



# Anisotropic behavior of energetic materials at elevated pressure and temperature

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## ABSTRACT

First principles and molecular dynamics methods were used to study energetic materials (EM) of varying sensitivity, particularly nitromethane (NM) and pentaerythritol tetranitrate (PETN). Molecular and electronic structure, as well as anisotropic elastic properties, variation of charge distributions, and stress-strain behavior of these three materials were investigated. Information obtained from different levels of theory is useful to reveal and assess the anisotropic sensitivity of the studied systems. For NM, we observe a crystallographic phase transformation and a drastic change in its mechanical behavior. PETN is observed to be mechanically stable within the studied pressure range, with a marked anisotropic behavior when compressed at elevated temperatures.

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## 1. Introduction

Applications for energetic materials (EM) range from initiators in safety bags to detonation charges, propellants and secondary explosives. It has been found experimentally that these materials may undergo detonation by un-planned stimuli. It is well known that high EM's display anisotropic sensitivity to heat and/or mechanical shock (Dick, 1984, 1993, 1997). Naturally, this has raised serious issues associated with safety, logistics, and time burdens related to handling of these materials, as well as the cost associated with these issues. To understand their behavior, various physical and chemical correlations have been proposed (Shaw, 1973; Zeman, 1995). Properties like the number and positions of the substituents, bond length, and partial charges of the molecular constituents in the gas phase, have been used to correlate the trends in sensitivity of these mostly nitro group containing molecular crystals (Brill & James, 1993).

For processing of plastic bonded explosives, crystals of EM's are fragmented and compressed with a polymer matrix binder. Localization of strain energy has been the suspect of the formation of reaction zones (Sewell, Menikoff, Bedrov, & Smith, 2003), or "hot-spots". Thus, a clear understanding of the relevant mechanical properties is essential. In addition to this, compression along a given plane can act as energy barriers and hinder a complete reaction, causing runaway reactions and unexpected behavior. In

this sense, observed reactivity and sensitivity of an explosive is influenced by an interplay between mechanical, chemical, and thermodynamic conditions. The prerequisite for the prevention of unexpected behavior while processing of EM's is to understand the phenomena at the molecular level, which requires assessment beyond empirical correlations.

Before any bond breaks and reactions occur, an orbital has to get polarized and charge localization increases at certain group atoms or chemical groups. Molecules interacting with each other, as in condensed phase, can give rise to charge localization not observable for the same isolated molecule. Even though there are numerous attempts to correlate the electronic properties as calculated from gas-phase and quantum chemical studies (Li, Huang, & Dong, 2005; Badders, Wei, Aldeeb, Rogers, & Mannan, 2006; Byrd & Rice, 2006; Hu, He, & Chen, 2002; Zhang, Shu, Huang, et al., 2005; Zhang, Shu, Zhao, et al., 2005; Manaa & Fried, 1998; Manelis, 2003), studies that relates charges in molecular crystal at different conditions are scarce (Byrd & Rice, 2007; Sorescu, Rice, & Thompson, 1999; Kuklja & Kunz, 1999). In case if only the gas phase studies used in correlations, the results will be in contradiction with observed experimental trends (Hu et al., 2002).

First principles based computational methods (ab initio quantum chemistry, density functional theory, molecular dynamics with accurate interaction potentials) are shown to be suitable to study different thermodynamic properties (Yuan & Smith, 2009; Woodward & Ketchum, 2001) at multiple length and time scales. This enable researchers to employ 'virtual experiments' to study the energetic behavior and crystallographic phase changes at elevated temperatures and pressures without the risk of exposure to unsafe conditions. For instance one can study the highly reactive

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molecular crystals at the ground state through the use of density functional theory (DFT)(Kohn & Sham, 1965). One can include the effect of temperature and pressure through the use of molecular dynamics (MD), employing time averages over the trajectory to determine thermodynamic properties. More specifically, DFT can also be used to determine pressure dependence of second order elastic constants, variation in charge localization under the influence of applied pressure or anisotropic mechanical loads, such as in response to uniaxial compression or applied shear stresses. More specifically MD is valuable to obtain molecular level information under extreme conditions such as shock or hypervelocity impact where fast evolution of thermodynamic states need to be observed and assessed within short time scales (Arman et al., 2011).

Herein, we present a systematic study of the mechanical properties as a function of external pressure for nitromethane (NM) and pentaerythritol tetranitrate (PETN), which have distinct impact and shock sensitivities (Gibbs, Popolato, & Baytos, 1980; Winey & Gupta, 2001). For example, PETN has a reported impact sensitivity which ranges between 12 cm and 27 cm (height for 50% chance of detonation) in drop hammer tests (Gibbs et al., 1980), as compared to a value higher than 320 cm for NM. PETN is known to be moderately sensitive to shock compression, while NM is sensitive to shock detonation. We will attempt to correlate these properties with overall thermodynamic behavior using DFT and MD methods. The main objective is to find information at the different level of theories employed, and compare and contrast system related information on the processes that could lead to unsafe behavior.

## 2. Theory and methods

By means of localized basis sets that are used to represent all-electron systems, we performed first principles calculations on the crystals of PETN and NM. These calculations are conducted within DFT(Kohn & Sham, 1965) level, with gradient corrected Perdew-Burke-Ernzerhof (PBE) functional for exchange and correlation(Perdew, Burke, & Ernzerhof, 1996). For these calculations we use extended basis sets(Gatti, Saunders, & Roetti, 1994) for carbon, hydrogen, nitrogen and oxygen, as implemented in the crystal06 package(Dovesi et al., 2007). Initial structures for these crystals are obtained from the Cambridge Crystallographic Database(CCSDB, 2007). Energy convergence was found for a mesh of  $4 \times 4 \times 4$  grid size used for inverse space sampling. Analytical gradients are used to relax the ionic degrees of freedom(Perry, 1978; Bernhard Schlegel, 1984) at different strained states.

An important part of the model used to represent properties and processes in nature lies in the level of accuracy and precision of the employed methods. The most common Gaussian or atom-localized basis sets of current use are the split valence basis sets (Towler, Zupan, & Causà, 1996; Binkley, Pople, & Hehre, 1980; Ditchfield, Hehre, & Pople, 1971). Quality of our basis sets have been validated by a set of calculations on the molecular crystal of urea(Civalleri, Doll, & Zicovich-Wilson, 2006) and other molecular crystal with known binding energy (BE) or sublimation enthalpy. One has to avoid the use of too few functions, which leads to drastic errors in reproducing experimental properties. Another effect to consider is the superposition of basis sets from neighboring atoms (BSSE); this is reduced if a large enough basis is used. We have employed three different type of sets; Ahlrichs' triple-split valence (TZP) basis set(Schafer, Horn, & Ahlrichs, 1992), the 6-21G basis and our modified 6-31G\* basis. For the latter two basis functions, the first digit indicates the number of Gaussian functions that represent core atomic orbitals, and the last two indicate the number of functions used for the valence orbitals. The TZP basis set is the largest one of the three sets employed here.

Full optimization with the different basis sets was performed. The results summarized in Table 1. Energies are reported to the last digit of the imposed tolerance for each self-consistent cycle ( $1 \times 10^{-7}$ ).  $V_0$  stands for the equilibrium unit cell volume in  $\text{\AA}^3$ , as calculated by relaxing all the cell and ionic degrees of freedom. The BE of the urea crystal was estimated to be  $-98.48$  kJ/mol, which compares well with the experimental(Ferro, Barone, Della Gatta, & Piacente, 1987) sublimation enthalpy of  $-94.3$  kJ/mol. From BE values, we see a basis set that reproduces qualitatively the experimental result. The BSSE lies between that of a contracted 6-21G\* basis, and the more expensive Ahlrichs basis set.

For calculations with localized basis sets, the effective pressure values corresponding to each compression value is obtained by fitting the results to a widely used Birch-Murnaghan (BM) equation of state (Birch, 1978). The fourth order BM equation of state has the following form;

$$P/B_0 = 3f(1+2f)^{\frac{5}{2}} \left[ 1 - \frac{1}{2} \left( \frac{\delta_3}{\delta_2} \right) f + \frac{1}{6} \left( \frac{\delta_4}{\delta_2} \right) f^2 + \dots \right] \quad (1)$$

Where;

$$V/V_0 = (1+2f)^{\frac{3}{2}} \quad (2)$$

And;

$$\frac{\delta_3}{\delta_2} = 12 - 3B'_0 \quad (3)$$

$$\frac{\delta_4}{\delta_2} = 9B_0 B''_0 + 9(B_0)^2 - 63B'_0 + 143 \quad (4)$$

This equation of state allows for larger range of volumes, pressures and other thermodynamic properties to be correctly predicted. Here,  $V$  is the unit cell volume at a given thermodynamic state,  $B_0$  stands for the equilibrium bulk modulus at zero pressure, while  $B'_0$  and  $B''_0$  represents the first and second derivative of the bulk modulus.

In order to obtain the anisotropic mechanical properties (namely the second order elastic constants) for NM and PETN, we use the finite strain method. By applying finite strains to the crystallographic unit cell, a new cell structure (representing the strained form) is obtained. The difference in energy (strain energy) can then be computed in terms of a polynomial expansion in strain tensor (Wallace, 1972);

$$E - E_0 = V_0 s_{ij} e_{ij} + \frac{V_0}{2} c_{ijkl} e_{ij} e_{kl} + \dots \quad (5)$$

In this case,  $E_0$  is the reference ground state energy, or the energy of zero-strain state;  $e_{ij}$  and  $e_{jk}$  are the Cartesian strain tensor components. The stress tensor components are  $s_{ij}$ , and  $c_{ijkl}$  is the elastic constants tensor. The first term vanishes in a zero-strain state. We can determine the corresponding elastic constants  $c_{ijkl}$ , by applying specific strain states to the reference system. Owing to the symmetry of the elasticity tensor, and to simplify, we employ

**Table 1**  
Formation energy of urea, as calculated from different basis sets. Total energy reported in atomic units (A.U.).

Basis set	Energy/A.U.	$V_0/\text{\AA}^3$	BSSE/KJ/mol	BE/KJ/mol
6-21G*	-449.7130153	136.345	97.05	-96.94
6-31G*M	-450.2513153	145.137	41.00	-98.48
Ahlrichs	-450.0698772	156.486	7.94	-88.38

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