Calculation of NMR Parameters in the Solid State

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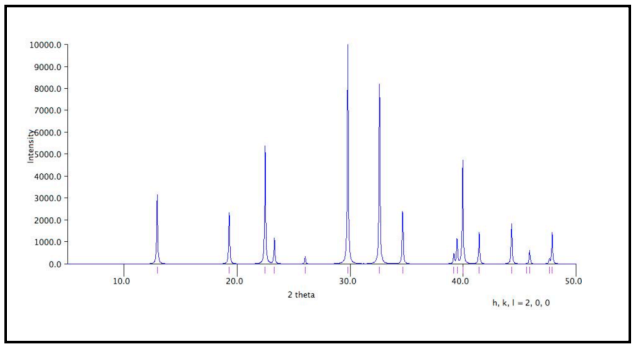
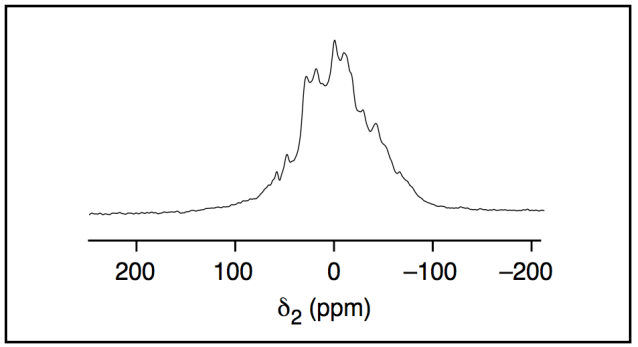
EaStCHEM

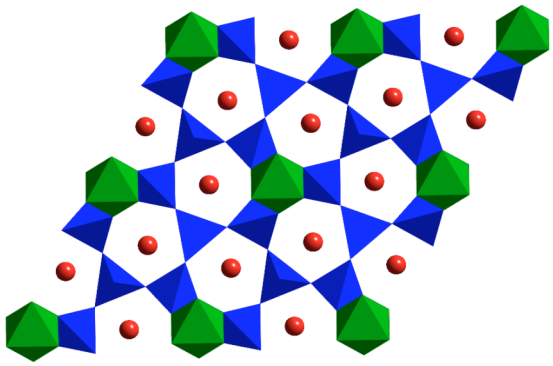
Obtaining structural information





$n\lambda = 2d \sin \theta$

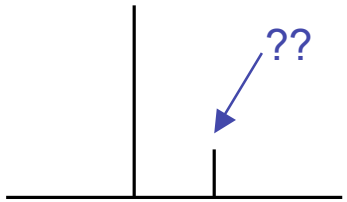
???



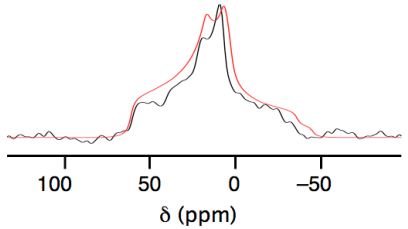
Why do we need calculations?

Spectral assignment

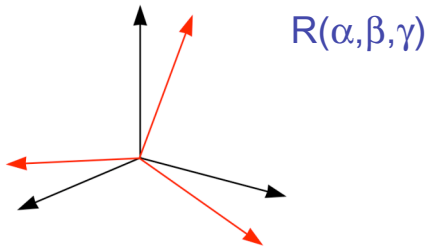
Spectral interpretation



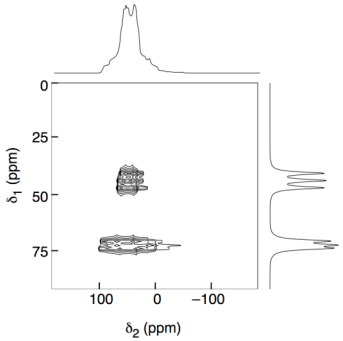
Confirmation of experimental parameters



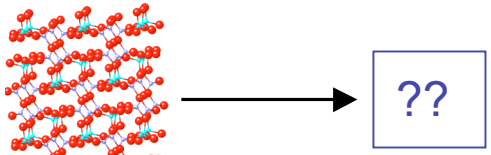
Additional information



Spectral prediction



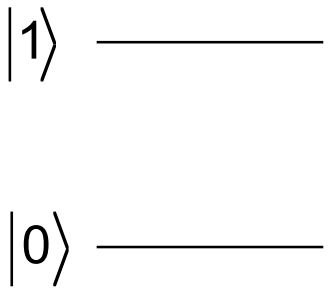
Testing of structural models/predictions



- Flexible way to study dependence of NMR parameters on local structure
- Models for disorder
- Information about dynamics

Quantum mechanics

- Magnetic resonance properties are inherently quantum mechanical



$$\alpha|0\rangle + \beta|1\rangle$$

- For one particle with two states we need to know two coefficients to describe the system

- For three particles with two states we now need eight coefficients

$$a|000\rangle + b|001\rangle + c|011\rangle + d|111\rangle + e|110\rangle + f|100\rangle + g|101\rangle + h|010\rangle$$

Number of coefficients 2^N

- In a material the number of states and the number of particles is very large
- Need to make some approximations

Quantum mechanics

- The many-particle Schrodinger equation cannot be solved

$$H = \text{nuclear kinetic} + \text{electron kinetic} + \text{nuclear/electron potential} + \text{nuclear/nuclear potential} + \text{electron/electron potential}$$

- Born-Oppenheimer approximation assumes nuclei are static

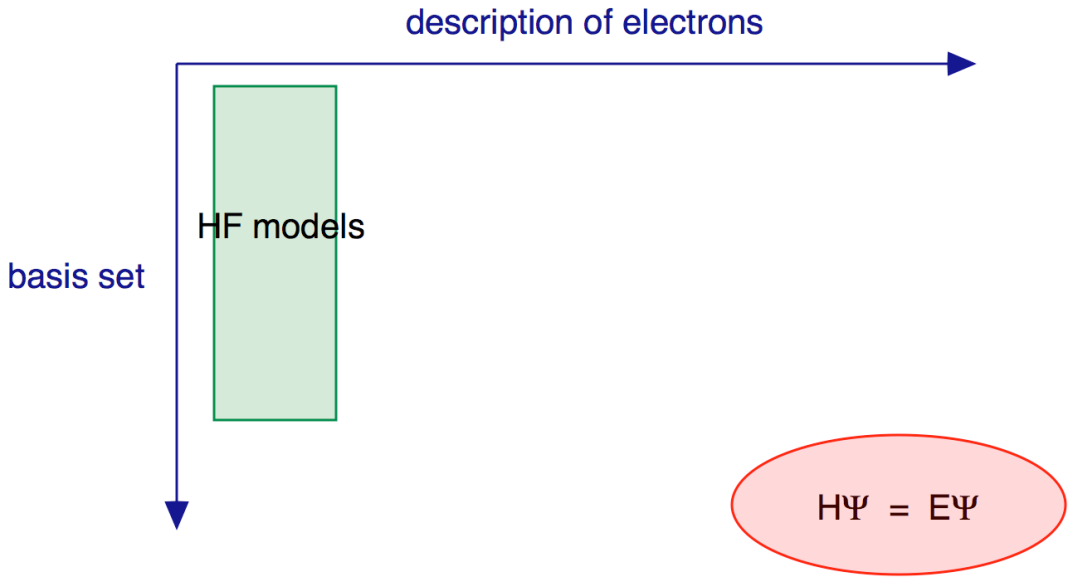
$$H_{el} = \text{electron kinetic} + \text{nuclear/electron potential} + \text{electron/electron potential}$$

$$E = E_{el} + \text{nuclear/nuclear potential}$$

Hartree-Fock theory

- The many-electron wavefunction is replaced by a sum of products of one-electron wavefunctions
- The electron-electron correlation is assumed to be zero (obviously incorrect)

- Wavefunctions are usually expressed as linear combinations of atomic orbitals (basis functions, B)
- Computational effort is $\propto B^4$ or B^3
- Restricted to first half of periodic table and moderate size molecules/systems



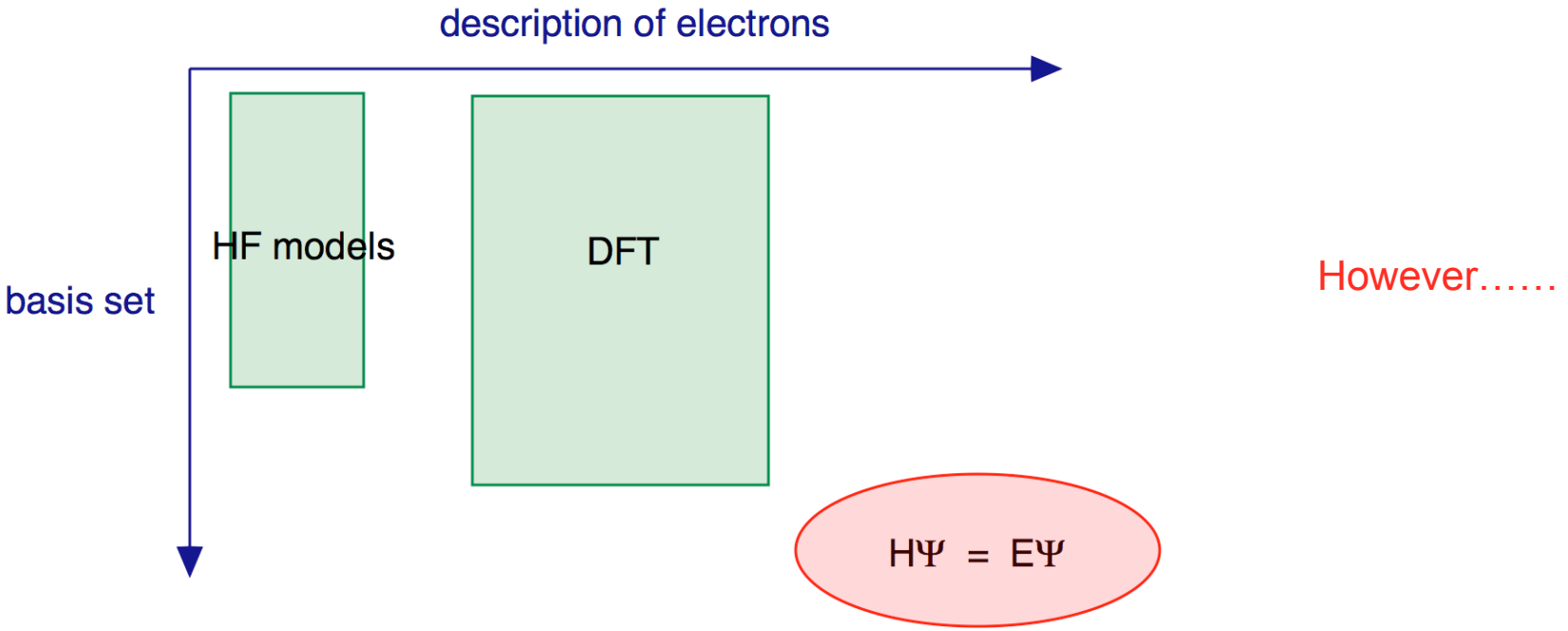
Not really commonly used for NMR calculations - too expensive to do accurately

Density functional theory (DFT)

- An alternative approach involves writing the total energy solely in terms of a functional of the density (relatively easily calculated at any point in space)

$$E[\rho] = E^{KE}[\rho] + E^{charge}[\rho] + E_{xc}[\rho] + E^{nuclear}[\rho]$$

- Generally computationally easier/faster/cheaper so can be performed for larger systems and for all/more of the periodic table



Density functional theory (DFT)

- The problem is we don't know the exchange/correlation energy
- Local density approximation (LDA)

$$E_{xc}[\rho] = \int \varepsilon_{xc}(\rho)\, \rho(r)\, d^3r$$

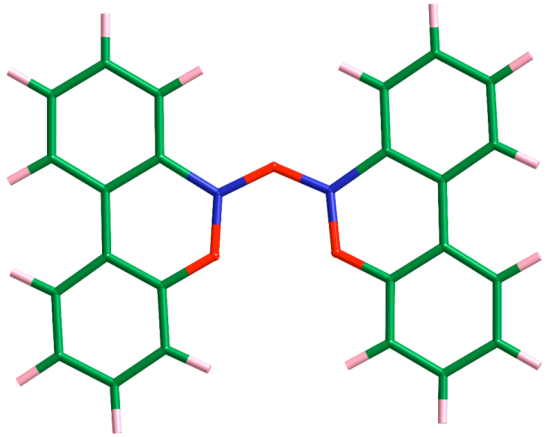
- Energy depends upon the local density only (calculated for a uniform electron cloud)
- "First-Principles"
- Generalized gradient approximation (GGA)

$$E_{xc}[\rho] = \int \varepsilon_{xc}(\rho, \nabla\rho)\, \rho(r)\, d^3r$$

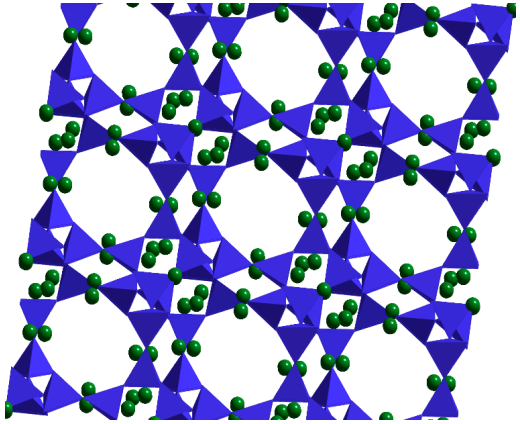
- Energy depends upon the gradient of the density
- Can be incorporated in a number of ways (PBE, BLYP)
- "First-Principles"?

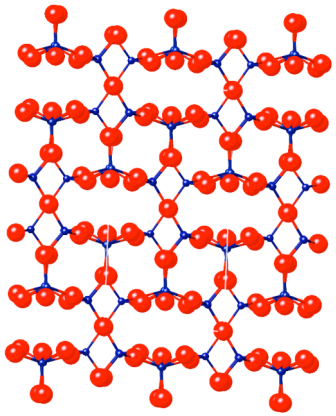
Extended systems

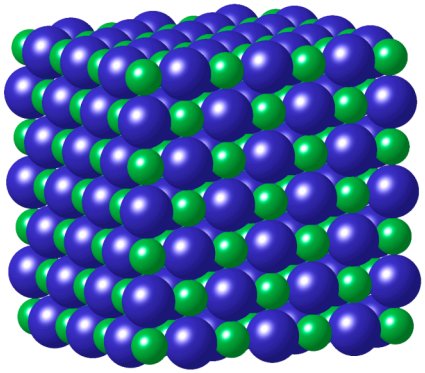
- For molecules the extent of the system is well defined and atomic orbitals (and their linear combinations) are a good basis set



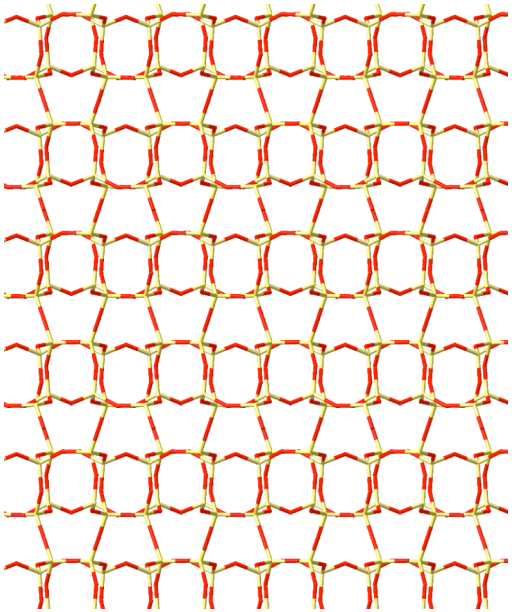
- What about the extended systems we regularly see in solids?





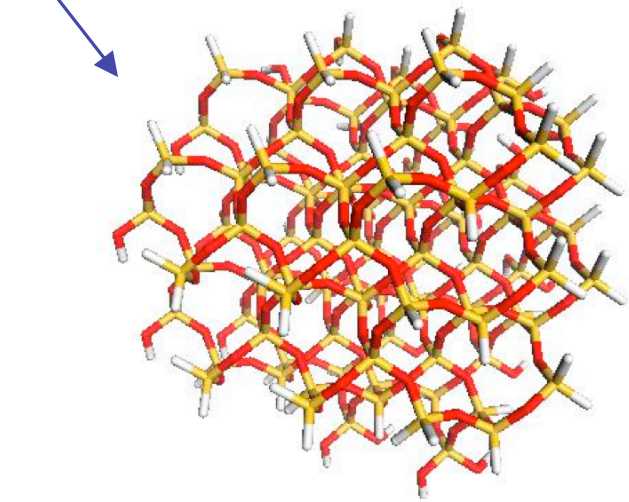


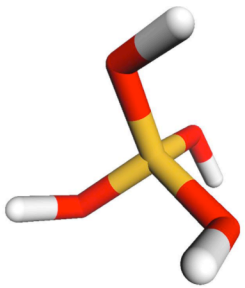
Cluster approximation



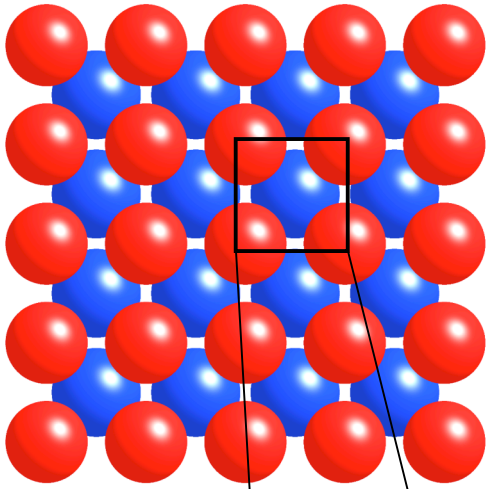
- Approximate an “infinite” solid as a cluster around a central atom
- Termination of dangling bonds, usually with ^{1}H
- Accurate results require larger and larger cluster sizes
- Large clusters become expensive quickly

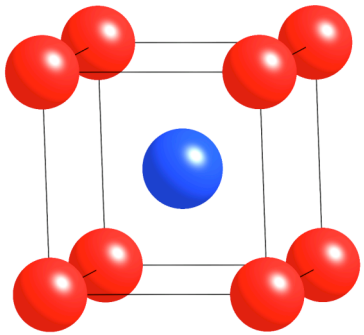
- Atom-based orbitals usually used as basis sets
- Accuracy determined by size/type of basis set and choice/position of termination





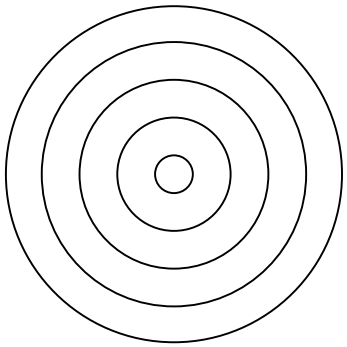
Periodic boundary conditions





- Exploit the translational symmetry of the structure
- Use the unit cell and impose three-dimensional periodic boundary conditions
- Long range effects reproduced well and no termination problems
- Accurate results for all atoms and atom types in the unit cell simultaneously

- Often used with plane waves as a basis set
- Quality of basis set controlled by a single number (E_{cut})



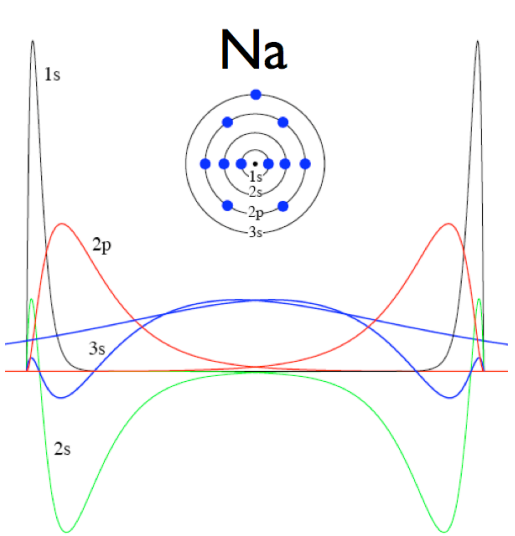
$$e^{i\,(4\sqrt{E_{cut}})\,.\,r}$$

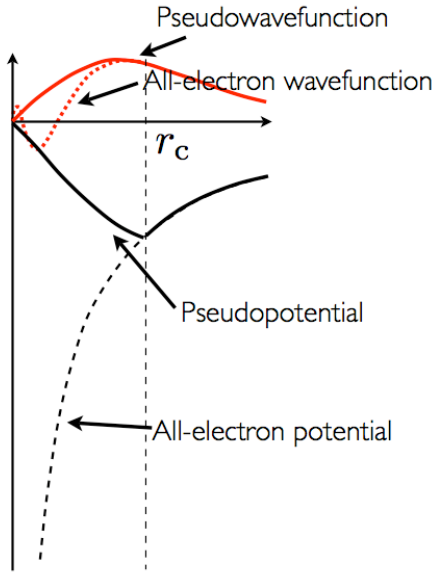
Pseudopotentials

- So how can we calculate an “infinite” number of atoms?
- Use a pseudopotentials to reduce calculation demands

frozen core

“smoothed” valence orbitals





- BUT, the core electron information is needed to calculate the NMR chemical shift!

- Can “fix up” wavefunctions near the nucleus (i.e., reconstruct the all electron wavefunction)
- PAW and GIPAW

Doing calculations

- Gaussian
- Implements a molecular/cluster approach
- HF or DFT
- Gaussian basis set
- Good for molecules, molecular solids

- WIEN
- Periodic solids with LAPW
- DFT
- Mixed basis set
- Very accurate all-electron approach for EFG only but long and costly to run

- CASTEP
- Periodic solids with GIPAW
- DFT
- Plane wave basis set
- Growing interest in use for chemical shift and quadrupolar calculations

Doing calculations

Choose

Computer

Code

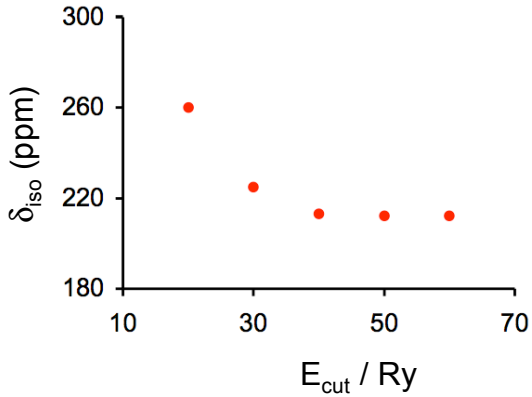
DFT functional

Pseudopotential

Converge

Basis set

Integration step



- CASTEP, GGA-PBE and ultrasoft pseudopotentials

20-60 atoms (depending on size) *in unit cell* on a pc

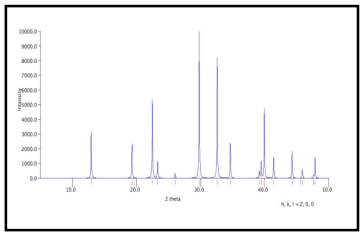
100-200 atoms *in unit cell* on a cluster

Up to 1000 atoms *in unit cell* on a supercomputer?

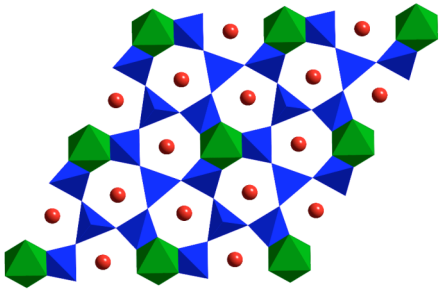
Initial structure

- Where do you get the initial structure from?

  Diffraction Neutron, powder X-ray, single crystal X-ray

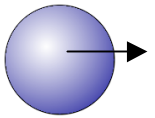


- Varying quality
- Protons typically misplaced
- “Average” occupancies of sites
- Flexibility of the structure



- How do you know if the structure/results are accurate?

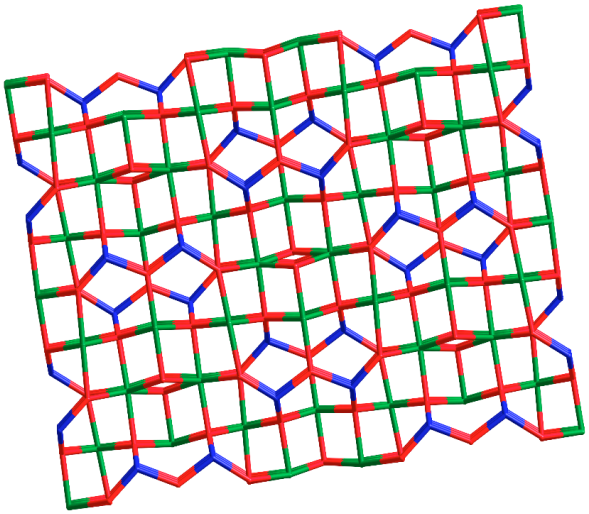
  Check the forces on the atoms



- Geometry optimization
  - Vary positions of some or all of the atoms
  - Fix or vary the unit cell size and shape
  - Retain or break the symmetry

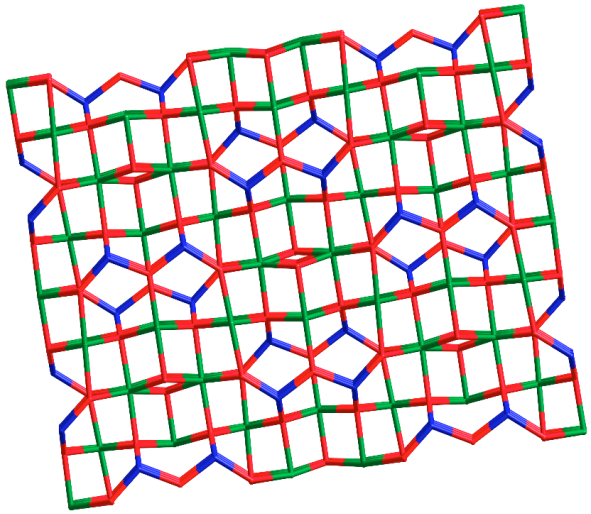
Geometry optimization

Rigid framework (neutron structure)



0-0.2 eV/Å

	δ_{iso} (ppm)	C_Q / MHz	η_Q
1	40.1	1.67	0.29
2	77.7	5.05	0.94
3	69.3	4.64	0.20
4	67.1	4.01	0.30

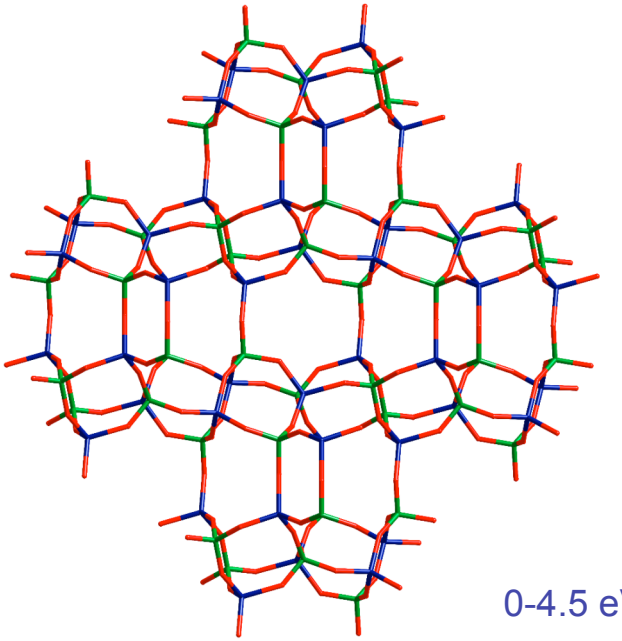


0-0.05 eV/Å

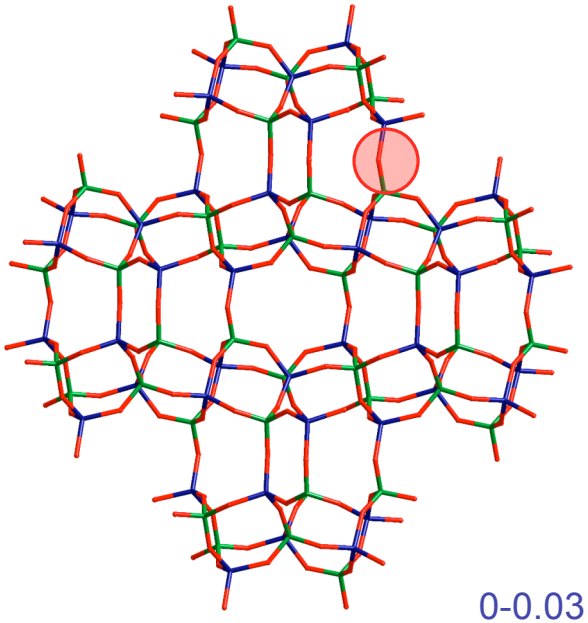
	δ_{iso} (ppm)	C_Q / MHz	η_Q
1	41.1	1.68	0.44
2	80.2	5.17	0.93
3	71.6	4.77	0.20
4	69.9	4.12	0.30

Geometry optimization

Flexible framework (powder X-ray structure)



0-4.5 eV/Å



0-0.03 eV/Å

	δ_{iso} (ppm)	C_Q / MHz	η_Q
1	38.5	5.30	0.08
2	48.6	9.69	0.26
3	40.3	5.55	0.74
4	55.9	7.04	0.57

	δ_{iso} (ppm)	C_Q / MHz	η_Q
1	46.5	3.72	0.95
2	46.8	3.44	0.48
3	41.8	2.22	0.37
4	48.7	4.50	0.27

Referencing

- Unlike experiment, it can be difficult to reference chemical shifts in calculations

- Need a simple reference structure (e.g., SiO_2, Al_2O_3, Y_2O_3, etc.,)
- Not all atom types in the real system are present?
- Geometry optimize?
- Converged to the same accuracy?

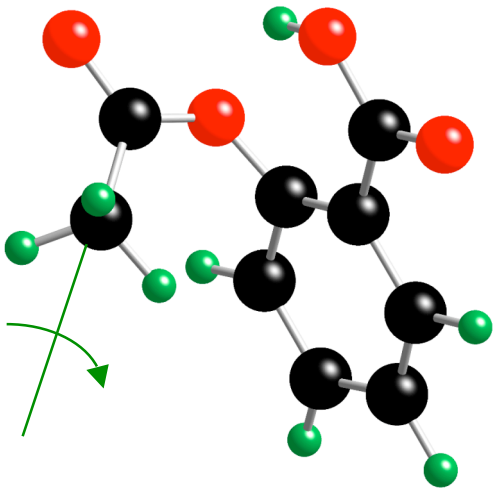
- Alternative approach is to reference within a calculation or between similar species
- Relative shifts converge much more rapidly than absolute shieldings
- All atom types are present
- Benefit from cancellation of errors

- As experimentalists we need to balance absolute accuracy both with cost but also with the level of information required for spectral analysis and interpretation

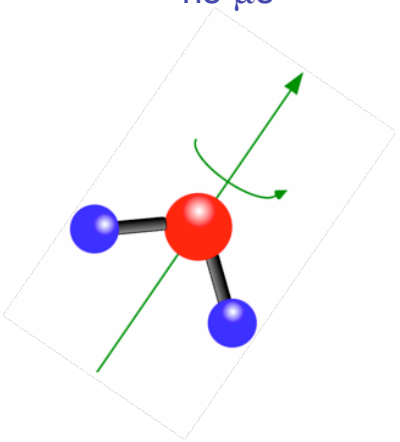
Dynamics?

- Calculations are typically performed at 0 K
- NMR is typically performed at 298 K
- Diffraction is typically performed at 120 K
- There is significant motion in the solid state over a range of timescales

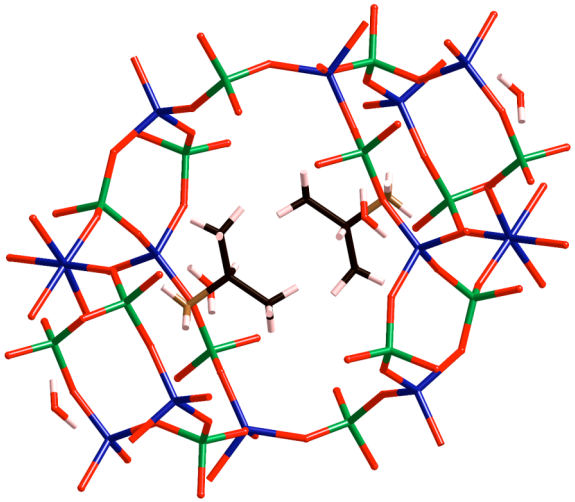
ps-ns



ns-μs



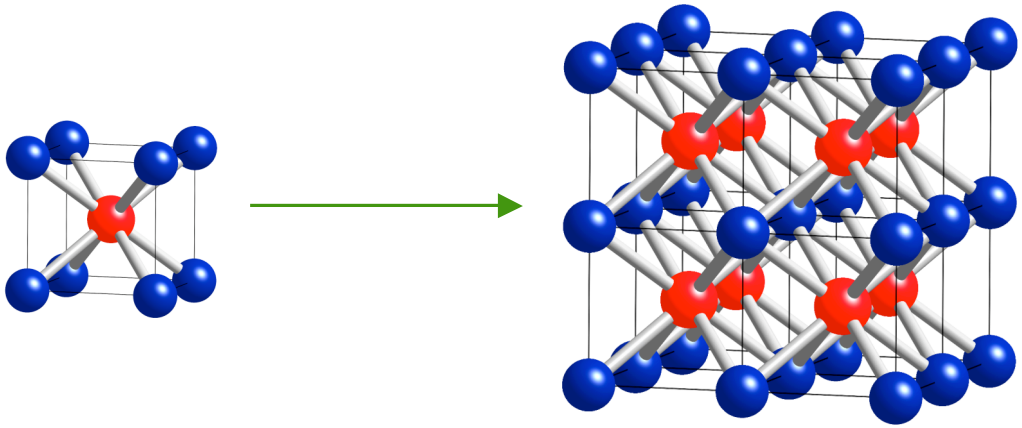
μs-ms



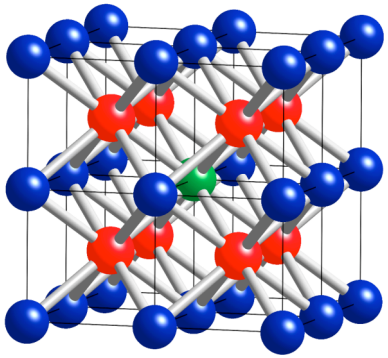
- Calculations can still be used to offer insight and help spectral interpretation
- Significant differences between experiment and calculation can suggest motion

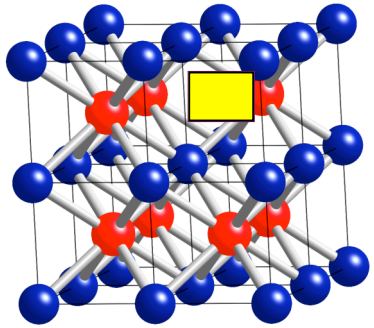
Supercells

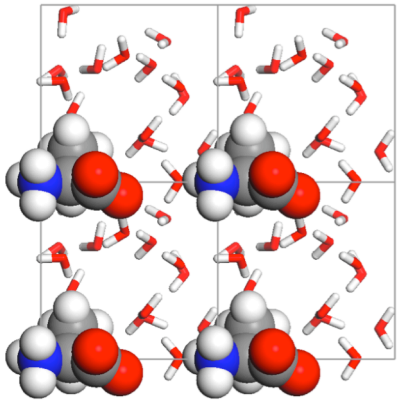
- Systems with lower periodicity can be studied using a supercell approach



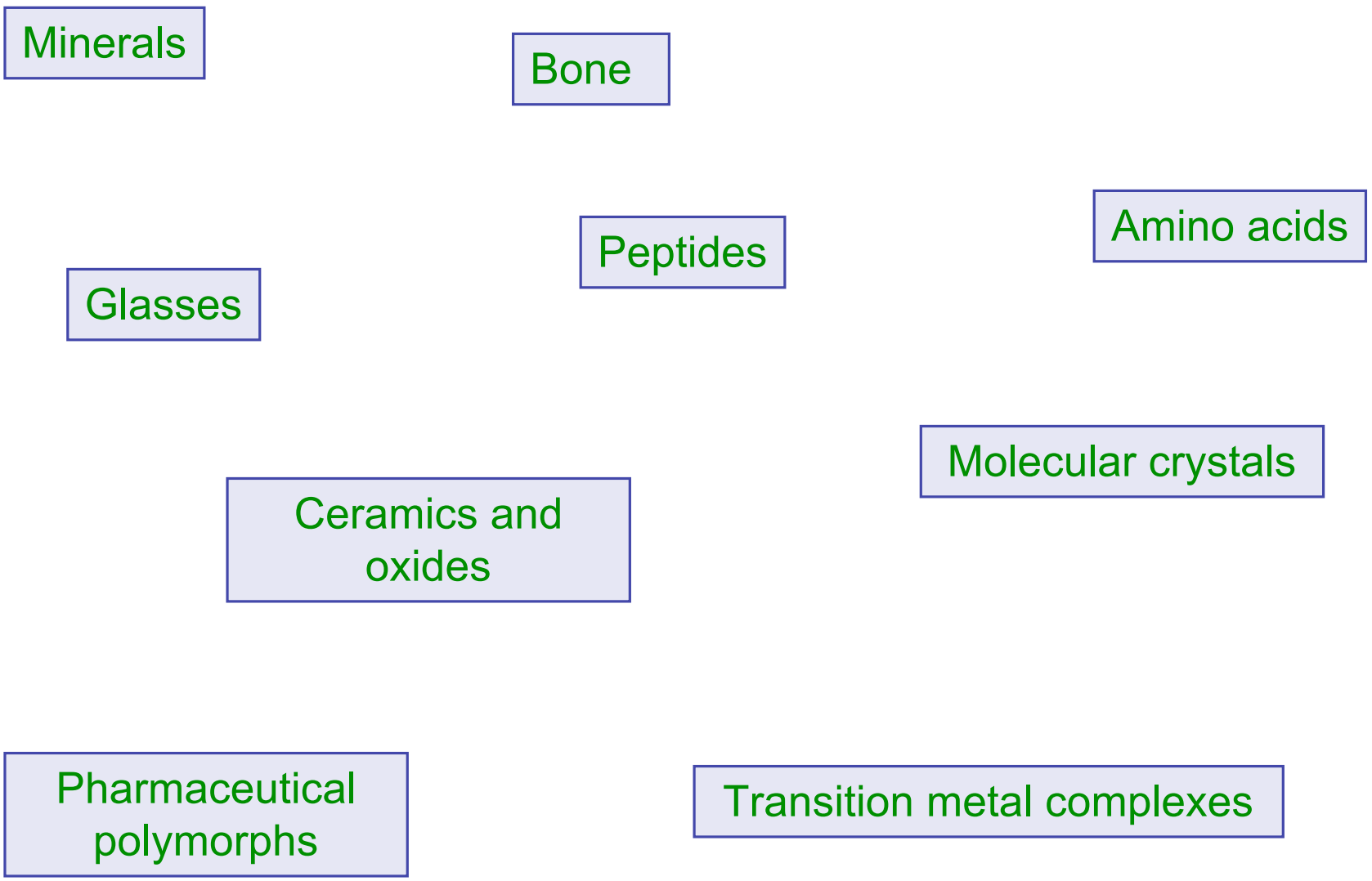
- Problems such as cation disorder, defects, solution





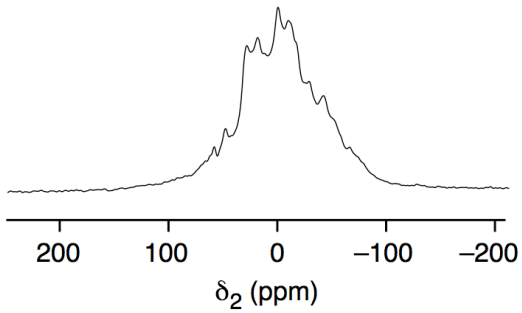


Applications

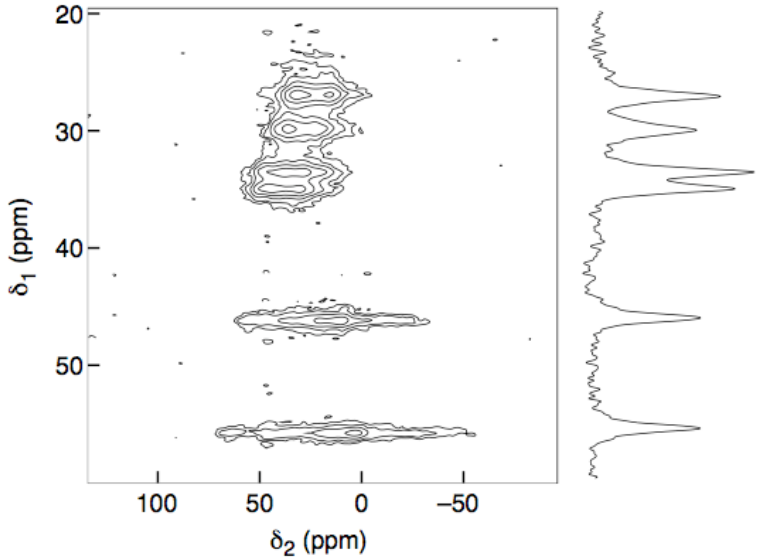


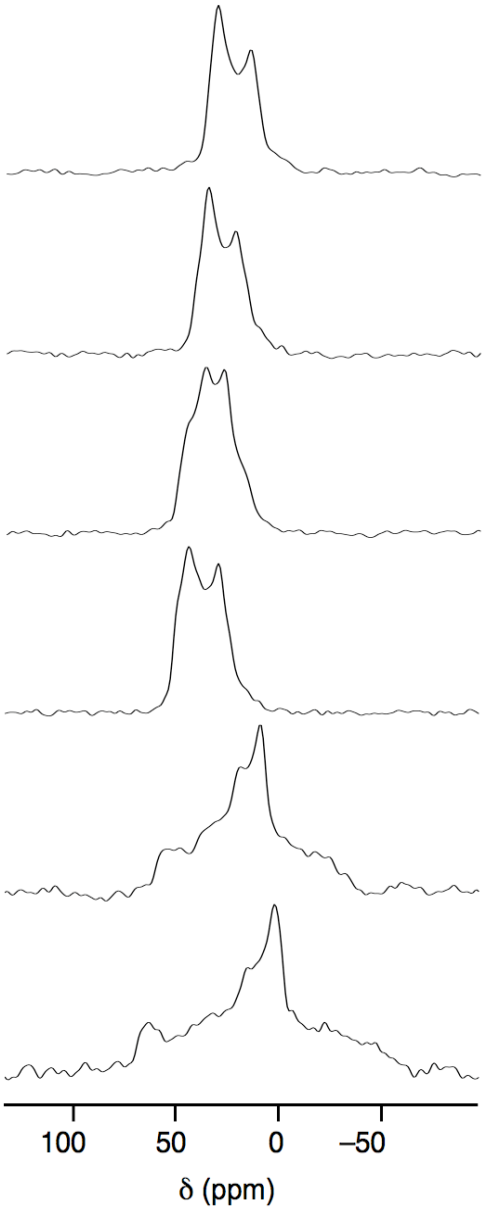
^{17}O NMR of enstatite

9.4 T MAS



9.4 T MQMAS





δ_{iso}	C_Q	η_Q
41 ppm	2.9 MHz	0.19
46 ppm	2.8 MHz	0.29
52 ppm	2.9 MHz	0.53
56 ppm	2.9 MHz	0.29
60 ppm	4.2 MHz	0.78
70 ppm	4.8 MHz	0.80

Ashbrook et al., J. Am. Chem. Soc. ***129****, 13213 (2007)*

^{17}O NMR of enstatite

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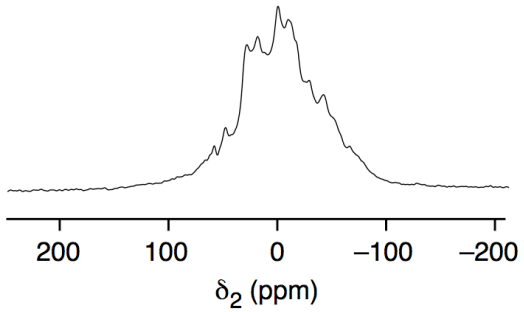
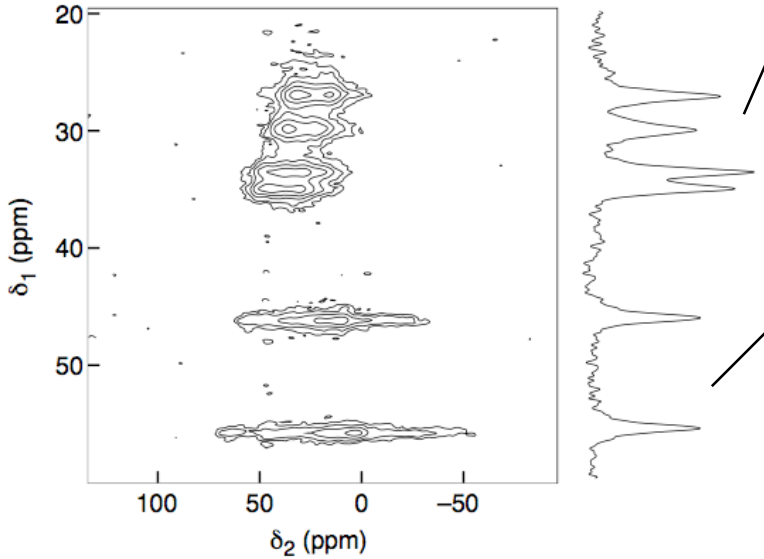
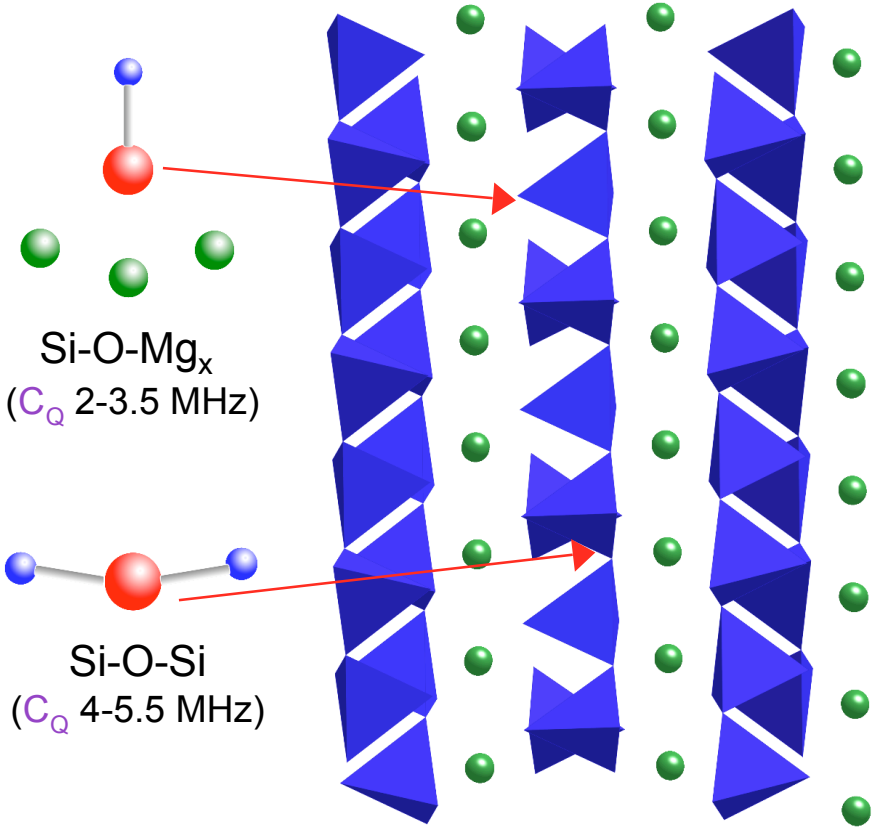


9.4 T MQMAS



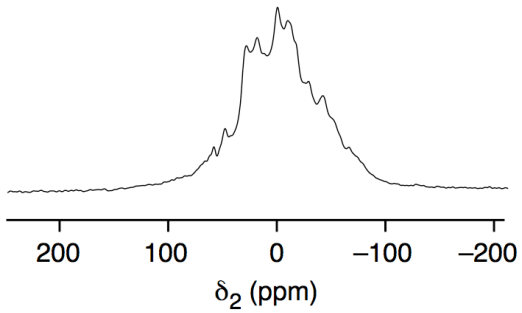


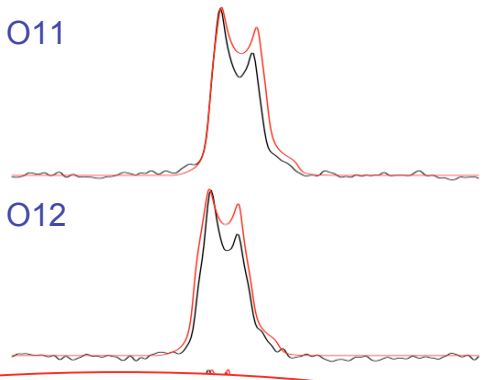
Ashbrook et al., J. Am. Chem. Soc. ***129****, 13213 (2007)*

^{17}O NMR of enstatite

12 cores for 4 days
80 atoms in unit cell
0.04 k-spacing, 60 Ry cut off

9.4 T MAS

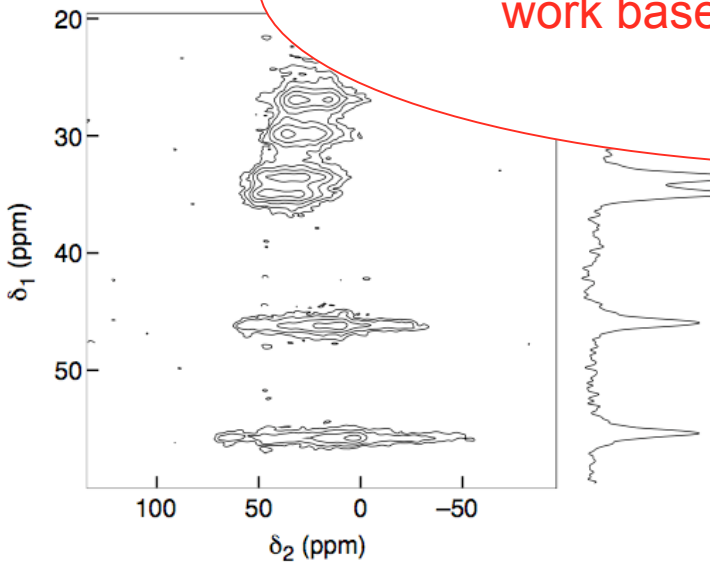


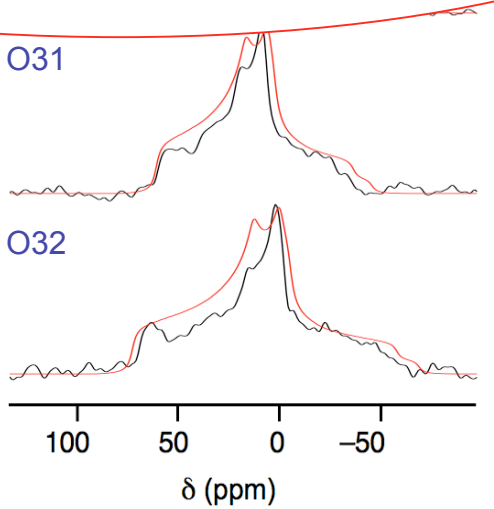


	δ_{iso}	C_Q	η_Q
O11	41 ppm	2.9 MHz	0.19
	41 ppm	3.06 MHz	0.21
O12	46 ppm	2.8 MHz	0.29
	47 ppm	2.96 MHz	0.29

Assignment is in contrast to previous literature work based on empirical correlations

9.4 T MQMAS



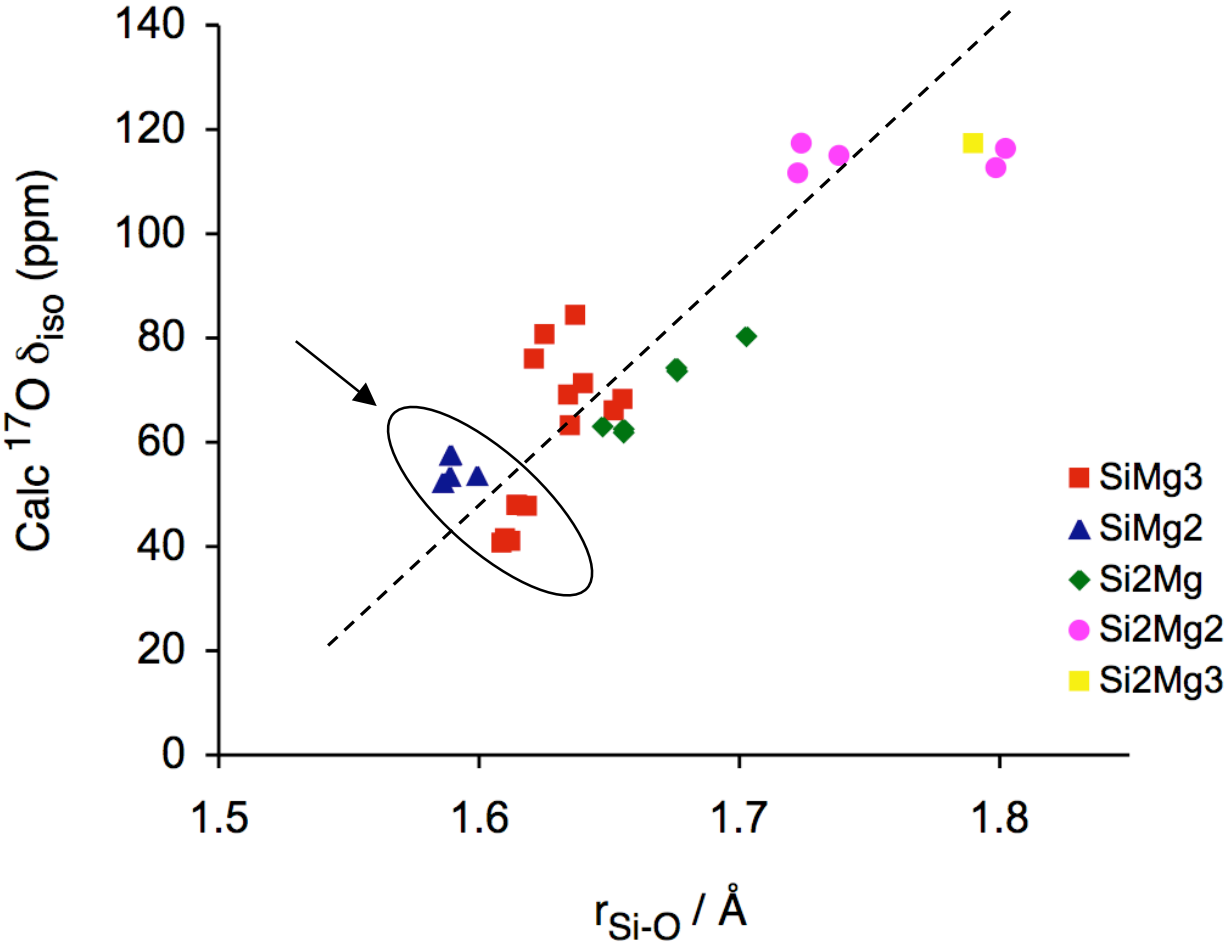


		2.9 MHz	0.53
		3.03 MHz	0.62
	ppm	2.9 MHz	0.29
	57 ppm	3.03 MHz	0.35
O31	60 ppm	4.2 MHz	0.78
	62 ppm	4.35 MHz	0.78
O32	70 ppm	4.8 MHz	0.80
	73 ppm	5.0 MHz	0.81

Ashbrook et al., J. Am. Chem. Soc. ***129****, 13213 (2007)*

^{17}O NMR of enstatite

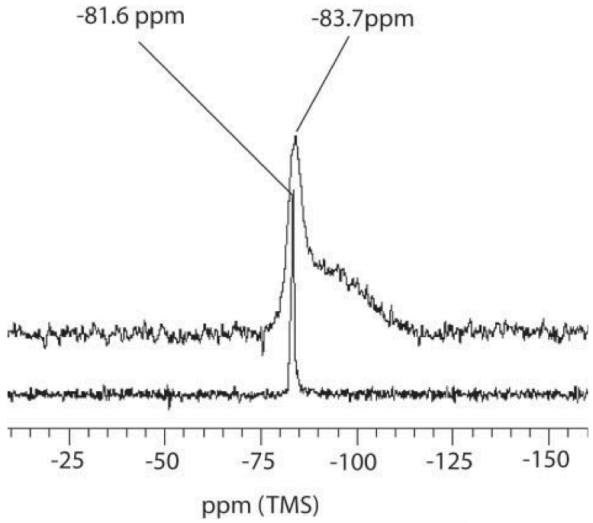
- Previous assignment based upon “empirical” relationships and the similarity of O environments to other known silicates

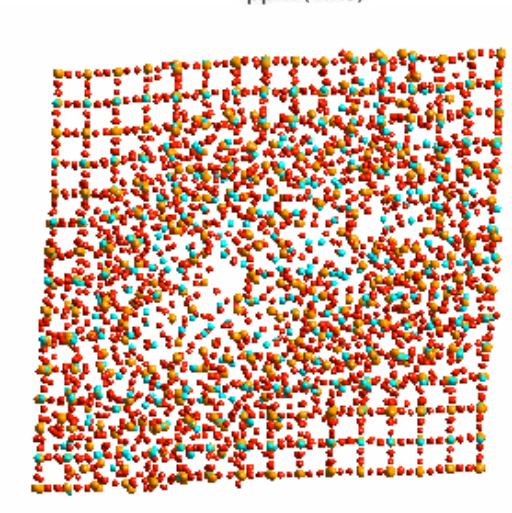


Ashbrook et al., J. Am. Chem. Soc. ***129****, 13213 (2007)*

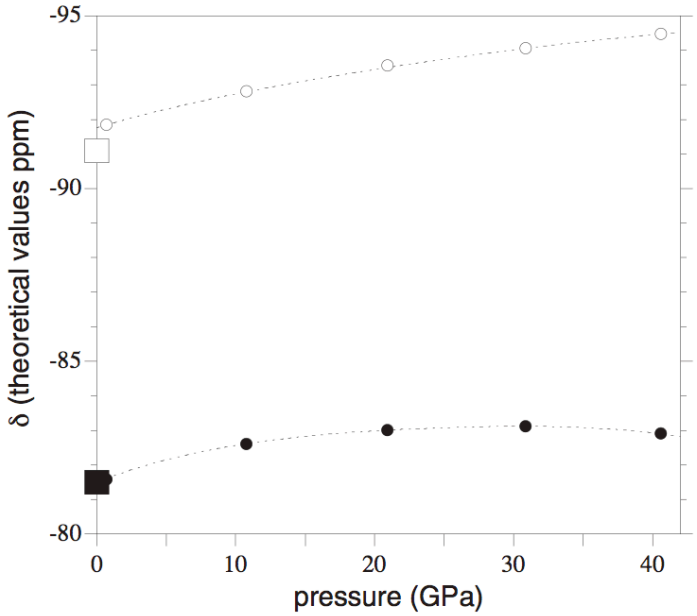
Radiation damage in $ZrSiO_4$

- Decrease in ^{29}Si chemical shift in radiation-damaged zircon
- Usually, δ increases with unit cell volume/bond length





volume swelling by 15%

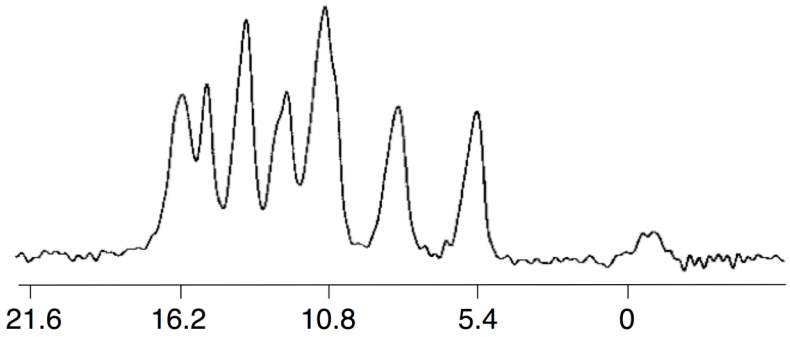


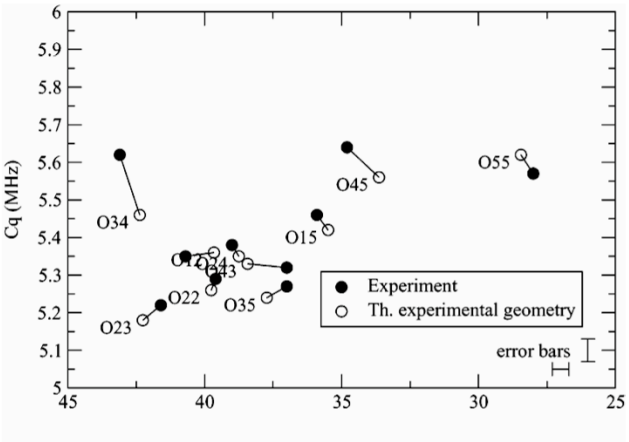
CASTEP calculations show shift becomes more negative as pressure increases - locally must be an increase in pressure

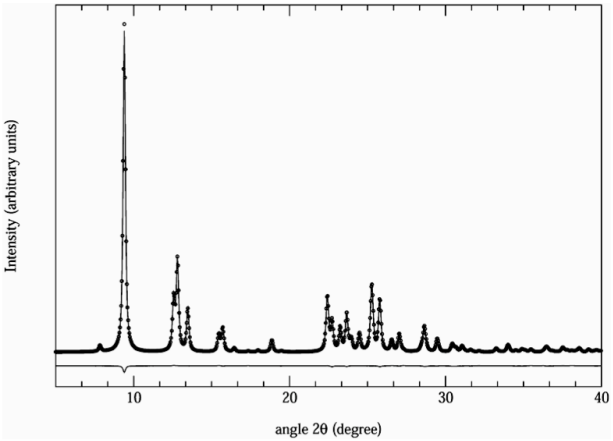
Farnan et al., Am. Mineral. ***88****, 1663 (2003)*

Ferrierite

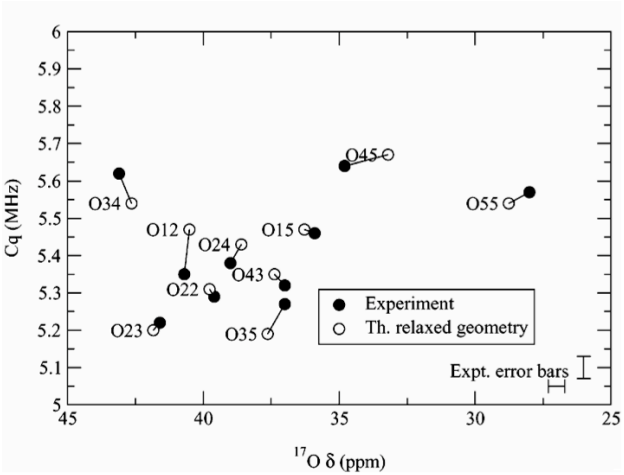
- Much debate in the literature over the assignment of the ^{17}O spectrum of ferrierite (a silica zeolite with 10 distinct O species)







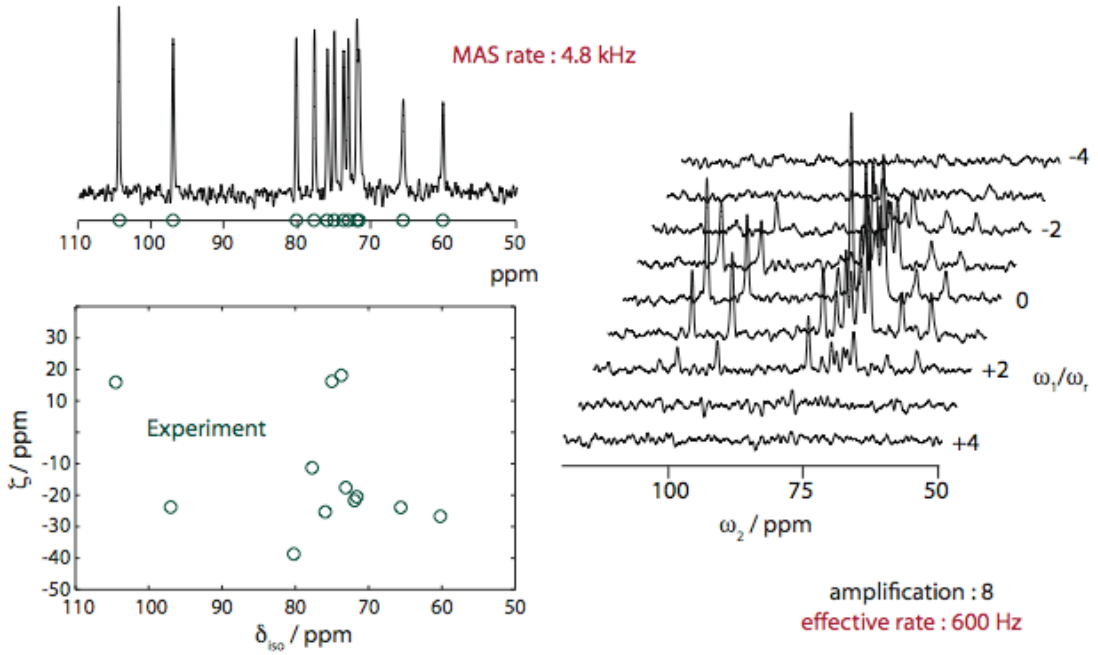
NMR parameters much more sensitive to geometry than diffraction

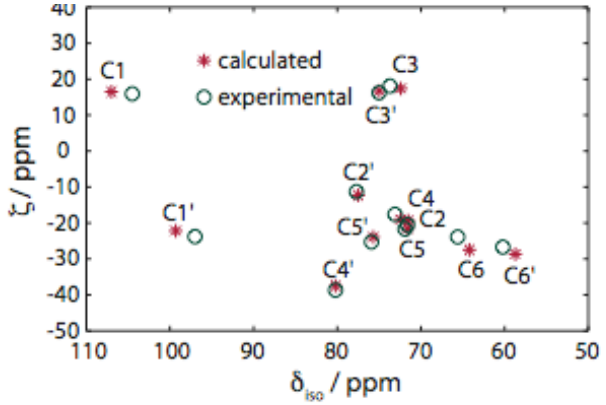


Profeta et al., J. Am. Chem. Soc. ***125****, 541 (2003)*

CSA calculations

- ^{13}C NMR spectrum of maltose contains closely spaced resonances which are difficult to assign
- CSAs measured using a 2D amplification technique





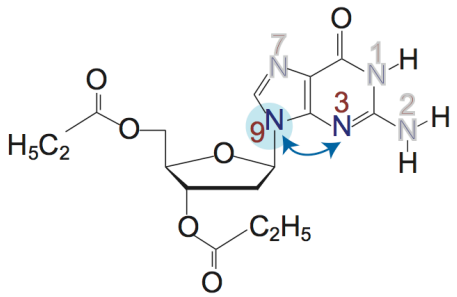
CASTEP calculations

- Spectral assignment
- Good agreement for isotropic shifts
- CSA consistently over estimated by 1.33 but can be rescaled

Shao et al., J. Phys. Chem. A ***111****, 13126 (2007)*

Calculation of J couplings

- Accurate calculation of scalar or J couplings in the solid state



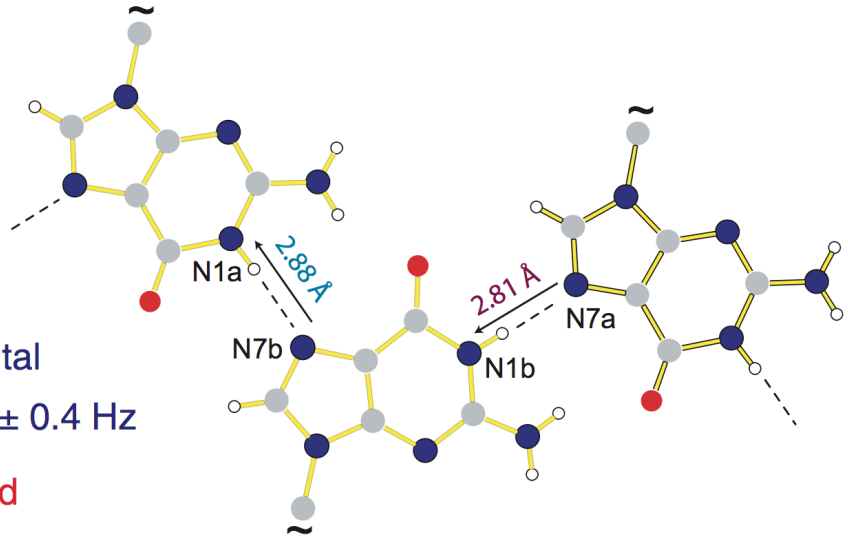
experimental

$^{2}J_{N9,N3}$ = 4.3 ± 0.2 Hz

calculated

$^{2}J_{N9,N3}$ = 4.2, 4.4 Hz

- Applications to the detection and characterization of intramolecular hydrogen bonds



experimental

$^{2h}J_{N7b,N1a}$ = 6.2 ± 0.4 Hz

calculated

$^{2h}J_{N7b,N1a}$ = 6.5 Hz

experimental

$^{2h}J_{N7a,N1b}$ = 7.4 ± 0.4 Hz

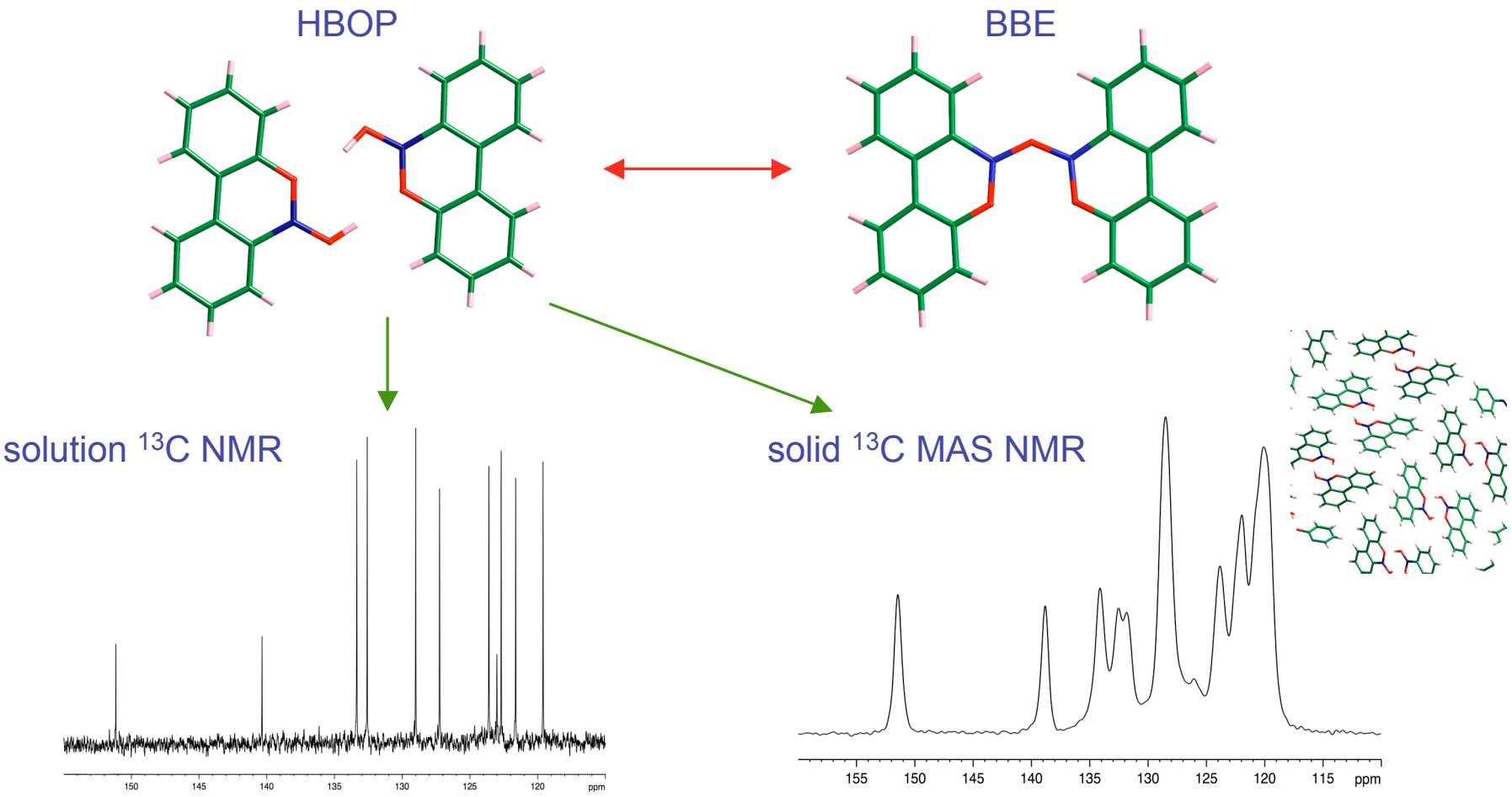
calculated

$^{2h}J_{N7a,N1b}$ = 7.7 Hz

Brown and Pickard, in preparation

Solid-state reactions

- Boroxophenanthrene undergoes reaction in the solid state but not in solution

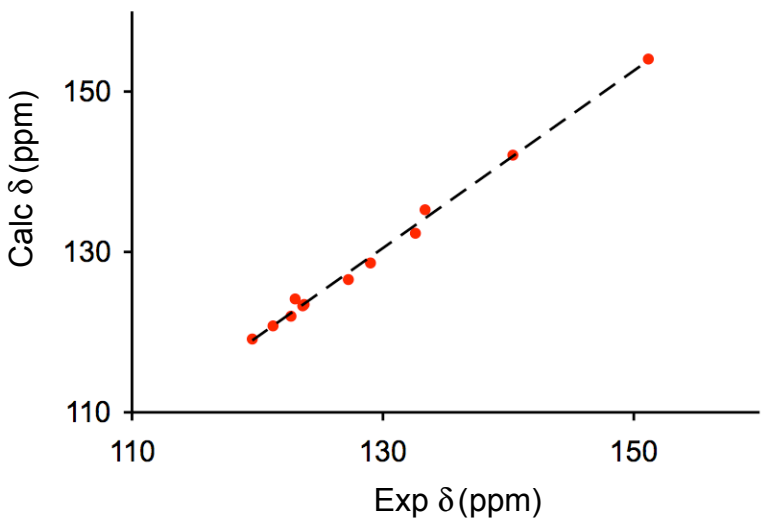


11 out of 12 carbons observed

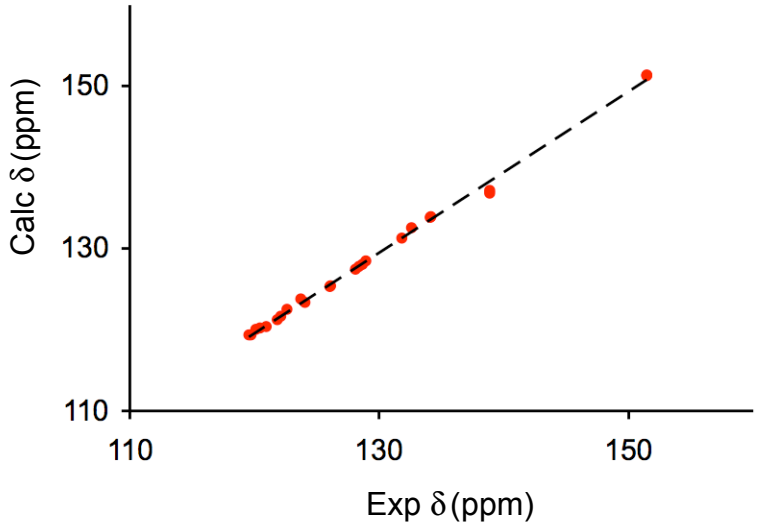
24 carbons

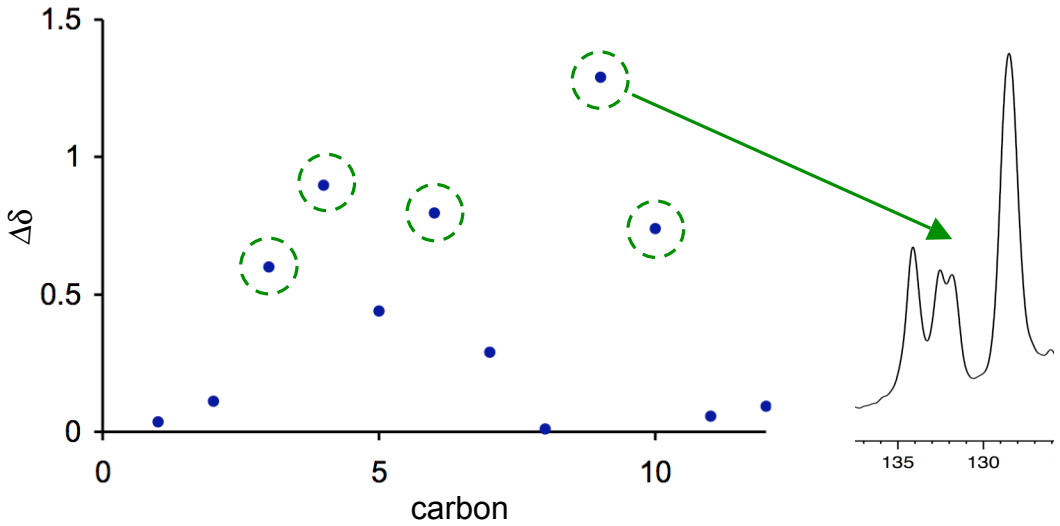
Solid-state reactions

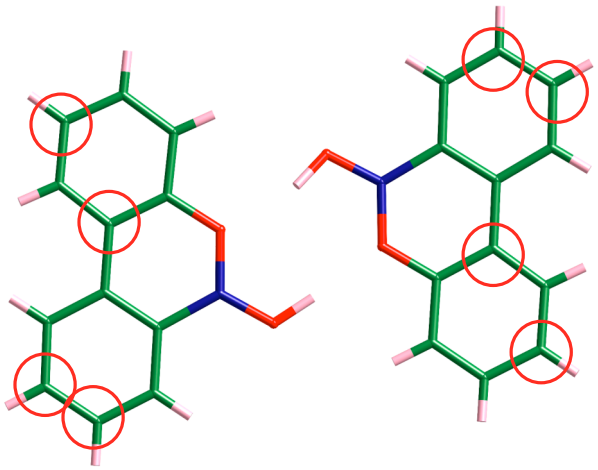
Solution (Gaussian calculation)



Solid (CASTEP calculation)



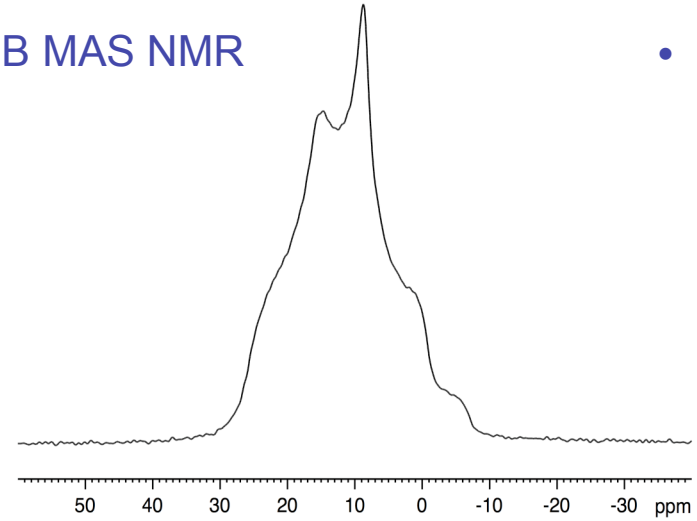




Most affected by π-stacking

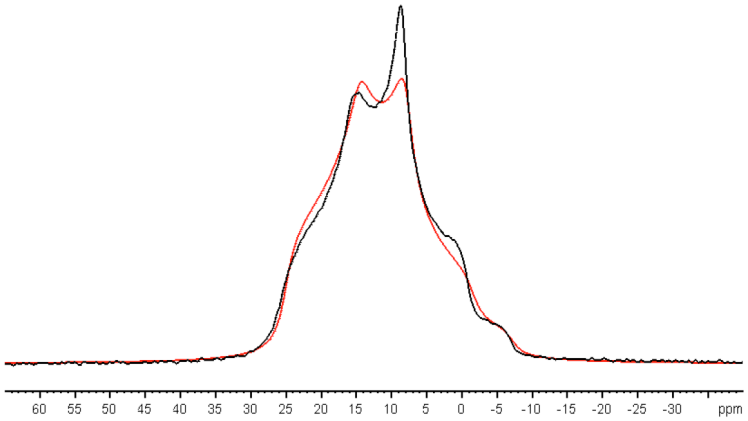
Solid-state reactions

^{11}B MAS NMR



- Should be two distinct ^{11}B species?

"Fit" with
δ = 25.6 ppm
C_Q = 2.9 MHz
η_Q = 0.60

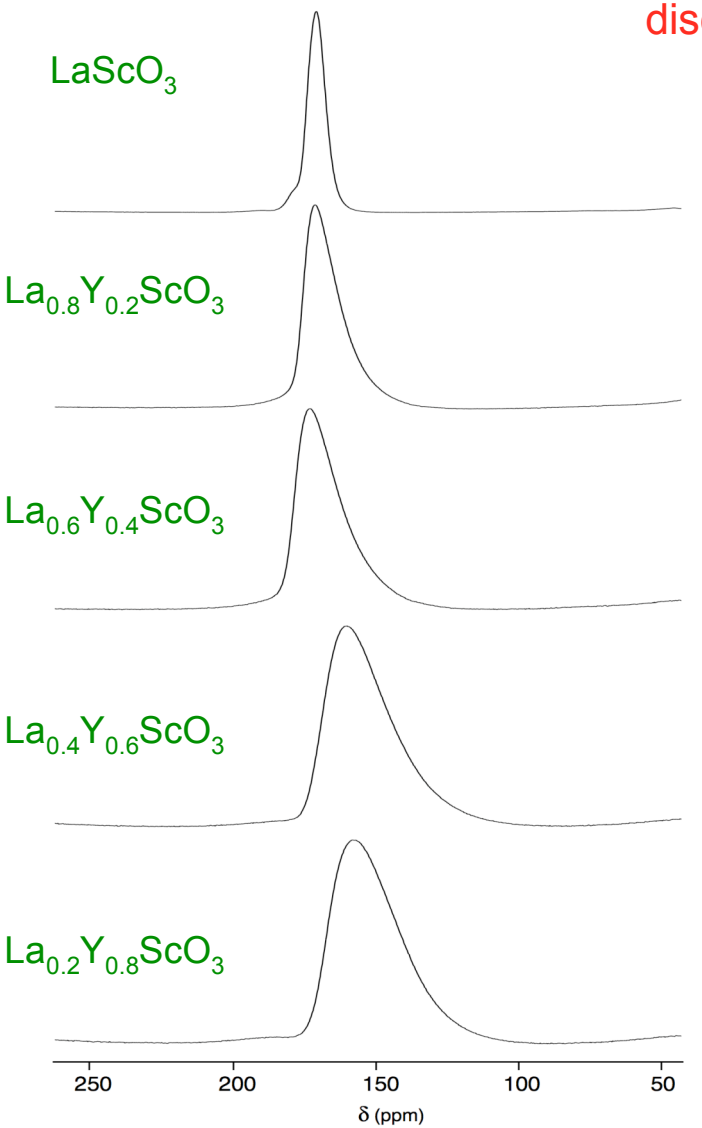


- Predicted to be identical by calculation

		σ (ppm)	C_Q / MHz	η_Q
Gaussian monomer	1	74.42	3.11	0.56
Gaussian dimer	1	73.97	3.09	0.65
CASTEP	1	68.32	3.32	0.64
	2	68.30	3.32	0.65

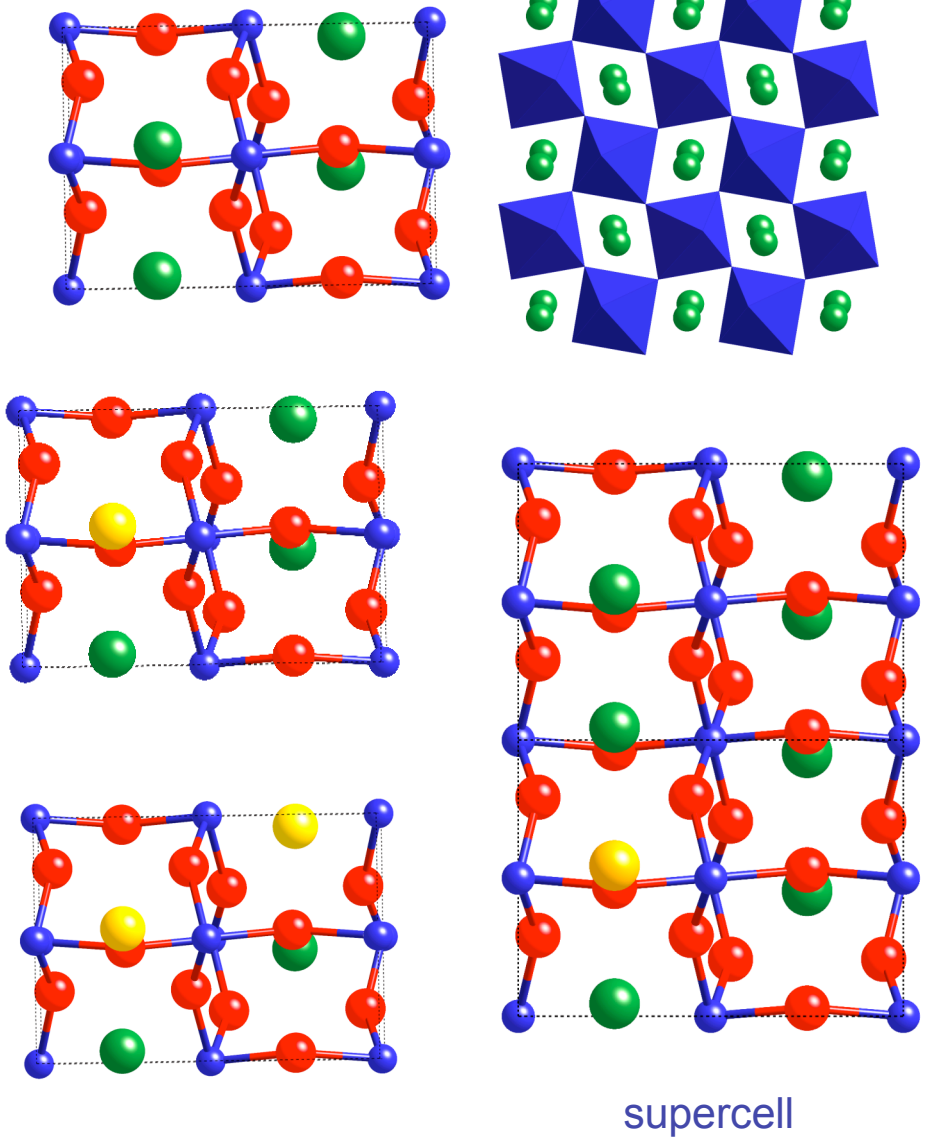
Sc-based perovskites

^{45}Sc MAS NMR



disorder

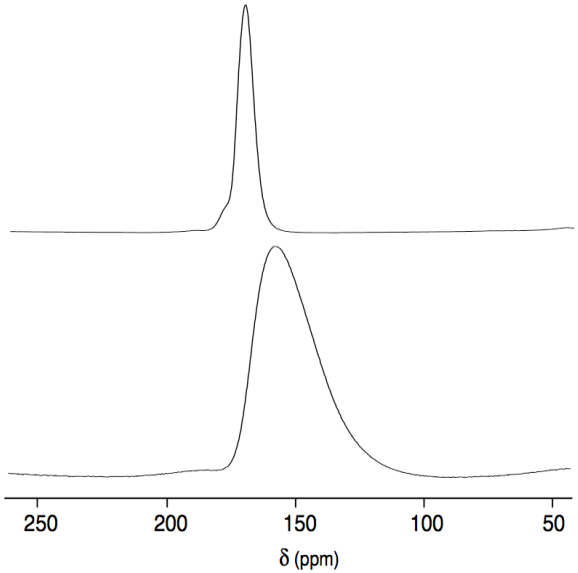
??

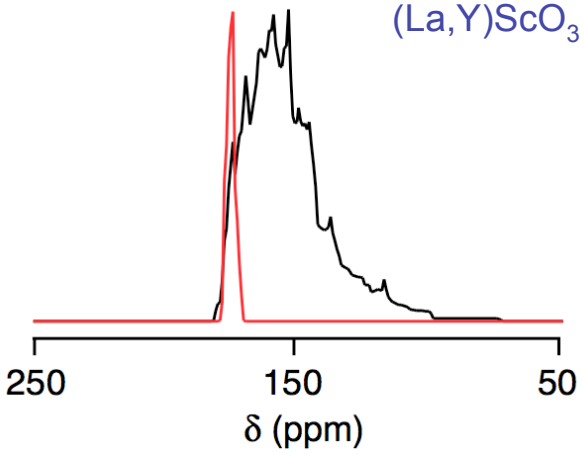


supercell

Sc-based perovskites

	δ_{iso} (ppm)	C_Q / MHz	η_Q
$LaScO_3$	189.71	3.19	0.64
$La_{0.75}Y_{0.25}ScO_3$	186.95	7.62	0.40
	192.71	−4.64	0.83
$La_{0.5}Y_{0.5}ScO_3$ (A)	187.57	6.59	0.92
$La_{0.5}Y_{0.5}ScO_3$ (B)	184.43	12.03	0.36
	192.57	8.25	0.82
$La_{0.5}Y_{0.5}ScO_3$ (C)	190.11	4.8	0.98
$La_{0.25}Y_{0.75}ScO_3$	185.45	9.76	0.38
	187.93	−7.77	0.49
$YScO_3$	184.06	−8.44	0.84
$La_{0.875}Y_{0.125}ScO_3$	186.41	8.48	0.26
	191.22	−4.39	0.58
	190.89	−3.79	0.85
	191.42	−6.06	0.73



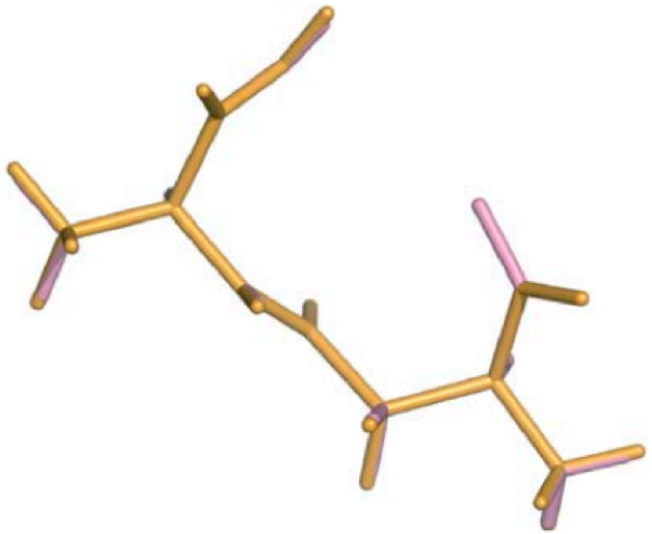


7.3 ± 2.6 MHz, 0.66 ± 0.24, 188.1 ± 3 ppm

Resolving crystal structures

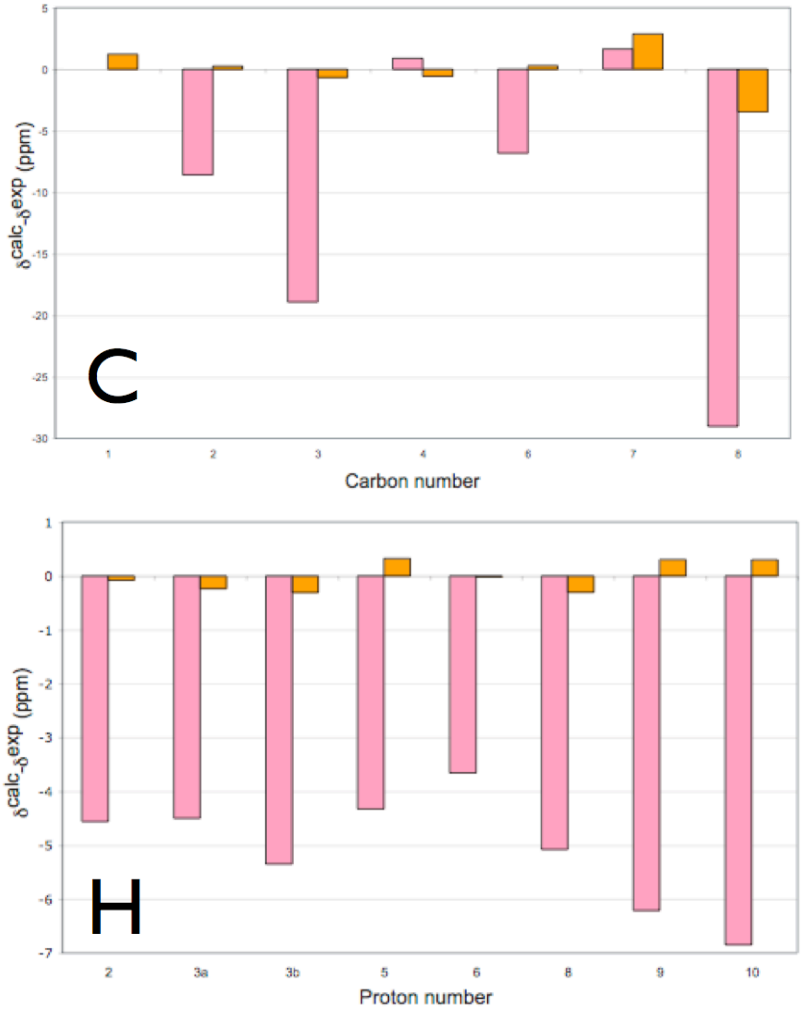
- Use of DFT (CASTEP) to refine the ^{1}H positions for X-ray structures and match the NMR parameters

β-L-aspartyl-L-alanine



Original structure

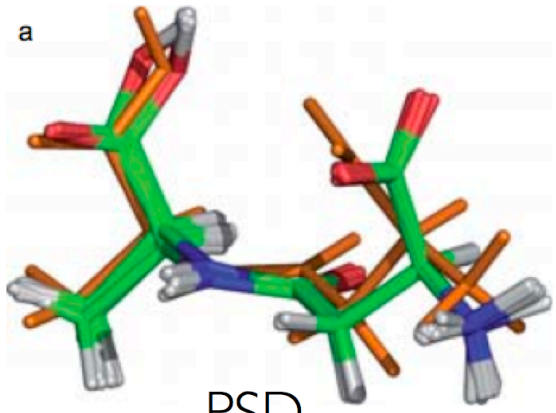
^{1}H optimization with DFT



Pickard et al., J. Am. Chem. Soc. ***129****, 8932 (2007)*

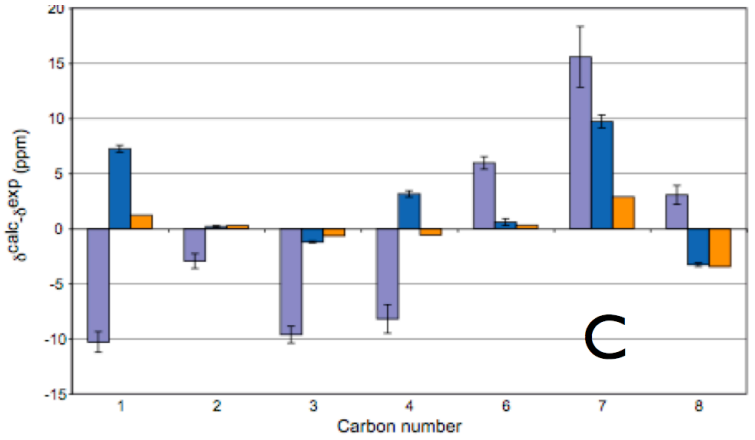
Resolving crystal structures

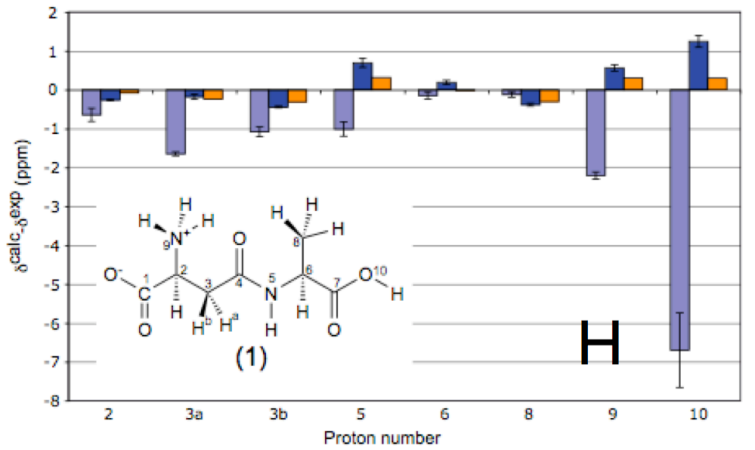
- Combination of experimental proton driven spin diffusion measurements with MM to produce candidate structures
- Geometry optimization using CASTEP and comparison of NMR data to refine the structures



PSD

PSD + CASTEP





input

DFT

x-ray + ^{1}H DFT

Pickard et al., J. Am. Chem. Soc. ***129****, 8932 (2007)*