**DFT Calculations of Temperature Dependent NQR Frequencies in β-HMX**

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**Introduction**

Nuclear quadrupole resonance (NQR) spectroscopy is an RF technique for solid materials that is similar to NMR in practice, however with some key differences in the underlying physics. Because NQR relies the interaction of the nuclear electric quadrupole moment with the local electric field gradient (EFG), a second rank tensor which depends on the electronic structure of the material, NQR frequencies are material specific and strongly temperature dependent. The theory of NQR T-dependence has long been discussed and various models have been proposed, with mixed results [1]. It has recently been shown that DFT methods can accurately predict solid state NMR and NQR parameters in the static lattice [2][3]. Work has been carried out to extend calculations of NMR parameters to systems at finite temperature by accounting for motional effects [4], but no such effort has been made to account for NQR T-dependence. This work concerns calculations of the NQR parameters in β-HMX, a well-known nitramine explosive compound whose NQR spectra has long been studied. [5]

**Experimental**

/Users/altoidnerd/Desktop/hmx1.pdfAll calculations are carried out using QUANTUM ESPRESSO software, using the PBE exchange-correlation functional and a plane-wave basis. Structure parameters for HMX crystal cells at eight experimental cell volumes [6] are relaxed and a set of modified structures is generated in each using NVE molecular dynamics (MD) simu-lations with cutoff energy 60 Ry, integration time step 3.87fs and initial kinetic energy corresponding to the cell measurement temperature. The EFG tensors at all nuclear sites are computed in each structure generated by the MD simulation using the GIPAW module with a cutoff energy of 80 Ry, and the modified tensor components are found in the coordinate system determined by the principal axes the EFG in the equilibrium structure.

**Results and Discussion**

Figure 1 shows preliminary results for computed temperature dependent NQR frequencies for the two inequivalent amine 14N sites in the HMX structure. The calculations overestimate the coupling constant showing an absolute error of ~150KHz for the equatorial sites and ~100KHz for the axial sites. However the combined effect of volume increase (which increases the computed coupling constant in the static lattice) and temperature increase (which results in a reduction of the observed constant) shows the correct trend. Better absolute agreement may be obtained cheaply by adjusting the DFT calculation (e.g using a different XC functional) in the computation of the static lattice coupling constants. The noise present in the computed values may be reduced by extending the total MD simulation time as well as averaging over various crystallographically equivalent nitrogen sites in the cell, or by computing space fixed tensor components differently. More analysis is needed to determine the degree to which the net temperature coefficients agree with experiment. This analysis is in its early stages and results may change.

**Fig.1** Comparison of computed 14N coupling constants v.s. experimental values. Axial sites (upper set of curves) are shown in black, the equatorial sites in blue. Experimental values are marked with a cross, calculated values with a circle.

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