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Surface Effects on the Crystallization of Cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) and the Consequences for its N K X-ray Emission Spectrum

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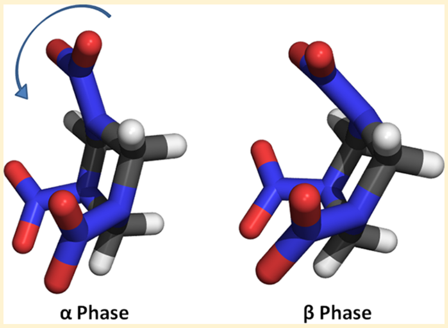
ABSTRACT: Recent studies of the crystallization of cyclotrimethylene-trinitramine (RDX) have shown that the presence of the *α*- and *β*-phases of the compound is sensitive to the substrate when using drop cast crystallization methods. The specific phase has potential consequences for measurements of the nitrogen K X-ray emission spectrum (XES) that were recently reported for this compound using samples crystallized on In metal substrates. We have determined that the crystallization of RDX on a clean In metal substrate starts out completely as the *β*-phase but progressively incorporates the *α*-phase as the film thickens. In addition, we have carried out additional molecular orbital calculations of the N 1s X-ray fluorescence from the valence band, comparing the results expected from the *α*-and *β*- phases. The differences due to the presence of the *β*-phase instead of, or in addition to, the *α*-phase appear to be minimal.



INTRODUCTION

The energetic material cyclo-1,3,5-trimethylene-2,4,6-trinitramine, commonly known as RDX, has been observed to occur in four known crystal phases designated *α*, *β*, *γ*, and *ε*.[1−5] Two of these phases, *γ* and *ε*, are only observed under high pressure.[2,5,6] There is also evidence of another high pressure phase, *δ*; however, no crystal structure has been determined yet.[7,8] Of the remaining phases, the *β*-phase is considered metastable,[4,9−11] and the *α*-phase is the phase that is normally assumed to be present at standard temperature and pressure (STP).

The X-ray absorption and emission spectra for RDX and other energetic nitrogen compounds have recently been studied both experimentally and theoretically.[12] Part of the motivation for these studies, aside from considerable chemical interest, is the possibility that the these emission spectra have potential for forensic identification. Reasonable qualitative agreement was attained in that work between the experimental N K X-ray emission spectra (XES) of RDX and theory, using two different methods of calculation that assumed the crystal structure of the *α*-phase. The experimental spectra were obtained by excitation with synchrotron radiation of RDX that was crystallized from solution on In metal foil substrates.

Recent work on the crystallization of RDX on ordered substrates using Raman spectroscopy has determined that the *β*-phase may be nucleated more commonly than previously suspected.[13,14] Furthermore, the *β*-phase may be more stable than has been reported.[14]

In light of this recent work on RDX, we have determined, using Raman spectroscopy, that RDX samples crystallized by drop casting from solution on In metal foil substrates, in the same manner used to fabricate the samples for the XES study, in fact crystallize initially almost exclusively in the *β*-phase. With continuing sample deposition, some *α*-phase is also observed to be present.

As a consequence of this unexpected result, we have also reanalyzed the X-ray emission spectrum calculations assuming the *β*-phase of RDX, which has a different molecular conformation and packing structure. The crystal symmetry of the *α*-phase is orthorhombic (*Pbca*). In that structure, two of the nitro groups are in pseudoaxial positions in relation to the carbon−nitrogen ring, and the last nitro group is in a pseudoequatorial position in relation to the ring. The *β*-phase, by way of contrast, has all three nitro groups in a pseudoaxial position in relation to the carbon−nitrogen ring, which leads to a C_{3v} crystal packing symmetry in the bulk. We focused on determining if different emission spectra arise from these structural differences in the *α*-and *β*-phases of RDX (Figure 1).

In our previous report[12] we used an older[1] crystallographic determination of the *α*-phase of RDX. Here we present results using a newer structural refinement[3] of this phase. Both of these structural determinations show that the *α*-phase is composed of

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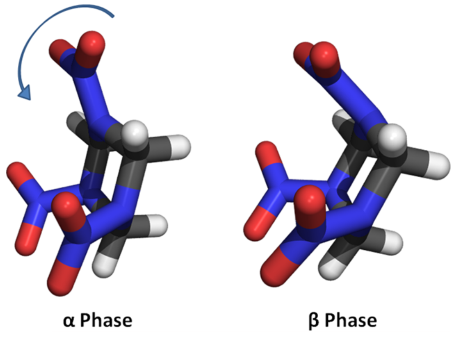

Figure 1. Structure of the symmetry-unique molecular units in the *α*- and *β*-phases of RDX. The arrow highlights the equatorial to axial change in the torsion angle of one of the NO_2 units, which is the most distinct difference between the two phases.

symmetry-unique molecules but show slight differences in the region surrounding the N atoms. As demonstrated in ref 12, these regions are key to understanding the observed emission spectra. The calculations were repeated for the structure of the *β* phase.[4] This phase is composed of two symmetry-unique RDX molecules and also has a small difference in the neighborhood of the N atoms.

EXPERIMENTAL SECTION

A commercial solution of RDX normally used as a purified standard was obtained at a concentration of 20 mg/mL in acetone. Drop-cast crystallization of 1 *μ*L drops of RDX solution was performed directly on the 99.999% MARZ-grade indium metal substrate. Each drop was allowed to evaporate completely before analysis by Raman spectroscopy. Initially, one drop of RDX solution was used for analysis; however, subsequent experiments were performed with additional drops of RDX solution directly on top of the previous one, up to 5 drops total.

Single crystal Raman spectroscopy was obtained with a confocal Raman microscope equipped with a 514 nm laser and a 2400 line/mm grating and calibrated against a Si wafer standard. The instrument was interfaced with an optical microscope for purposes of alignment and focus and a magnification factor of 20× or 100× was typically used. Spectra were collected in extended scan mode from 100 to 3200 cm^{-1}. One accumulation required a 10 s exposure time after background removal. This range and these conditions enabled unambiguous identification of individual crystal forms.

THEORETICAL

The theoretical methods used here are described in detail in ref 12. Briefly, we compute the nonresonant X-ray emission intensity within the "frozen-orbital" approximation as implemented in the StoBe-deMon[15] density functional theory (DFT) code. This approach uses Kohn−Sham molecular orbitals as single-particle states, and the excited states are represented by a single Slater determinant formed from the ground state orbitals. The basis set and exchange−correlation functional are those used in ref 12. The spectra were uniformly broadened to match experimentally observed broadening of the principal features. The structural models were built on the basis of the crystallographic structures determined in refs 1, 3, and 4. As in ref 12, we find that intermolecular interactions have a negligible effect on the emission spectra, resulting in single-molecule models that provide converged results.

RESULTS

The experimental results comparing Raman spectra of bulk *α*-RDX and RDX crystallized on In foil are shown in Figure 2.

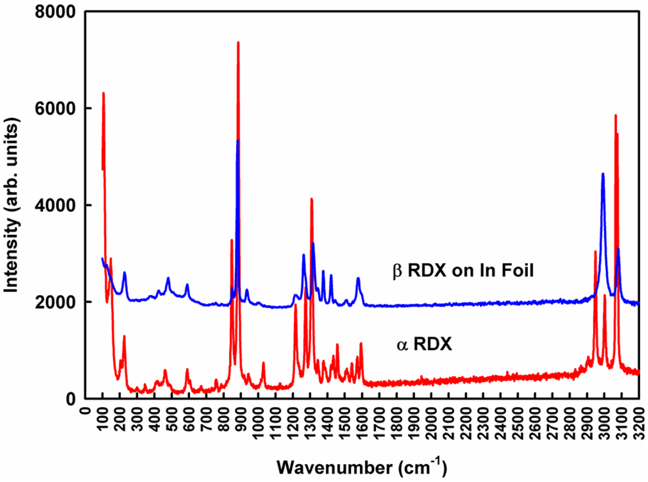

Figure 2. Raman spectra of *α*-RDX (red) and *β*-RDX grown on In foil (blue).

The RDX crystallized on In foil shows unmistakable characteristics of the *β*-phase. The two forms can be distinguished in three separate regions of the spectra. In the ring breathing mode, the *β*-RDX peak is downshifted by 6 cm^{-1} and centered at 877 cm^{-1} as compared to that for *α*-RDX, which is centered at 833 cm^{-1}. The downshifting of the *β*-RDX peak indicates less ring strain than in *α*-RDX. In the N−O stretching region *β*-RDX has one broad peak centered at 1574 cm^{-1}, and *α*-RDX has three sharp peaks centered at 1540, 1570, and 1594 cm^{-1}. In the C−H stretching region *β*-RDX has two peaks centered at 2989 and 3075 cm^{-1}, and *α*-RDX has four peaks centered at 2947, 3000, 3065, and 3075 cm^{-1}. The higher symmetry of the *β*-RDX conformation reduces the number of peaks seen in the N−O and C−H stretching regions as compared to the *α*-RDX spectrum.[13]

Figure 3 shows the theoretical X-ray emission spectra for the different structures. The structures of the RDX molecules determined by Choi and Prince[1] and Hakey et al.[3] for the *α*-phase have an rms deviation of the atomic positions of only 0.08 Å^2 and are very similar. The rms deviation between the *α*-

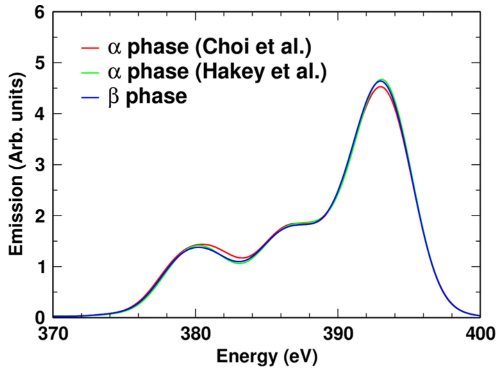

Figure 3. Theoretical N 1s K X-ray emission spectra of the *α*- and *β*-phases of RDX. For the *α*-phase, two structural models are shown, whereas for the *β*-phase, the average spectrum from the symmetry-unique RDX molecules is shown.

and β-phase molecules is larger, at about 0.40 Å^2. This larger difference arises mostly from the different orientation of one of the NO_2 units, as shown in Figure 1. The local structure around the N atoms, however, remains mostly unaffected. On average, the CN bonds in the Choi structure are 1.45 Å, compared to 1.46 Å in the Hackey structure and 1.45 and 1.46 Å in the two RDX molecules of the β-phase. The NN bonds are also quite similar with an average bond distance of 1.38 Å (Choi), 1.39 Å (Hakey), and 1.40 Å for either molecule of the β-phase. Finally, the NO bonds are 1.21 Å (Choi), 1.22 Å (Hakey), and 1.21, 1.22 Å for the β-phase.

Given that the X-ray emission spectra are dominated by the p density of states (pDOS) around the N atoms, and considering that none of the structural changes described above have a large effect on the pDOS, we expect minimal changes in the theoretical XES. For the β-phase we find that the symmetry-unique molecules give emission spectra that differ in intensity by, at most, 3%.

■ CONCLUSIONS

The crystallization of RDX on clean In foil clearly favors the formation of the β-phase. A potential model for this has been suggested in DFT calculations carried out by Guadarrama-Pérez et al.[16] They calculated the conformation of the RDX molecule in the presence of a 16 atom complex that models an Al surface. They showed that in the presence of the metal surface, the conformation of the RDX molecule tends to change from having a single NO_2 group in an equatorial conformation (AAE), to a much more symmetrical axial conformation (AAA). This is essentially the difference between the α- and β-phases shown in Figure 1.

As for the consequence of the β-phase in the XES, the theoretical results show only minor differences in the spectra. The spectrum derived from the most recent α structure is very similar to the β-phase spectrum. The most noticeable differences are in a slight increase in intensity of the main peak (393 eV) and a decrease in the intermediate region (380–384 eV). We have previously shown[12] that the main peak of RDX arises from complex excitations involving a variety of orbital types of mostly π-character on the NN and NO bonds. The intermediate region, on the other hand, is dominated by σ-character orbitals around the NC bonds. The conclusions and assignment of molecular orbitals to the XES in our previous work remains unchanged.

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Notes

The authors declare no competing financial interest.

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