

Study of Thermal Instability of HMX Crystalline Polymorphs with and without Molecular Vacancies Using Reactive Force Field Molecular Dynamics

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Abstract

The sensitivity of energetic materials can be identified by heat, friction, impact, shock, electrostatic charge, etc. A complexity of various factors may influence the sensitivity and among them are the crystal structure and the defects within the crystal very important. The explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) may exist in four crystalline polymorphs, denoted α , β , γ , and δ . It has been shown that β -HMX has the lowest impact sensitivity of them whereas δ -HMX has the highest, and that the density of the polymorphs decreases with increasing sensitivity. Knowledge and understanding of the relationship between polymorphism and chemical decomposition processes in crystalline HMX phases may enable improvement of existing energetic compounds or development of novel materials. Thermal instability may be strongly related to mechanical instability due to hot-spot mechanisms. In this work we apply reactive force field molecular dynamics (ReaxFF-MD) to study how the thermal stability of α - and β -HMX is affected by crystalline structure, molecular vacancies, and density. We have found decomposition temperatures of around 1550 K for both

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polymorphs, which is significantly higher than experimental results of around 550 K. However, by introducing molecular vacancies into the crystals the decomposition was calculated to occur at 400-600 K, in agreement with experimental values. The α polymorph was more sensitive than the β polymorph when vacancies were present. We also discovered that the β polymorph had better resistance against rupture of the N-NO₂ bond at higher crystal densities. These results may hint on the different impact sensitivity of the two polymorphs and highlight the influence of crystal structure, crystal defects, density, and temperature on the sensitivity.

Keywords: HMX, Crystalline polymorphs, Reactive force field, Molecular dynamics, ReaxFF-MD

1 Introduction

Thermal instability may be strongly related to mechanical impact due to the hot spot mechanism [39, 40]. Dissociation of molecules can proceed in various ways; by intermolecular vibrations caused by the so-called doorway modes, by thermal ionization, or by electronic excitations [7]. After electronic excitation the molecule can relax back to the ground state and release the energy as a photon, or undergo a non-radiative transition to the vibration stage (conversion). It may also decompose from the excited state and release an excess energy as nuclear motion. (See [12] for a review on electronic excitations). Phonons have in general wavenumbers less than 200 cm⁻¹, where molecular vibrations relevant to bond rupture have wavenumbers above 1000 cm⁻¹. Phonon energy must thus be converted to higher vibrations by the “multiphonon up-pumping” where the lowest modes are termed “doorway modes”. The dominant mechanism is inharmonic coupling of the excited phonon modes with low wavenumber molecular vibrations. These intermolecular vibrations lead to unimolecular endothermic or weakly exothermic decompositions which finally give excited vibration states of intermediate product series. The internal vibration energy of the products increases enormously since most of the chemical energy is initially released into vibration modes (see [36] for details). A strong correlation has been found between the number of doorway modes in the region 200-1000 cm⁻¹ and the impact energy [8, 45]. Fried and Ruggiero [8] reported that the energy transfer rate at a vibration frequency of 425 cm⁻¹ increases linearly with the impact sensitivity. This wavenumber corresponds to the nitro group motion. However, the different sensitivities of the polymorphs of HMX could not be explained [45]. A mechanism for hot-spot formation, based on defects inducing local increases in a harmonic coupling, has also been discussed [38].

It is reasonable to assume that lattice vacancies are the dominating structural point defects in molecular crystals. Interstitials are not favored energetically since displacement energy of a molecule into an interstitial position strongly exceeds

that of a vacancy formation. Moreover, as covalent bonds are much stronger than van der Waals interactions between molecules it should be much easier to create a molecular vacancy than an atomic or ionic vacancy. By quantum mechanics Kuklja [13] showed that cleavage of the N-NO₂ bond in RDX requires less energy if the molecule is isolated than if the molecule is placed in the bulk of the solid. It should be noted that even less energy is required to break the N-NO₂ bond if the molecule is located near a free crystal surface (*i.e.* at crystallographic molecular vacancies). Although energy barriers for the decomposition of molecules are reduced on surfaces with defects, the defects may also be able to accumulate or focus mechanical energy of impact/shock wave (hot-spot) and transfer it into sufficient energy to start a chemical reaction.

HMX is one of the most important energetic materials, as it is widely used in applications like explosives and rocket propellants. The molecule is an eight-membered ring system with four N-NO₂ groups and four CH₂ units. HMX may exist in four different crystalline polymorphs, denoted α , β , γ , and δ . The β polymorph has a chair conformation while the others have a boat conformation. The number of molecules in the unit cell is eight, two, two and six for the α , β , γ , and δ form, respectively. The unit cell of the γ polymorph includes a water molecule. The sensitivity order is: β (least sensitive) < α < γ < δ (most sensitive) and the sensitivity of the different polymorphs is anti-correlated with the density.

HMX decomposes by many possible mechanisms which are still debated in the literature. It appears that the N-NO₂ bond rupture is the first reaction step and that molecular vacancies lead to increased sensitivity [11, 29]. Kohno *et al.* [10] discovered a close relationship between the impact sensitivity of the different polymorphs and the total energy. They also introduced a parameter for HMX, defined as the difference between the N-N bond length in the gas phase and the N-N bond length in the crystal. The parameter correlated well with the impact sensitivity of the different HMX polymorphs. Lewis [15] performed DFT calculations of energetic profiles of intermolecular hydrogen transfer along an arbitrary least resistance trajectory. He concluded that the sensitivity trend may be due to the density variations. Reduced volume due to crystal packing hinders conformational changes in the molecules as the intermolecular hydrogen transfer progresses. Intermolecular hydrogen transfer can occur between adjacent molecules since it is a weak hydrogen-bonding-like interaction from a C-H bond in one molecule to the oxygen atom of a NO₂ group in an adjacent molecule (HONO reaction). Kuklja [14] concluded that a surface induced effect on electron charge is much more pronounced in δ -HMX than in β -HMX. For β -HMX the activation barrier for the cleavage of an N-NO₂ bond on the surface is approximately 30 kJ/mol lower than in the bulk, while this reduction is significantly larger for δ -HMX. The decrease of the activation barrier was assumed to be due to the polar nature of the (100) surface of HMX. It was speculated that the interaction between the dipole moment of the β -HMX molecule and the polar (100) surface induces an electronic density redistribution, which in turn could explain the difference in sensitivity [14].

Redistribution of charges only near the crystal surfaces would not necessarily explain the difference in crystal density of the polymorphs. Indeed, the crystal density for a given compound is dependent on the electrostatic and the van der Waals forces that describe the intermolecular interactions. Due to different conformations (chair/boat) the N-NO₂ units may be twisted in separate ways. The corresponding charges in the NO₂ group can thus deviate from α -HMX (or δ -HMX) to β -HMX.

Molecular dynamics (MD) can be used to study non-steady conditions during heating caused by hot-spots. The approach is to perform a number of density functional theory (DFT) calculations to compute interatomic forces by quantum mechanics and simultaneously calculate the position time history of the atoms. MD is capable of revealing changes in the atomic and electronic structures that may not be captured by steady state calculations [17, 18, 24, 25, 30], see also a review by Rice and Byrd [26]. However, DFT based MD methods are currently computationally too costly to describe most processes at realistic conditions, especially when chemical reactions need to be described. MD has been most useful for understanding unimolecular and simple bimolecular processes of small molecules.

The limitation of DFT based MD has to some extent been overcome by the development of reactive force field molecular dynamics (ReaxFF-MD) that can describe chemical reactions in a much more computationally efficient way [2, 20, 32-34, 41, 42, 46, 48]. ReaxFF-MD is now a practical tool for high-temperature and high-pressure MD of realistic and chemically reacting systems. ReaxFF-MD does not assume a fixed connectivity assignment for the chemical bonds, as the bond order is calculated from the interatomic distance which changes continuously throughout the reaction coordinate. Formation and rupture of bonds is therefore allowed during a simulation. This concept was first introduced by Tersoff [37]. The parameters of the interatomic potentials are “trained” to best fit thousands of DFT calculations on small clusters of various combinations of atomic species. The parameters of the nitramines are for instance based on a large number of *ab initio* quantum mechanical (QM) calculations. More than 40 reactions and more than 1600 equilibrium molecules have been used. The major non-trivial problem is whether the potential in ReaxFF-MD is able to produce reasonable dynamics on systems outside its training set. ReaxFF-MD has been applied to describe the thermal decomposition of RDX [21, 33], TATP [42], TATB and HMX [46, 48]. ReaxFF-MD predicts that within 30 ps TATB decomposition initiates the formation of large carbon clusters, whereas HMX decomposition will yield small product molecules. This is in full agreement with experimental observations and demonstrates that ReaxFF-MD is a viable method [46].

Zhang *et al.* [47] developed a method for rapid assessment of impact sensitivity by using ReaxFF-MD in combination with rapid compression of RDX and HMX crystals. The simulation suggested a critical compression ratio of 40 % at detonation

speed. For the different polymorphs of HMX it was found that impact sensitivity increases in the order $\beta < \alpha < \gamma < \delta$. Zhou *et al.* [52] showed by using ReaxFF-MD that shock directions normal to the (100) and (011) planes of β -HMX are less sensitive than a shock direction normal to the (010) plane. The reason for this difference in sensitivity is the large shear stress barriers arising from steric overlap of molecules in adjacent slip planes during shear motion induced by shock direction normal to (010) plane.

Wen *et al.* [43] used ReaxFF-MD to demonstrate that twinned HMX crystals are much more shock sensitive than perfect HMX crystals. Long and Chen [16] studied the reaction kinetics of HMX by using ReaxFF-MD and observed that the detonation velocity and pressure agreed very well with experimental results. Zhou *et al.* [49] applied ReaxFF-MD to examine compression effects on thermal shock initiated β -HMX. Their calculations showed initiation of a thermal shock wave with an average velocity of 3.32 km/s and also that compression accelerated the thermal-mechanical wave significantly. Zhou *et al.* [50] used ReaxFF-MD when they found that δ -HMX was less sensitive to shock normal to the (001) plane. They obtained significant anisotropies in the thermo-mechanical and chemical response. In another work Zhou *et al.* [51] performed ReaxFF-MD calculations to show that α -HMX was sensitive to shock in the direction normal to the (010) plane. The molecular origin of the anisotropic sensitivity was suggested to be the intermolecular steric arrangements across a slip plane induced by shock compression. Wen *et al.* [44] applied ReaxFF-MD to study cluster evolution during the early state of heating of explosives and its relationship to sensitivity. It was observed that clustering tendencies for explosives like β -HMX, TATB and PETN became less pronounced when the oxygen balance was increased. That is, clusters can form more readily in a high explosive with a more negative oxygen balance. Clusters may retard detonation reactions and widen the reaction zone. Sewell *et al.* [28] used molecular dynamics simulation to study the elastic properties of different polymorphs of HMX.

In this work we have applied ReaxFF-MD to study the thermal decomposition of the α - and β -HMX polymorphs at different densities, with and without molecular vacancies defects. The simulations were performed with the ADF (rev.-2014.01) program package. By applying a constant heating rate and a maximum temperature, we mimicked hot-spots at different locations. The decomposition time (or temperature) was recorded for the two polymorphs when assuming various numbers of vacancies and different densities. Molecular vacancies were modeled by initially removing at least one HMX molecule from the unit cell. The quantum chemical calculations were carried out at the B3LYP/6-31(d) level. Section 2 presents the HMX polymorphs and shows some important parameters. Section 3 shows results from the ReaxFF-MD, while conclusions and some discussions are given in Section 4.

2 The HMX polymorphs and some important parameters related to sensitivity

The orthorhombic α -HMX has a boat conformation while the monoclinic β -HMX has a chair conformation, as shown in Figure 2.1. In the boat conformation all four NO₂ groups are on the same side of the ring, while in the chair conformation two neighboring NO₂ groups are on one side of the ring and the other NO₂ groups are on the opposite side of the ring. So the β -HMX is less polar and more symmetric compared to the α -HMX.

The experimental densities are 1.84 and 1.96 g/cm³ for the α and β form, respectively. Various crystal properties are given in Table 1.

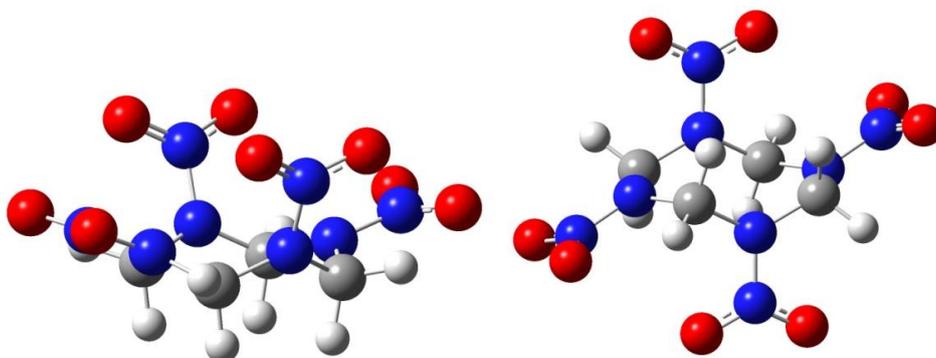


Figure 2.1: The α -HMX (left) and the β -HMX (right) conformation

It has so far not been developed any general theory making it possible to calculate the sensitivity precisely for all the groups of energetic molecules. High correlation applies for shock sensitivity and shock initiation pressure and for shock sensitivity and the largest positive Mulliken charge [35]. A close relationship between the dissociation energies and the electrostatic potential of has been found for the C-NO₂ bond. Thus, the electrostatic potential is a structural parameter related to the strength of the C-NO₂ bond [22]. Pospíšil *et al.* [23] examined a possible crystal volume factor in impact sensitivities of some energetic materials.

For energetic materials with similar structure or with similar thermal decomposition mechanism, Zhu and Xiao [53] experienced that the smaller the band gap, the easier the explosive ignitions during impact, and the easier the electron transfer from the valence band to the conduction band. For HMX it has been found that the band gap decreases with increasing hydrostatic pressure [54]. A strong correlation between impact sensitivity and shock sensitivity has also been observed [31].

The Gaussian09 program package [9] has been used to calculate some of the above mentioned sensitivity parameters of HMX. In Table 1 it is shown that β -HMX is slightly more stable than α -HMX which has a lower total energy than the β -HMX by 10 kJ/mol. The energy of the weakest N-NO₂ bond is 167 kJ/mol and 170 kJ/mol for α -HMX and β -HMX respectively. The distance from the hydrogen atom to the nearest NO₂ group is 2.12 Å for α -HMX and 2.15 Å for β -HMX. The Mulliken charge for the NO₂ group is -0.11 a.u. and -0.14 a.u. for the α - and β -polymorph, respectively. The number of molecular vibration modes in the range 200 to 700 cm⁻¹ is 16 for α - as well as for β -HMX.

Table 1: Properties of α - and β -HMX polymorphs

Polymorph	α -HMX (Boat)	β -HMX(Chair)
Space group	Fdd2 ^a	P2 ₁ /c ^b
Lattice constants a (Å) x b (Å) x c (Å)	15.14 x 23.89 x 5.91 ^a	6.54 x 11.05 x 8.70 ^b
Molecules in unit cell	8 ^a	2 ^b
Total energy (kJ/mol)	-3141522 ^c	-3141532 ^c
Experimental impact energy (kg/cm ²)	0.20 ^d	0.75 ^d
Experimental impact energy (J)	-	7.2 ^e
Calculated impact energy (J)	7.6 ^c	7.6 ^c
Bond energy (kJ/mol)	167 ^c	170 ^c
Minimum distance H-(ONO) (Å)	2.120 ^c	2.147 ^c
Mulliken charges NO ₂ (a.u.)	-0.11 ^c	-0.14 ^c
Doorway modes 200-700 cm ⁻¹	16 ^c	16 ^c
HOMO/LUMO gap (eV)	6.35 ^c	5.87 ^c
Experimental density (g/cm ³)	1.84 ^a	1.96 ^f
Predicted density (g/cm ³)	1.90 ^g	1.97 ^g

a: Ref [3]. b: Ref [4]. c: This work, Gaussian B3LYP/6-31G(d). d: Ref [53]. e: Ref [27]. f: Ref [19]. g: This work, Materials Studio 7.0.

The HOMO/LUMO difference is somewhat larger for α -HMX than for β -HMX. The calculated impact sensitivity of β -HMX seemed to be in good agreement with the experimental values. These impact sensitivities were calculated by using a model derived by Rice and Hare [27] based on the correlation between the electrostatic potential and the impact sensitivity. However, this model could not distinguish between the conformations. The deviations in calculated properties

between the boat and the chair conformation may be too small to explain the observed difference in impact energy. The density of a crystal is sensitive to the electrostatic and the van der Waals energy. By applying charges set by the Compass force field within the Materials Studio 7.0 Polymorph predictor [1, 5], only the β -HMX values did fit well to the experimental results. The spread within the different space groups could not explain why α -HMX did not fit. It appears that a significant difference in charges of atoms on α -HMX and β -HMX are necessary to explain the difference in density between the two polymorphs.

3 ReaxFF-MD results

The unit cells were first combined into super-cells which consisted of either $2 \times 1 \times 3$ unit cells for α -HMX or $4 \times 2 \times 3$ unit cells for β -HMX. Both super-cells contained 48 molecules. Then the cell constants and molecules were allowed to relax in order to find the energy minimum of the system at ambient pressure and $T = 0$ K. The high energy force field was applied in all MD calculations. The number of unit cells was $2 \times 1 \times 3$ for α -HMX and $4 \times 2 \times 3$ for β -HMX. The initial temperature was set to zero degrees K. The heating rate was set to a constant of 2 K per fs up to maximum temperature. One iteration corresponded to 0.1 fs. We used 2000 K, 3000 K, or 4000 K as the maximum temperatures during heating. The defects were introduced by initially deleting molecules in the crystal and in this way create vacancies. By deleting several molecules from the structure, vacancies may be connected into larger cavities within the crystal.

Figure 3.1 shows the decomposition of β -HMX for a run to a maximum temperature of 2000 K. We observe that the N-NO₂ bond starts to dissociate after about 4500 iterations which corresponds to approximately 1550 K. The HONO molecule is formed after about 7000 iterations.

Figure 3.2 displays the temperature of the first dissociation of the N-NO₂ group. The numerical simulation shows consistency as the choice of maximum temperature did not affect the dissociation temperature. The number of defects strongly influences the dissociation temperature: the higher number of defects, the lower the dissociation temperature. For two or three defects the dissociation temperature is around 400 K. This is below the melting point of 282 °C (555 K) which is close to the dissociation temperature. The simulated dissociation temperature is thus in reasonable agreement with the measured value. The literature reports that thermal stability of α -HMX is somewhat higher than β -HMX. Figure 3.3 shows the corresponding result for the β -HMX. The results are much the same as for α -HMX with small differences that may not be significant.

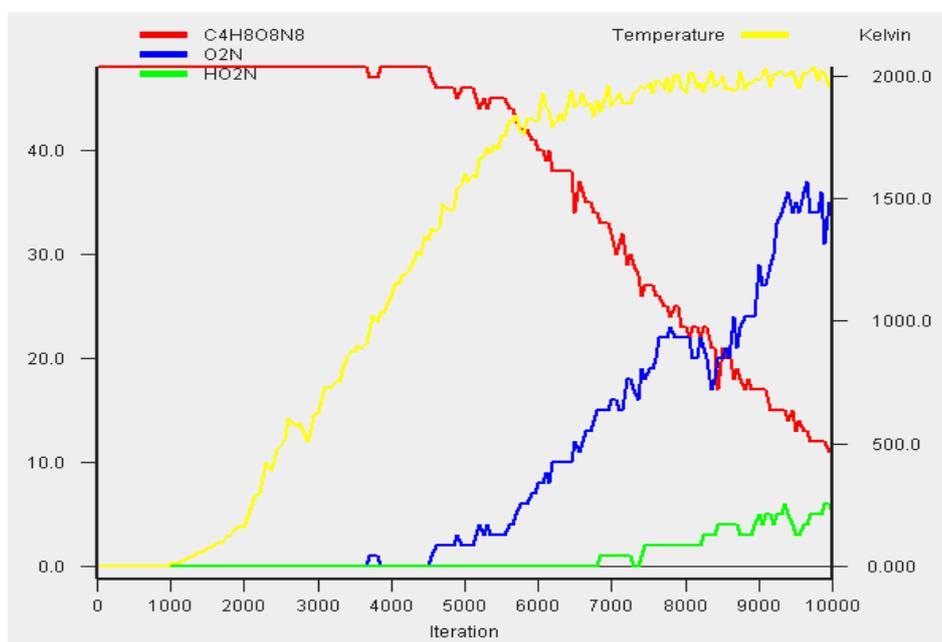


Figure 3.1: Decomposition of β -HMX using ReaxFF. The number of molecules (left axis) and the temperature (right axis) vs. the number of iterations

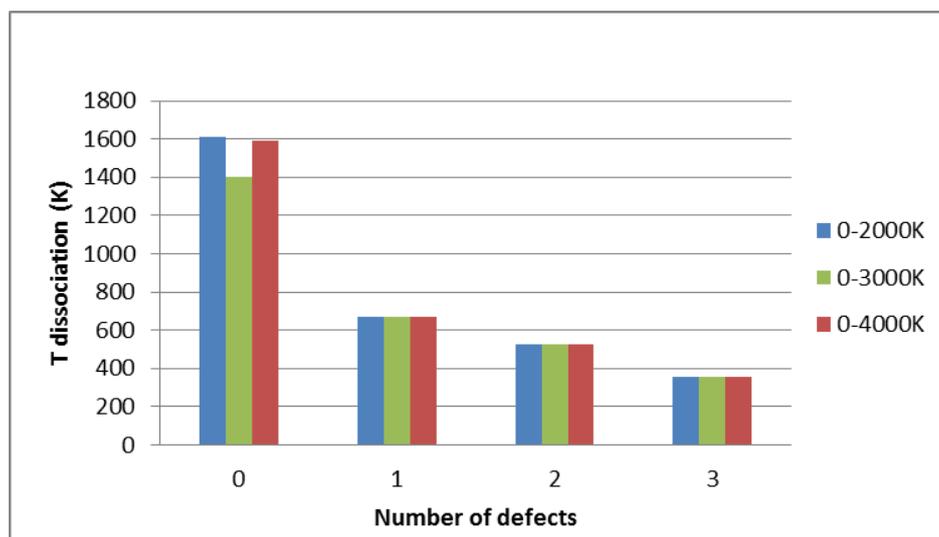


Figure 3.2: The temperature of the first dissociation of N-NO₂ of α -HMX, density 1.85 g/cm³

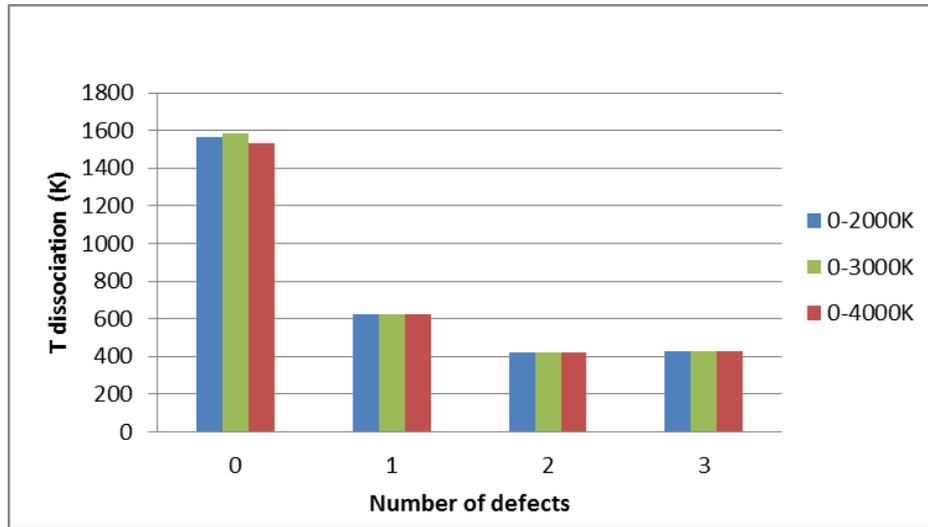


Figure 3.3: The temperature of the first dissociation of N-NO₂ of β -HMX, density 1.85 g/cm³

During shock or impact the density at dissociation is larger than the crystal density at ambient conditions. The density in the detonation front is around 1.5 times the crystal density. We apply a pressure of 40 GPa on the structure to mimic the detonation density. Figure 3.4 shows the simulated dissociation temperature of N-NO₂. Without vacancies the dissociation temperature is slightly higher than in Figure 3.2 where a lower density was applied. When one vacancy is introduced in the structure, the dissociation temperature decreases significantly.

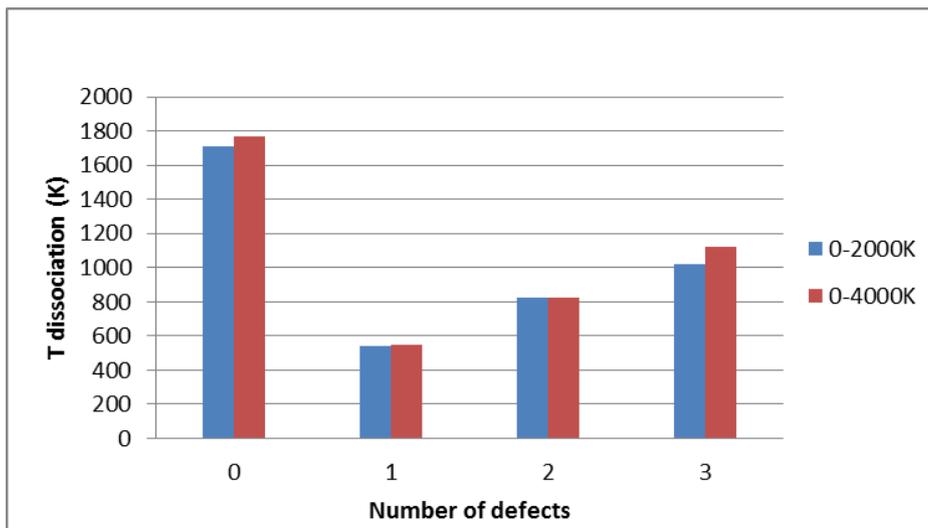


Figure 3.4: The temperature of the first dissociation of N-NO₂ of α -HMX, density 2.83 g/cm³

Figure 3.5 shows the corresponding results for β -HMX. Without crystal defects we predict a similar dissociation temperature for β -HMX as for α -HMX. For vacancies the dissociation temperature is somewhat lower than without vacancy. For one, two or three defects the dissociation temperature of N-NO₂ for β -HMX seems to be larger than for α -HMX. N-NO₂ bond rupture seems to be less dependent on defects at higher densities.

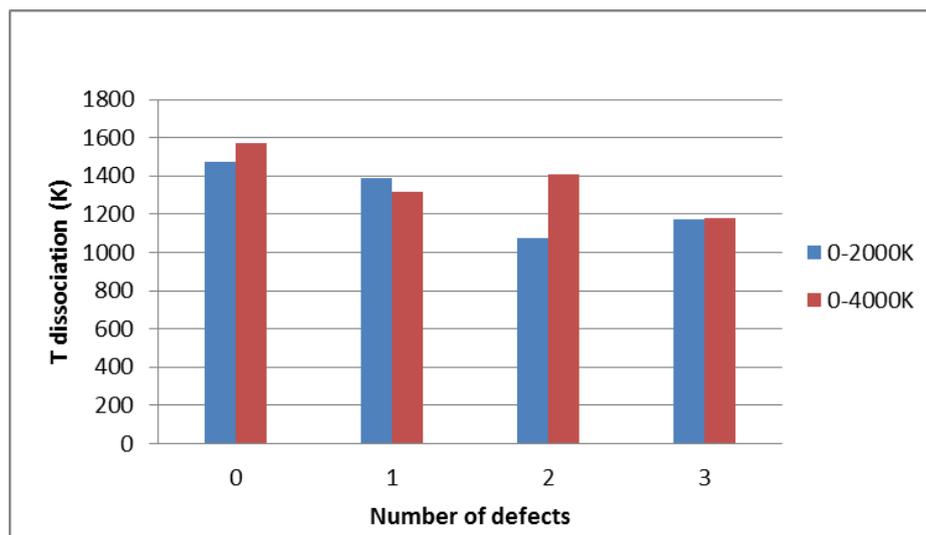


Figure 3.5: The temperature of the first dissociation of N-NO₂ of β -HMX, density 2.87 g/cm³

By studying the molecular reactions as a function of temperature carefully it appears that also dimerization took place at high density. In this reaction two HMX molecules combine into one molecule.

In Figure 3.6 we compare the dissociation temperatures of HMX polymorphs (density 1.85 g/cm³) with that of triaminotrinitrobenzene (TATB), a compound that is much less shock sensitive and substantially more stable than HMX [44]. We see that defects do not affect the dissociation temperature of TATB. (The small difference seen in Figure 3.6 is probably within the error margin). This may be explained by the fact that the initial reaction of TATB is found to be completely due to dimerization and not to C-NO₂ dissociation. It may be suggested that dimerization is only modestly influenced by crystal defects. When two TATB molecules are dissociated due to dimerization, they are squeezed together and C-NO₂ bonding on the vacancy surfaces may be of less importance. It is notable that Doherty and Watt [6] concluded that impact sensitivity was not a good predictor of shock sensitivity for three different types of RDX. This indicates that hot-spot enhancement by crystalline defects is less important during impact than in shock. In our ReaxFF-MD simulations the crystal structures of the HMX polymorphs seemed to melt at higher temperatures and become fluid-like.

This may explain the equality of the simulated high dissociation temperatures of α -HMX and β -HMX when vacancies are not applied. It is forecasted that at higher temperatures the N-NO₂ bond dissociation may not be a good indicator of sensitivity. Reactions taking place before the N-NO₂ bond is broken may be important, *e.g.* dimerization and intermolecular hydrogen transfer to the NO₂ group.

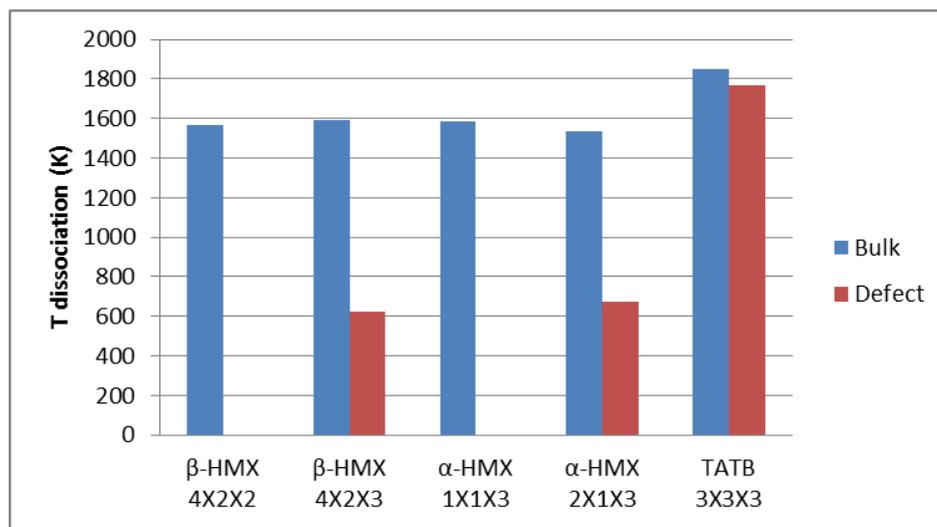


Figure 3.6: The temperature of the first dissociation of N-NO₂ of α -HMX and β -HMX and dimerization of TATB. The density is 1.85 g/cm³ for HMX and 2.20 g/cm³ for TATB

For all cases without structural modeled defects the dissociation temperature of N-NO₂ is around 1600-1800 K, regardless of the type of polymorph. By making a structure with only one defect the N-NO₂ dissociation temperature is reduced to 600 K for both α -HMX and β -HMX.

Finally, to show numerical consistency Figure 3.6 show that the number of unit cells did not influence the result. We apply two sets for α -HMX and β -HMX.

4 Discussion and conclusion

Energetic materials may be sensitive to several external stimuli. The impact sensitivity of explosives may be determined by a series of material characteristic, *e.g.* crystal structure and defects, whereas the thermal instability may have strong relation to mechanical instability. We have studied two of the crystalline HMX polymorphs (α and β), where the α polymorph is the most sensitive. Their thermal stability was investigated as a function of crystalline structure, molecular vacancies, density and temperature. By applying reactive force field molecular dynamics (ReaxFF-MD) on perfect HMX crystals decomposition temperature of

around 1550 K was calculated. This value was 1000 K above experimental results, but when defects were introduced into the structures, the calculated decomposition temperature became close to measured values. We also found that calculations on HMX crystals with vacancies discriminated between α - and β -HMX regarding sensitivity. The α polymorph was the most sensitive one, which is in agreement with practical observations.

This may hint on differences in impact sensitivity of the two polymorphs and highlights the influence of crystal defects possess on sensitivity. At high temperatures the crystal structure of α -HMX and β -HMX disappears and they become fluid-like. This effect may explain why the differences between the bond dissociation temperatures are relatively small for the α -HMX and β -HMX with no vacancies. It is forecasted that at higher temperatures the N-NO₂ bond dissociation may not be a good indicator of sensitivity. Reactions like dimerization and intermolecular hydrogen transfer to the NO₂ group may be important, as they might occur before the N-NO₂ bond is broken.

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Appendix A

Table A1: Density and energy calculated for HMX polymorphs (Materials Studio 7.0)

HMX polymorph	Space group	Density (g/cm ³)	Total energy (kJ/mol)	van der Waals energy (kJ/mol)	Electrostatic energy (kJ/mol)
α	C2/c	1.895	-1108.04	-24.45	-1063.58
α	P2 ₁ /c	1.930	-1107.96	-25.63	-1062.65
α	P2 ₁	1.967	-1106.17	-32.99	-1053.57
α	P2 ₁ 2 ₁ 2 ₁	1.899	-1103.75	-28.05	-1062.04
α	Pbca	2.000	-1102.86	-37.36	-1047.70
α	P-1	1.844	-1099.69	-23.70	-1057.59
β	P2 ₁ /c	1.967	-1107.34	-31.82	-1062.14
β	P2 ₁	1.975	-1106.67	-24.70	-1071.80
β	P2 ₁ 2 ₁ 2 ₁	1.924	-1103.23	-28.29	-1058.81
β	Pbca	1.938	-1102.73	-30.56	-1058.80
β	C2/c	1.894	-1101.75	-23.55	-1063.90
β	P-1	1.870	-1101.13	-22.50	-1063.98

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