Abstract Submitted
for the SHOCK11 Meeting of
The American Physical Society

Comparative analysis of decomposition reactions in gaseous and crystalline β-HMX ONISE SHARIA, MAIJA KUKLJA, University of Maryland College Park — Most quantum chemical studies focus on determining reaction paths and reaction barriers. We will illustrate that knowing only those parameters is insufficient for finding the dominant mechanism. One needs to calculate both the activation barriers and the reaction rates. We present a density functional theory based modeling of several possible detonation initiation reactions in HMX, including its gas phase, a perfect crystal, and a crystal containing vacancies, voids or internal surfaces. We show that the N-NO_2 homolysis is the most favorable decomposition reaction in the gas phase. In the crystalline phase, this reaction has a higher activation barrier and becomes much slower due to the densely packed structure of HMX. As a result, two other reactions, the HONO elimination and NONO rearrangement, would compete with the N-NO_2 homolysis in an ideal crystal. Practical samples however contain a lot of imperfections hence we also studied an effect of voids on the chemical decomposition. We established that a large space in the vicinity of voids facilitates the N-NO_2 break, and, similarly to the gas phase, the N-NO_2 reaction proceeds with the highest rate. The conclusions and revealed trends help to provide a consistent interpretation to experimental data.

Onise Sharia
University of Maryland College Park

Date submitted: 16 Feb 2011 Electronic form version 1.4