Thermal Decomposition of Nitromethane using Reactive Molecular Dynamics

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The development in recent years of reactive interatomic potentials has enabled, for the first time, the accurate simulation of the thermal- or shock-induced decomposition of energetic materials under realistic loading conditions. Reactive molecular dynamics (MD) simulations provide a molecular-level, full-chemistry, and full-physics description of the chemistry and mechanical processes in energetic materials making no assumptions or simplifications other than those intrinsic to the force field description of the interactions, the fact that we use classical mechanics to describe atomic dynamics and the size of the simulation cell. Such molecular level characterization is essential for the development of predictive, physics-based, materials models.

We study the decomposition of liquid and solid samples on nitromethane (CH_3NO_2) at high temperatures (2000–3000 K) and high density (1.97 g/cm³) using molecular dynamics with the first-principles-based reactive force field ReaxFF. The first chemical reactions observed in the decomposition of nitromethane are either an intermolecular proton transfer leading to the ions CH_3NOOH and CH_2NO_2 (favored at higher temperatures) and an isomerization reaction involving the scission of the C-N bond the formation of a C-O bond to form methyl nitrate (CH_3ONO) (favored for the lower temperature cases studied). Also early in the decomposition process we observe intramolecular proton transfer events leading to the aci-acid form: CH_2NO_2H.

We show in Fig. 1 five snapshots of the isomerization reaction obtained from our MD simulation starting from a liquid structure at T = 2500 K; the time elapsed between the second and forth snapshots is 20 fs. The central structure depicts roughly the transition state, the corresponding C-N and C-O bond distances at this point in the reaction are 1.89 and 1.60 Å, respectively. There has been some controversy in the literature regarding the structure of the transition state between nitromethane and methyl nitrate; see for example [1]. Some authors have predicted a loose transition state (with C-N and C-O bond distances longer than 3 Å) while others predict a tight transition state with bond distances around 2 Å. Our MD simulations predict a tight transition state in agreement with the most recent and accurate *ab initio* results [1].

In Fig. 2 we show the time evolution of the population of nitromethane as well as several important products (H_2O, CO, N_2, and NH_3) and the intermediate (H_3CNOOH) for both liquid and crystalline structures and two temperatures. As already mentioned the formation of CH_3NOOH via a proton transfer is the first reaction that appears in the populations plot. The formation of H_2O (the main product) occurs after most of the original nitromethane molecules have undergone the initiation reactions. The final population of H_2O is not very sensitive to temperature; we find about 0.8 H_2O molecules per nitromethane. Other important products are N2, CO_2, and NH_3. As expected the population of these small molecules is larger at T = 3000 K than at T = 2000 K, in particular we find almost no N_2 molecules at T = 2000 K.
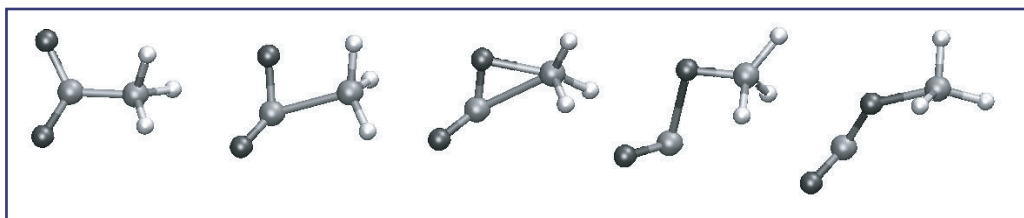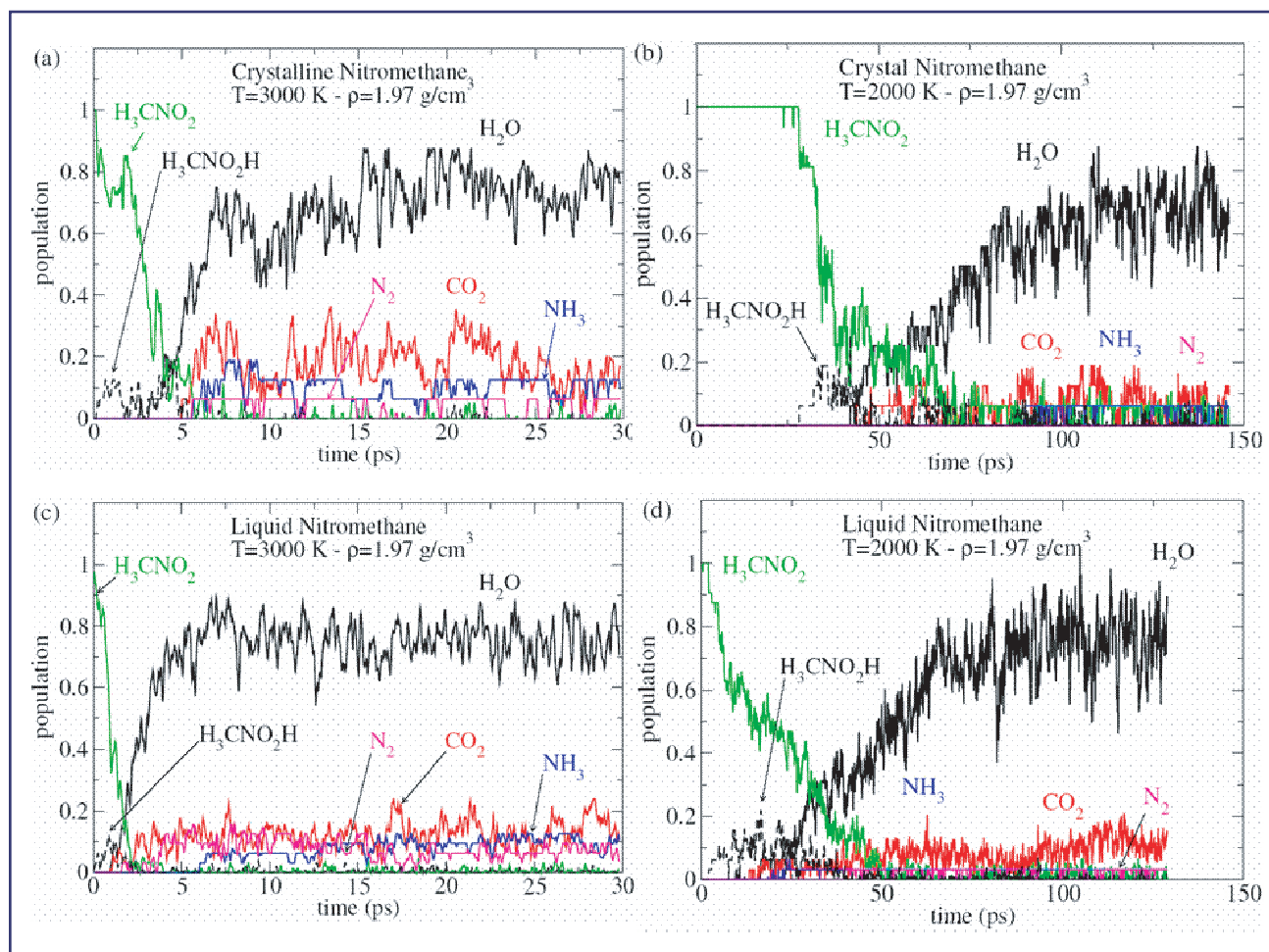

Figure 1—
Molecular dynamics snapshots of the process of isomerization of nitromethane leading to methyl nitrate.

Our results for the crystalline sample at T = 3000 K are in excellent agreement with recent quantum mechanically (QM)-based MD simulations [2] regarding the detailed chemistry of decomposition and the time-scales associated with the reactions. Furthermore the pressures obtained from our simulations at T = 1000 and 4000 K and high pressure ρ = 2.2 g/cm³ are in excellent agreement with the QM results. Note that while *ab initio* data on nitromethane has been used to develop ReaxFF (chemical reactions and vibrational properties) none of the QM MD results in Ref. [2] were included in any way into the ReaxFF parameterization. This provides an important direct validation of the ReaxFF description of interatomic forces in energetic materials.

[1] M.T. Nguyen, et al., *J. Phys. Chem.* **107**, 4286 (2003).
[2] M.R. Manaa, et al., *J. Chem. Phys.* **120**, 10146 (2004).

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