Ground-state Structure and Dynamics

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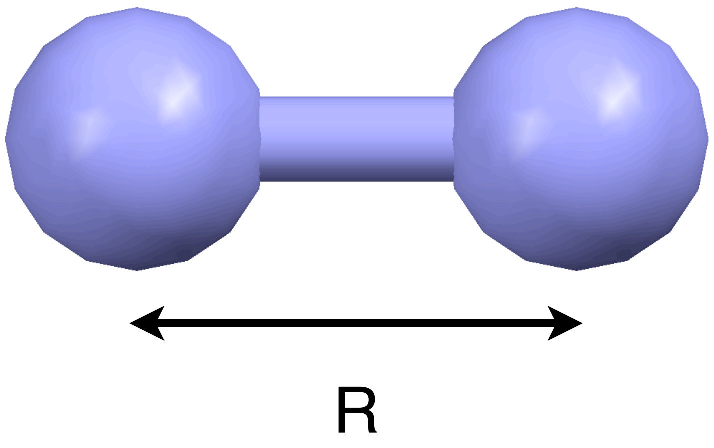
The Born-Oppenheimer Approximation

Compared to electrons, nuclei are massive and slow. This has two consequences:

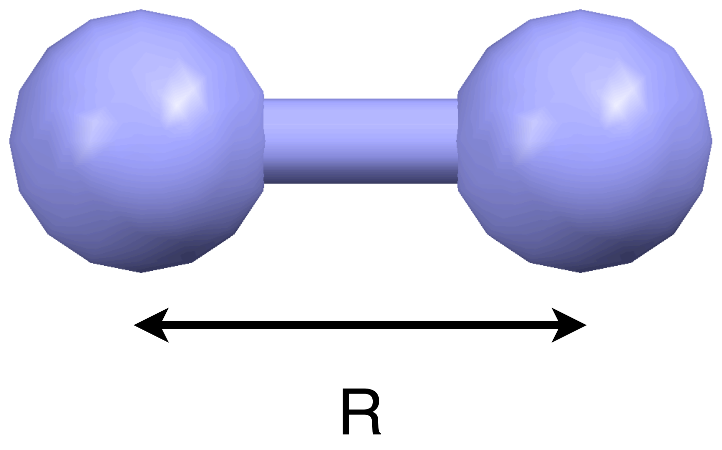
- Whenever a nucleus moves, the electrons react so quickly that it may as well be instant.
- The wavefunctions for the nuclei are zero except in a very small region – we may as well forget the wavefunction and just say ‘there they are’!



Forces

For a given set of atomic positions the ions will experience a force

$$F = \frac{dE}{dR}$$



After minimising the energy of the electrons PWSCF can compute the ionic forces

(v. cheap using Hellman-Feyman theorem)

```
***************** Symmetrised Forces *****************
*                                                    *
*            Cartesian components (eV/A)             *
* -------------------------------------------------- *
*                   x            y            z      *
*                                                    *
* N         1      0.56342      0.00000      0.00000 *
* N         2     -0.56342      0.00000      0.00000 *
*                                                    *
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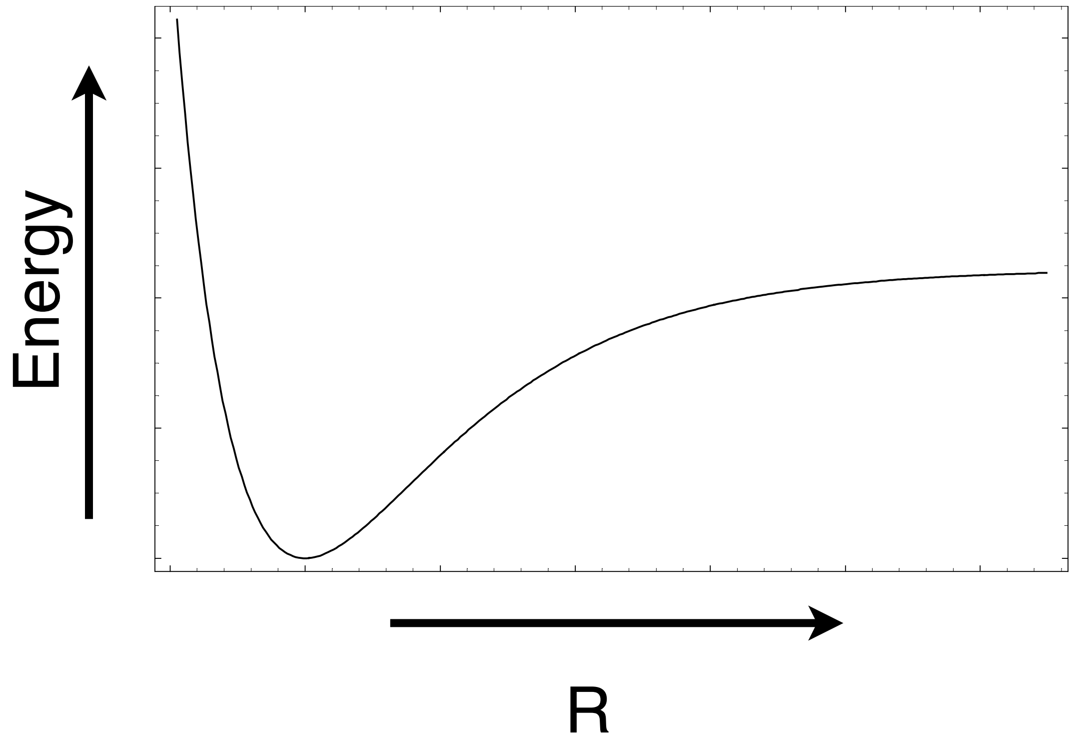


Rule of Thumb Force>1.0 eV/Å is a large force

1 Ry/a.u. = 25.7110 eV/Å

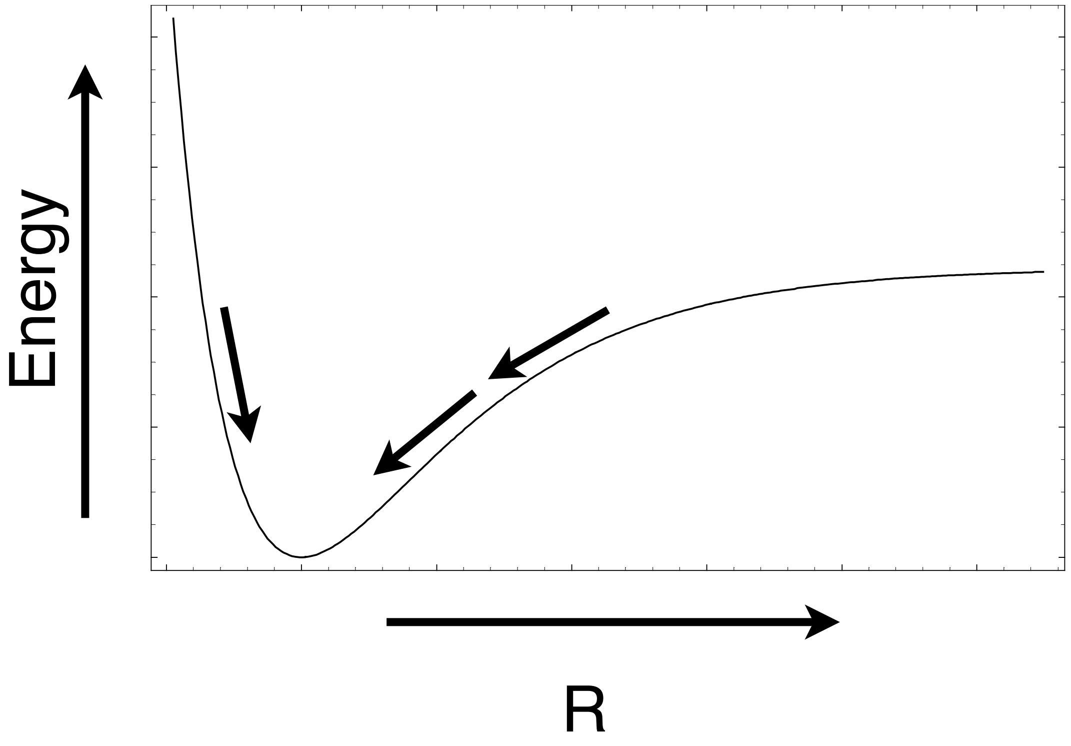
Crystalline materials

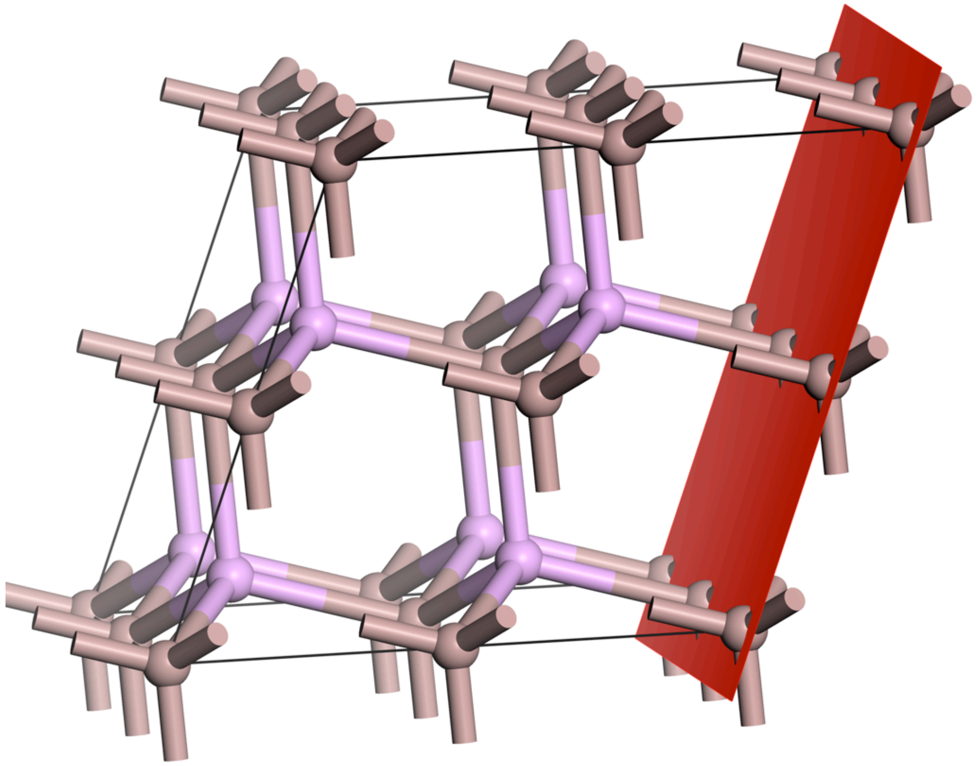
Ground-state structure at zero Kelvin corresponding to a minimum in the energy (all ionic forces are zero)

If we consider a crystalline material ground-state structure is a minimum in the Enthalpy (zero force and stress)

We can use the forces, and stress to guide us to the minimum

More precisely we use a minimisation algorithm called BFGS (Broyden–Fletcher–Goldfarb–Shannon)





Minimisation

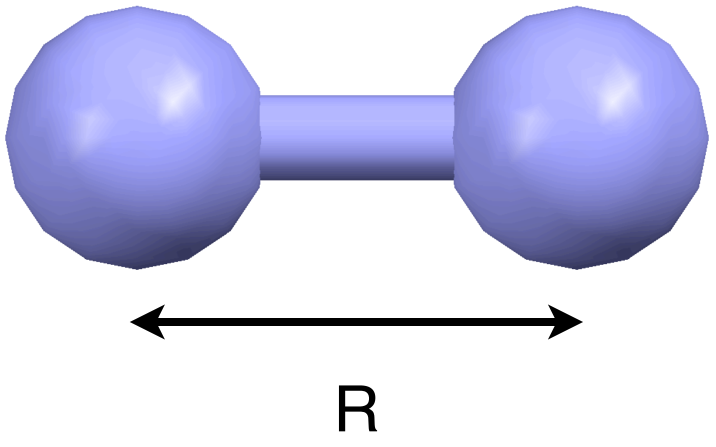
To find ground-state of system

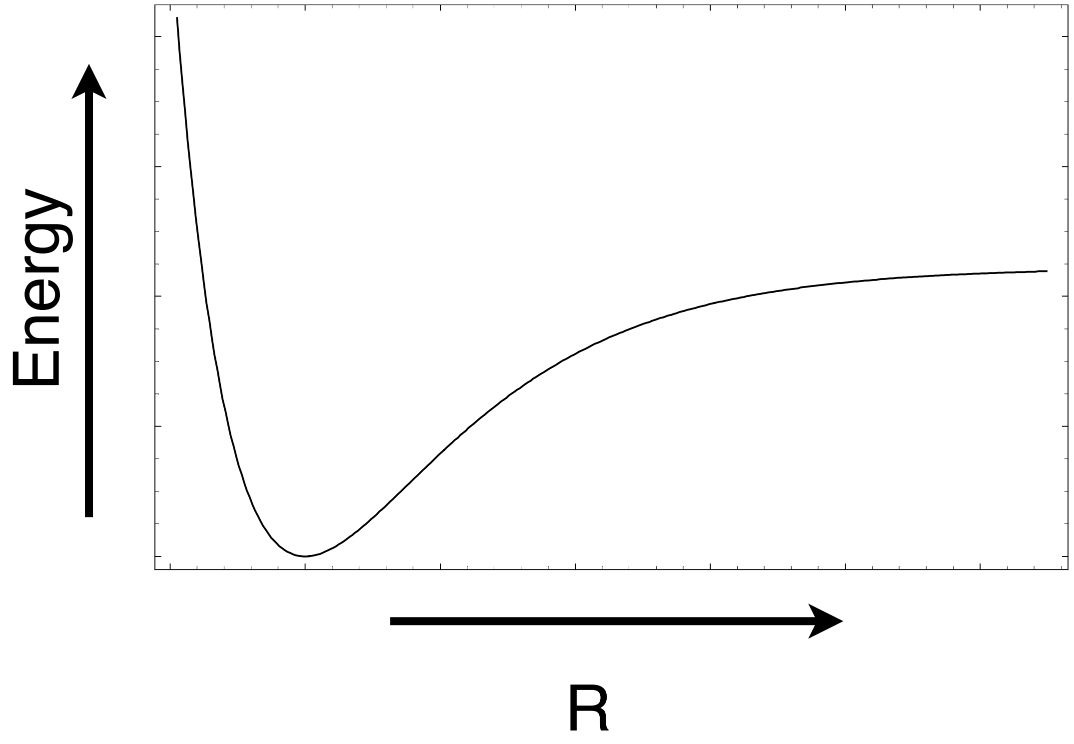
1- Minimise energy of electrons for fixed ionic positions

2- Evaluate forces on ions (+stress)

3- Move ions, unit cell according to BFGS algorithm

Repeat steps 1-3 until the maximum force / stress is below a specified value (plus a few other conditions)





Important note: BFGS will find the closest local minimum - this might not be the global minimum

Constraints

We can apply contraints to system during minimisation

- Fix positions of an atom or a set of atoms (for example fix heavy atoms and only allow H atoms to move)
- Fix unit cell (all or only allow given lattice vectors or angles to change)
- Fix centre of mass
- Apply a pressure to the unit cell: for example to find structure at given pressure - study phase changes

Note: We can also fix bond lengths, or bond angles. These are ‘non-linear contraints and so harder to apply.

What it can tell you

- Equilibrium bond lengths and angles
- Equilibrium cell parameters
- Discriminating between competing structures
- Elastic constants
- Surface reconstructions
- Pressure-driven phase transitions
- Starting point for many advanced investigations …

CONVERGE RESULTS (pw cutoff, k-points)

What is the right structure?

Need to think carefully about your problem

BFGS will find nearest minima.

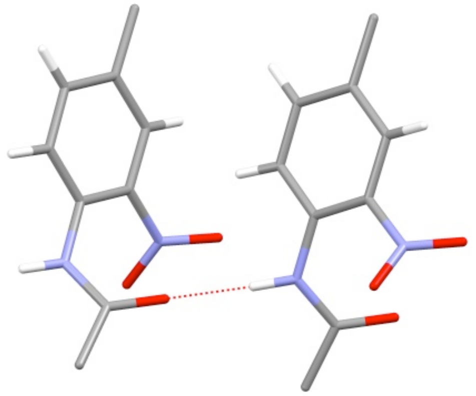
- Is this what you want?
- Maybe there are multiple minima
- Can compare total energy of minima to find the lowest
- If the energies are close these might all be physically relevant

Does your system have some disorder?

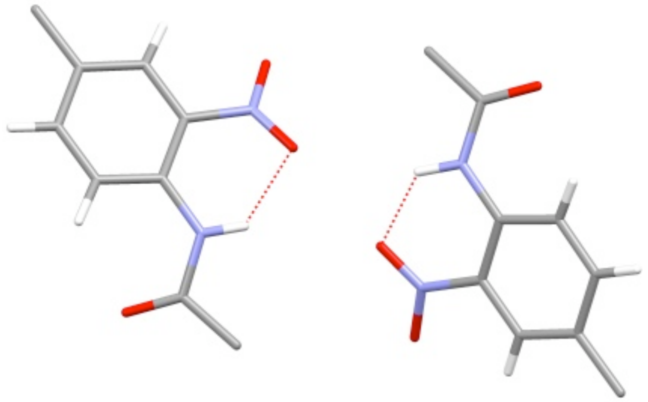
- Is it static disorder
- Is there a time-scale involved

Minimisation will give the 0K structure.

- A diffraction experiment would have been performed at a finite temperature.
- A spectroscopic measurement might have been made at a different temperature.



Two polymorphic forms of MNA
both are stable at rtp



The ground-state energies of the systems are close. But the spectroscopic signatures (NMR, vibrational) are quite different.

Where to get your crystal structure

Diffraction: Structures deposited in the ICSD (inorganic) and CSD (organic)

X-ray Diffraction: Many structures available (and equipment is common), but hydrogen positions inaccurate

Neutron Diffraction: Good resolution for light elements - but few structures available

For symmetric molecules or 1 or 2 dimensional systems (eg nanotubes): work out by hand, or use a programs such as tubegen.

Phonons

The first step in a calculation of the phonon frequencies is to perform a geometry optimisation to obtain a structure with no forces on the ions.

Harmonic lattice dynamics is based on a Taylor expansion of the total energy about the equilibrium coordinates - assumes first order term (ie groundstate force) is zero

Formalism valid for finite stress - so can compute change in phonon frequency with pressure

The presence of negative eigenvalues (“imaginary frequencies”) shows we are not at a minimum of the energy - maybe a saddle point. This might indicate the system is unstable to a distortion

Knowledge of the phonons tells us something about the system’s response to temperature - can incorporate this information into property calculations at finite temperature

Comparison of ND and XRD

Sucrose - 3 structures in CSD

- **NRD** Neutron diffraction, G.M. Brown and H.A. Levy *Acta Cryst.* B**29**, 790-797 (1973).
- **XRD-91** X-ray diffraction, R. C. Hynes Y. Le Page , *J. App. Cryst.*, 24 (1991) p352
- **XRD-73** X-ray diffraction, J. C. Hanson L. C. Sieker L. H. Jensen , *Acta Crysta, B*, 29 (1973) p797

Compare Forces (eV/Å) for Expt and Partial Relaxed (PR = only H atoms can more) structures

		NRD		XRD-91		XRD-73	
		Expt	PR	Expt	PR	Expt	PR
Hydrogen	Mean Force	0.6065		7.1615		12.7606	
	Maximum Force	3.8200		20.7193		66.0071	
Heavy Atoms	Mean Force	0.6028		6.4252		11.4669	
	Maximum Force	3.9187		19.9329		65.7079	

NRD max force (3.8eV/Å) on O-H of length = 0.912 Å

XRD-73 max force (66eV/Å) on O-H of length = 0.636 Å

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		NRD		XRD-91		XRD-73	
		Expt	PR	Expt	PR	Expt	PR
Hydrogen	Mean Force	0.6065	0.0011	7.1615	0.0014	12.7606	0.0037
	Maximum Force	3.8200	0.0027	20.7193	0.0036	66.0071	0.0081
Heavy Atoms	Mean Force	0.6028	0.2613	6.4252	0.3285	11.4669	0.2028
	Maximum Force	3.9187	0.4565	19.9329	0.9787	65.7079	0.3764

NRD max force (3.8eV/Å) on O-H of length = 0.912 Å

XRD-73 max force (66eV/Å) on O-H of length = 0.636 Å

Relaxed bond length = 0.977 Å

Note: We kept the unit cell fixed during the relaxation. This is important when using standard functions LDA/GGA as they do not describe dispersion/Van der Waals forces well - and these have a large contribution to the cohesion of molecular crystals.

AlPO-14 calcined: calculations

Experimental

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	43	4.0	0.8
Al2	43	3.4	0.2
Al3	38	2.5	0.6
Al4	45	4.9	0.3
P1	−21.4		
P2	−26.7		
P3	−31.5		
P4	−26.7		

Calculated

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	38.5	5.30	0.08
Al2	48.6	9.69	0.26
Al3	40.3	5.55	0.74
Al4	55.9	7.04	0.57
P1	−33.5		
P2	−24.0		
P3	−35.7		
P4	−35.8		

CASTEP

48 atoms in unit cell (8 $AlPO_4$)

GGA/PBE
Ultrasoft pseudopotentials
60 Ry cut-off energy
0.04 Å^{-1} k-point spacing

NMR calculation: 12 processors for 2 days

Referenced to berlinite ($AlPO_4$)

Forces up to 4 eV / Å

slides from Sharon Ashbrook (St Andrews)

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P1	−21.4		
P2	−26.7		
P3	−31.5		
P4	−26.7		

Calculated
optimized (fixed cell)

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	46.5	3.72	0.95
Al2	46.8	3.44	0.48
Al3	41.8	2.22	0.37
Al4	48.7	4.5	0.27
P1	−19.3		
P2	−25.6		
P3	−30.3		
P4	−24.5		

Forces up to 0.02 eV / Å

Calculated
optimized

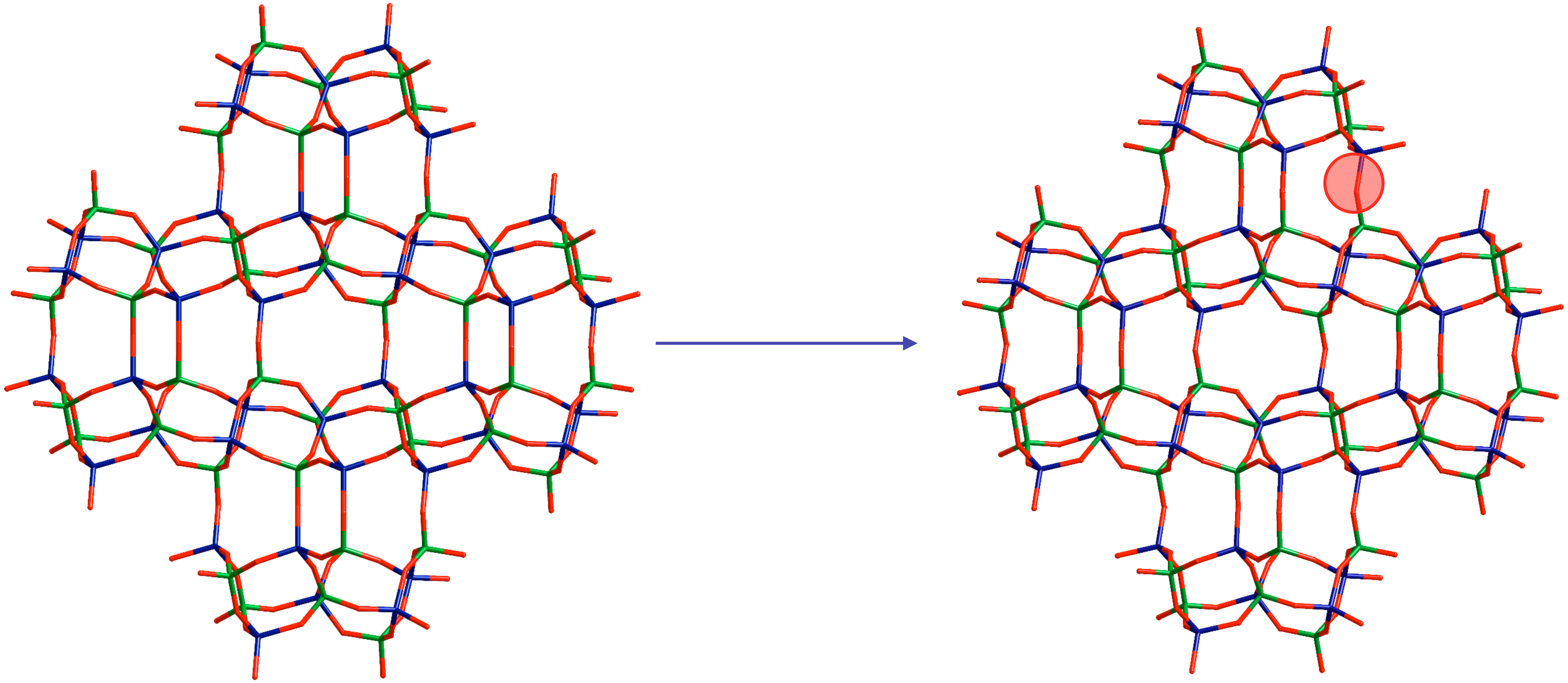
	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	43.2	4.54	0.74
Al2	43.8	3.57	0.25
Al3	38.0	2.80	0.71
Al4	46.6	4.96	0.26
P1	−21.4		
P2	−26.6		
P3	−32.9		
P4	−25.3		

Forces up to 0.015 eV / Å

slides from Sharon Ashbrook (St Andrews)

AlPO-14 calcined: calculations

- How much have we changed the structure?



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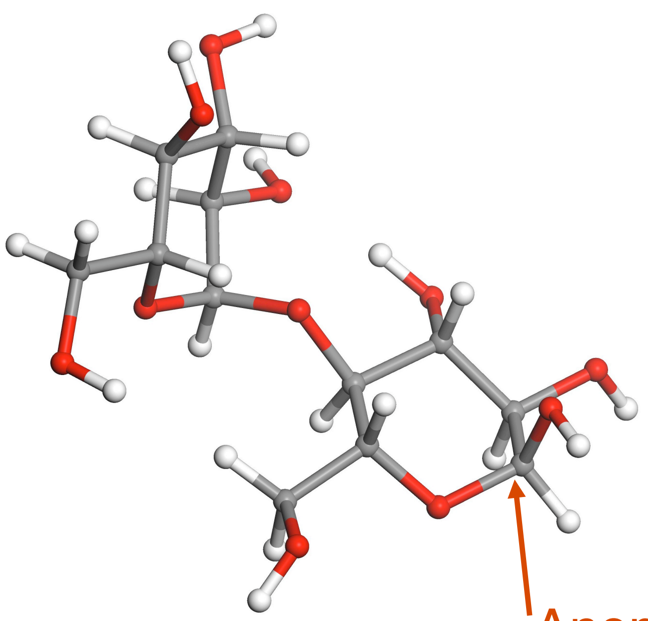
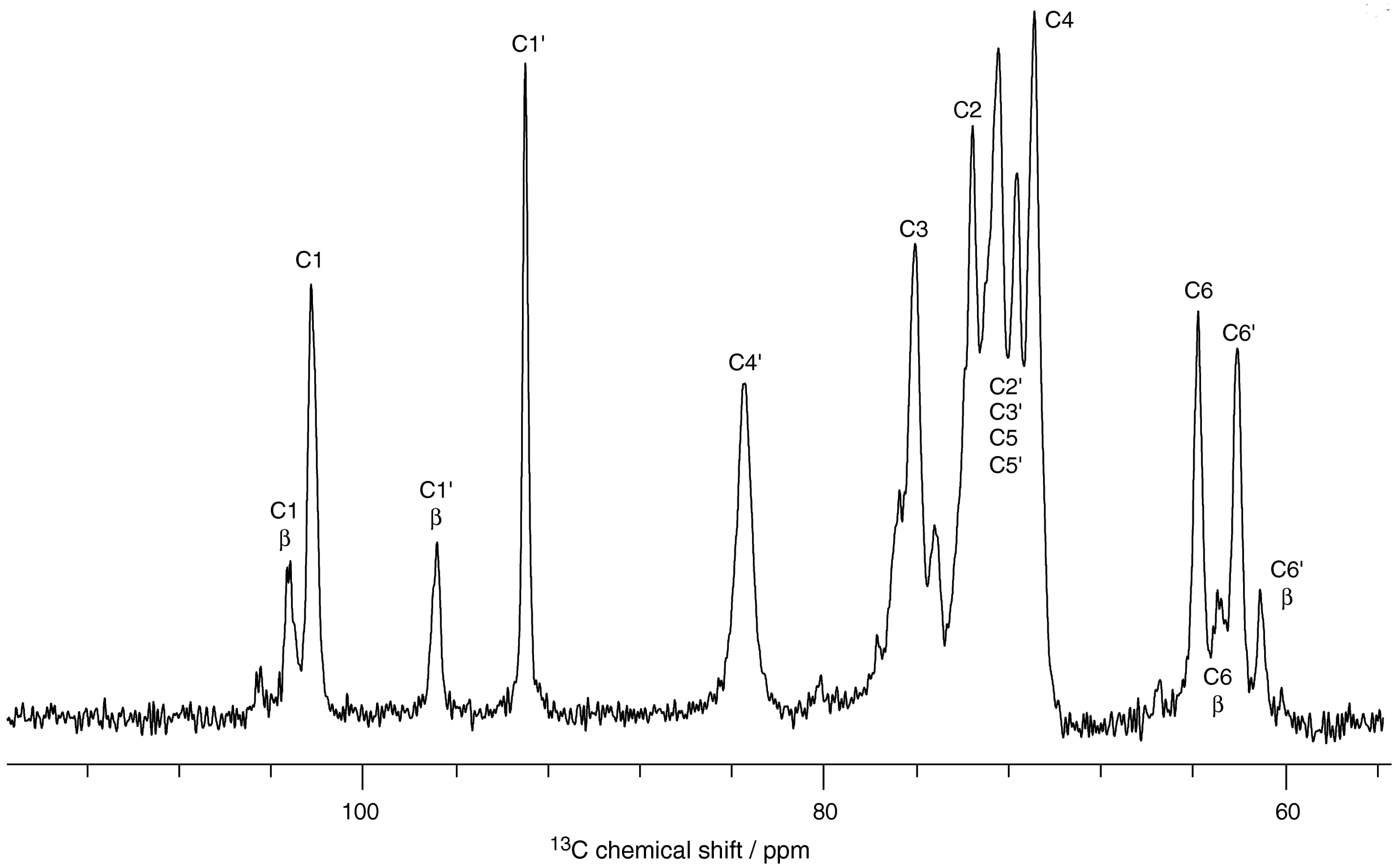
Static ‘Disorder’



Anomeric Carbon

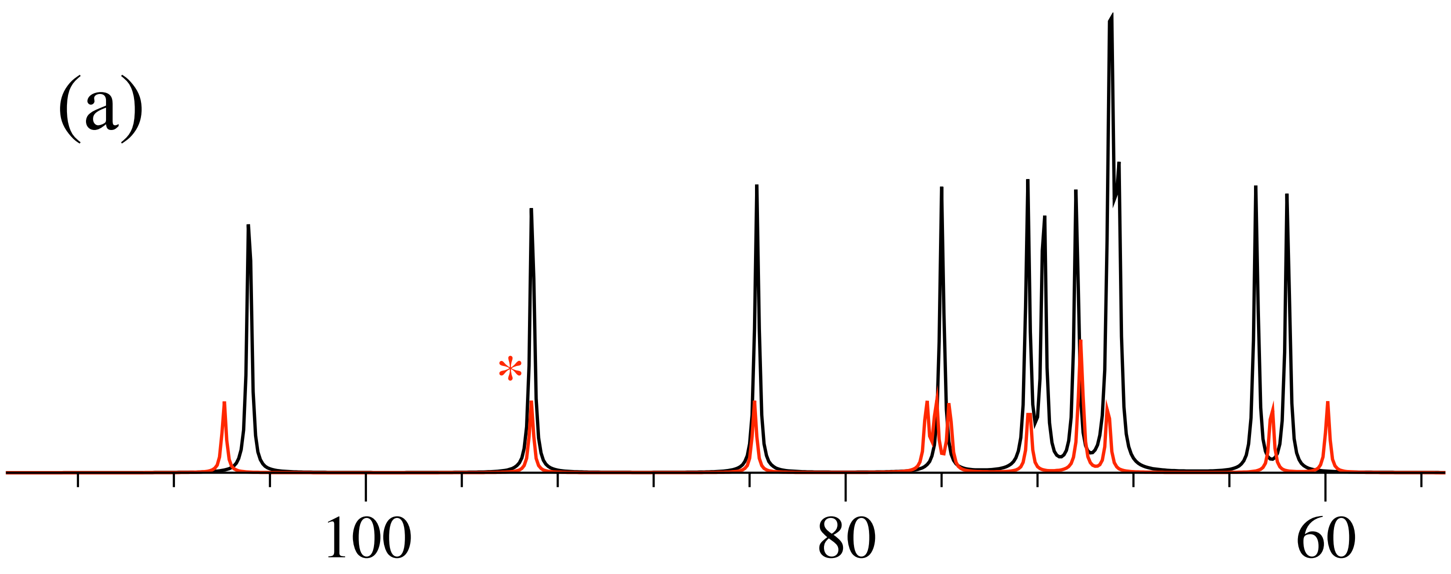


Crystallises as:

80% α-Maltose

20% β-Maltose

Compute spectra for both structures separately and superimpose



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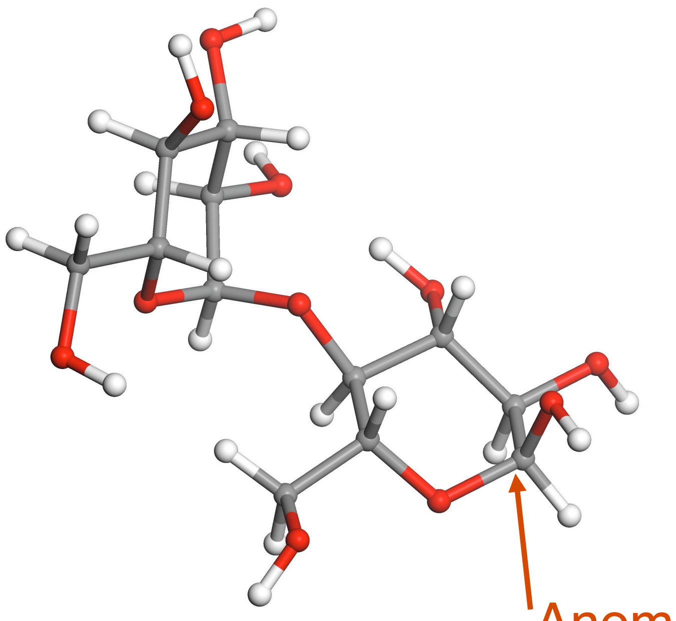

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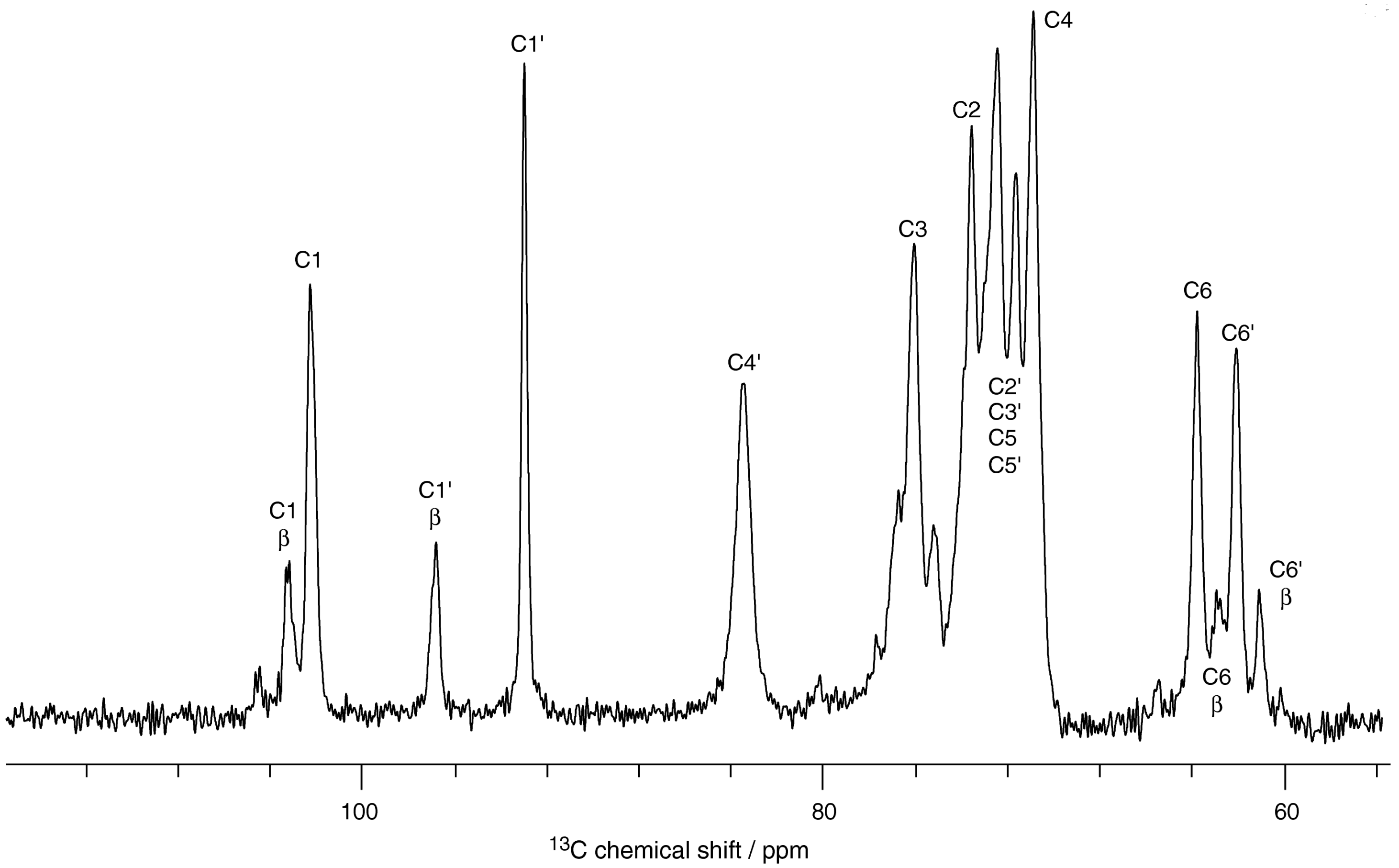
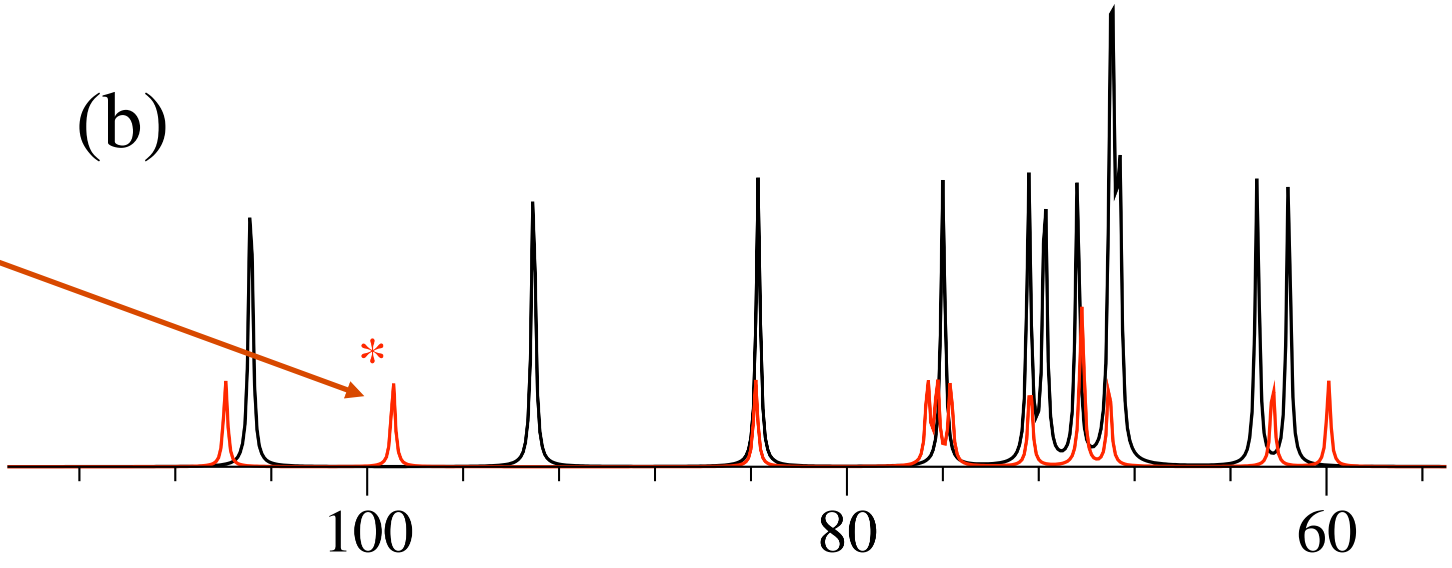


After relaxing neighbouring atom O1’ which had large force / thermal ellipsoid



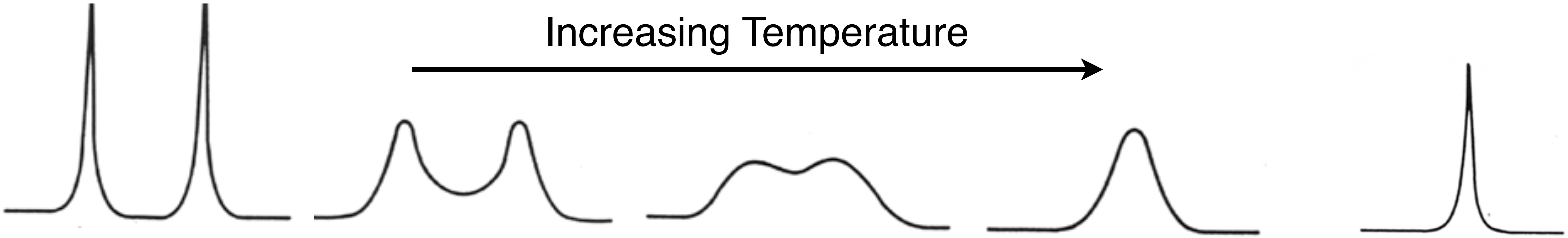
Thermal Motion

- *Vibration of atoms around equilibrium*
- *Hopping (exchange) between two minimum*

NMR “time scale” is “slow” - Lamor frequency ~<1GHz

Bond-vibrations ~1-100THz are much faster than NMR timescale: so nucleus feels average magnetic field (note: not the same as magnetic field from average structure). No line broadening.

Exchange processes - faster than NMR timescale => single peak
comparable to NMR timescale => broad peak
slower than NMR timescale => two (or more) peaks



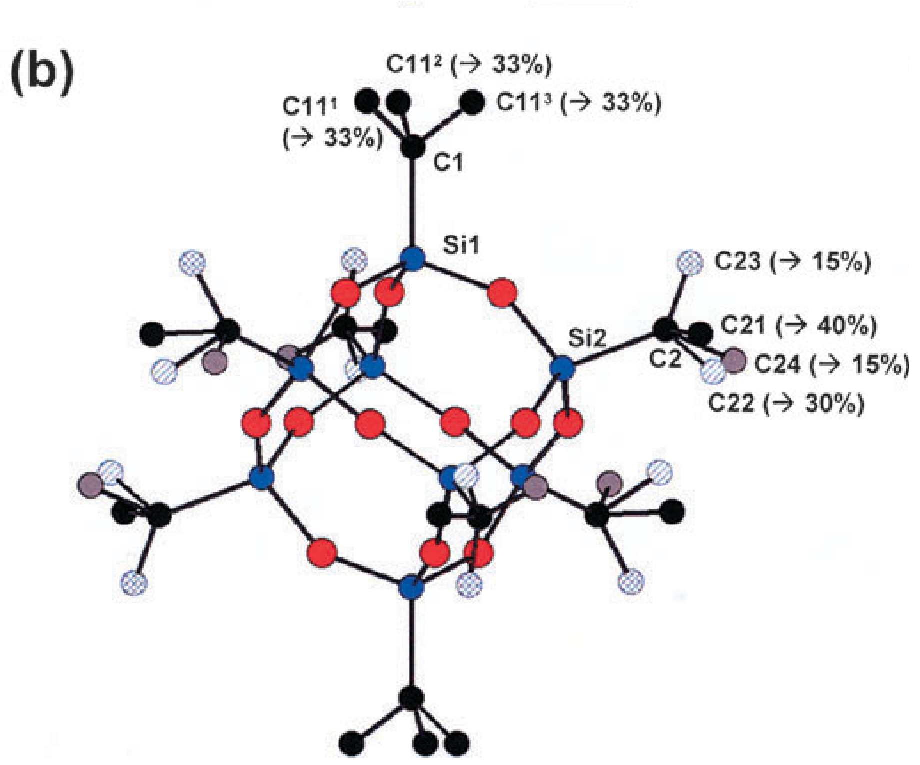
Many different timescales in NMR - can be a sensitive probe of dynamics

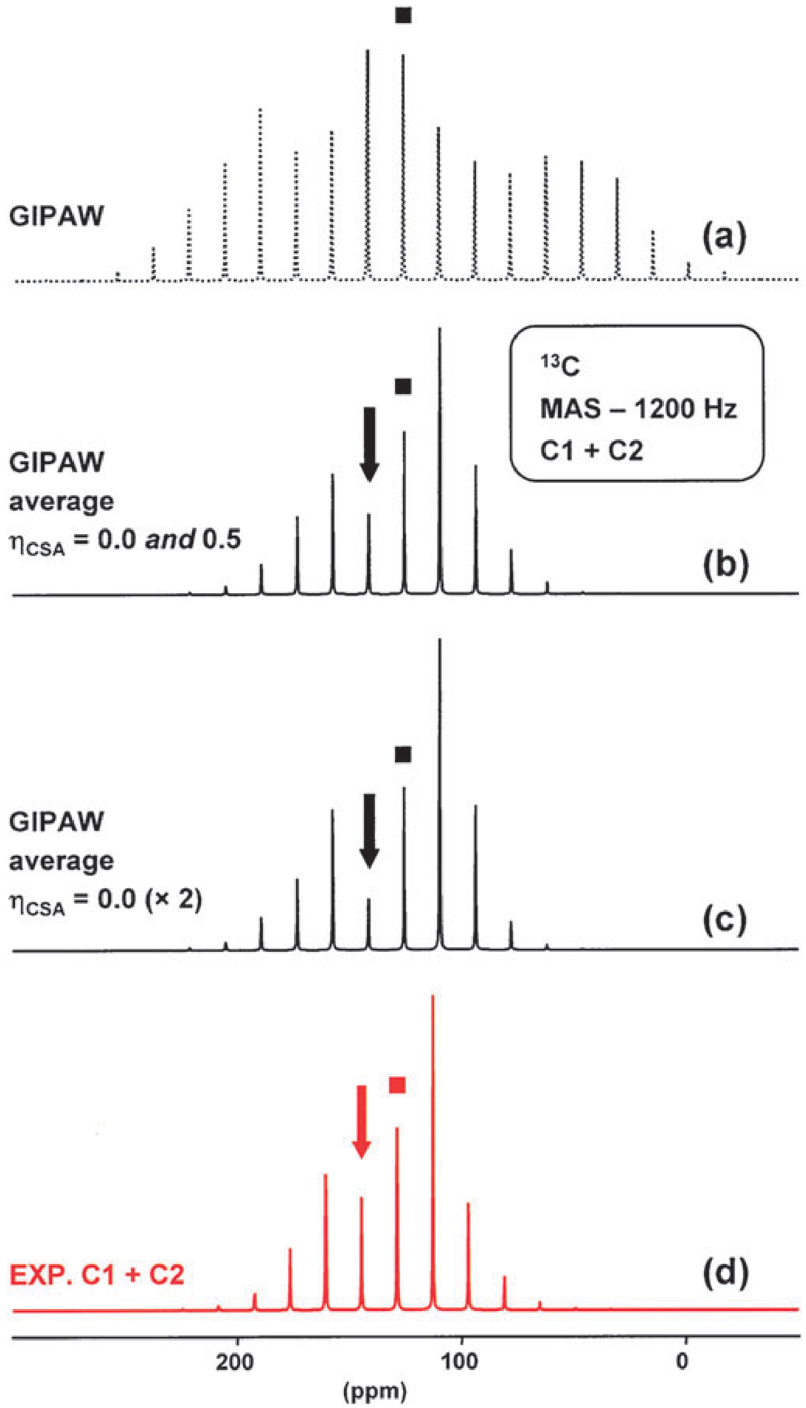
eg effect on STMAS
J. M. Griffin, S. Wimperis, A. J. Berry, C. J. Pickard and S. E. Ashbrook, *J. Phys. Chem. C*, 2009, **113**, 465

Phys. Chem. Chem. Phys., 2009, **11**, 6953 - 6961, **DOI:** 10.1039/b907450c

GIPAW (gauge including projected augmented wave) and local dynamics in ^{13}C and ^{29}Si solid state NMR: the study case of silsesquioxanes $(RSiO_{1.5})_8$

Christel Gervais, Laure Bonhomme-Coury, Francesco Mauri, Florence Babonneau and Christian Bonhomme





Variable Temperature (experiments)

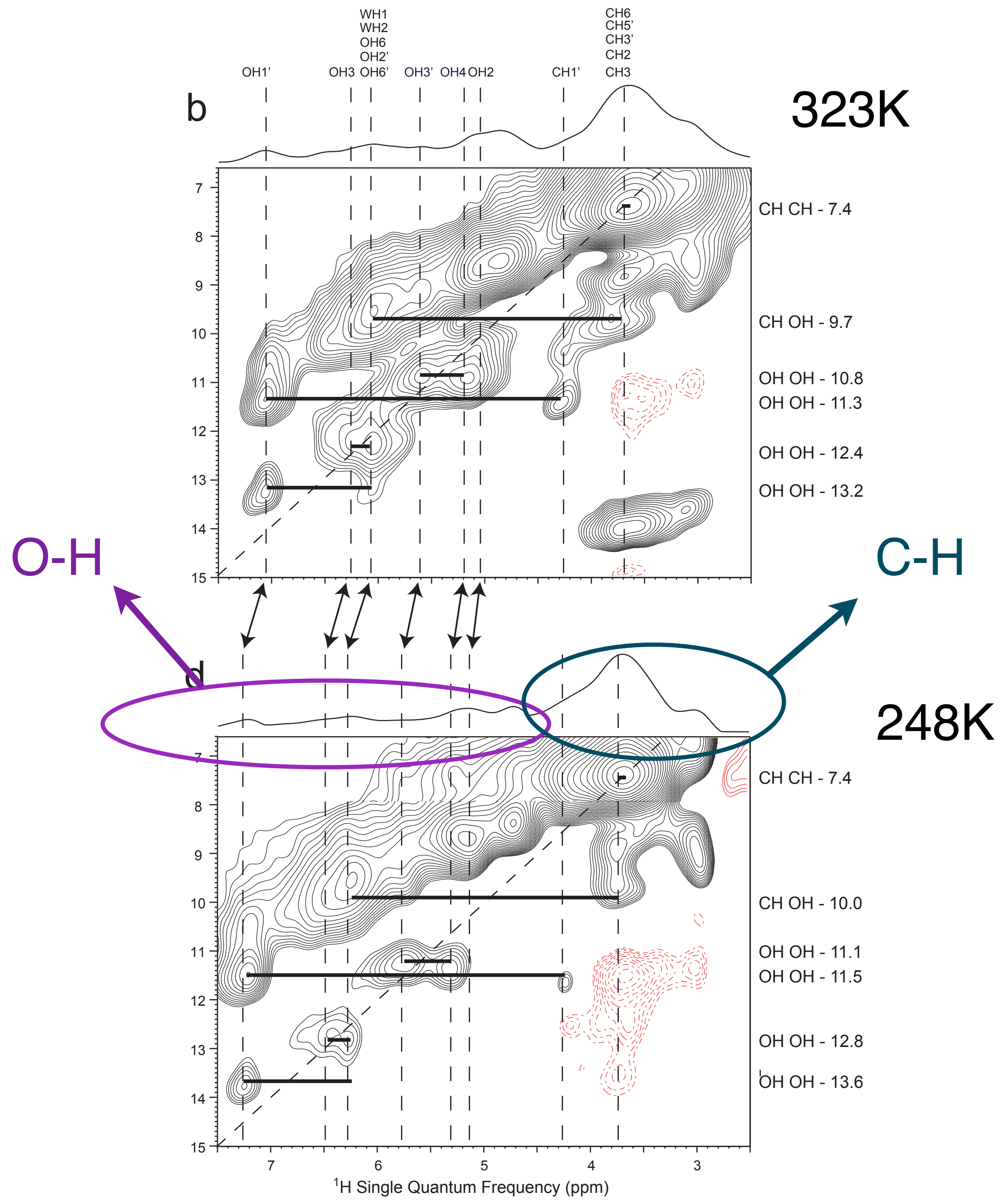
In NMR experiments it is possible to vary the temperature of the sample (eg via the gas used to spin the rotor) and hence investigate the effect of temperature

Maltose (again!)

Compare Calculation with rtp experiment
- C-H max error 0.3ppm (mean 0.1ppm)
- O-H max error 0.6ppm (mean 0.4ppm)

Compare Calculation with experiment extrapolated to 0K
- C-H (no change)
- O-H max error 0.4 ppm (mean 0.1ppm)

Thermal motion appears to affect O-H but not C-H hydrogens. Extrapolating measurements to 0K gives much better agreement with calculations



Experimental work performed in groups at Warwick (S. Brown) and Lyon (L. Emsley)

Variable Temperature (calculations)

Ways to incorporate thermal effects:

Use a crystal structure obtained at finite temperature

Take into account vibrations:

Compute the phonon frequencies.
Generate an ensemble of structures corresponding to a population of phonons.
Average results.
Note this gives a correction even at 0K (zero point motion)

Molecular dynamics

see Dumez and Pickard *J. Chem. Phys. 130, 104701 (2009)*

Molecular Dynamics

Compute the forces on the ions, then evolve their positions in time using classical (Newtonian) mechanics

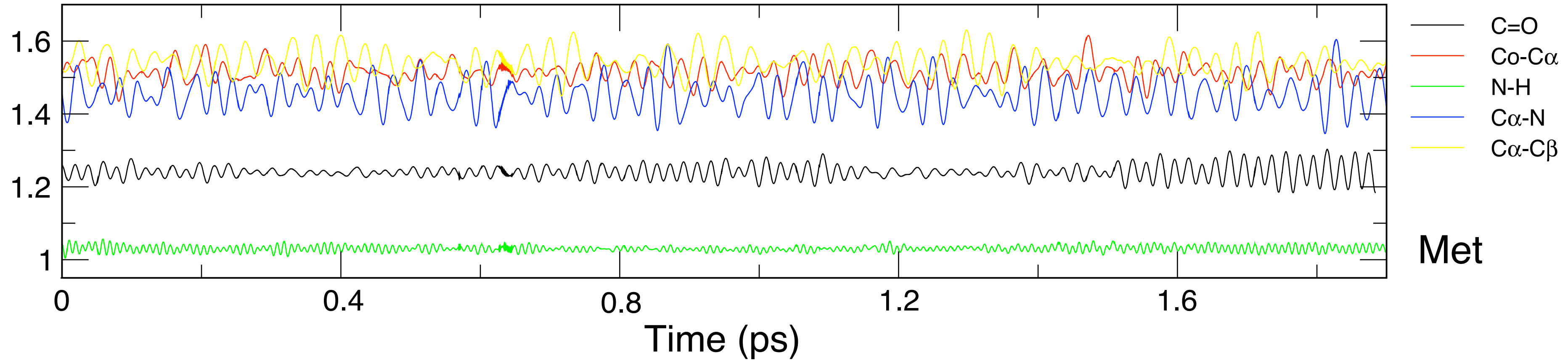
Includes effects beyond the Harmonic approximation

QM of ions can be treated with path-integral molecular dynamics (not routine)

Can only simulate short timescale (~10ps) ok for vibrations - longer timescales not captured (generate forces from a classical method such as empirical potentials?)

Need to think carefully about thermodynamics (microcanonical / canonical ensemble)

Variation in bond lengths during MD simulation of a di-peptide at 293K



Met

Summary

A good geometry optimisation is an essential starting point for almost all investigations

Essential to think carefully about your simulation

also see this afternoon's practical

S. Rossano, F. Mauri, C. J. Pickard and I. Farnan, *J. Phys. Chem. B*, 2005, **109**, 7245

Y. J. Lee, B. Bingoel, T. Murakhtina, D. Sebastiani, W. H. Meyer, G. Wegner and H. W. Spiess, *J. Phys. Chem. B*, 2007, **111**, 9711

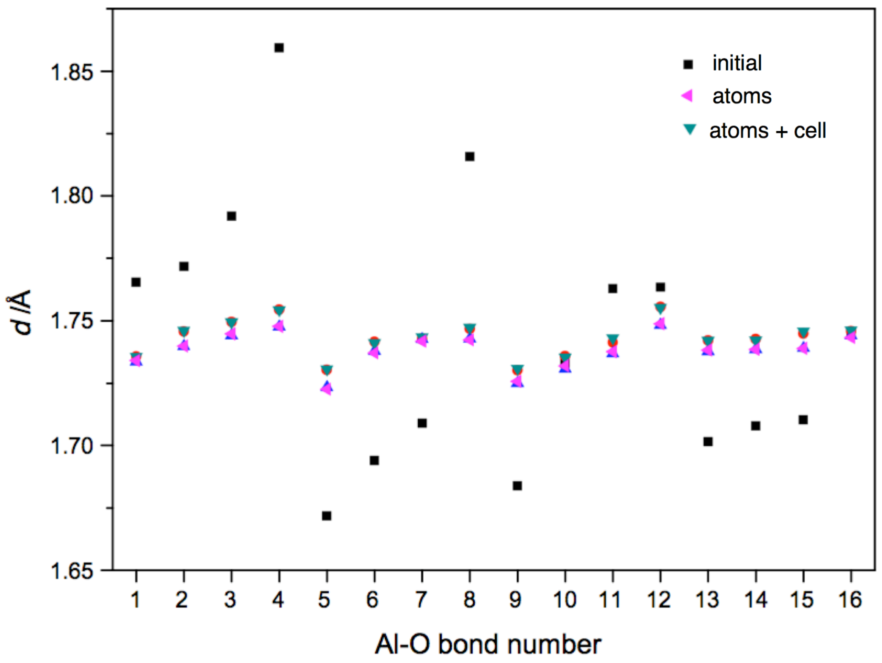
J. M. Griffin, S. Wimperis, A. J. Berry, C. J. Pickard and S. E. Ashbrook, *J. Phys. Chem. C*, 2009, **113**, 465

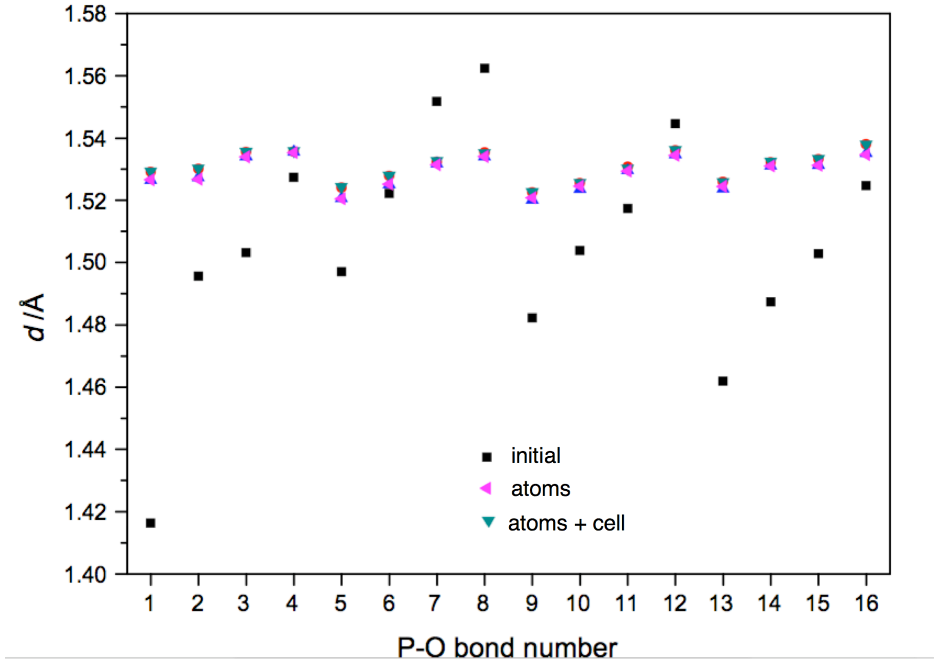
A. Soleilhavoup, M. R. Hampson, S. J. Clark, J. S. O. Evans and P. Hodgkinson, *Magn. Reson. Chem.*, 2007, **45**, S144 .

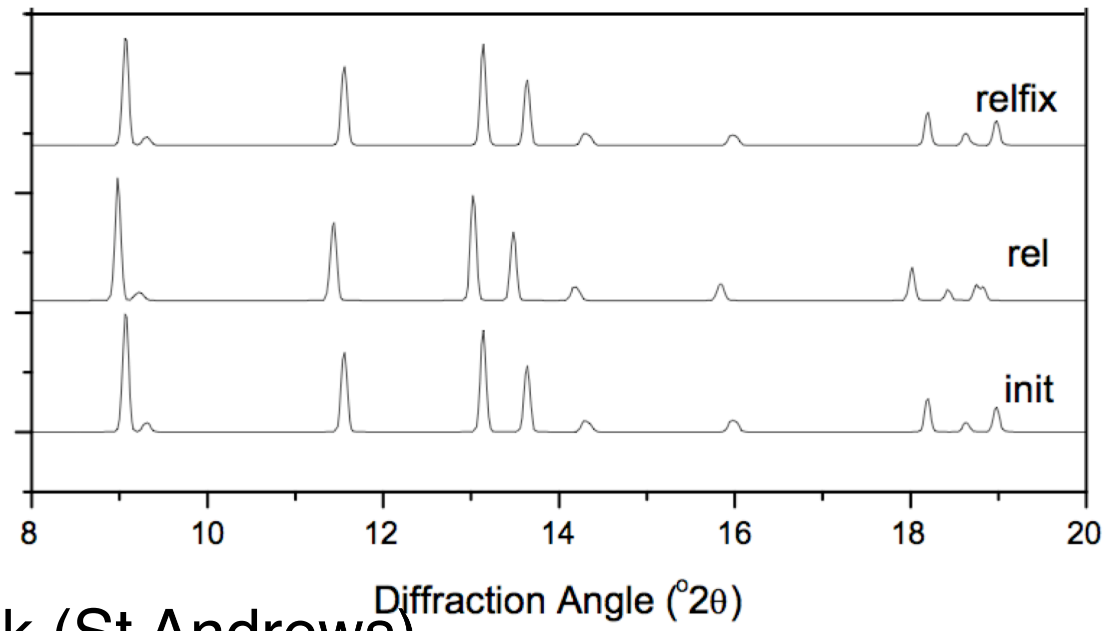
J-N. Dumez and C.J. Pickard *J. Chem. Phys. 130, 104701 (2009)*

AlPO-14 calcined: calculations

- How much have we changed the structure?







slides from Sharon Ashbrook (St Andrews)