.S. Electron population analysis on LCAO-MO molecular wave functions. *J. Chem. Phys.* **23**, 1833-1840 (1955).
44. CP2K code, <http://www.cpk2.berlios.de>. Copyright CP2K developers group 2000–2006.
45. Van de Vondele, J *et al.* *Comput. Phys. Comm.* **167**, 103 (2005).

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## **Author Contributions**

C. J. W. originated the central idea, performed and analyzed the PETN MD simulations, and wrote the paper; L. E. F. developed the molecular analyzer code; L. H. Y. carried out Quantum MD code development; N. Goldman contributed to Mulliken charge analysis; S. Bastea performed conductivity and dielectric calculations; all authors contributed to discussions and editing of the manuscript;

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