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Pressure dependent Raman spectra used to validate DFT EOS of Hexanitrostilbene (HNS)

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Abstract. Due to its thermal stability and low vapor pressure, Hexanitrostilbene (HNS) is often used in high-temperature or vacuum applications as a detonator explosive or in mild detonating fuse. Toward improving the accuracy of the equation of state used in hydrodynamic simulations of the performance of HNS, we have measured the spectra of this material under static pressure in a diamond anvil cell. Density functional theory calculations were used to simulate the pressure dependence of the Raman spectra along the Hugoniot and 300K isotherm for comparison and to aid in interpreting the data. We discuss changes in vibrational signatures of HNS under pressure, validation of a DFT predicted equation of state, and using this data as a basis for understanding future pulsed Raman measurements on dynamically compressed HNS samples.

INTRODUCTION

Due to its thermal stability and low vapor pressure, Hexanitrostilbene (HNS) is often used in high-temperature or vacuum applications as a detonator explosive or in mild detonating fuse. Static compression data is useful for building equations of state for use in hydrocode simulations. Gump[1] previously reported x-ray diffraction data for the isotherm of HNS. In this work, we report Raman spectra of fine particle HNS at a series of pressures up to 6 GPa. The HNS used in this study has a lower level of impurity (<0.05%) than the material used in Gump's work (~0.6%), which could allow for more accurate comparison with theory. To our knowledge, single crystal shock data for HNS has never been collected. This work is partially motivated by a desire for an alternate means of validating a DFT predicted crystalline equation of state.

EXPERIMENTAL PROCEEDURE

Raman Spectra of HNS in DAC

Raman Spectra and pressure measurements were taken using a WiTec Confocal Raman microscope. Diamond anvil cells (DACs) were loaded with fine particle HNS. Head space gas analysis was used to verify HNS contained < 0.05% residual DMF (99.95% pure). Dow Corning 200 Fluid (5 centistokes), reported to be hydrostatic to 10 GPa (ref), was added as a pressure medium for compression experiments in an attempt to create hydrostatic conditions. A ruby microsphere next to HNS grain was used to monitor pressure. Ruby fluorescence measurements were carried out using a 0.2 second illumination averaged over 10 scans (532 nm) to prevent damage to adjacent HNS. Raman spectra where taken using a 785nm cw laser and collected over 3-5 minute intervals per scan. Background spectra of the Dow Corning oil were also taken next to the HNS grain under identical conditions. HNS and background spectra were normalized to Dow Corning oil peak between 450-550 cm^{-1}.

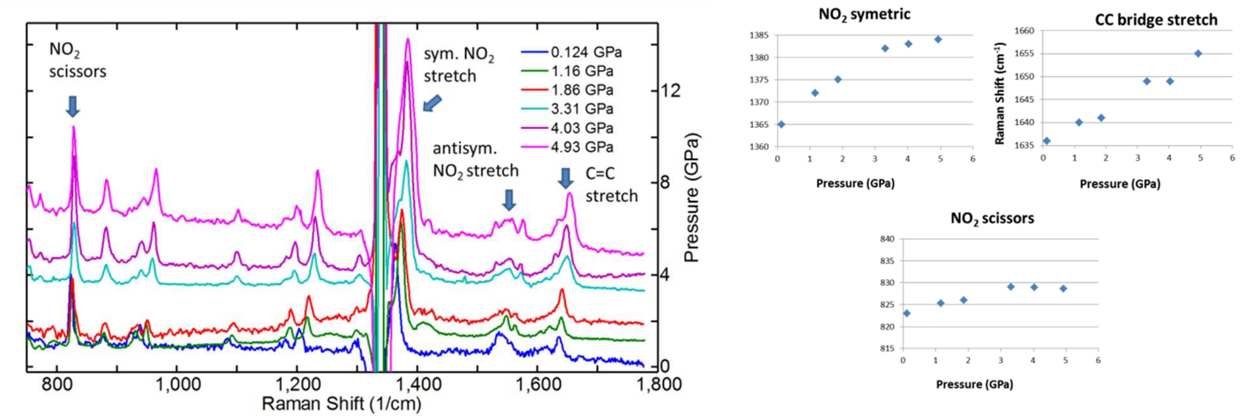
DFT EOS Model

Density functional theory (DFT) based molecular dynamics simulations of HNS were used to calculate pressure/volume behavior of HNS on the 300K isotherm. Our DFT-MD calculations with the AM05 [2] functional were performed using the Vienna ab-initio simulation package (VASP 5.2) [3-5], using strictly converged settings[6-7]. The plane-wave cut-off was set to 800 eV and k-point sampling with mean-value point (1/4,1/4,1/4) was used. The reference state run (equilibrium volume, 300K) was repeated with (4x4x4) Monkhorst Pack sampling to verify convergence of the total energy, which was better than 0.001 eV. The ionic time-step was set to 0.4 fs. A velocity auto-correlation was extracted from the molecular dynamics trajectories for particular groups of atoms in HNS.

RESULTS AND DISCUSSION

Raman Spectra of HNS in DAC

Raman data for HNS taken at 300K are shown below from 750-1800 cm^{-1}(Fig. 1). NO_2 scissors, symmetric stretch and antisymmetric stretch have been identified along with the C=C stretch of the carbon bridge. [8] Features, with the exception of the antisymmetric NO_2 stretch, blue shift with pressure, but do not split into new bands. The symmetric NO_2 stretch and CC bridge stretch are most sensitive to pressure, blue shifting ~ 20 cm^{-1} from 1 atm to ~ 6 GPa. Data above 6 GPa were had poor signal to noise and are not shown.



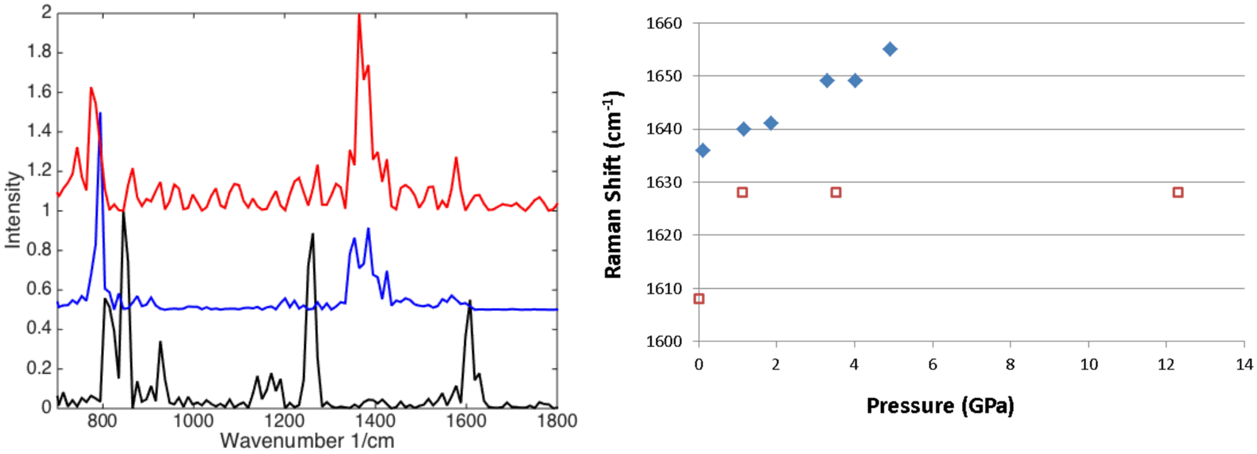
(a)

(b)

FIGURE 1. (a.) Raman Data of HNS taken from 0.24 to 5.0 GPa. (b) Raman peak frequency ploted as a function of pressure.

Comparison to DFT Calculations

As a first attempt to compare Raman data to our DFT calculation, we took the power spectrum of a velocity auto-correlation for specific groups of atoms. This was done to isolate the bridge carbons and nitrogen/oxygen associate modes respectively (Fig. 2). The peak near 1608cm^{-1} from C=C autocorrelation is 30 cm^{-1} to the red of C=C stretch in our Raman data. Like the Raman modes, the normal modes blue shift with pressure, but the shift occurs at low pressure and then appears to be independent of the pressure change. Longer simulations are underway, which will improve frequency resolution, and we will identify Raman active modes for a more direct comparison. However, it is encouraging that for C=C stretch there appears to be a correlation between the simulated vibrational spectra and the Raman data. Bands that appear in both spectra (examples) identify coupling between groups.



(a) (b)

FIGURE 2. (a.) Velocity autocorrelations of bridge carbons (black), nitrogen (blue) and oxygen (red) atoms ofHNS. (b) Plot of C=C peak shift vs. pressure.

CONCLUSIONS

The vibrational spectra obtained from DFT-MD reproduce many key features of the Raman spectra, including blue shift of Raman active modes at low pressures 1-6GPa. Efforts to improve the calculation for better frequency resolution and comparison to data taken at higher pressure with a new pressure medium are underway. .

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