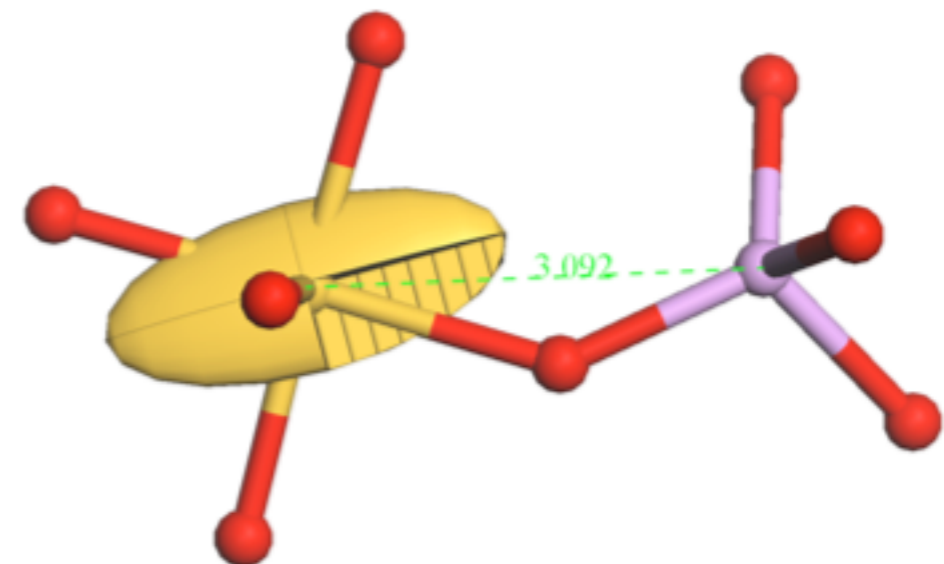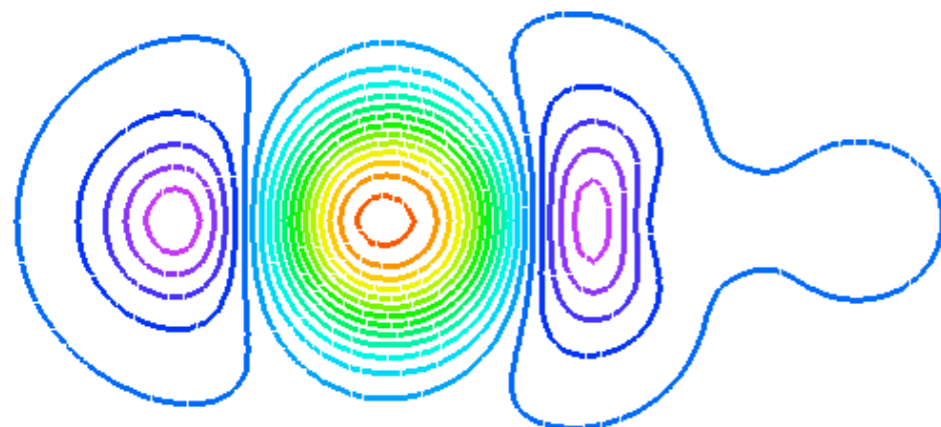# Prediction of NMR parameters in the solid-state
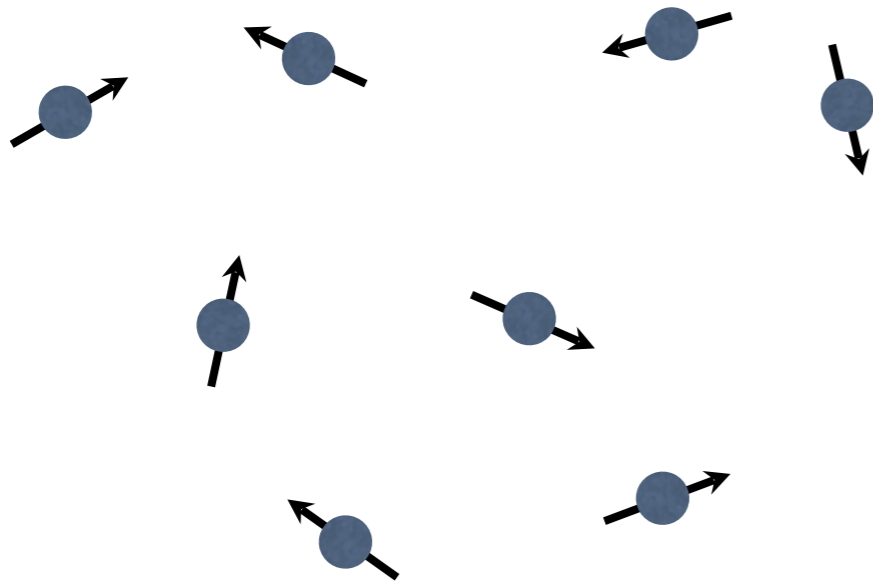
Jonathan Yates

Materials Modelling Laboratory, Oxford Materials

Nuclear Magnetic Resonance

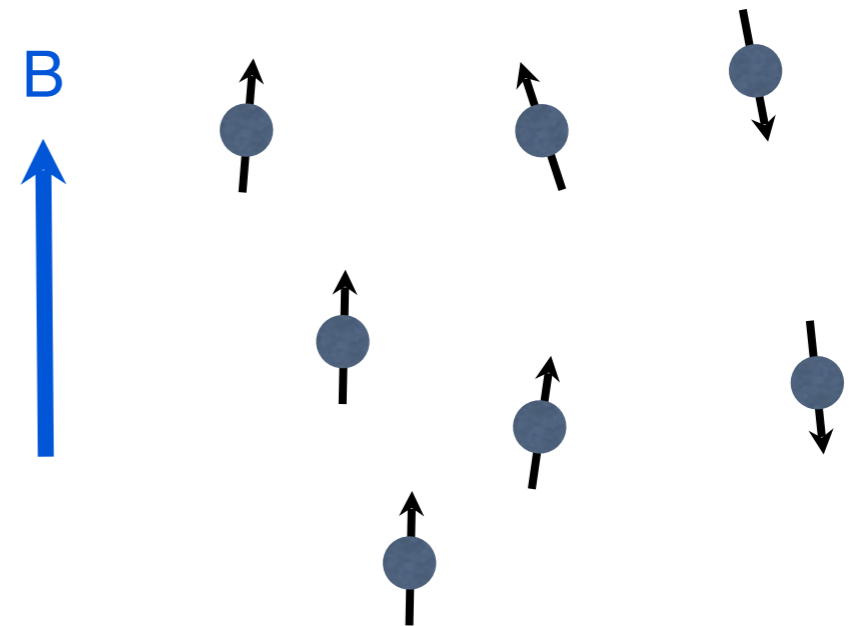**Zero Field**

Applied Field

B

$$\omega = \gamma B$$

magnetogyric ratio
fundamental nuclear constant

NMR signal is proportional to population difference
For ^1H in 9.4T at 298K

ΔE = 2.65×10^{-25} J

n_{upper}/n_{lower} = exp $(-\Delta E / kT)$

     = 0.999935

Sensitivity is an issue! Need Large γ and/or B

Materials
Modelling
Laboratory

OxfordMaterials

Common Isotopes

Isotope	Spin	γ 10^7 T^{-1} rad s^{-1}	Freq MHz @ 9.4T	Abundance %
^{1}H	1/2	26.75	400	100
^{13}C	1/2	6.73	100.6	1.1
^{29}Si	1/2	-5.32	79.6	4.7
^{31}P	1/2	-10.84	162.1	100

Common Isotopes

Isotope	Spin	γ 10^7 T^{-1} rad s^{-1}	Freq MHz @ 9.4T	Abundance %
^{1}H	1/2	26.75	400	100
^{13}C	1/2	6.73	100.6	1.1
^{29}Si	1/2	-5.32	79.6	4.7
^{31}P	1/2	-10.84	162.1	100
^{17}O	5/2	-3.63	54.1	0.04
^{49}Ti	7/2	-1.51	22.6	5.41

Solid-State NMR Spectrometers

600 MHz 14.1 T
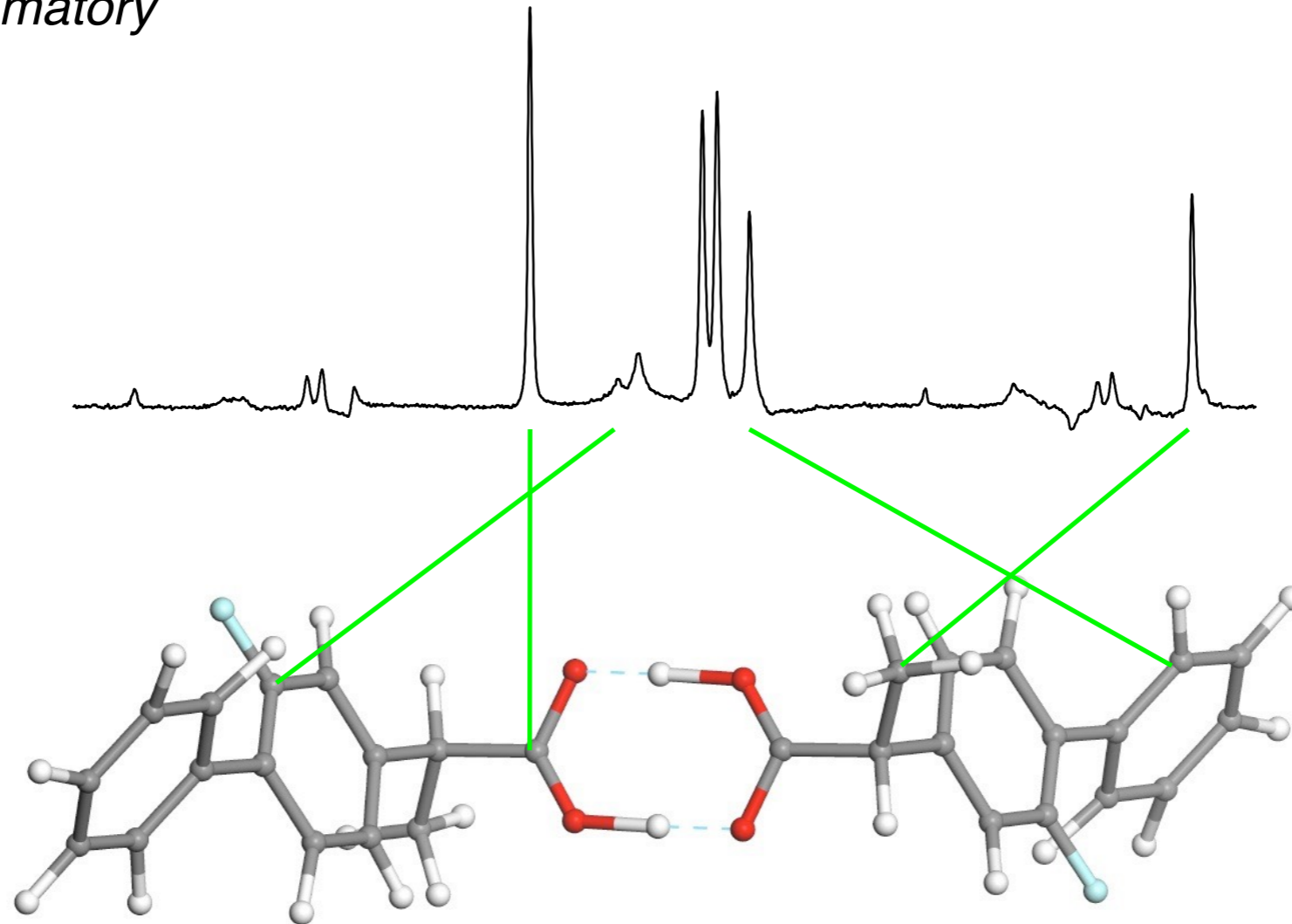~£800,000

400 MHz 9.4 T
~£300,000

Image courtesy Sharon Ashbrook (St Andrews)

Materials Modelling Laboratory

OxfordMaterials

Magnetic Shielding

Flurbiprofen
non-steriodal anti-inflamatory

Each distinct C atom experiences a different magnetic field and resonates at a unique frequency.

Measure the change wrt a standard (for ^{13}C this is liquid tetramethylsilane)

Magnetic Shielding

Measure Larmor frequency

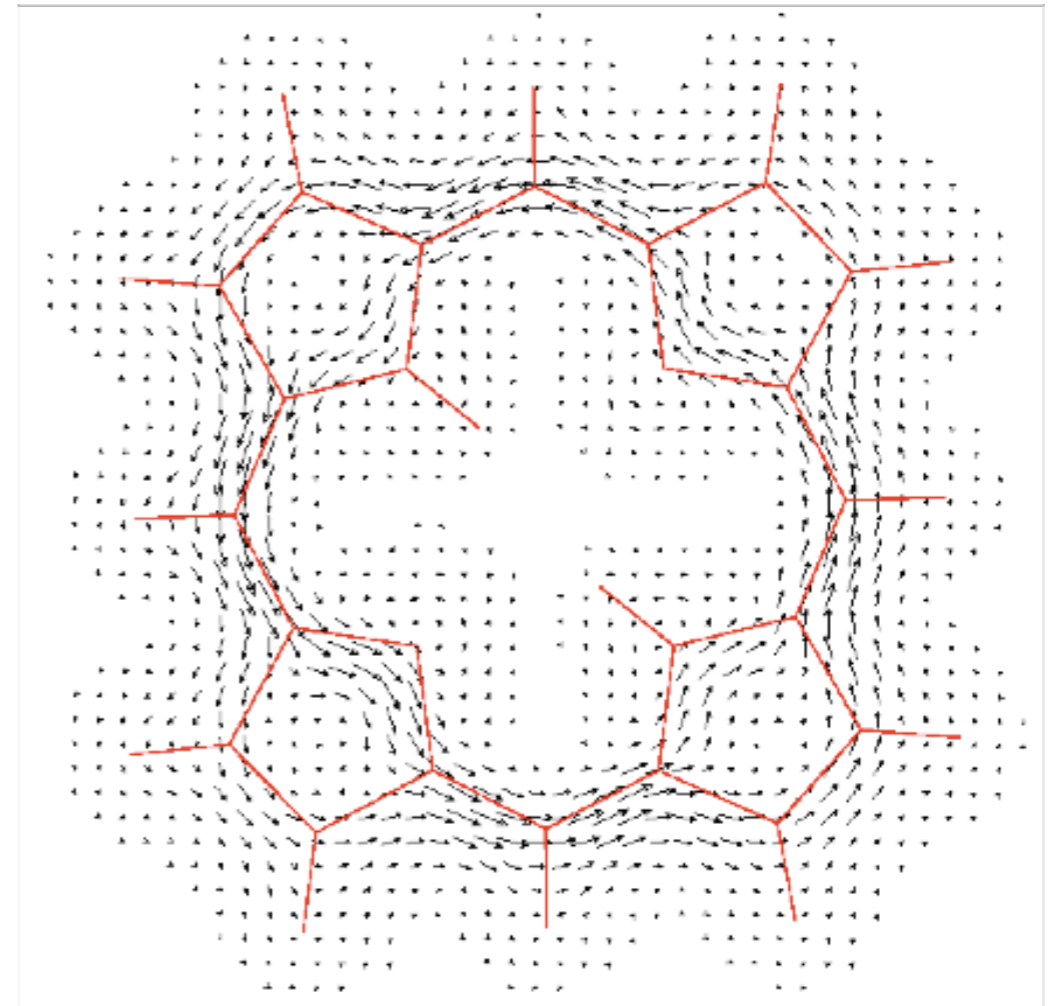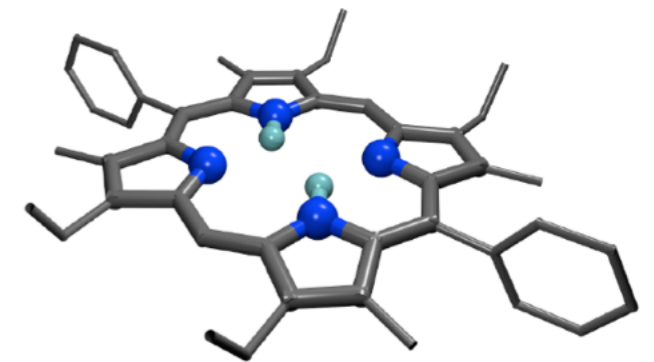$$\omega = \gamma\, B_{local}$$

What is the local field?

$$B_{local} = B_0 + B_{induced}$$

$$B_{local} = (1-\sigma)B_0$$

magnetic shielding

Orbital Current induced by B-field in Porphyrin ring

Induced Current

To compute the chemical shifts we just need to calculate the current induced by the external magnetic field
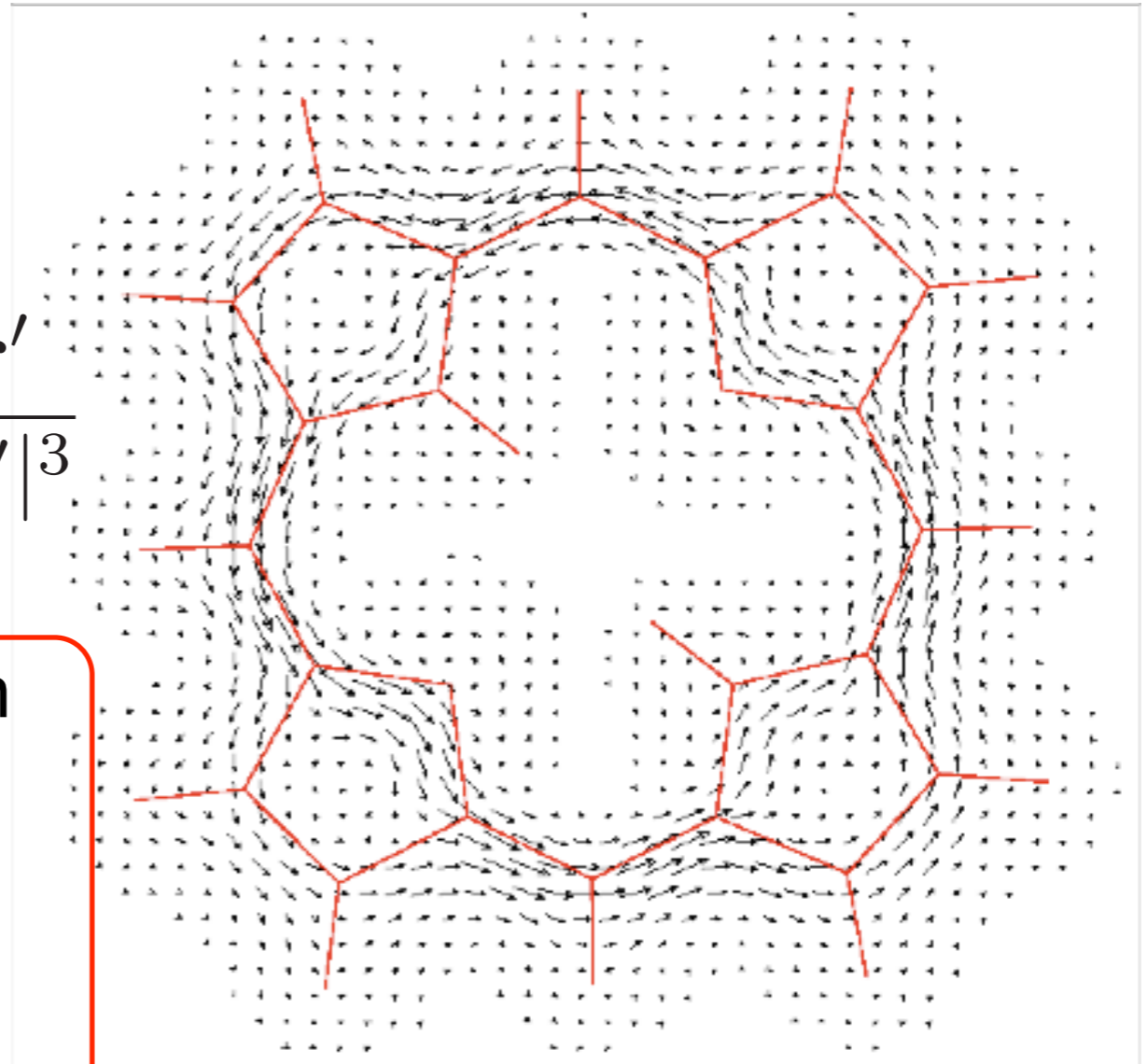
Biot-Savart

$$\mathbf{B}_{\text{in}}(\mathbf{r}) = \frac{1}{c} \int d^3 r' \mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}$$

Obtain current within perturbation theory (linear response)

$$O = O^{(0)} + O^{(1)} + \mathcal{O}(\mathbf{B^2})$$

spin contribution averages to zero in a diamagnetic insulator

$B = (1-\sigma) B_0$

$B_{\text{in}} = -\sigma B_0$

note: σ is a rank 2 tensor

First-principles NMR

Crystal Structure
X-ray, Neutron diffraction
Cambridge Structural Database

```
C1 -0.602 -0.537 6.384
C2  0.135  0.622 5.689
H1  0.257  0.361 4.639
```
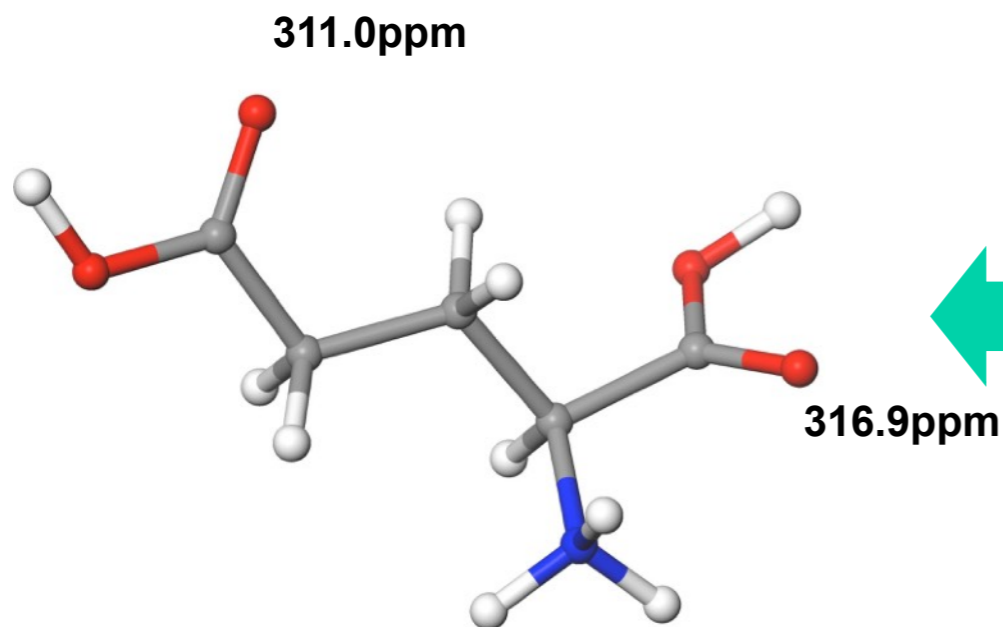**. . .**

**Calculate forces
refine structure**

**Calculate chemical
shifts**

311.0ppm

316.9ppm

Materials
Modelling
Laboratory

OxfordMaterials
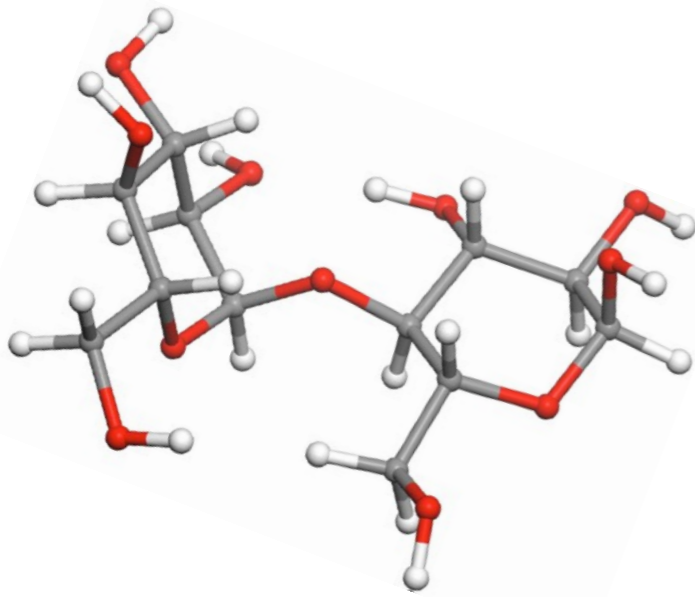
furosemide

Examples

Maltose
sugar used in brewing

MAS-J-HMQC

¹³C axis

¹H axis

Materials Modelling Laboratory

OxfordMaterials
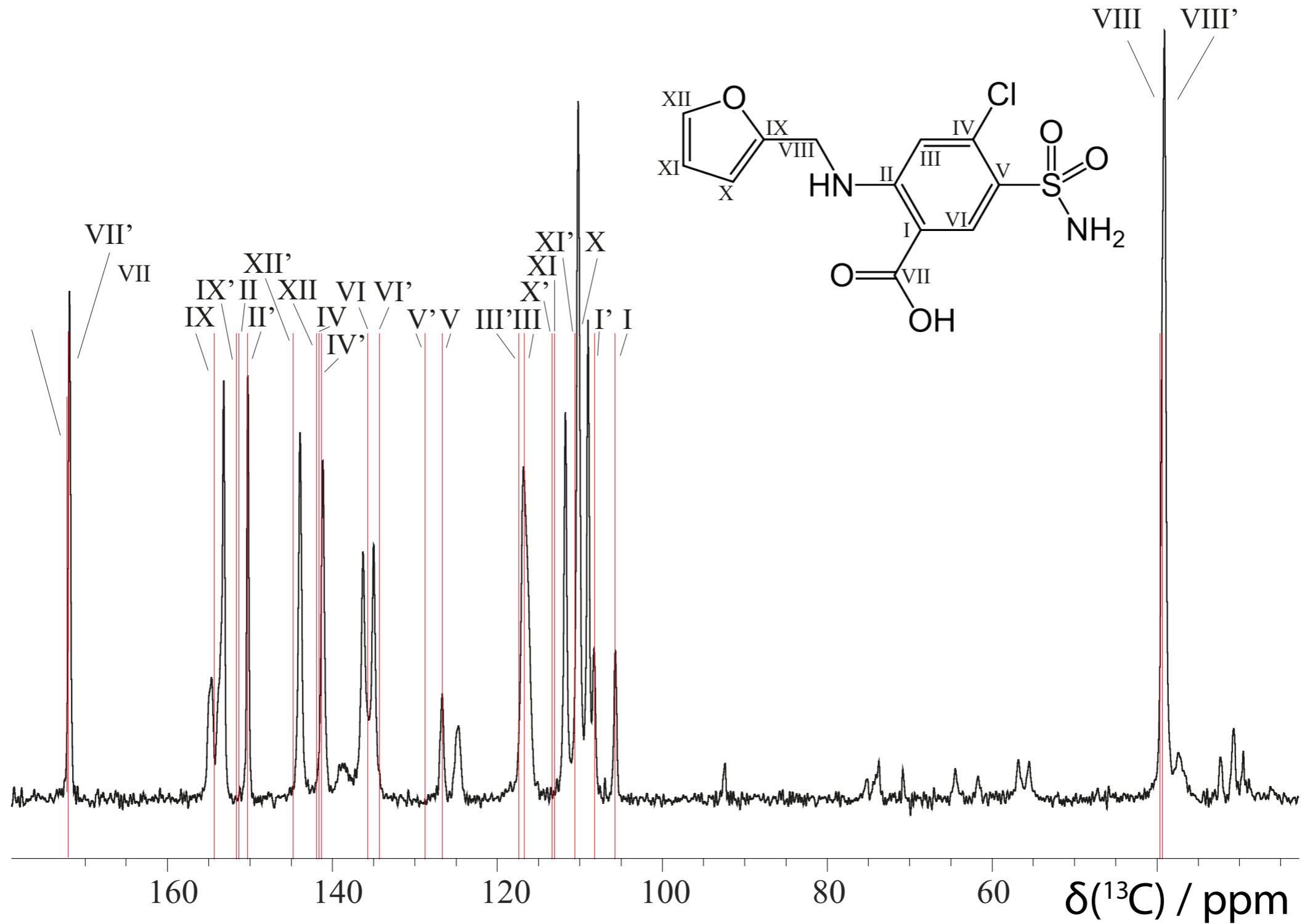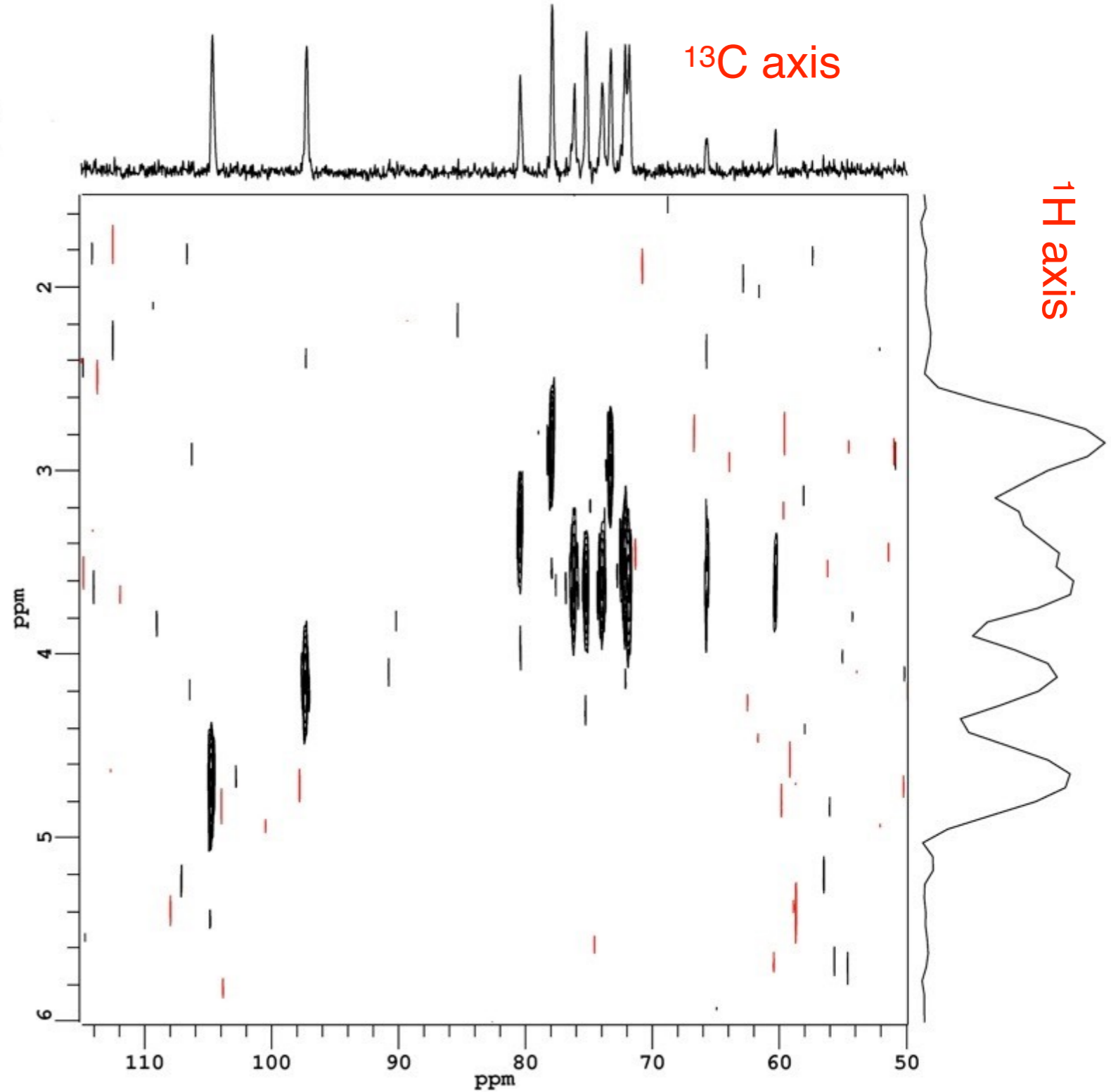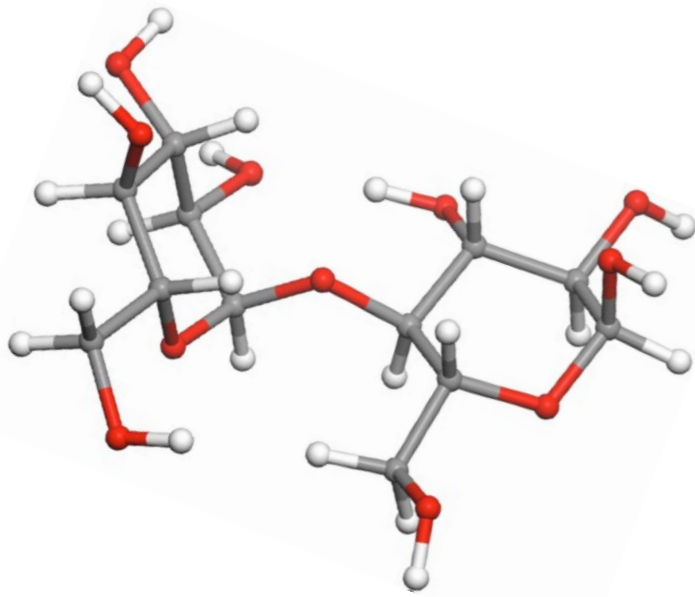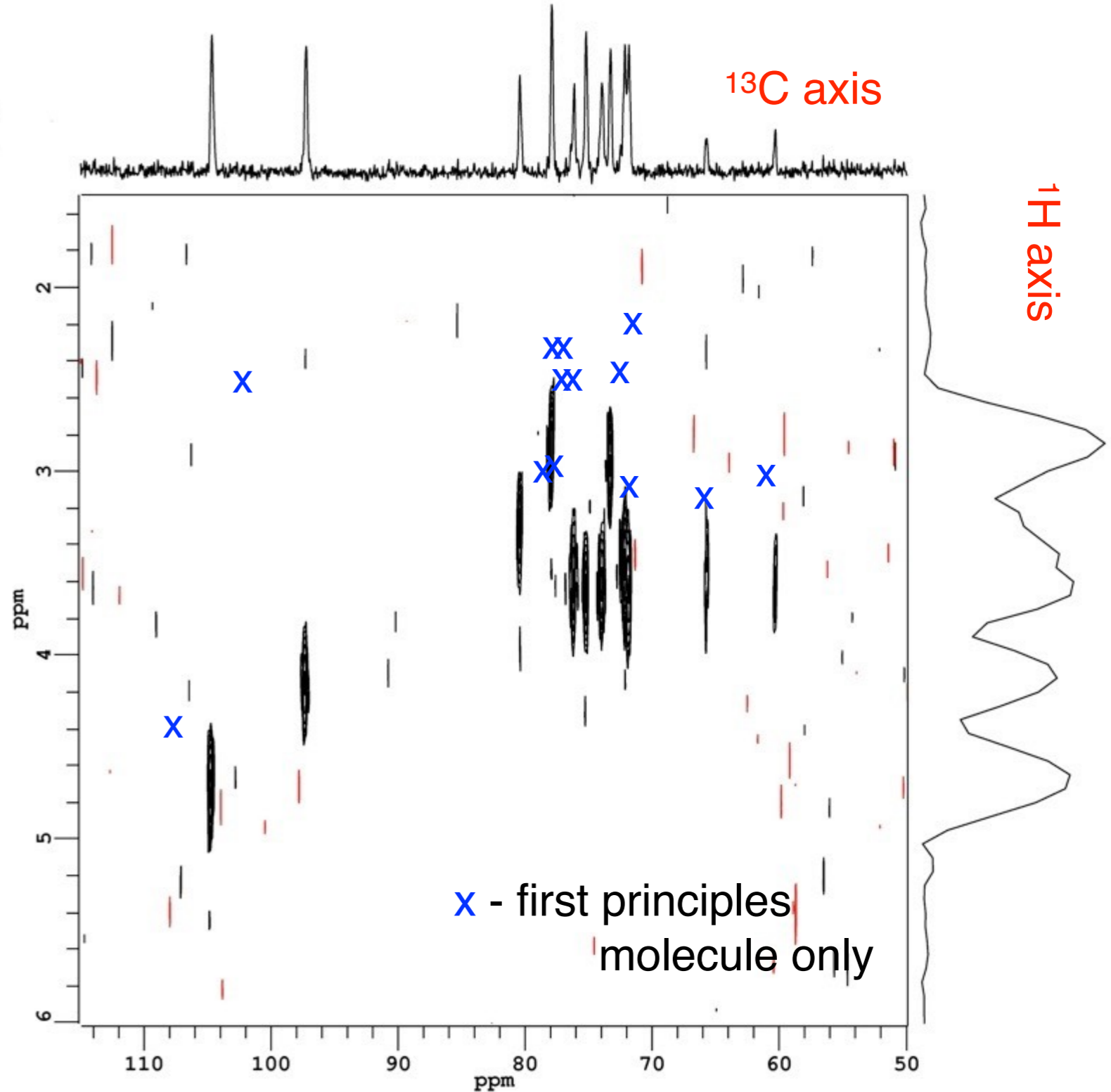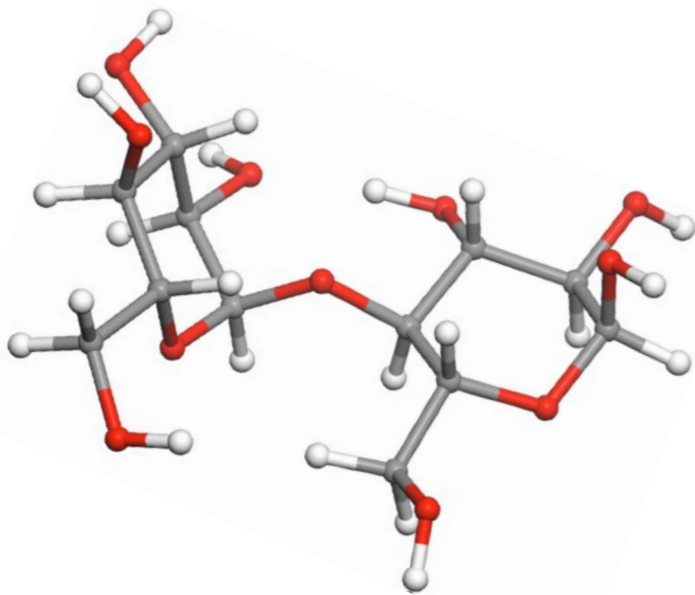
Examples

Maltose
sugar used in brewing

MAS-J-HMQC

Examples

Molecule to solid variation due to intermolecular interactions (weak hydrogen bonds)

J. Am. Chem. Soc. 127 10216 (2005)

¹³C axis

¹H axis

x - first principles full crystal
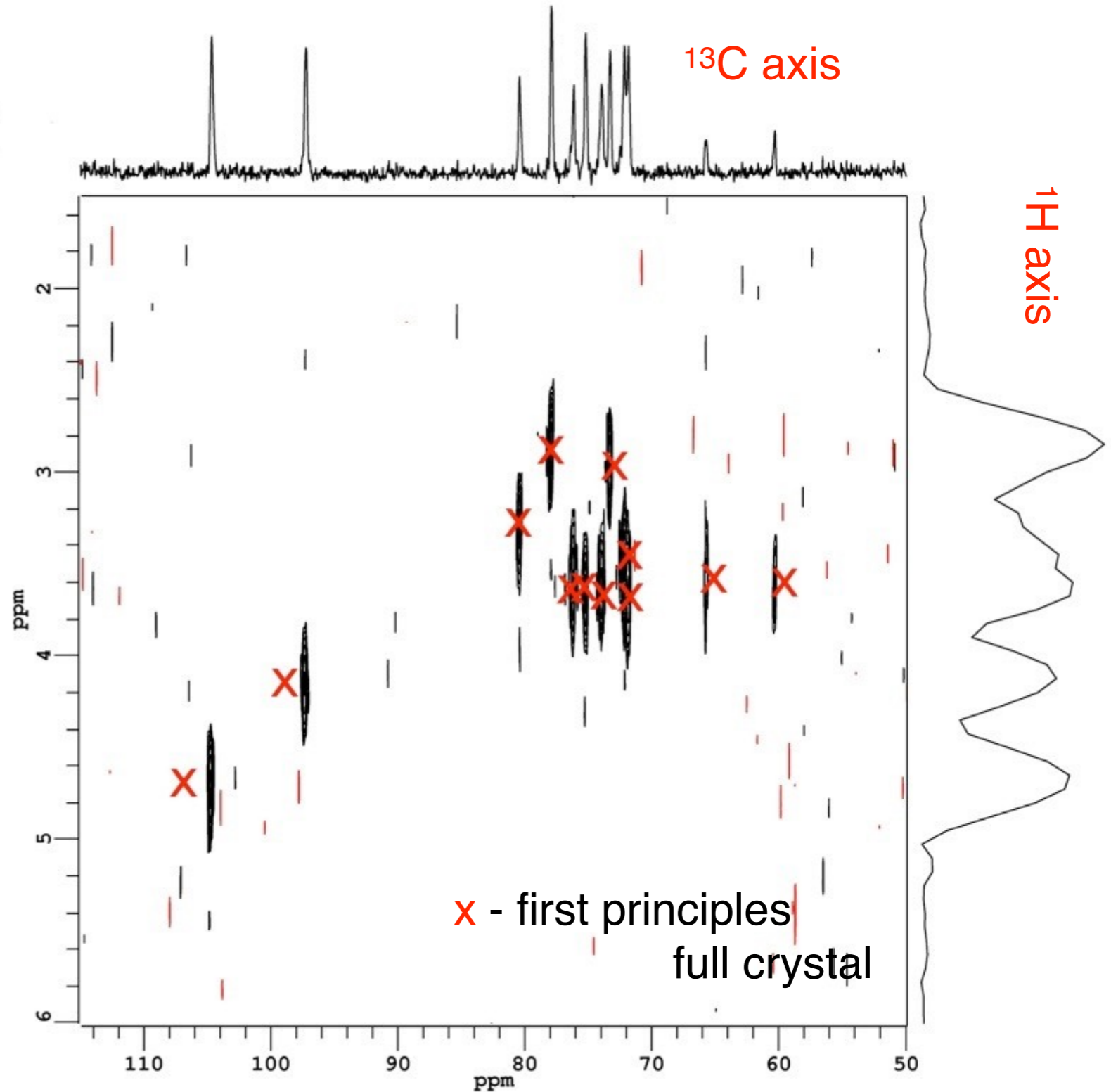
Magnetic Shielding vs Chemical Shift

Experiment - Chemical Shift

$$\delta_{\mathrm{iso}} = \frac{(\omega - \omega_{\mathrm{ref}}) \times 10^6}{\omega_{\mathrm{ref}}}$$

Result is now independent of the spectrometer frequency and isotope
Standard compounds for reference frequency
 beware of those with two standards (eg N)

Calculation - Magnetic Shielding

$B_{\mathrm{loc}} = (1-\sigma)\, B_0$ σ magnetic shielding

$\omega = \gamma\, B_{\mathrm{loc}}$ Larmor frequency

$$\delta = \frac{\sigma_{\mathrm{ref}} - \sigma_{\mathrm{sample}}}{1 - \sigma_{\mathrm{ref}}}$$ $|\sigma_{\mathrm{ref}}| \ll 1$ $\delta = \sigma_{\mathrm{ref}} - \sigma_{\mathrm{sample}}$

Materials
Modelling
Laboratory

OxfordMaterials

Magnetic Shielding vs Chemical Shift

$$\delta = \sigma_{\text{ref}} - \sigma_{\text{sample}}$$
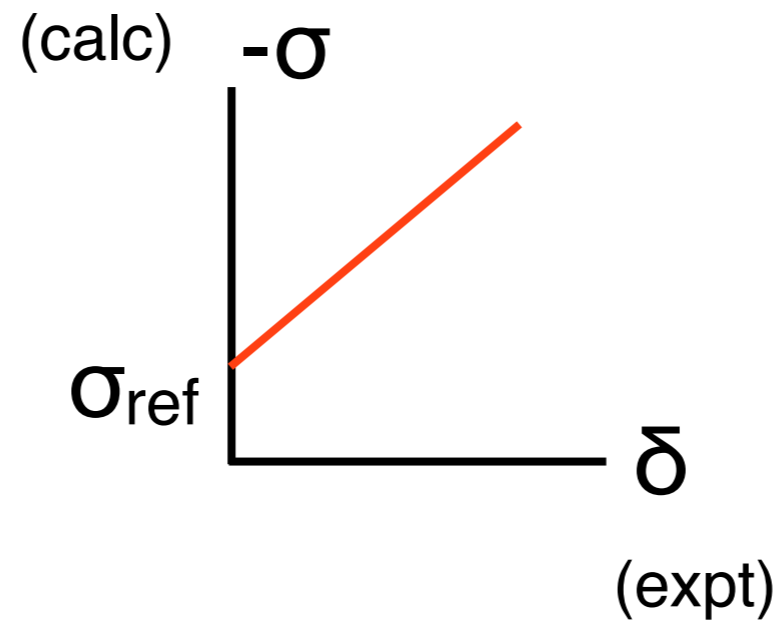
Compute reference compound
Compute secondary reference
Use literature value
Adjust to match average

Magnetic Fields - an aside

Can create a magnetic field in two ways:
  1- Intrinsic spin of electrons (i.e. a magnetisation density)
  2- Charge of electrons (moving charge gives magnetic field)

Induced Field

$$\mathbf{B}_{\text{in}}^{(1)}(\mathbf{R}_K) = \frac{\mu_0}{4\pi} \int \mathbf{m}^{(1)}(\mathbf{r}) \cdot \left[\frac{3\mathbf{r}_K\mathbf{r}_K - |\mathbf{r}_K|^2}{|\mathbf{r}_K|^5} \right] d^3\mathbf{r} + \frac{\mu_0}{4\pi} \frac{8\pi}{3} \int \mathbf{m}^{(1)}(\mathbf{r}) \delta(\mathbf{r}_K) d^3\mathbf{r}$$

$$+ \frac{\mu_0}{4\pi} \int \mathbf{j}^{(1)}(\mathbf{r}) \times \frac{\mathbf{r}_K}{|\mathbf{r}_K|^3} d^3\mathbf{r}.$$

Spin Dipolar

Fermi Contact

Orbital

Materials
Modelling
Laboratory

OxfordMaterials

NMR Interactions

Chemical Shift

orbital currents create magnetic field

Direct Dipolar Coupling

magnetic field created by neighbouring nuclei

n.b. function of atom positions only i.e. not directly an electronic property

Quadrupolar coupling

nuclei with I>1/2 interact with gradient of electric field (non-spherical charge density)

spin-spin coupling (J-coupling)

magnetic field induced by neighbouring nuclei but mediated via valence electrons

---

**Simulation of Observed Spectra**

In general not a simple function of NMR interaction tensors. Need to consider experimental conditions (which NMR experiment). Several sophisticated codes to handle this e.g. SIMPSON, Spinevolution (virtual spectrometers)

Materials Modelling Laboratory

OxfordMaterials

J-coupling

Electron-mediated interaction
of nuclear spins

Nucleus A causes a magnetic field at
nucleus B (and vice versa)
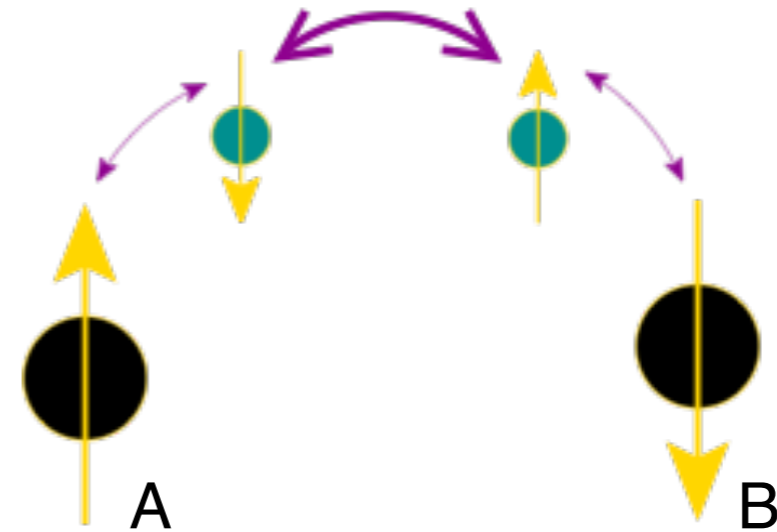
No J-coupling

with J-coupling

J

parallel

anti-parallel
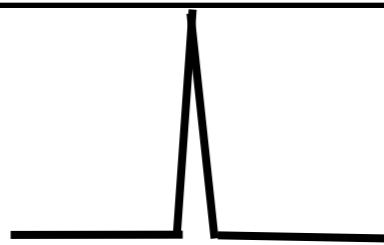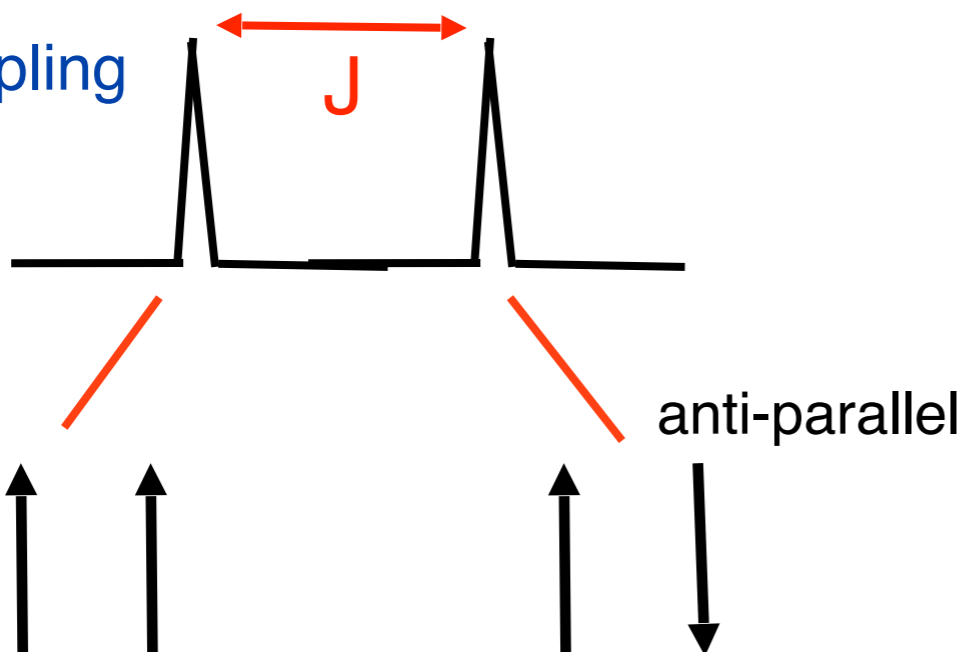
In solids J is rarely revealed in splitting
of peaks in 1D spectra (anisotropic
interactions broaden peaks)

Increasing use of techniques, eg those
using spin-echo modulation, to
measure J in solids.

Materials
Modelling
Laboratory

OxfordMaterials

Spin-Spin (J) coupling

Effective Hamiltonian

$$H = \sum_{K<L} \mathbf{I}_K (\mathbf{D}_{KL} + \mathbf{J}_{KL}) \mathbf{I}_L$$

Bare   Dressed
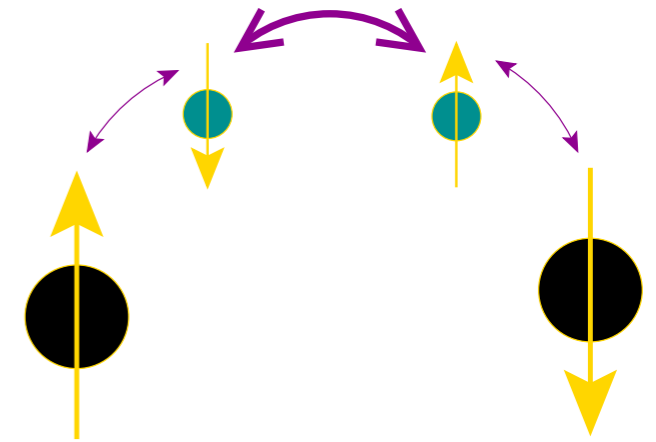
Indirect Coupling

$$\mathbf{J}_{KL} = \frac{\hbar \gamma_K \gamma_L}{2\pi} \frac{\partial^2 E}{\partial \boldsymbol{\mu}_K \partial \boldsymbol{\mu}_L}$$

(note E here omits the nuclear-nuclear magnetic interaction)

$$\mathbf{B}_{in}^{(1)}(\mathbf{R}_K) = \frac{2\pi}{\hbar \gamma_K \gamma_L} \mathbf{J}_{KL} \cdot \boldsymbol{\mu}_L$$

Orbital Magnetic dipole induces orbital motion of electrons

Spin Magnetic dipole induces spin density
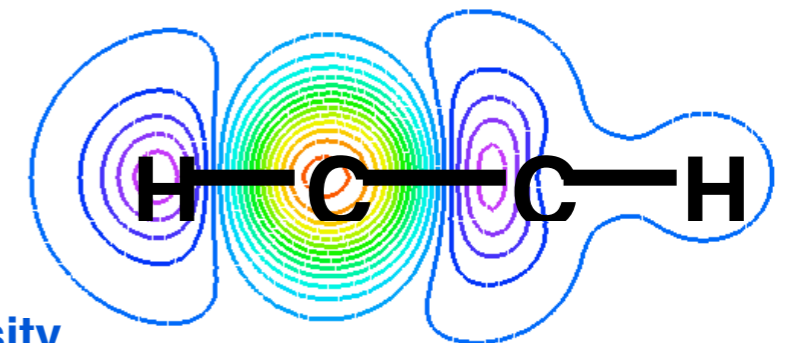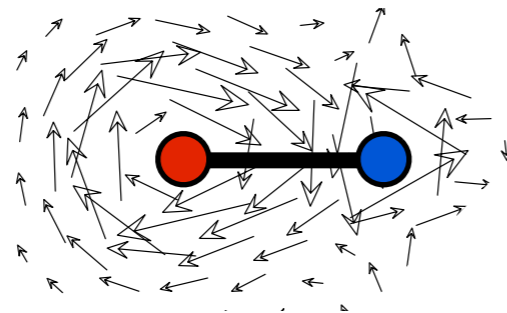
Orbital Current

Induced Spin density

Materials Modelling Laboratory

Oxford Materials

J-coupling

Guanosine
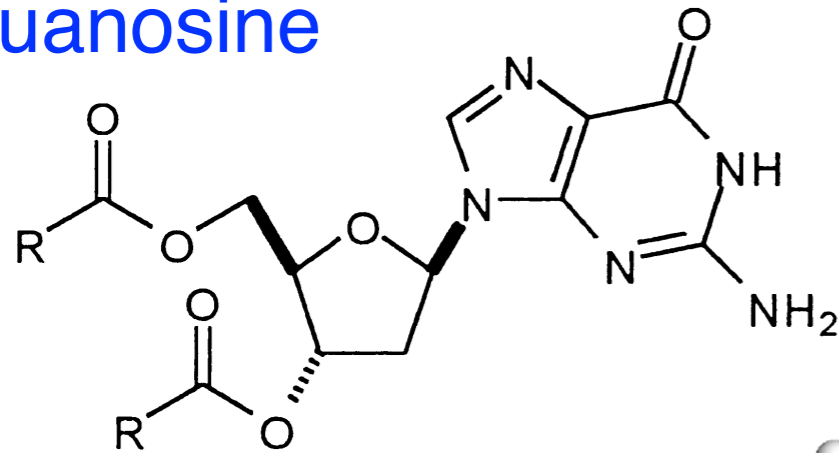
self-assembles into ribbons
molecular electronics (FET)

$^{2h}J_{N7a,N1b}$
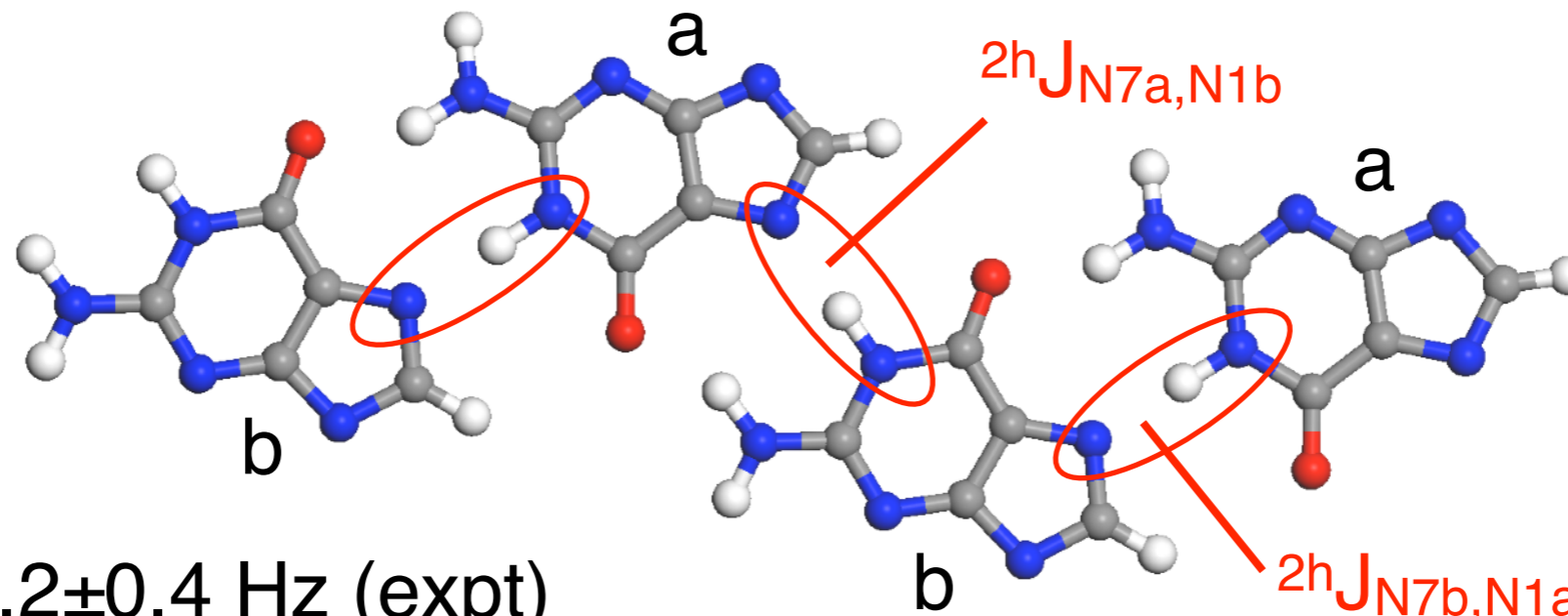
$^{2h}J_{N7b,N1a}$

$^{2h}J_{N7b,N1a} = 6.2 \pm 0.4$ Hz (expt)
$\phantom{^{2h}J_{N7b,N1a} =}$ 6.5 Hz (calc)
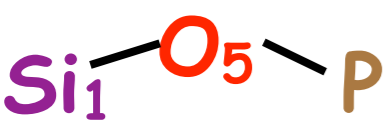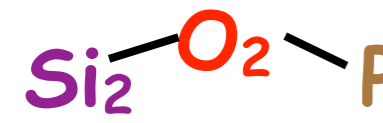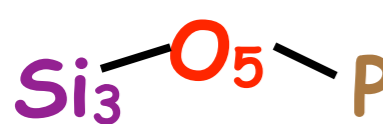
$^{2h}J_{N7a,N1b} = 7.4 \pm 0.4$ Hz (expt)
$\phantom{^{2h}J_{N7a,N1b} =}$ 7.7 Hz (calc)

J. Am. Chem. Soc. **130**, 12663 (2008)

Materials
Modelling
Laboratory

OxfordMaterials

Silicophophates

Christian Bonhomme *(Paris)*

Si$_5$O(PO$_4$)$_6$

$^2J_{SiP}$		Expt	Theory
Si$_1$—**O$_5$**—**P**		15±2 Hz	17 Hz
Si$_2$—**O$_2$**—**P**		14±2 Hz	16 Hz
Si$_3$—**O$_5$**—**P**		12±2 Hz	14 Hz
Si$_2$—**O$_2$**—**P**		4±2 Hz	1 Hz
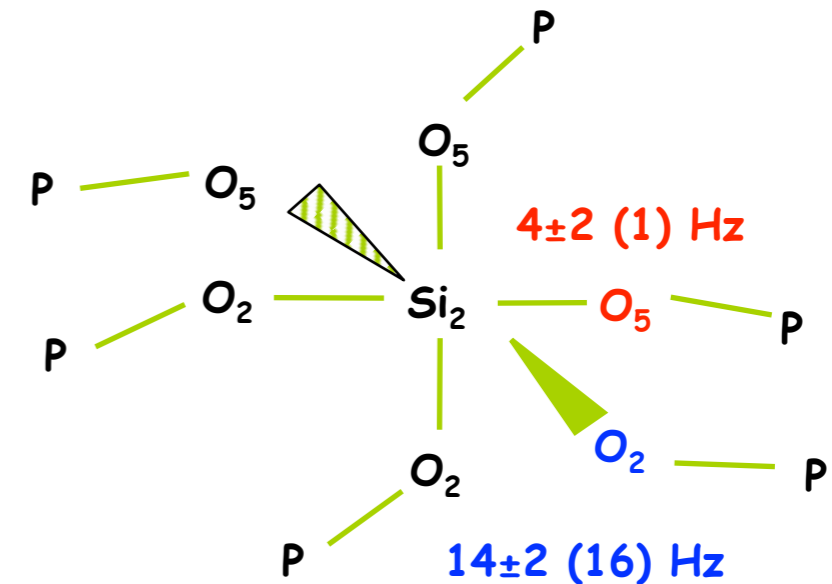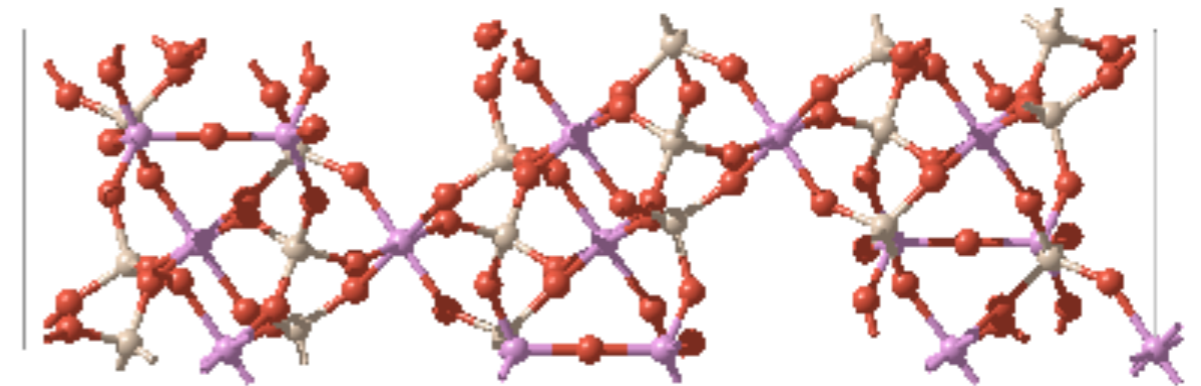
Expt: Inorg. Chem. 46, 1379 (2007)
Calc: J. Chem. Phys. 127, 204107 (2007)

4±2 (1) Hz

14±2 (16) Hz

Materials Modelling Laboratory

OxfordMaterials

Role of Calculations of J

Design and optimisation of NMR experiments
Interpretation of experiment

Through-space J-coupling

$^{1i}J_{FF}$	Expt	Calc
F1-F3:	18 Hz	12.5 Hz
F1-F7:	2.6 Hz	3.6 Hz

2.74Å

3.18Å

F3   F7   F1
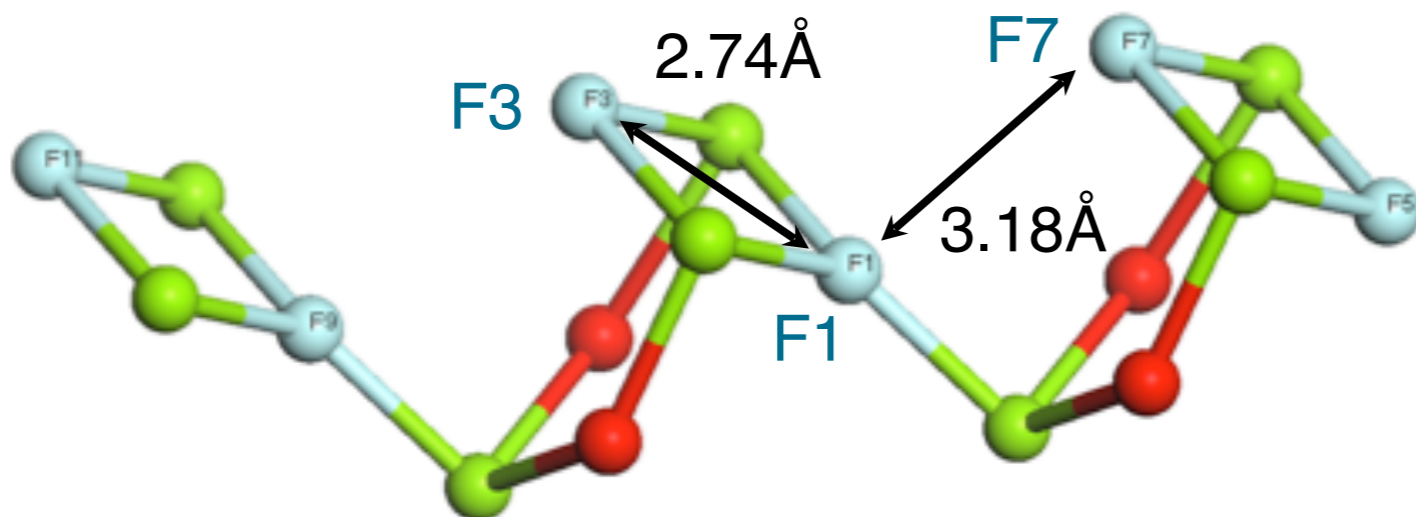
fluorine-substituted deuterated hydrous magnesium silicate

J. Am. Chem. Soc. 132 15651 (2010

Distributions of J in amorphous solids

Si-O-Si (deg)

silica glass

Materials
Modelling
Laboratory

OxfordMaterials
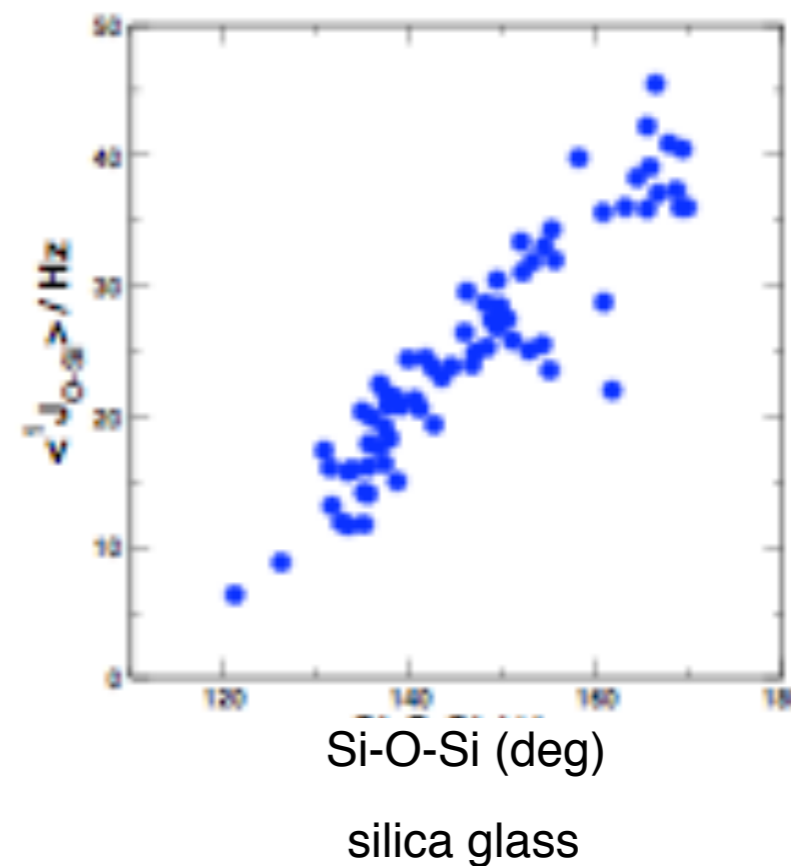
Electric Field Gradients

Function of the charge density - ie ground-state property.
Also computed by all-electron codes such as Wien2k, Crystal

charge density

EFG
$$V_{\alpha\beta}(\mathbf{r}) = \int d^3 r \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|^3} \left[\delta_{\alpha\beta} - 3 \frac{(r_\alpha - r'_\alpha)(r_\beta - r'_\beta)}{|\mathbf{r} - \mathbf{r}'|^2} \right]$$

Eigenvalues

$$V_{xx}, V_{yy}, V_{zz} \qquad |V_{zz}| > |V_{yy}| > |V_{xx}|$$

Quadrupolar Coupling

$$C_Q = \frac{eQV_{zz}}{h}$$

Asymmetry

$$\eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

Note: The quadrupolar moment, Q, is a nuclear property. Most recent values given in "*Year-2008 Standard Values of Nuclear Quadrupole Moments*": P. Pyykkö, Mol. Phys. 106, 1965-1974 (2008)
But note Q appears as a simple scaling factor
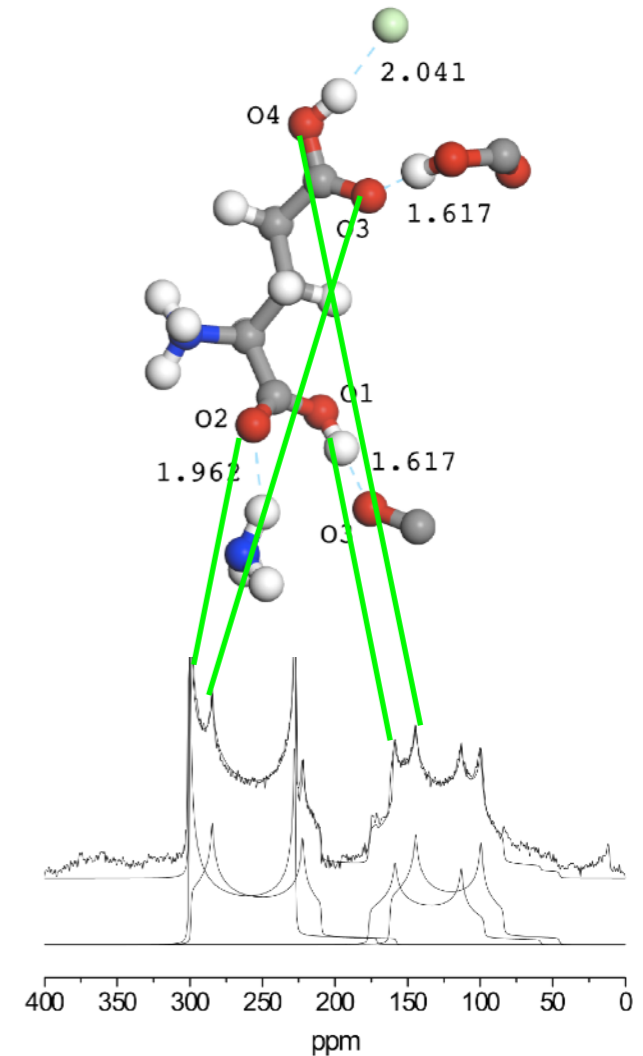
^{17}O MAS Glutamic Acid . HCl

Materials Modelling Laboratory

OxfordMaterials

*.param file

```
task          : magres
magres_task : shielding
                    efg
                    nmr
              jcoupling
```

→ chemical shift/shielding

→ electric field gradient

→ both

Must use on-the-fly pseudopotentials

Highly sensitive to geometry (optimise H X-ray positions)

CONVERGE
(basis cut-off & k-points)

*.castep file

```
============================================================
|              Chemical Shielding Tensor                   |
|----------------------------------------------------------|
|     Nucleus                    Shielding tensor          |
|   Species    Ion          Iso(ppm)    Aniso(ppm)   Asym  |
|      H        1             23.81        5.27       0.40  |
|      H        2             24.75       -3.35       0.85  |
|      H        3             27.30       -5.79       0.90  |
|                                                          |
|      O        5            -43.73      504.95       0.47  |
|      O        6            -63.53      620.75       0.53  |
|      O        7            -43.73      504.95       0.47  |
|      O        8            -63.53      620.75       0.53  |
============================================================
```

Anisotropy

Asymmetry

$$\sigma_{\mathrm{aniso}} = \sigma_{\mathrm{zz}} - 1/2(\sigma_{\mathrm{xx}} - \sigma_{\mathrm{yy}})$$

$$\eta = 3(\sigma_{\mathrm{yy}} - \sigma_{\mathrm{xx}})/2\sigma_{\mathrm{aniso}}$$

Materials
Modelling
Laboratory

OxfordMaterials

*.magres file

```
============
Atom: O     1
============

O     1 Coordinates        1.641     1.522      5.785    A


TOTAL Shielding Tensor


            218.1858       12.1357      -25.7690
             13.4699      191.6972       -7.2419
            -25.9178       -6.5205      216.3180


O     1 Eigenvalue  sigma_xx      185.6127 (ppm)
O     1 Eigenvector sigma_xx         0.5250      -0.8103       0.2603
O     1 Eigenvalue  sigma_yy      193.8979 (ppm)
O     1 Eigenvector sigma_yy         0.4702       0.5310       0.7049
O     1 Eigenvalue  sigma_zz      246.6904 (ppm)
O     1 Eigenvector sigma_zz        -0.7094      -0.2477       0.6598


O     1 Isotropic:       208.7337 (ppm)
O     1 Anisotropy:       56.9351 (ppm)
O     1 Asymmetry:         0.2183
```
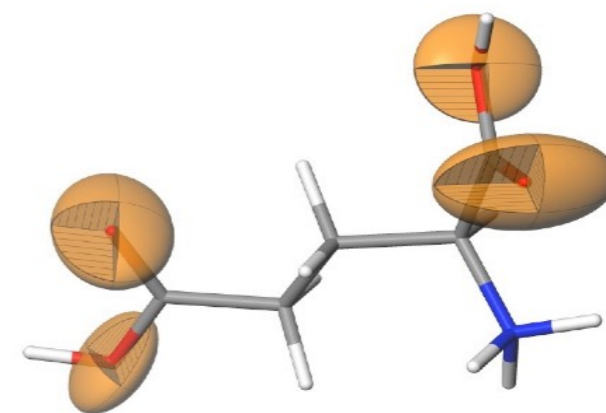
Note: shielding tensor has a symmetric and an antisymmetric component.
Typical NMR experiments are only sensitive to the symmetric part.
Therefore we only diagonalise the symmetric part of the shielding tensor

Materials
Modelling
Laboratory

OxfordMaterials
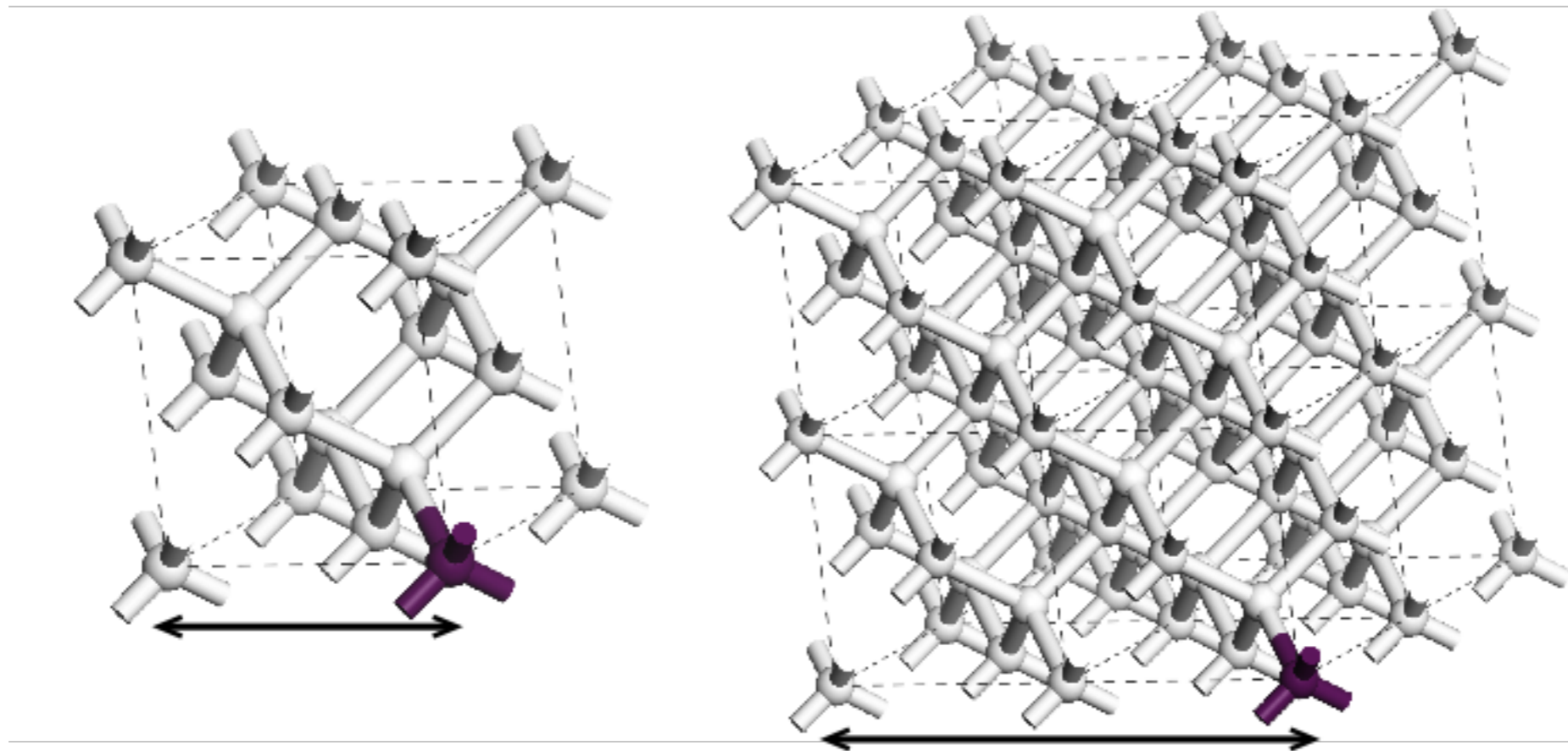
A single calculation give the coupling between one (perturbing) atoms and all others. Might need several calculations to get all of the couplings of interest.

Perturbing atom breaks periodicity - if the unit cell is small you might need to build a supercell to inhibit the interaction with periodic images

Materials
Modelling
Laboratory

OxfordMaterials

J-coupling

Contributions to J-coupling

Spin: Fermi Contact (FC)   Spin Dipolar (SD)

Charge: Paramagnetic (PARA) and Diamagnetic (DIA) - terms similar to shielding

note: *only total J is observable*

```
=================================================================================
|                          Isotropic J-coupling                                 |
|-------------------------------------------------------------------------------|
|       Nucleus                        J-coupling values                        |
|    Species    Ion       FC           SD          PARA         DIA      TOT(Hz) |
|       O        1       25.37         0.31        -5.61        0.10       20.18  |
|**     Si       1        _._          _._          _._         _._        _._   |
|       Si      10       12.41        -0.04         0.41        0.01       12.79  |
|       Si      16       17.97         0.07         0.43        0.01       18.48  |
|       Si      30       14.40         0.23         0.39        0.01       15.03  |
```

Perturbing atom → (points to the `** Si 1` row)

```
          Bond          Length (A)   1st image      Iso(Hz)        Aniso(Hz)
        ==================================================================
        Si 001 --  O 001   1.61808     12.06908       20.18          57.86
        Si 001 -- Si 038   3.02674     11.25096       12.90           3.09
        Si 001 -- Si 010   3.03908      7.70290       12.79           3.47
        Si 001 -- Si 016   3.09623      9.83675       18.48           6.54
        Si 001 -- Si 030   3.17013     11.91281       15.03           8.39
```

Practical Things

Some practical things to keep in mind

Structure

    NMR is very sensitive to structure!

    XRD atom positions are often not sufficient for accurate simulation of NMR parameters

Dynamics

    Atoms move - spectra are recorded at finite T.

    How to account for that in (static) calculations?

Accuracy

    How good are our present (approximate) density functionals?

Materials
Modelling
Laboratory

OxfordMaterials

Challenges

Effects of Relativity
   scalar relativistic effects easy to treat (relativistic_treatment)
   *spin-orbit interaction is much harder - but needed for eg shifts on light atoms bonded to heavy atoms*

Localised d/f Electrons
   Local Density Approximation not enough

Paramagnetic Materials
   Magnetic fields from electronic spin
      Curie type paramagnetism is hard
      Pauli (i.e. Knight Shift) now implemented

Materials
Modelling
Laboratory

OxfordMaterials

Limitations
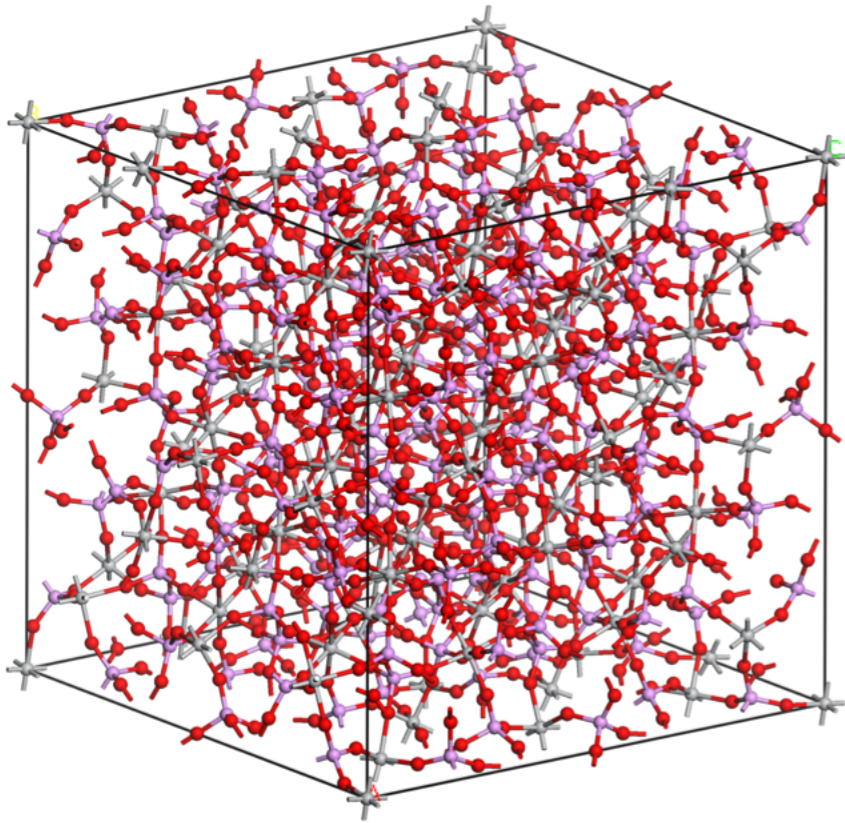
TiP$_2$O$_7$
1020 atoms 8000 electrons
~42 hours on 384 cores (2Tb RAM)
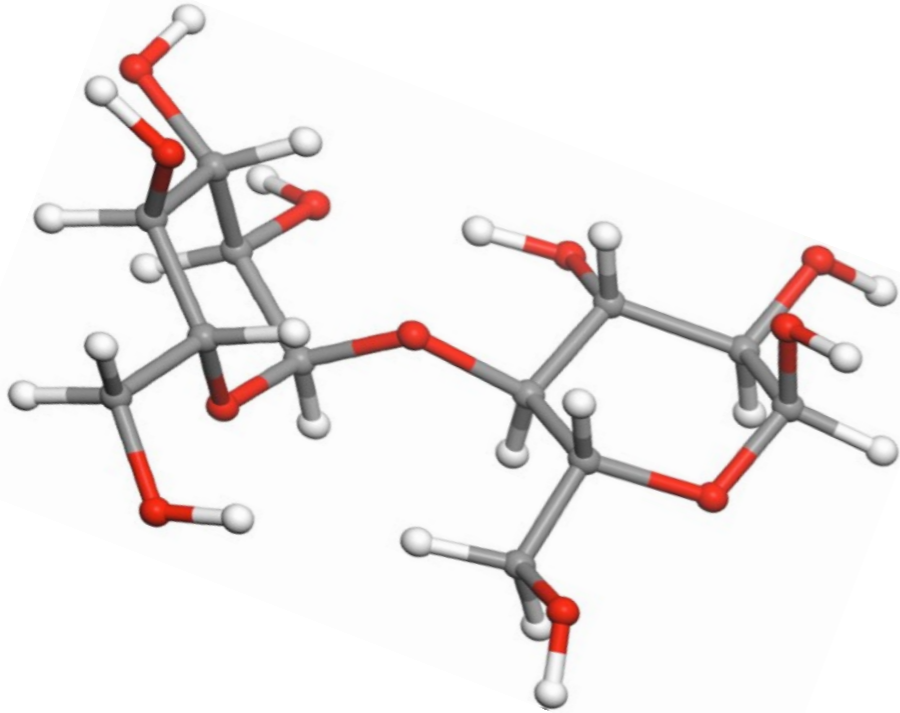"archer" UK national facility

Pharmaceutical
980 atoms 3000 electrons
~24 hours on 96 cores
local cluster
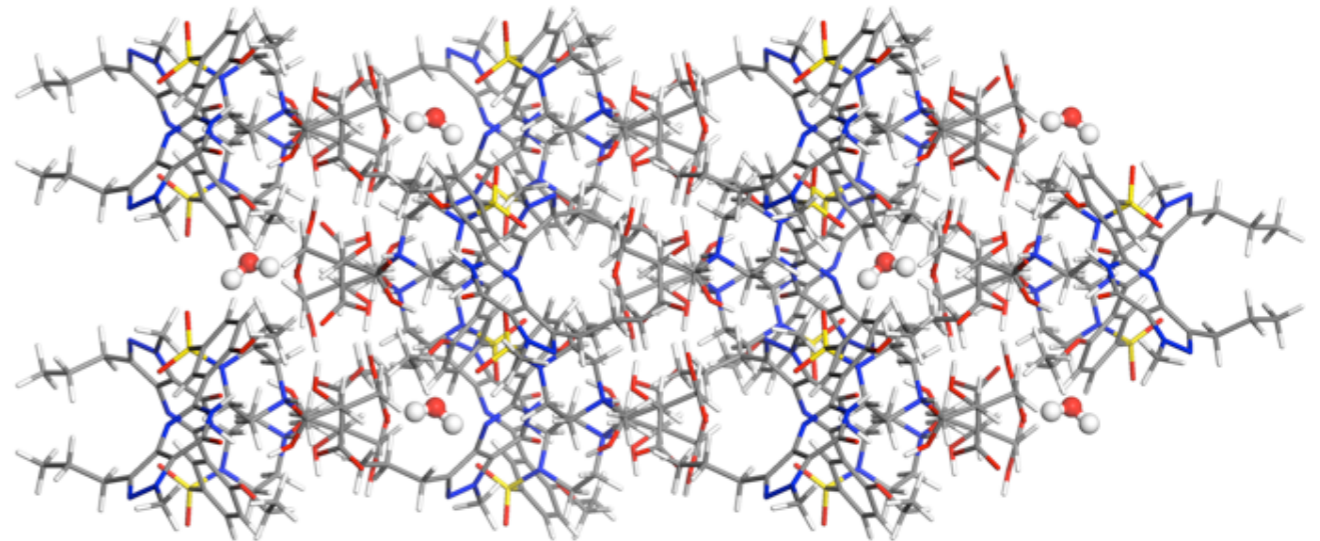
Maltose Again

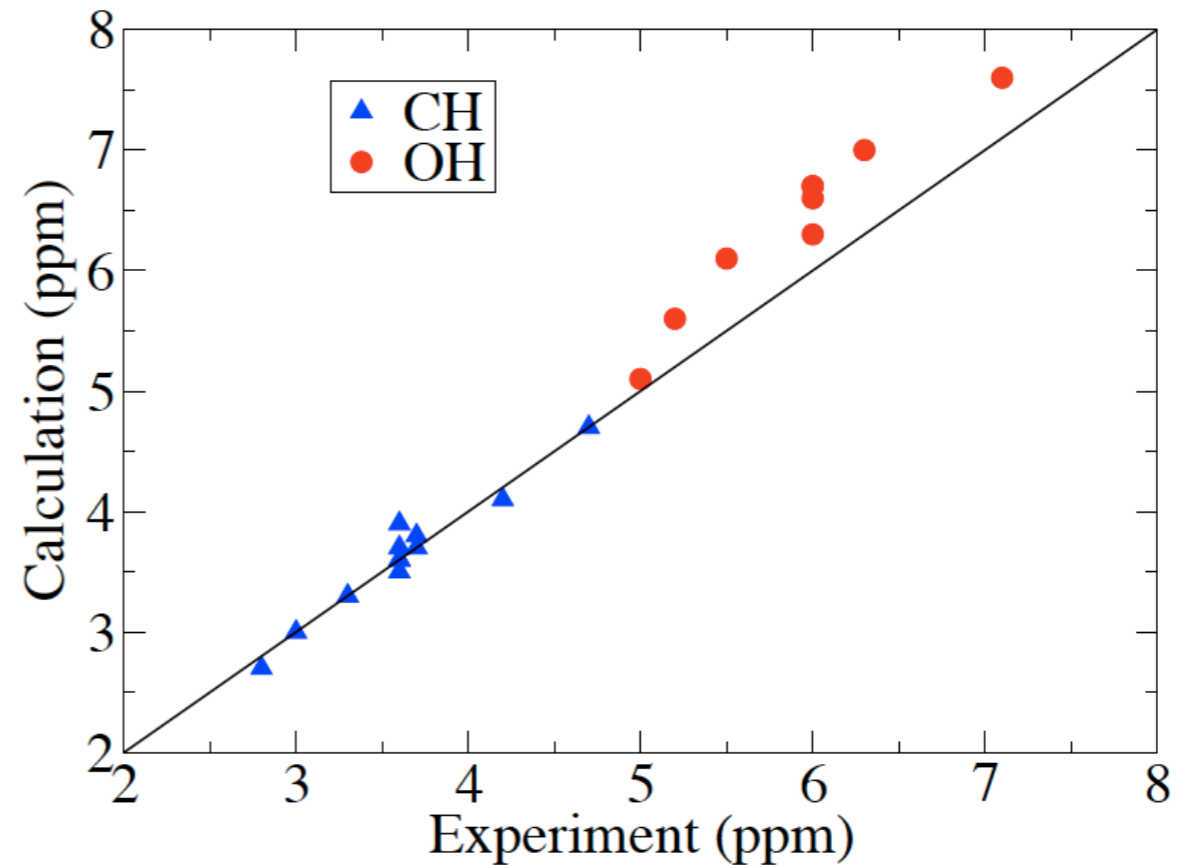

CH
J. Am. Chem. Soc. 127 10216-10220 (2005)

OH
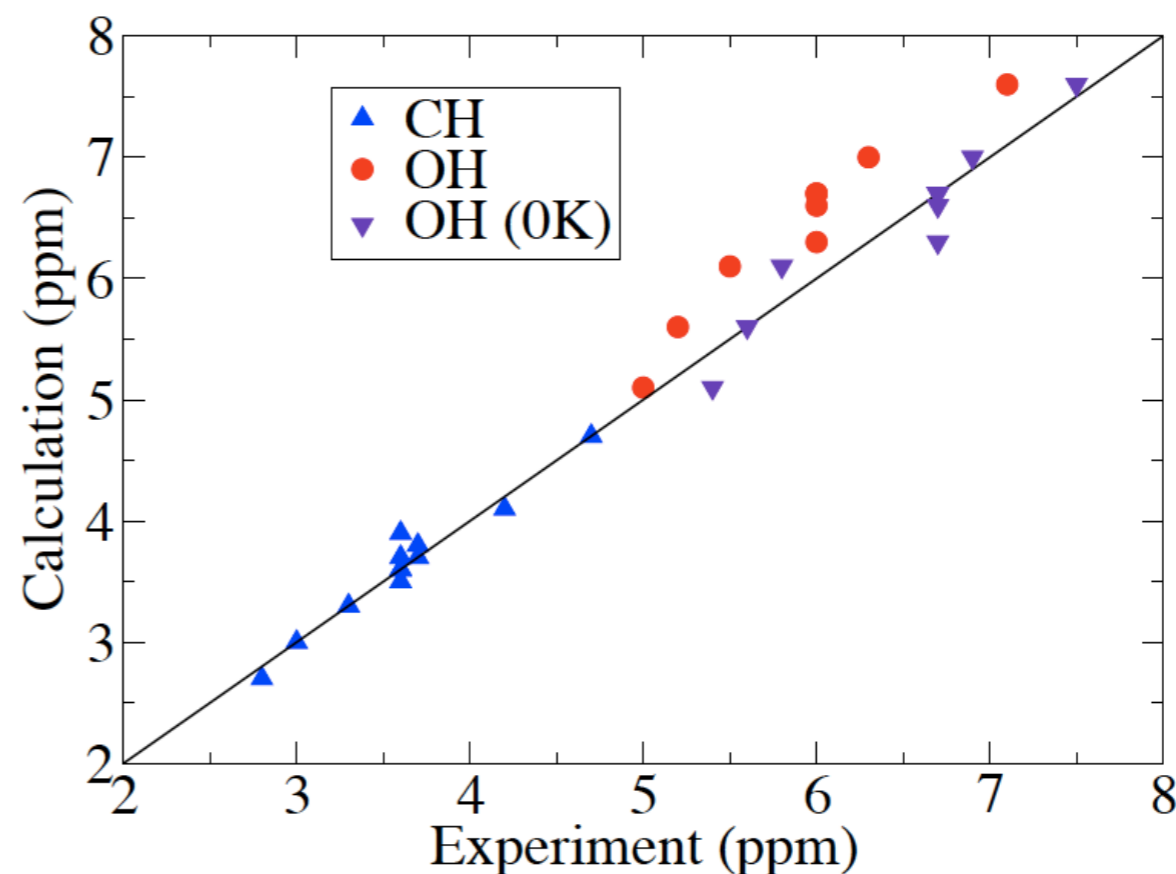Phys. Chem. Chem. Phys., 12, 6970 (2010)
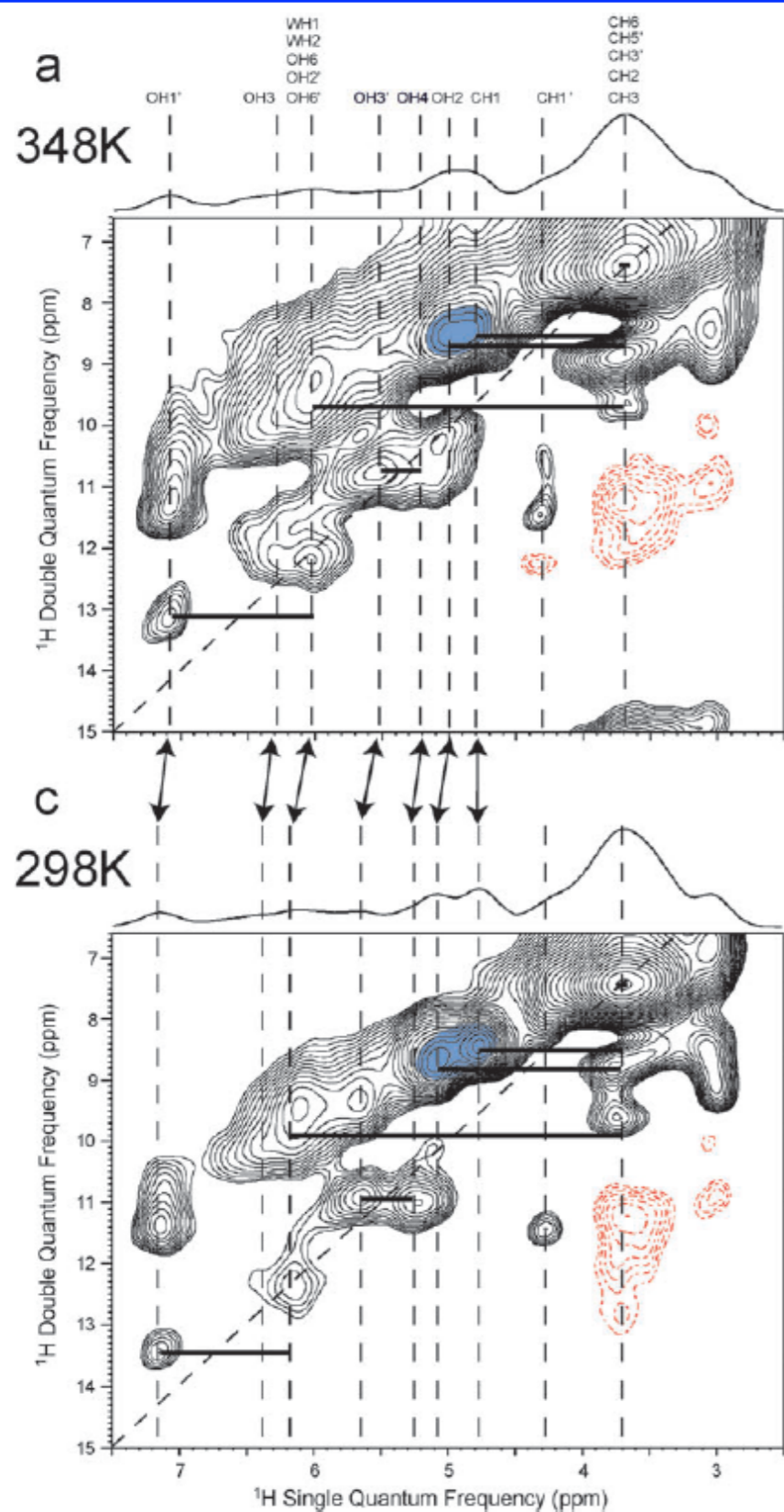
Compare Calculation with experiment
C-H max error 0.3ppm (mean 0.1ppm)
O-H max error 0.6ppm (mean 0.4ppm)

Why are there larger errors for hydroxyl protons?

Materials
Modelling
Laboratory

OxfordMaterials

Variable Temperature
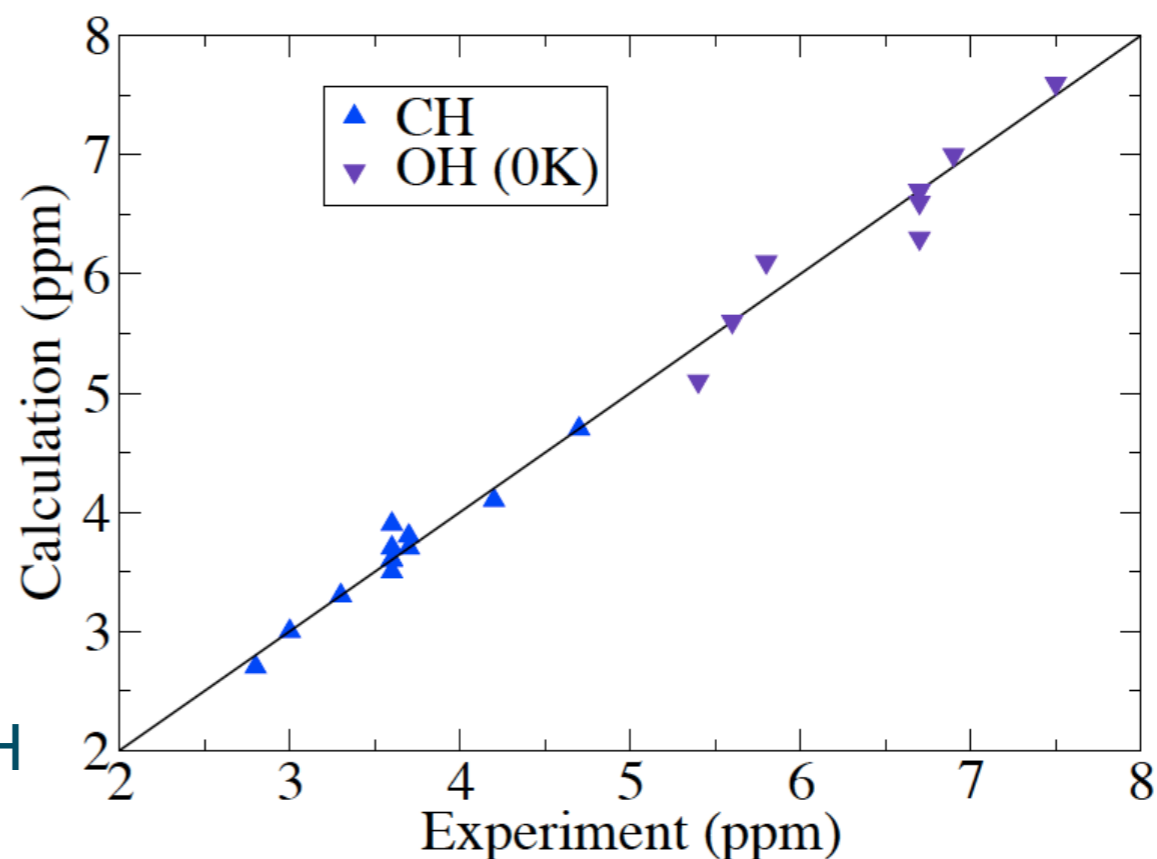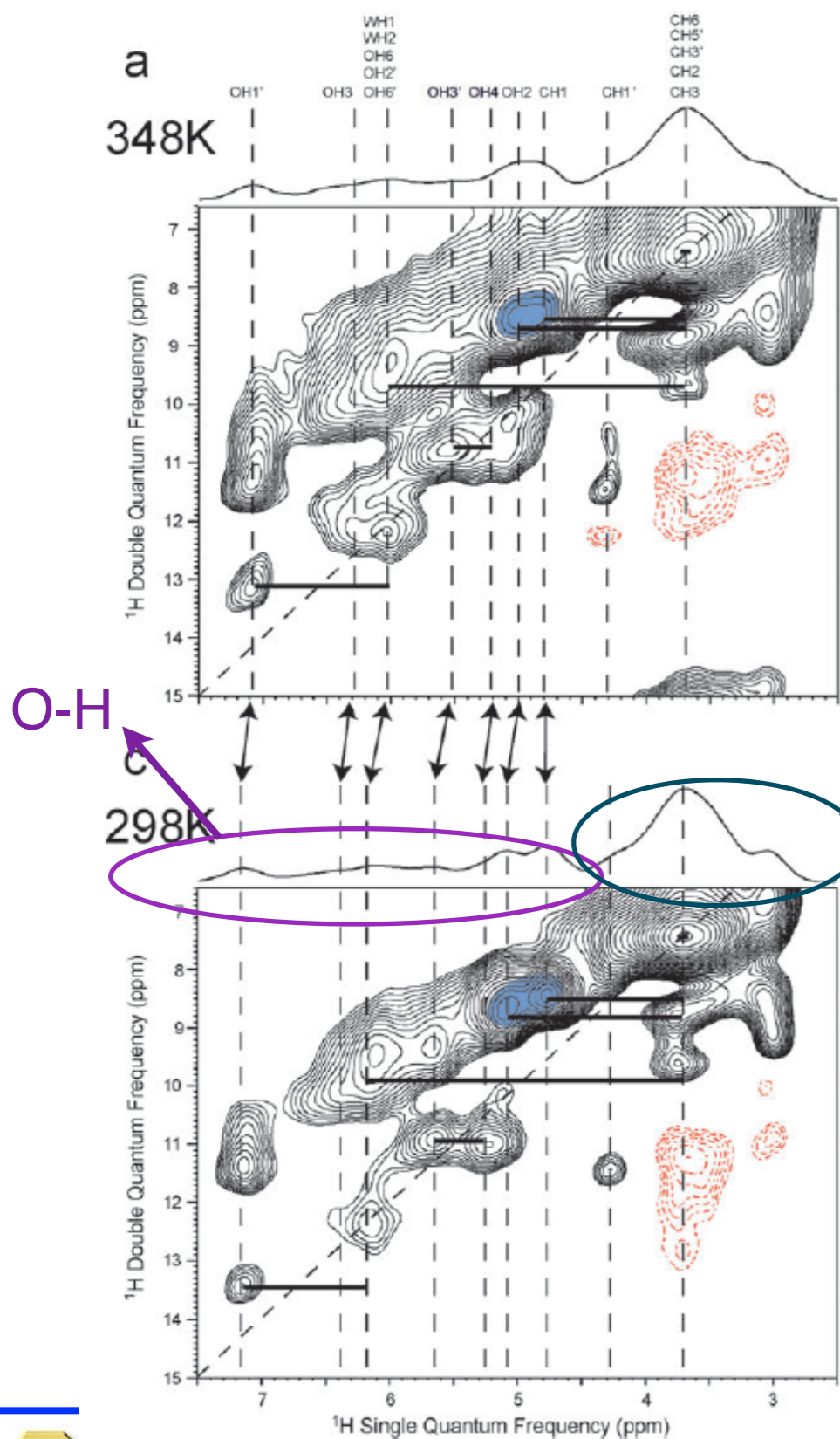

Compare to room temp experiment
C-H max error 0.3ppm (mean 0.1ppm)
O-H max error 0.6ppm (mean 0.4ppm)

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

Variable Temperature

Compare to room temp experiment
 C-H max error 0.3ppm (mean 0.1ppm)
 O-H max error 0.6ppm (mean 0.4ppm)

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

Thermal motion

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)*

Materials Modelling Laboratory

OxfordMaterials

Getting more information

NMR Books

Good Introduction

Nuclear Magnetic Resonance (Oxford Chemistry Primers)

P. J. Hore

More advanced

Spin Dynamics: Basics of Nuclear Magnetic Resonance

Malcolm H. Levitt

Solid state NMR

Solid-State NMR: Basic Principles and Practice

David Apperley, Robin Harris, Paul Hodgkinson

Useful survey of applications

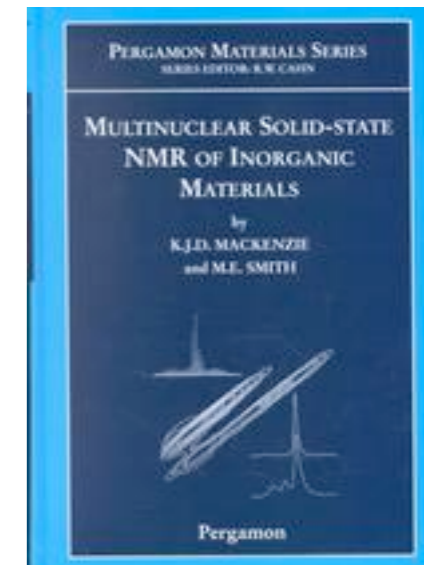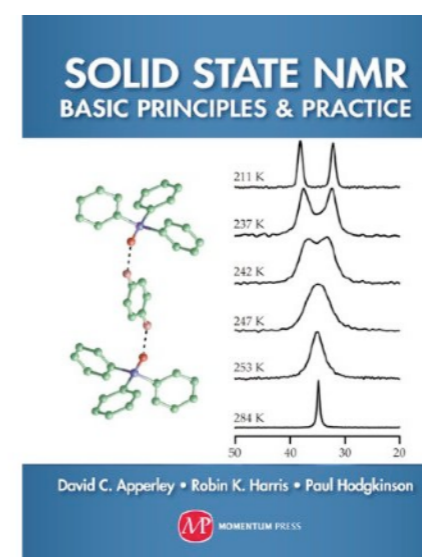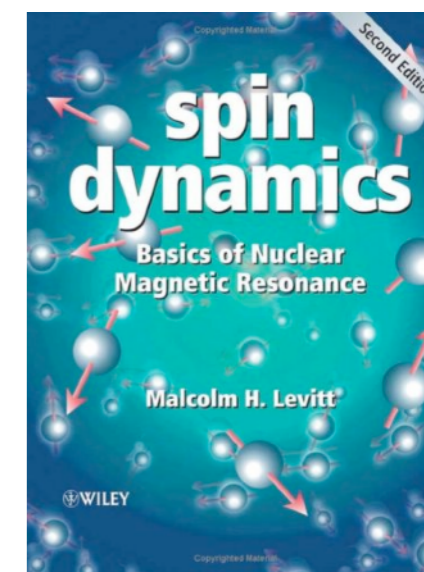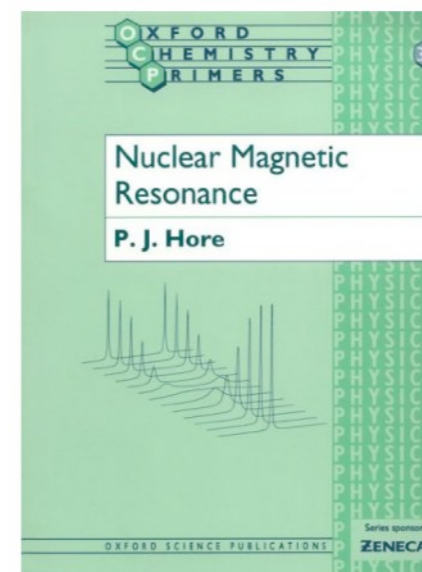Multinuclear Solid-State Nuclear Magnetic Resonance of Inorganic Materials

Kenneth J.D. MacKenzie, M.E. Smith

Recent Review Articles

Perspective: Current advances in solid-state NMR spectroscopy
J. Chem. Phys. 149, 040901 (2018); https://doi.org/10.1063/1.5038547
Sharon E. Ashbrook and Paul Hodgkinson

Materials Modelling Laboratory

Oxford Materials

GIPAW Theory

Exhaustive (and exhausting!) review of applications and theory

First-Principle Calculation of NMR Parameters Using the GIPAW (Gauge Including Projector Augmented Wave) Method: a Chemist's Point of View

Bonhomme, Gervais, Babonneau, Coelho, Pourpoint, Azais, Ashbrook, Griffin, Yates, Mauri, Pickard,

Chemical Reviews 112 (11), 5733-5779 (2012)

Original Theory Papers:

All-electron magnetic response with pseudopotentials: NMR chemical shifts,

Chris J. Pickard, and Francesco Mauri.

Phys. Rev. B, 63, 245101 (2001)

Calculation of NMR Chemical Shifts for extended systems using Ultrasoft Pseudopotentials

Jonathan R. Yates, Chris J. Pickard, and Francesco Mauri.

Physical Review B 76, 024401 (2007)

A First Principles Theory of Nuclear Magnetic Resonance J-Coupling in solid-state systems

Sian A. Joyce, Jonathan R. Yates, Chris J. Pickard, Francesco Mauri

J. Chem. Phys. 127, 204107 (2007)

Materials
Modelling
Laboratory

OxfordMaterials