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A Computational Study of the Vibrational Spectrum of Crystalline RDX

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Abstract

We are presenting results on the eigenmode spectrum of the RDX crystal from a computer model including molecular and lattice degrees of freedom. The model is based on the force field by Boyd et al [1] . We have calculated vibrational eigen spectra for various large models of the molecular crystal, and compared the modal distribution with the modes of isolated molecules. Projections of the eigenmodes onto various molecular and lattice degrees of freedom are presented. Our results indicate that dihedral rotations and wagging motions of the nitro groups are capable of coupling with lattice modes in the region between 175 and 220 cm^{-1}.

Background

The vibrational spectrum of this high-energetic material is of interest due to two main questions:

(1) There have been increased efforts to develop the possibility of unobtrusive explosives detection using Terahertz spectroscopy - a frequency region dominated by slower molecule modes and lattice vibrations.

(2) During the initiation of a detonation, shock wave energy is transferred from lattice degrees of freedom to internal degrees of freedom of the molecules. Certain vibrational modes – so-called doorway modes- may provide a mechanism for this energy transfer.

Model

- periodic model with 3×3×3 primitive cells (4536 particles, 216 molecules)
- Geometry optimizations using conjugate gradient method
- Ring structure presents as chair (C), boat (B) or twist (T).
- The three nitro groups can be in axial (a) or equatorial (e) orientation.
- Most stable free conformer: Caaa
- Present in α-RDX: Caae
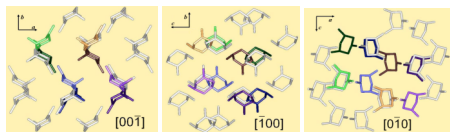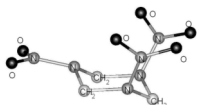
Primitive cell (Pbca symmetry); O and H are omitted.

Force field

Bending and torsional parameters, as well as the long-range interactions have been fitted in order to stabilize the Pbca crystal while allowing flexible molecules.

$$U_{intra} = U_{bond} + U_{bend} + U_{tors} + U_{vdW} + U_{Coulomb} .$$

$$U_{bond} = \sum_{bonds} D_e^{ij}\left(1 - e^{-\alpha\left(r_{ij} - r_{ij}^0\right)}\right)^2$$

$$U_{bend} = \sum_{bends} k_{ijk}\left(\vartheta_{ijk} - \vartheta_{ijk}^0\right)^2$$

$$U_{tors} = \sum_{torsions} \sum_{m=1}^{3} a_m^{ijkl}\left(1 - \cos b_m^{ijkl}\,\varphi_{ijkl}\right)$$

Long-range:

$$U_{VdW} = \sum_{i<j} A_{ij}\exp\left(-B_{ij}r_{ij}\right) - \frac{C_{ij}}{r_{ij}^6}$$
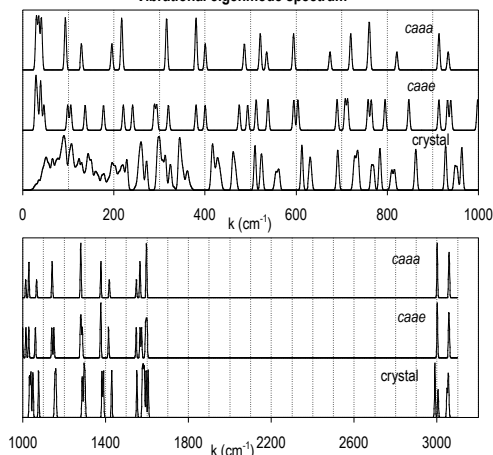
$$U_{Coulomb} = \sum_{i<j} f_{cut}(r_{ij})\frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}}$$

Long-range interactions were handled using smooth cutoff functions with a range of 15 Å.

## Projections of eigenmodes onto internal degrees of freedom

Center-of-Mass motion

Rotations

Translations

Bond stretches

NO, NN, CH, CN

Bending Motions

HCH, NCH, ONO, NNO, CNN, NCN

Dihedral Motions

(CNC)-N, CNNO, CNCH, CNCN
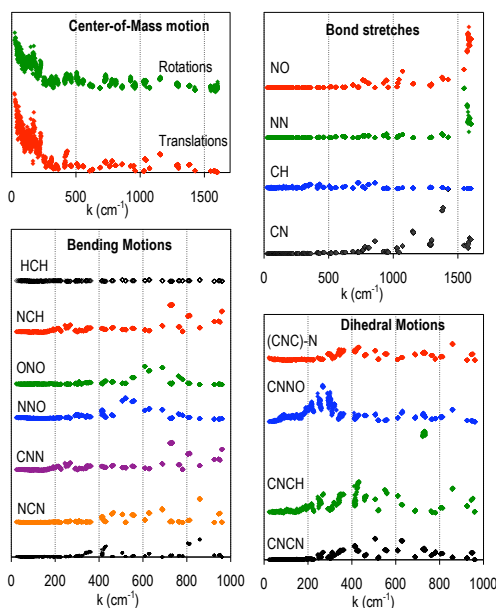
Vibrational eigenmode spectrum

caaa, caae, crystal

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Correlations

There are groups of eigenmodes in the crystalline system for which nitro dihedral rotations and lattice motions are correlated. Two correlation maps for the contributions of center-of-mass translations and molecular dihedral rotations in the crystal eigenmodes are shown below.
The red and blue modes are found between 175 and 220 cm^{-1}.

Center-of-mass translation — CNNO dihedral rotation

Center-of-mass translation — CNCH dihedral rotation
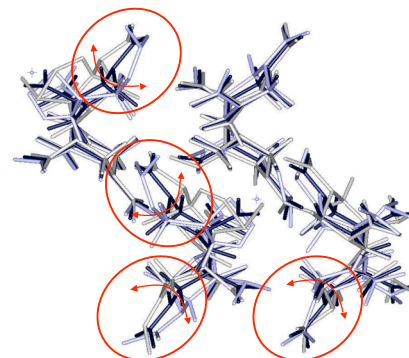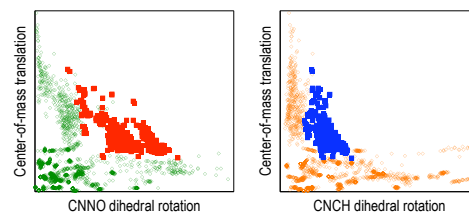
Conclusions

(1) The vibrational eigenmode spectrum of two molecule conformers and crystalline α RDX has been analyzed.

(2) Bond and bending modes are not significantly changed if the molecule is embedded in the crystal. Most lattice modes can be found in the range below 500 cm-1.

(3) The eigen modes have been projected onto various internal degrees of freedom. Lattice modes can be identified by center-of-mass motions of the molecules.

(4) Potential doorway modes have been identified between 175 and 220 cm^{-1}, in which modes combine significant center-of-mass motion with rotations of the nitro side group. These modes can facilitate the transition of energy from lattice to internal degrees of freedom. In particular, the involvement of the nitro group would indicate a pathway for the initial break-down of a molecule.

(5) Further work is directed at the influence of vacancies, as well as at the influence of high pressure onto the vibrational properties of the crystal.

[1] Sylke Boyd, Matthew Gravelle, and Peter Politzer, *Nonreactive molecular dynamics force field for crystalline hexahydro-1,3,5-trinitro-1,3,5 triazine*, J. Chem. Phys. 124, 104508 (2006).