

Ab initio calculations of properties of molecular crystals under deformation

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Overview

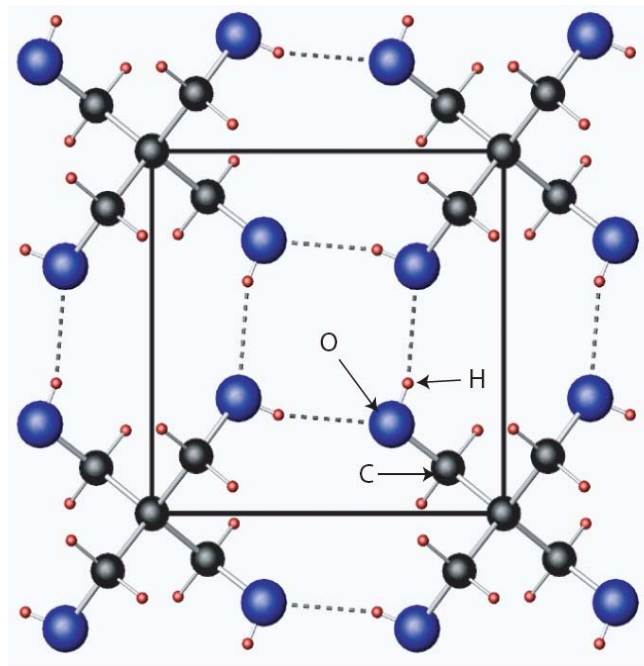
- ◆ The need for first-principles studies
- ◆ Issues associated with organic molecular crystals (OMC's)
- ◆ Energetic materials are organic molecular crystals
- ◆ Computational difficulties with molecular crystals; often many atoms per unit cell and low symmetry
- ◆ Atomistic calculations; require quantum mechanics (non-relativistic)
- ◆ Accurate calculation of organic molecular crystal (OMC) properties requires consideration of 3 structural levels
 - Electronic: responsible for optical properties
 - Intra-molecular: relatively strong binding
 - Inter-molecular: relatively weak, van der Waals interaction.
- ◆ Inter-molecular interaction responsible for mechanical and elastic properties.
- ◆ Characterization of the inter-molecular potential is valuable for understanding the shock initiation-to-detonation transition.
- ◆ Understanding the intra-molecular potential is required for crystal deformations which invalidate the rigid-molecule approximation.

Why we need first-principles theory/modeling

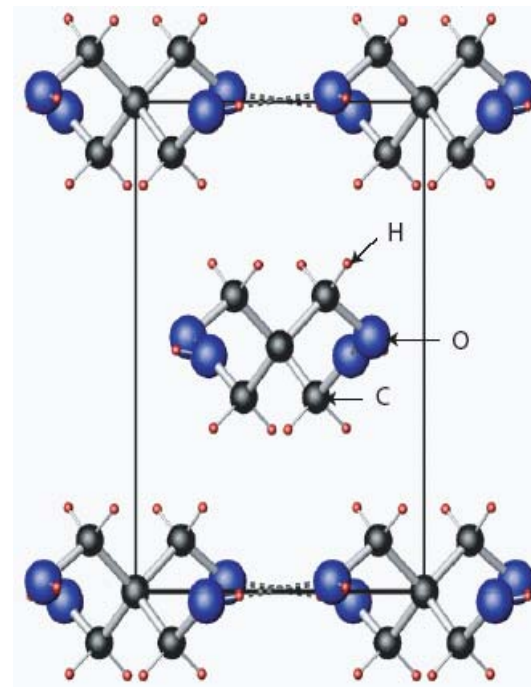
- ◆ **Practicality:** theory can, in principle, reduce the number of experiments made
- ◆ **Inspiration:** a detailed understanding of a process in a system can suggest new experiments
- ◆ **Necessity:** application of first-principles ideas simply necessary for some properties in some systems (e.g. PE O-H stretching mode)
- ◆ **Philosophy:** science is furthered when we understand what we have measured
- ◆ **Note the distinction between “theory” and “modeling”**

The problem

- ◆ All high-energetic materials (HE's) are molecular crystals
- ◆ Molecular crystals are hydrogen and van der Waals bonded, sometimes both (e.g. PE)



ab plane

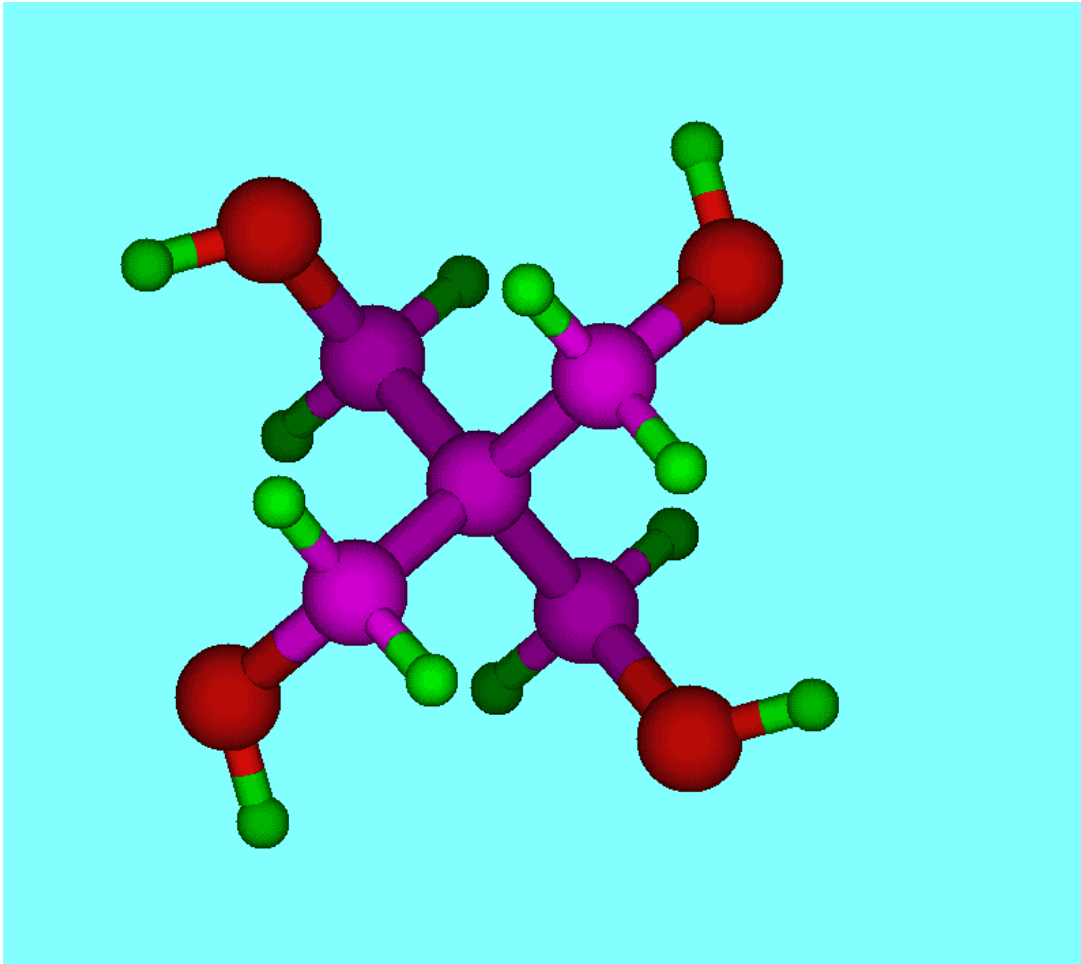


ac plane

The problem...

- ◆ **Effects of compression, via hydrostatic pressure and uniaxial strain:**
 - on mechano-chemistry?
 - on shock initiation-to-detonation transition?
- ◆ **OMC's often anisotropic, e.g. tetragonal PE**
- ◆ **BOTH intramolecular and intermolecular potentials must be accurately accounted for**
- ◆ **Studies on PE predict pressures which are too high if a rigid-molecule approximation is taken: “relaxation” of atomic positions is required**
- ◆ **This requires an n-parameter optimization procedure**
- ◆ **The intermolecular potential, often van der Waals, yields $\sim 1/r^6$ and commonly-used exchange-correlation density-functional theory technique is not well-suited**
- ◆ **OMC's can have many electrons in the unit cell: e.g. RDX has 912.**

Variation of internal geometry in PE with pressure



- ◆ Hydrogen
- ◆ Oxygen
- ◆ Carbon

The equations to solve

Schrödinger equation with independent-particle approximation

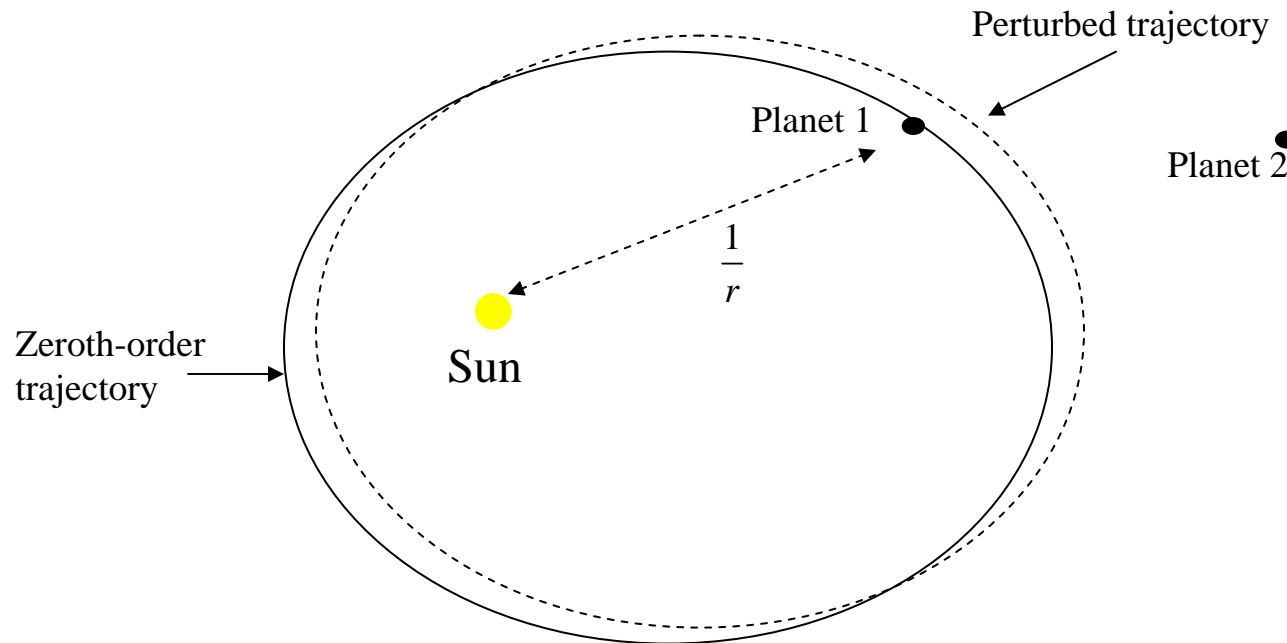
$$H\Psi_i = E_i\Psi_i \quad (1)$$

with the Hamiltonian, H , yields the Hartree-Fock equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + \frac{e^2}{4\pi\epsilon_o} \sum_{k \neq j} \int \frac{|\phi_k(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\tau' \right] \phi_j(\vec{r}) - \frac{e^2}{4\pi\epsilon_o} \sum_{k \neq j} \int \frac{\phi_k^*(\vec{r}')\phi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d\tau' \phi_k(\vec{r}) = E_j\phi_j(\vec{r}) \quad (2)$$

- ◆ Where $V(r)$ is the potential due to the lattice ions, and the sums are the direct and exchange terms, respectively.
- ◆ Difficulties:
 - The direct and exchange terms depend on the ϕ_k 's, which are the functions we seek.
 - The exchange term depends on j , so there is a different Hartree-Fock equation for each electron.
 - And there is no “correlation”...

The $1/r$ potential and the many-body problem



- ◆ This can be solved analytically only for $n=2$. We need the particle positions (electron density) to determine the potential (intra- and inter-molecular). What will we do for OMC's, with *hundreds* of e's?
- ◆ There is no (commercially-available) answer to this question

What is known about exchange-correlation

- ◆ It typically cannot be neglected.
- ◆ Hartree-Fock (exchange is “perfect,” but there is NO correlation), grossly overestimates band gaps, gives ambient volumes which are too large (correlation tends to increase the intermolecular attraction)
- ◆ Density-functional theory: attempts to reproduce both the exchange and correlation by means of an appropriate electron density
 - Problems:
 - Where does it come from, that is, what theoretical justification is used?
 - There is NO proof that you have “the” functional!!
- ◆ Many-body perturbation theory, aka, Rayleigh-Schoedinger, Moller-Plesset (MP2), is possible, used in atomic and molecular work, but expensive
- ◆ Likewise for coupled-cluster approaches

What can we do and are we doing?

- ◆ Use different software programs which use different basis sets and functionals
- ◆ Program in our own functionals
- ◆ Explore other methods, such as MP2 or coupled-cluster
- ◆ Extract what information we can about response of crystal to compression by studying, for example, vibrational spectra shifts as a function of pressure
- ◆ Use all-electron approach and compare with pseudo-potential

Density functionals: an example

- ◆ X3LYP DFT functional (Goddard, et al)

$$E_{XC}^{X3LYP} = a_o E_x^{exact} + (1 - a_o) E_x^{Slater} + a_x \Delta E_x^X + a_c E_c^{VWN3} + (1 - a_c) E_c^{LYP}$$

- Where :

$$\Delta E_x^X = a_{x1} F^{B88}(s) + a_{x2} F^{PW91}(s)$$

- And $\{a_o, a_x, a_c\} = \{0.218, 0.709, 0.129\}$ and $\{a_{x1}, a_{x2}\} = \{0.765, 0.235\}$

Limitations of what we are doing

- ◆ Time independent
- ◆ Zero Kelvin
- ◆ No “exact” answer for correlation (although H-F gives exact exchange)
- ◆ Difficult to establish meaningful error bars
- ◆ And those basis sets....

Application of hydrostatic pressure

(uniform stress, not uniform strain)

- ◆ Begin by optimizing atomic positions (talk by C. Zicovich)
- ◆ Choose volumes around equilibrium
- ◆ For tetragonal systems (e.g., PE, PETN), at each volume, find c/a ratio which minimizes total energy
- ◆ At that c/a ratio, re-optimize atomic positions
- ◆ Recalculate total energy at that volume
- ◆ Fit to Murnaghan EOS:

$$E(V) = B_o V_o \left[\frac{1}{B' (B' - 1)} \left(\frac{V_o}{V} \right)^{B' - 1} + \frac{V}{B' V_o} - \frac{1}{B' - 1} \right] + E_o,$$

F. D. Murnaghan, Proc. Natl. Acad. Sci USA 30 (1944) 244

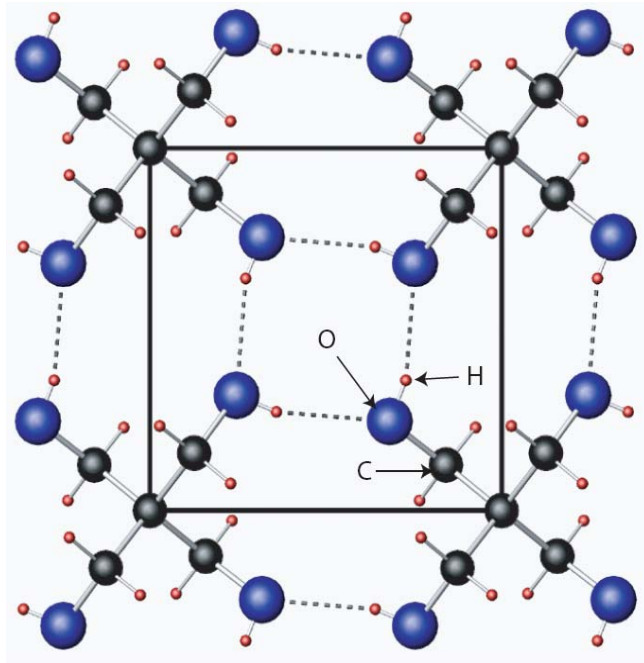
Vibrational spectra

- ◆ Begin by optimizing atomic positions (talk by C. Zicovich)
- ◆ Create $n_{\text{runs}} = 3N(n_{\text{pts}} - 1)$, where N =number of atoms and n_{pts} is the number of points in the numerical 2nd-derivative (first derivative is analytic and comes from Crystal03 program)
- ◆ Create cartesian Hessian of terms in 2nd-derivative of total energy:

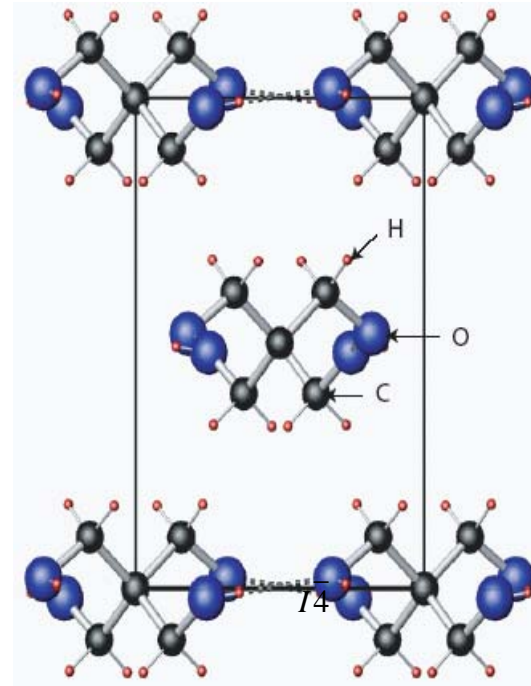
$$f_{\text{cart},ij} = \left(\frac{\partial^2 V}{\partial \zeta_i \partial \zeta_j} \right)_0$$

- ◆ Convert to mass-weighted system
- ◆ Diagonalize
- ◆ Write eigenvectors to a file for viewing with Molden
- ◆ Eigenvalues are the vibrational frequencies

PE: a case study



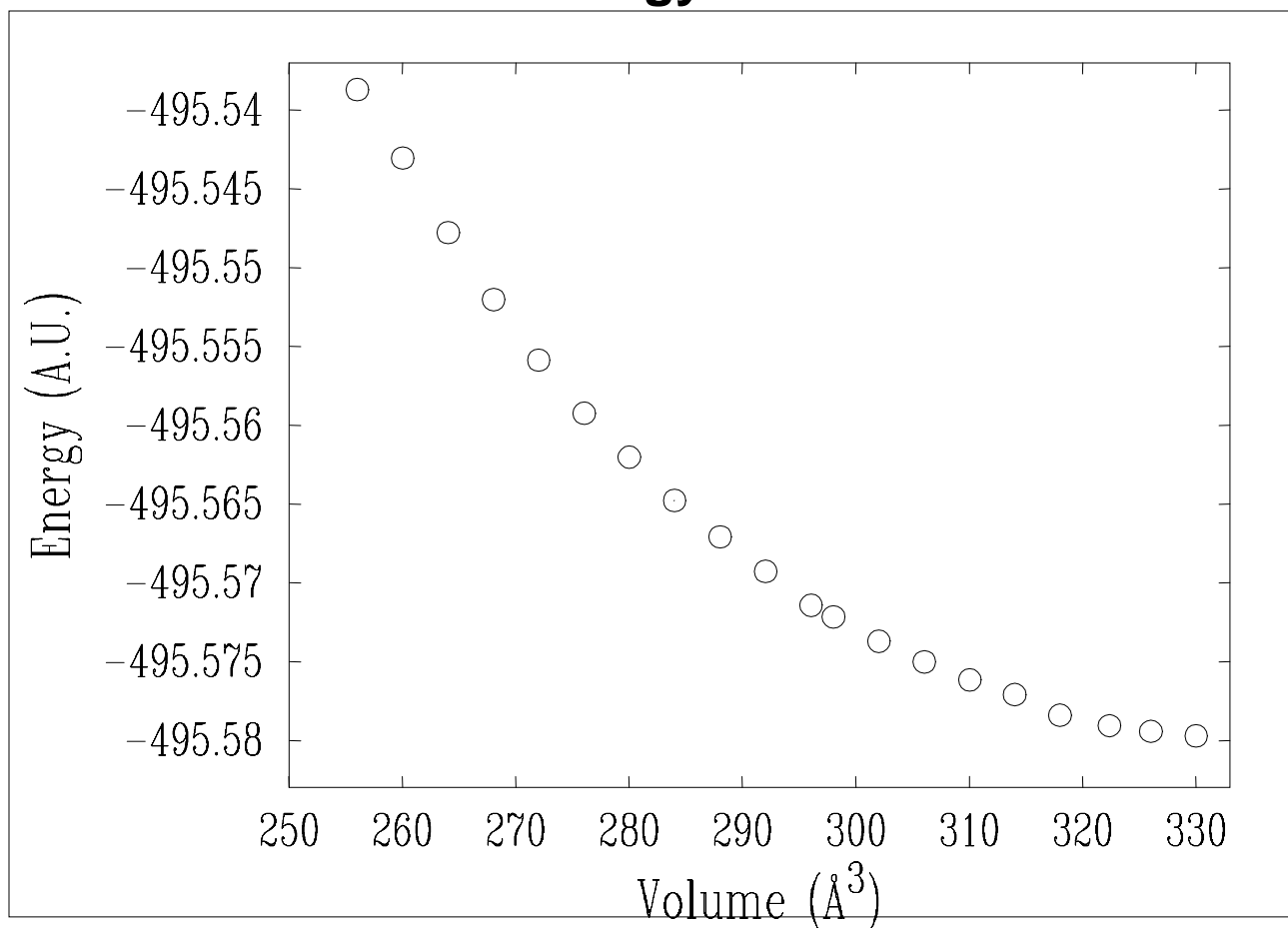
ab plane



ac plane

- Tetragonal, space group
- C (CH_2OH)₄, 21 atoms per unit cell

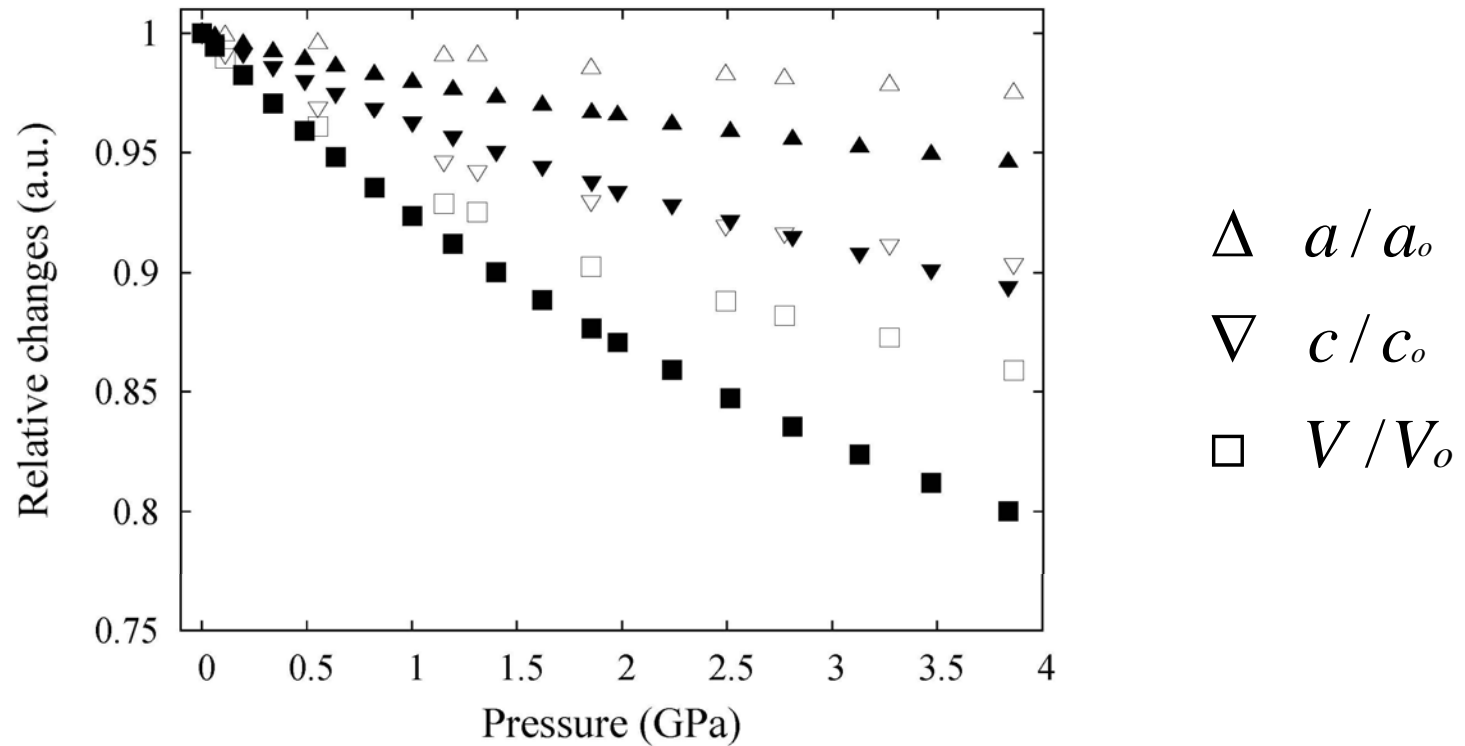
PE Total Energy vs. Volume



PE Total Energy vs. Volume, HF/6-31G

=> Relaxation of internal co-ordinates essential!!

PE lattice parameters and volume as function of pressure



Calculated (solid), experiment (open), Hartree-Fock 6-31G

PE Lattice parameters as a function of pressure

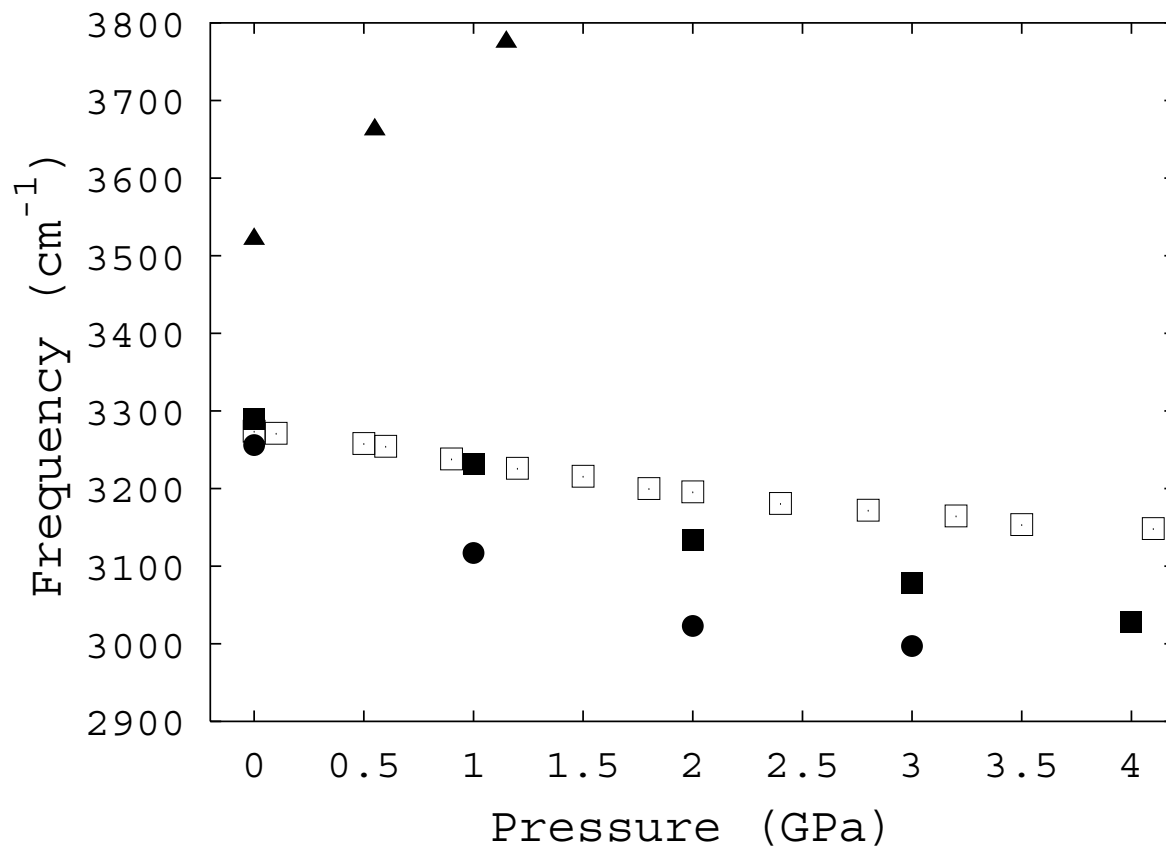
GPa	Method	Lattice		
		a	c	Volume
0	Expt [1]	6.075	8.733	322.30
	Expt [2]	6.079	8.745	323.2
	HF/631G	6.168	8.935	339.92
	B3LYP/631G**	6.145	8.866	334.75
1	Expt[3]	6.017	8.267	299.30
	HF/631G	6.026	8.562	310.88
	B3LYP/631G**	5.981	8.403	300.57
2	HF/631G	5.950	8.349	295.62
	B3LYP/631G**	5.907	8.168	285.01
3	HF/631G	5.881	8.140	281.56
	B3LYP/631G**	5.846	7.947	271.58

1. D. Eilerman and R. Rudman, Acta Cryst. B35 (1979) 2458-2460.
2. D. Semmingsen, Acta Chem. Scand. A42 (1988) 279-283.
3. T.-R. Park, Z.A. Dreger, Y.M. Gupta, J. Phys. Chem. B 108 (2004) 3174-84.

PE vibrational study

- ◆ 57 internal modes
- ◆ 2 lattice modes

OH stretching mode vibrational frequency with hydrostatic pressure



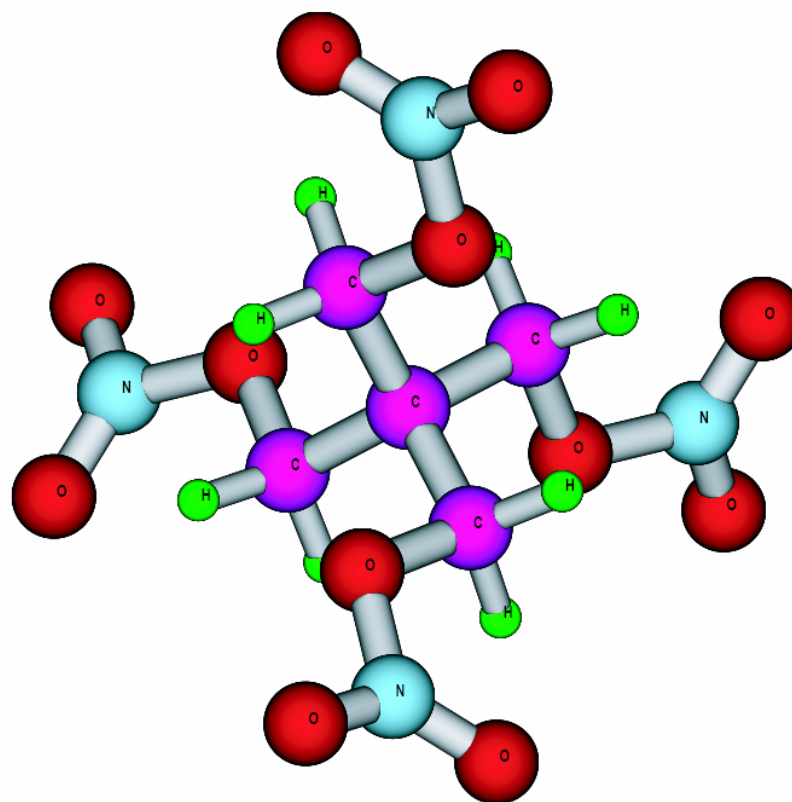
Hartree-Fock/631G (solid square); B3LYP/631G** (solid circle); Semi-Empirical (solid triangle, Ramamoorthy et al, Crys. Res. Technol.36 (2001) 169-182); Experiment (open square)

Lattice modes of PE using B3LYP/6-31**, compared with experiment

Pressure(GPa)	Frequency (cm ⁻¹)		
	Calculated		Experiment
	L1	L2	L2
0	55	75	78
1	100	116	91
2	101	116	104
3	58	84	112
4	95	121	124

Penta-erythritol tetranitrate (PETN)

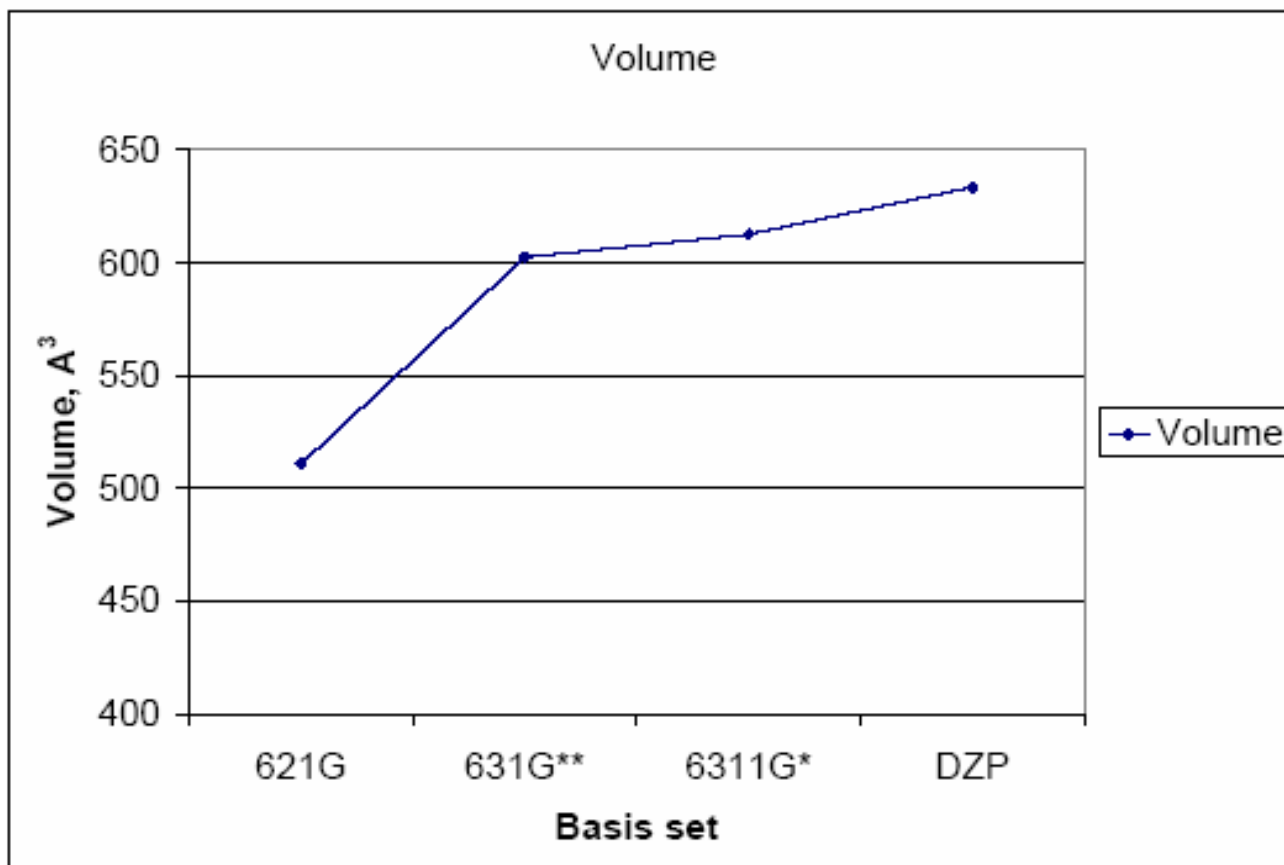
- ◆ PETN has 29 atoms per molecule, 2 molecules/unit cell
- ◆ Crystal structure – body centered tetragonal
- ◆ $C(CH_2ONO_2)_4$
- ◆ Two molecules per unit cell
- ◆ Space group – $P42_1c$
- ◆ Molecular point group – S_4
- ◆ 81 (20A + 21B + 20E modes) x 2 = 162 internal modes
- ◆ Both van der Waals (intermolecular) and covalent (intramolecular) bonding
- ◆ Gas-phase vibrational frequencies calculated (Gruzdikov, et al, 2004); need for pressure-dependence



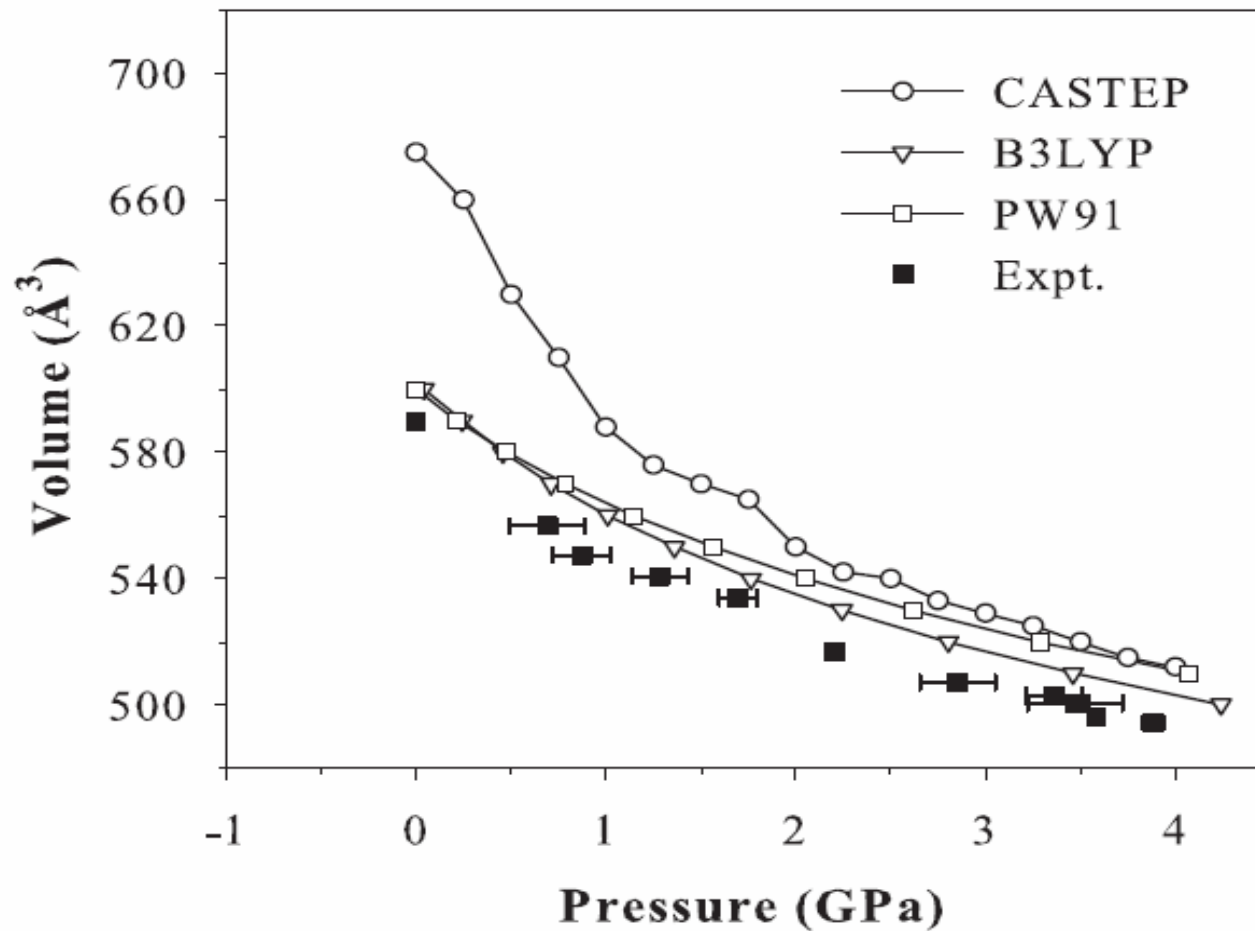
PETN ambient lattice constants

	Experiment		Theory				
	Cady, Larson	Conant,et al	Gan, et al	Brand	CRYSTAL03		CASTEP
					B3LYP	PW91	PW91
a(Å)	9.383	9.378	9.425	9.2546	9.439	9.431	9.868
c(Å)	6.711	6.708	6.756	6.6636	6.762	6.746	6.925
V(Å³)	590.8	589.9	600.3	593.7	602.4	599.0	674.3

PETN volume as function of basis set



Volume vs. Pressure for PETN



Crystal03 B3LYP and PW91 (631**) compared with CASTEP PW91 and Experiment.

Selected vibrational frequencies for the PEIN crystal from current and previous theoretical calculations compared with experimental data. IrrRep refers to the irreducible representation; CA, B3, PW, and G98 refer to the CASTEP, CRYSTAL03-B3LYP, CRYSTAL03-PW91, and Gaussian 98 calculations, respectively; IR and Raman refer to the infrared and Raman spectroscopy results

		Theory						Exp.
Assignment	IrrRep	CA	B3	PW	G98	IR		
CH2 rock	A	303	324	319	319	319		
CCC def. + ON stretch + NO2 rock	E	375	458	437	453	460	459	
C5 skeletal + CH2 wag + ON stretch	B	479	538	502	536	539		
CC bend + ONO2 rock	A	509	594	568	585	589		
C5 skeletal + ONO2 rock 619	B	566	566	627	598	617	618	
CCC def. + ONO2 rock	E	582	632	599	623	624	624	
ON stretch + CC stretch + NO2 scissors	A	592	685	634	673	676		
ON stretch + CCC def. + NO2 rock	E	634	712	666	710	704	704	
CCC def. + ON stretch	B	679	750	709	753	746	746	
ONO2 umbrella	E	776	758	721	756			
ONO2 umbrella	A	781	759	721	757			
ONO2 umbrella + CCC def. 755	B	784	784	760	722	760	755	
CC stretch	A	750	845	785	842	839		
ON stretch	E	795	864	801	855	852	854	
ON stretch	B	810	888	820	860	869	869	
ON stretch + CC stretch	A	849	903	840	886	873		
CCC def. + CH2 rock	B	864	928	899	934	900		
CH2 torsion + CCC def.	E	865	938	902	952	939	939	
CH2 rock + CO stretch	A	898	1009	972	1023	995		

◆	CO stretch + CCC def.	E	946	1019	994	1038	1003	1004
◆	CO stretch + C5 skeletal + NO2 rock	B	1037	939	1054	1026	1074	1038
◆	CH2 torsion + CC bend	A	1058	1059	1030	1071	1044	
◆	CH2 wag + C5 skeletal	B	1161	1188	1152	1194	1159	
◆	CCC def. + CH2 wag	E	1175	1202	1164	1212	1193	1195
◆	CH2 bend	A	1254	1260	1214	1274	1253	
◆	CH2 bend + C5 skeletal	E	1269	1288	1235	1295	1257	
◆	CH2 bend + C5 skeletal + ONO2 rock	B	1273	1291	1303	1254	1319	1272
◆	NO2 stretch + CH bend + C5 skeletal	E	1286	1303	1326	1278	1336	1285
◆	NO2 stretch + CH2 wag	A	1274	1344	1292	1351	1294	
◆	CH2 wag + C5 skeletal + NO2 rock	B	1376	1327	1351	1298	1352	1306
◆	CH2 wag + CCC def.	E	1368	1408	1347	1417	1387	
◆	CH2 wag + CCC def.	B	1398	1412	1352	1422	1396	1397
◆	CH2 wag + CC stretch	A	1497	1428	1367	1435	1406	
◆	CH2 scissors	A	1472	1519	1475	1535		
◆	CH2 scissors	B	1477	1519	1477	1536	1509	1512
◆	CH2 scissors	E	1734	1525	1481	1541	1474	1474
◆	NO2 stretch (a)	A	1751	1726	1697	1775	1633	
◆	NO2 stretch (a)	B	1751	1735	1706	1776	1661	1665
◆	NO2 stretch (a)	E	2976	1750	1719	1778	1648	1650
◆	CH2 stretch (s)	B	3106	3106	3027	3102		
◆	CH2 stretch (s)	E	2975	3109	3029	3103	2940	
◆	CH2 stretch (s)	A	2975	3112	3030	3105	2985	2987
◆	CH2 stretch (a)	A	3043	3173	3089	3159		
◆	CH2 stretch (a)	E	3042	3175	3091	3161	3023	3025
◆	CH2 stretch (a)	B	3033	3178	3094	3163	2916	2918

PETN vibrational results synopsis

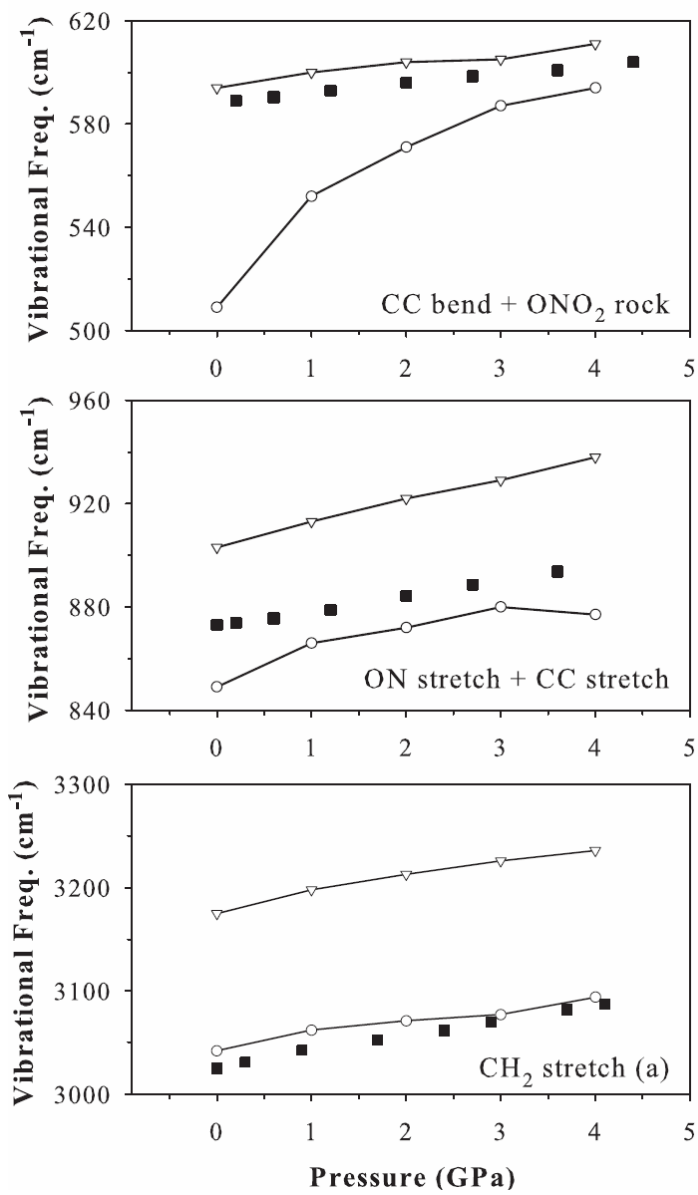
- ◆ Average deviation of the calculated vibrational frequencies using the CASTEP code compared with the experimental values is about 5.1%.
- ◆ The CRYSTAL03 gave average deviation from the experimental values of 2.4% for the B3LYP functional and 3.0% for the PW91 functional.
- ◆ For the higher-energy vibrational modes (greater than 1100 cm), the CASTEP calculations with the PW91 functional agree with the experimental data better than the CRYSTAL03-B3LYP results. However, the average deviation of the CASTEP PW91 results from the experimental values increases to 8.2% for frequencies lower than 1100 cm, while the deviation is only 1.3% for the CRYSTAL03-B3LYP calculations.
- ◆ Overall, the CRYSTAL03-B3LYP calculations tend to overestimate the higher vibrational frequencies, while the CASTEP-PW91 calculations tend to underestimate the lower vibrational frequencies. The CRYSTAL03-PW91 results appear to be intermediate between the other two cases.
- ◆ The better description of vibrational frequencies by the CRYSTAL03-B3LYP calculations in the range from 300 to 1100 cm correlates with the fact that the CRYSTAL03-B3LYP calculations predict bond lengths that are closer to the experimental values than CASTEP-PW91.

Selected PETN vibrational modes as function of pressure

Castep PW91- circles

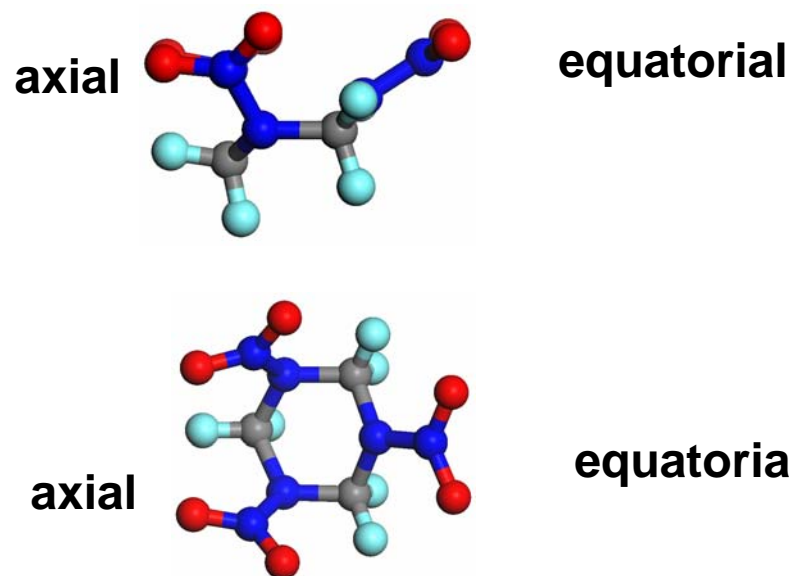
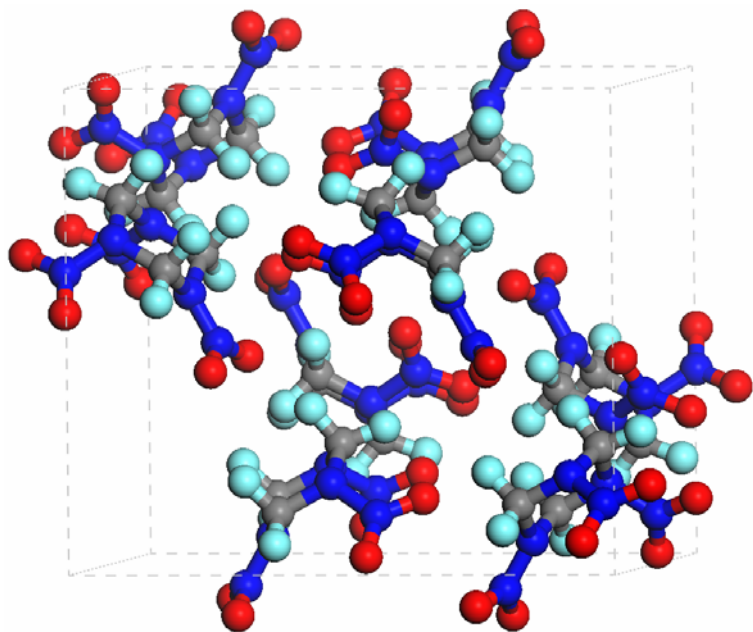
Crystal B3LYP-triangles

Experiment-squares



The next OMC (work done with J. Zhao)

- ◆ RDX ($C_3H_6N_6O_6$), organic molecular crystal
- ◆ Orthorhombic, space group $Pbca$, 8 molecules per unit cell (168 atoms)
- ◆ Molecular C_s point group, AAE configuration (A: axial, E: equatorial)
- ◆ Intramolecular: covalent bonds; Intermolecular: van der Waals bonding



Objective: examine compression-induced changes to lattice and molecular geometry; role of non-hydrostaticity

Previous work for RDX under compression

Experimental

- ◆ Crystal structure (Choi and Prince, 1972)
- ◆ Hydrostatic P-V data (Olinger et al., 1978; Yoo et al. 1998)
- ◆ Phase diagram from vibrational spectra (Baer et al., 1990; Miller et al.. 1991)
- ◆ Currently at ISP: optical spectroscopy under shock loading (Patterson);
Raman spectroscopy under hydrostatic loading (Dreger)

Theoretical

- ◆ Molecular packing simulation (Sorescu et al., 1997, 1999)
- ◆ Monte-Carlo simulation (Sewell et al., 1998, 2000)
- ◆ Reactive force field MD (Goddard et al., from 2003).
- ◆ Hartree-Fock calculation (Kuklja and Kunz, 1999-2002) based on rigid-molecule approximation and uniform rescaling of lattice constants

Computational methods

- ◆ **Density functional theory: generalized-gradient approximation (GGA-PW91 functional), implemented in CASTEP code**
 - Norm-conserving pseudopotentials for electron-ion interactions
 - Plane wave basis set for electron wave function (1000 eV cutoff)
 - Sampling of reciprocal space by Γ point approximation
- ◆ **Model crystal using one unit cell (eight RDX molecules)**
- ◆ **Full optimization of lattice parameters and internal coordinates with space group constraints – no rigid molecule approximation**
- ◆ **Hydrostatic loading up to 3.65 GPa applied using stress theorem**

RDX crystal at ambient conditions

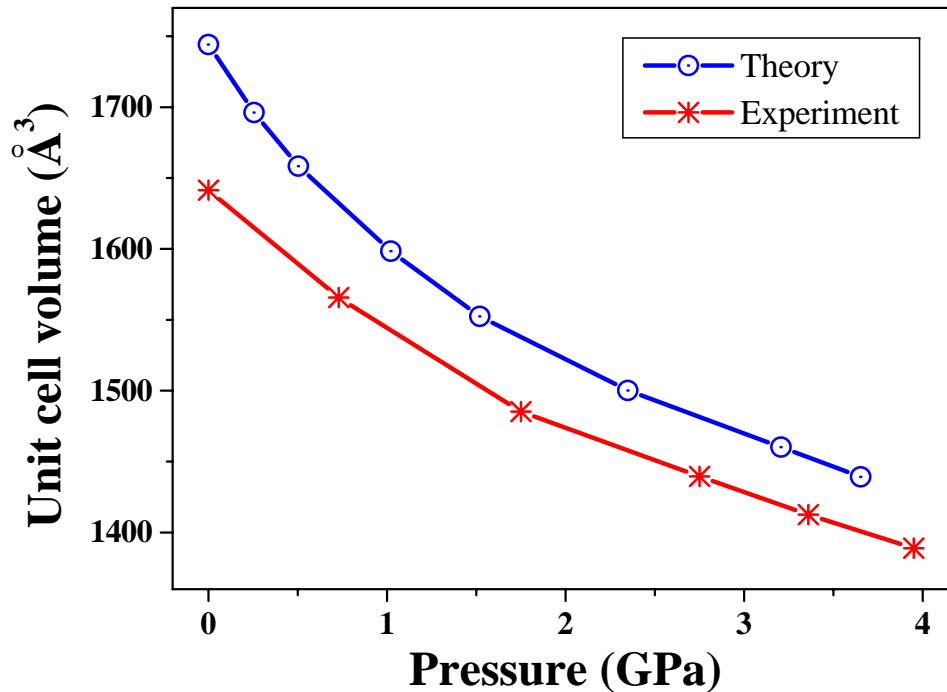
- ◆ Our GGA calculations overestimate the cell volume by ~6.3%

DFT with GGA can't reproduce the intermolecular vdW interaction (work with Mike Desjarlais, Ann Mattsson, Sandia Labs)

	a (Å)	b (Å)	c (Å)	V (Å ³)
Experiment (Choi, 1972)	13.182	11.574	10.709	1633.86
Experiment (Olinger, 1978)	13.200	11.600	10.720	1641.45
GGA (current results)	13.490	11.643	11.105	1744.20

- ◆ Computed lattice energy is 0.5 eV per molecule (experiment: ~1.35 eV)
- ◆ Experimental intramolecular geometry reasonably reproduced, e.g., average deviation of bond lengths: 0.015 Å (~1.2%)

P-V relation under hydrostatic loading



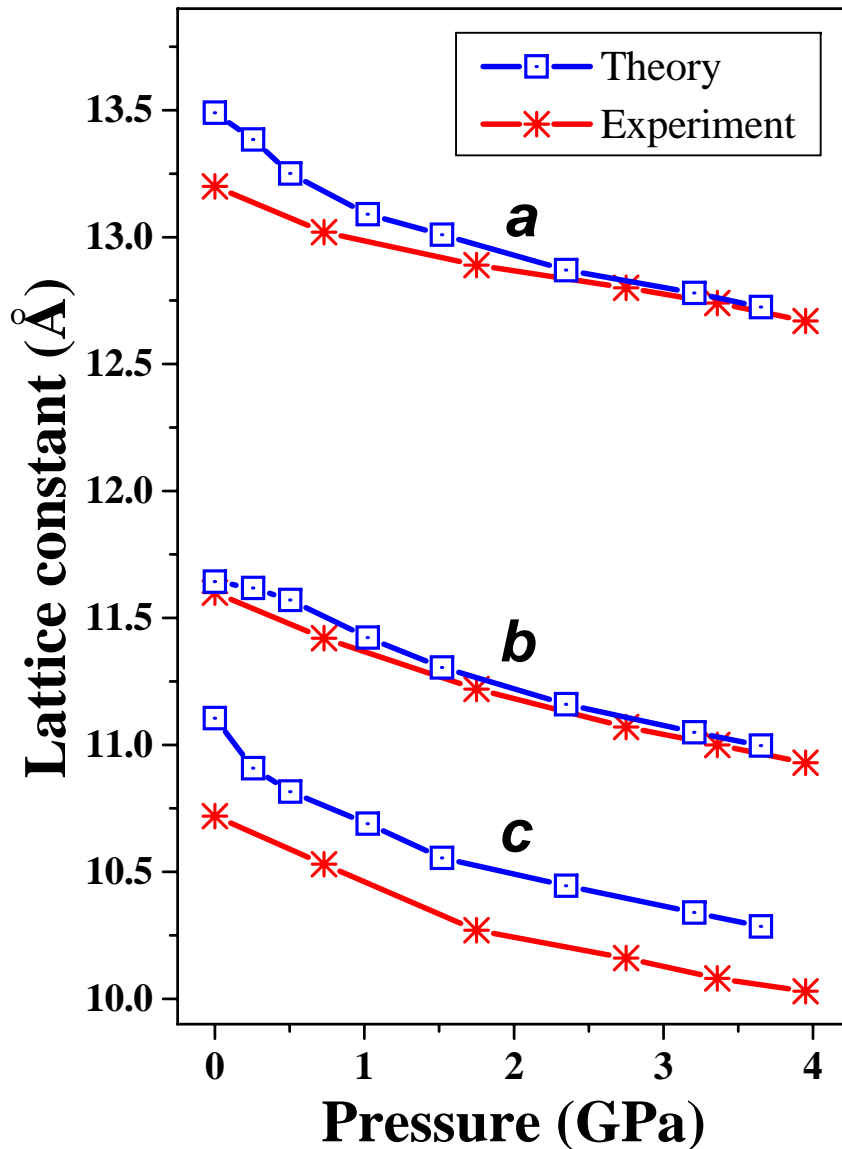
- ◆ Discrepancy between theory and experiment for unit cell volume decreases from ~6.3% at 0 GPa to ~2.7% at 3.65 GPa
- ◆ Our GGA calculation underestimated the overall stiffness of RDX crystal

◆ Fit P-V response using Murnaghan equation

$$P = \frac{B_0}{B_0'} \left[\left(\frac{V}{V_0} \right)^{-B_0'} - 1 \right]$$

	B_0 (GPa)	B_0'
Experiment	12.61	6.95
GGA	8.04	7.97

Change of lattice constants under hydrostatic loading

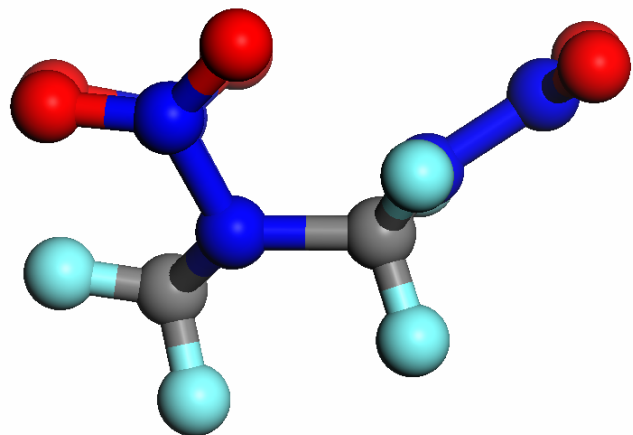


- ◆ Reduction of lattice constants of RDX crystal up to 3.65 GPa

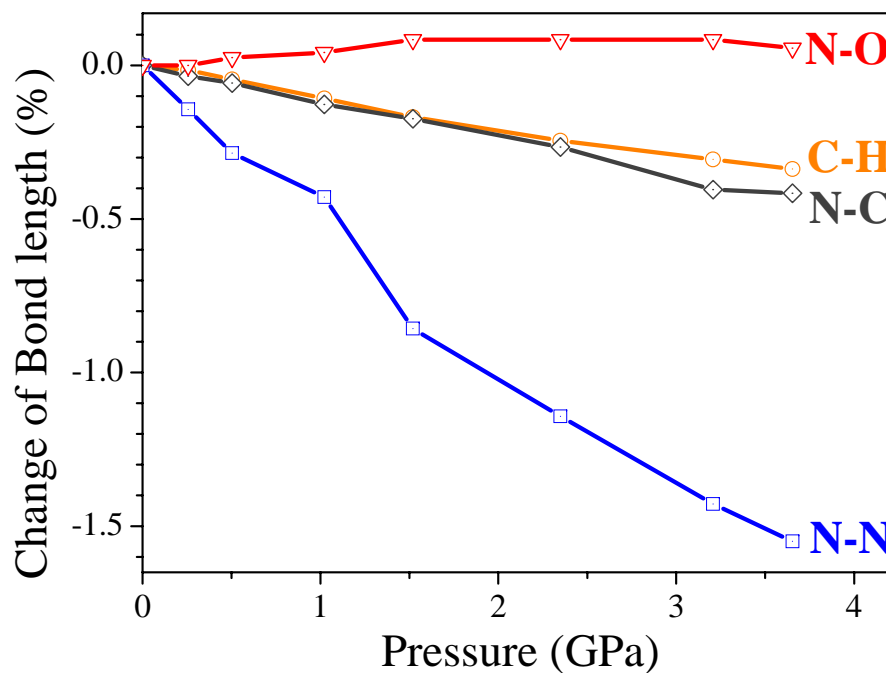
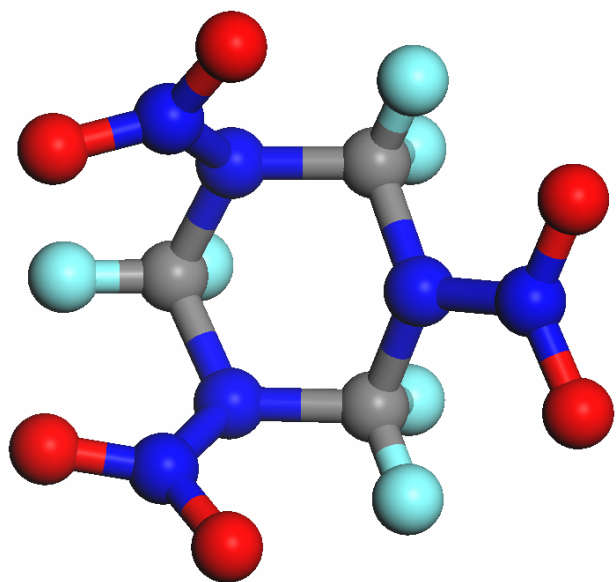
	Δa (%)	Δb (%)	Δc (%)
Experiment	4.02	5.78	6.44
GGA	5.67	5.55	7.38

- ◆ Our GGA calculations describe the *b* axis reasonably well, results for other two axes not as good.
- ◆ *c* axis is most compressible, consistent with experiment

Changes in intramolecular geometry

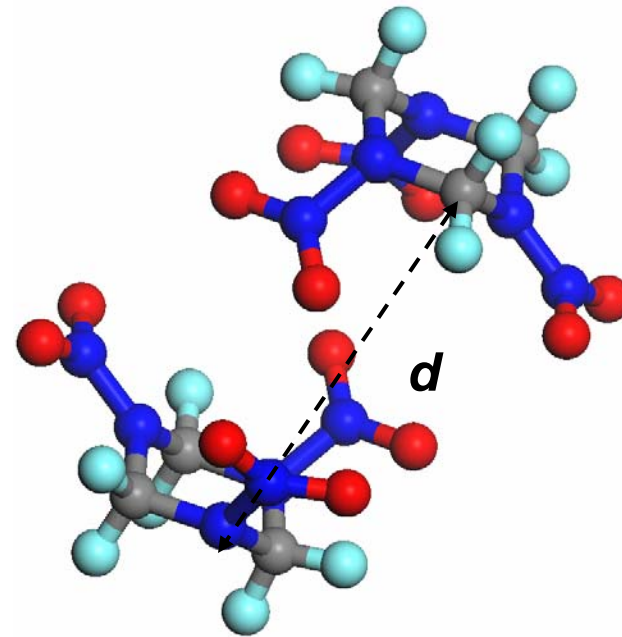
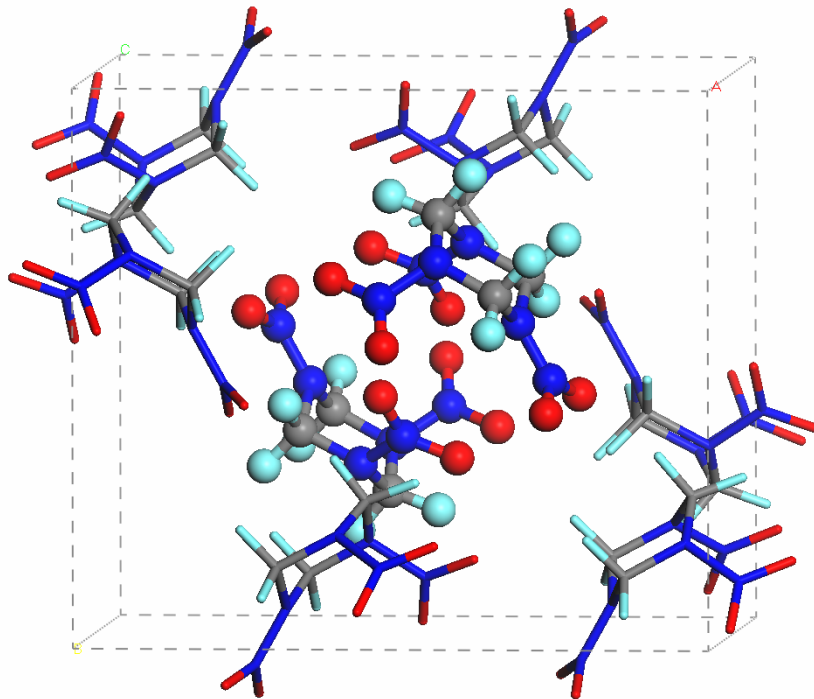


- ◆ N-N bond is most compressible
- ◆ Small deformation of C₃N₃ six-member ring (change of bond length <0.01 Å, bond angle <1°)
- ◆ Angle of NO₂ group with respect to C₂N plane changes slightly (~ 1° to 3°)



Changes in intermolecular distances

- ◆ RDX molecules form pairs in crystal structure packing
- ◆ We define the intermolecular distance d as distance between the centers of C_3N_3 six-member rings of adjacent RDX molecules, typically $d = 6\sim 7$ Å
- ◆ Up to 3.65 GPa, distance d between molecules within a pair reduces by 0.66 Å, compared to 0.3~0.4 Å for the other intermolecular distances d



Changes of band gap under compression

- ◆ Ambient condition, band gap at Γ point at GGA level is 3.87 eV
 - Previous Hartree-Fock calculation with 2nd-order many-body perturbation correction predicts a gap of 5.25 eV (Kuklja and Kunz, 1999)
 - Experiment: optical band gap = 3.4 eV (Marinkas, 1977)
- ◆ Under hydrostatic loading, our GGA calculations predict a reduction of band gap by 0.21 eV for 3.65 GPa pressure
 - Previous Hartree-Fock/MP2 calculations predict a modest reduction of gap, for pressures up to ~ 4GPa
 - Experiment: shift of optical adsorption edge by ~0.5 eV under 16.4 GPa hydrostatic pressure

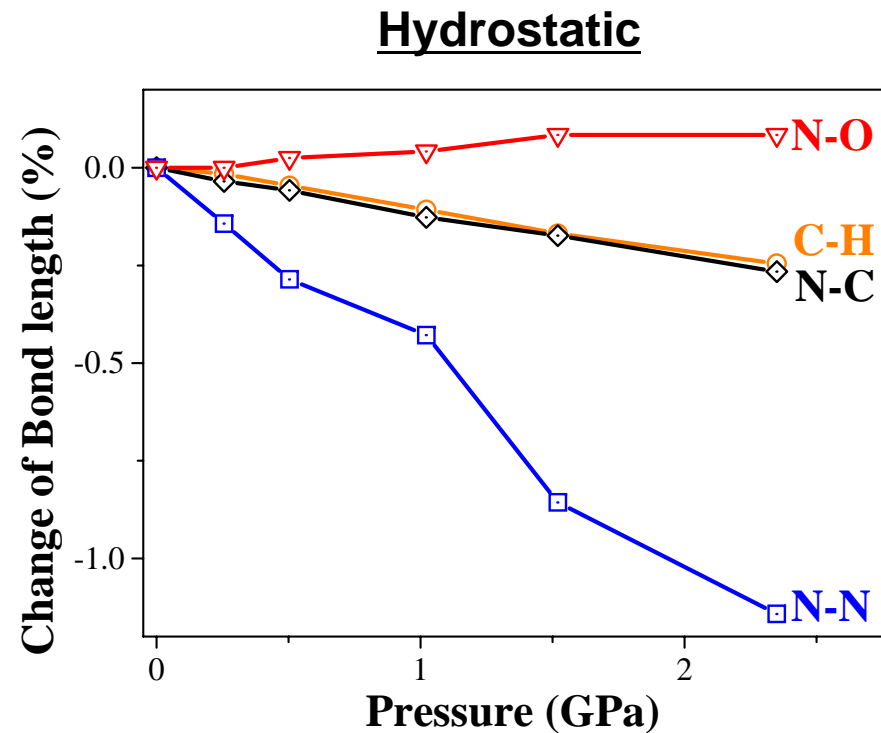
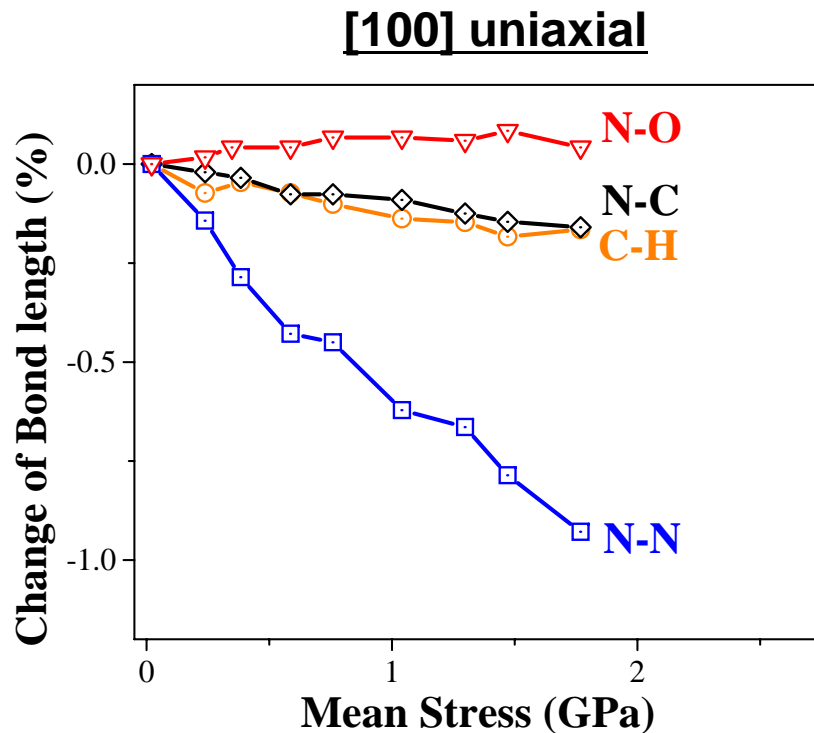
Summary of findings

- ◆ Intramolecular bonding is well described while intermolecular interaction (and crystal stiffness) is underestimated (with GGA)
- ◆ Unit cell volume of RDX overestimated by 6.3% at 0 GPa and by 2.7% at 3.65 GPa hydrostatic pressure
- ◆ Intramolecular N-N bonds most compressible
- ◆ RDX molecular pairs show significant reduction of intermolecular distances under pressure
- ◆ Uniaxial strain along different crystal orientations is underway

First-principles simulations can provide insight into structural changes under compression

Future directions

- ◆ Vibrational analysis for RDX in solid phase
- ◆ Uniaxial compression along [100], [010], [001], etc.
- ◆ Preliminary results on [100] uniaxial compression:



Summary/Future Directions

- ◆ We have developed systematic procedures for ab initio, all-electron, quantum-mechanical calculations of ambient volumes, hydrostatic compression of tetragonal crystals, and vibrational frequencies; need to compare with Crystal06
- ◆ Study uniaxial strain in PE, PETN, RDX
- ◆ MP2 code with Torino group: is it feasible for OMC's?
- ◆ DFT functional development: the need to climb "Jacob's ladder"
- ◆ Must examine more sophisticated basis sets for ambient volume:
 - TZP?
 - "Hybrids?"
 - Prior work showed that simple, but optimized, sets do not help
- ◆ Will use VASP (Maosheng/ISP) for RDX ambient volume and compare with Crystal06
- ◆ *Always work to close the gap between what we should do and what we are doing.*