

# Anisotropic Interactions and High-Resolution NMR in Solids

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## Overview

- Quick reminder of NMR theory from yesterday
- Introduction to anisotropy and why it matters
- The effects of anisotropic interactions
- Removing anisotropic interactions in solids

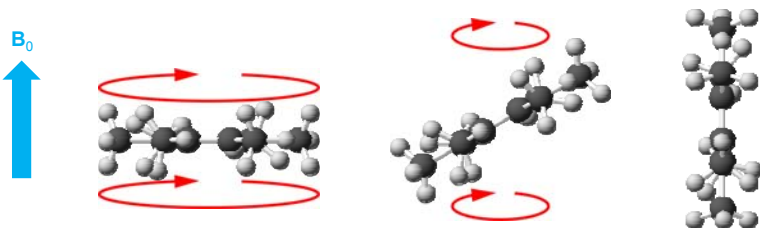
## “NMR in a Nutshell” in a Nutshell

- Magnetically-active nuclei interact with a magnetic field to give an NMR signal (intensity, frequency).
- Electrons interact with external magnetic fields to create small internal magnetic fields.
- When we look at nuclei surrounded by electrons (*i.e.*, stuff), the exact resonance frequency depends on where the electrons are (*i.e.*, chemistry).
- NMR spectroscopy can be used to probe of structure, connectivity and 3D conformation.

## 1. Anisotropic Interactions in NMR

# Anisotropy

- “Anisotropic” means “not the same in all directions” and applies to many molecules.



- We expect a different magnetic response, *i.e.*, shift, for the same  $^{13}\text{C}$  nucleus at the same  $B_0$  strength depending on the molecular orientation.
- So why do we see sharp lines in solution for this anisotropic molecule?

# Liquids vs Solids

- In liquids, molecules tend to tumble rapidly compared to the Larmor frequency.
  - $\tau_c$  around  $10^{-12}$  s (small molecules) to  $10^{-7}$  s (biomolecules)
  - $1/\nu_0$  around  $10^{-9}$  s (1 GHz) to  $10^{-8}$  s (100 MHz)
- Over the course of one nuclear oscillation, there is no memory of molecular orientation.
  - Caveat: this isn't always true for biomolecules, which have longer  $\tau_c$  and may behave more like small solid particles under certain conditions.
- In a typical solid, motion is (nearly) absent owing to molecular packing, rigid ionic lattice potentials, *etc.*, so it matters which way up your crystallite is.

# Some Maths, Unfortunately

- We have seen chemical shifts reported as  $\delta$ , but this is the orientation-averaged isotropic value. In solids, we must represent the chemical shift as an interaction tensor.

lab frame

$$\delta^{\text{lab}} = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix}$$

axes fixed relative to the lab (and  $B_0$ )  
arbitrary orientation of the molecule

interaction frame

$$\delta^{\text{PAS}} = \begin{pmatrix} \delta_{zz} & 0 & 0 \\ 0 & \delta_{yy} & 0 \\ 0 & 0 & \delta_{xx} \end{pmatrix}$$

$$\delta_{\text{iso}} = \frac{\delta_{zz} + \delta_{yy} + \delta_{xx}}{3}$$

$$|\delta_{zz} - \delta_{\text{iso}}| \geq |\delta_{xx} - \delta_{\text{iso}}| \geq |\delta_{yy} - \delta_{\text{iso}}|$$

axes fixed relative to the interaction  
arbitrary relative orientation of  $B_0$

rotation transform between frames

# Some Maths, Unfortunately

- All shifts must be between  $\delta_{zz}$  and  $\delta_{xx}$ , and are distributed according to:

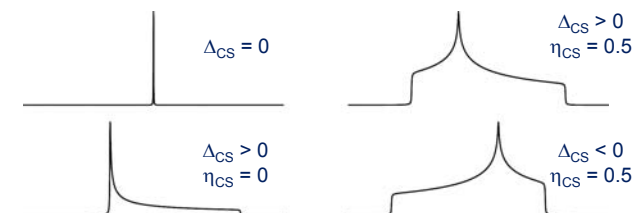
$$\delta = \delta_{\text{iso}} + \frac{\Delta_{\text{CS}}}{2} \left[ (3\cos^2\theta - 1) + \eta_{\text{CS}} (\sin^2\theta \cos 2\phi) \right]$$

orientation independent

orientation dependent

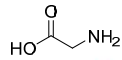
$$\Delta_{\text{CS}} = \delta_{zz} - \delta_{\text{iso}} \quad \text{Anisotropy "size"}$$

$$\eta_{\text{CS}} = \frac{\delta_{yy} - \delta_{xx}}{\Delta_{\text{CS}}} \quad \text{Asymmetry "shape"}$$



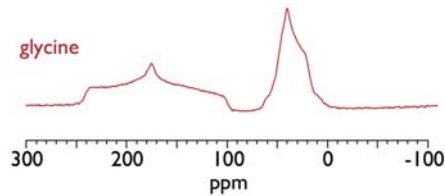
# The Problem with Anisotropy

- Having a spectrum where we can identify all three components of the shift tensor gives us more information than the average  $\delta_{iso}$  from solution, and more information is good, right?



sp<sup>2</sup> C have a larger CSA as their symmetry is lower

glycine



sp<sup>3</sup> C have approximately tetrahedral electron density, so have a small CSA

- Broad signals are a problem when we have multiple resonances in the spectrum (*i.e.*, in most materials of interest).

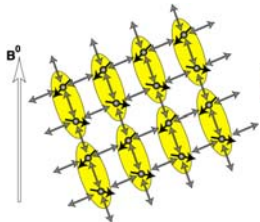
# Other Anisotropic Interactions

- If the molecule is anisotropic, all interactions present will be anisotropic.

Interaction	Size	Liquids	Solids
Zeeman	10 <sup>7</sup> – 10 <sup>9</sup> Hz	yes	yes
RF pulses	10 <sup>3</sup> – 10 <sup>5</sup> Hz	yes	yes
chemical shift	10 <sup>4</sup> – 10 <sup>5</sup> Hz	isotropic	anisotropic
J coupling	1 – 10 <sup>3</sup> Hz	isotropic	anisotropic
dipolar coupling	10 <sup>3</sup> – 10 <sup>5</sup> Hz	no	anisotropic
quadrupolar coupling	10 <sup>3</sup> – 10 <sup>7</sup> Hz	no	anisotropic

# Dipolar Couplings

- Nuclear spins generate a magnetic dipole, which can interact directly with other nuclear dipole moments through space.



$$\omega_D = \frac{\omega_D^{PAS} (3\cos^2\theta - 1)}{2}$$

$$\omega_D^{PAS} = -\frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi r_{IS}^3}$$

$$D = \begin{pmatrix} +D & 0 & 0 \\ 0 & -D/2 & 0 \\ 0 & 0 & -D/2 \end{pmatrix}$$

# Quadrupolar Nuclei

- Nuclei with spin  $I > 1/2$  have a nuclear electric quadrupole moment  $Q$ , which interacts with an electric field gradient,  $V$ .

$$V^{PAS} = \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix}$$

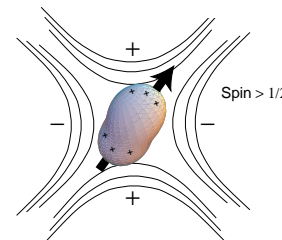
$$C_Q = \frac{eQV_{zz}}{h}$$

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

$$|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$$

$$V_Q^{PAS} = \frac{3C_Q}{4I(2I-1)}$$

$$P_Q = C_Q \left(1 + \frac{\eta_Q^2}{3}\right)^{1/2}$$

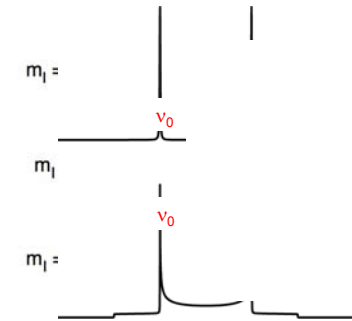


## Nuclei with Integer Spins

- Only seven natural NMR-active nuclei have integer spins.
  - $I = 1$ :  $^2\text{H}$ ,  $^6\text{Li}$ ,  $^{14}\text{N}$
  - $I = 3$ :  $^{10}\text{B}$
  - $I = 5$ :  $^{138}\text{La}$
  - $I = 6$ :  $^{50}\text{V}$
  - $I = 7$ :  $^{176}\text{Lu}$
- All exhibit combinations of very unfavourable properties.
  - Low abundance, low receptivity, large quadrupolar coupling...
- Can still be used to provide information.
  - More on that later.

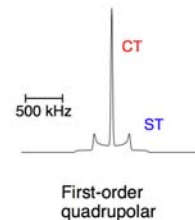
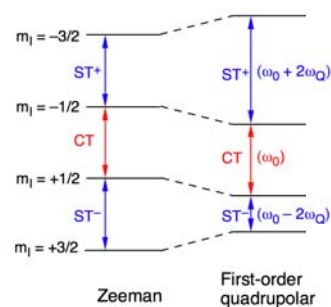
## Quadrupolar Nuclei: $I = 1$

- For  $I = 1$ , three allowed Zeeman states give two allowed transitions.
  - These are degenerate when  $V_{zz} = 0$  but the quadrupolar interaction perturbs these energy levels, normally only to first order.
- $$\nu_Q = \nu_Q^{\text{PAS}} \frac{1}{2} \left[ (3\cos^2\theta - 1) + \eta_Q (\sin^2\theta \cos 2\phi) \right]$$
- Two transitions observed in the spectrum.



## Quadrupolar Nuclei: $I = 3/2$

- For half-integer spins the Central Transition (CT) is unaffected by the first order transition.



## Quadrupolar Nuclei: $I = 3/2$

- The quadrupolar frequency has a complicated orientation dependence:

$$\nu_Q = \frac{(\nu_Q^{\text{PAS}})^2}{\nu_0} \left[ A + B d_{00}^2(\theta) + C d_{00}^4(\theta) \right]$$

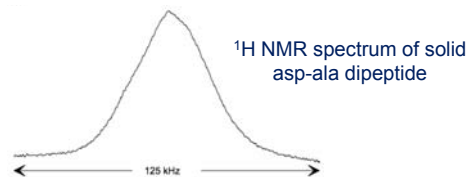
A: isotropic

B: first-order  $d_{00}^2(\theta) \propto 3\cos^2\theta - 1$

C: second-order  $d_{00}^4(\theta) \propto 35\cos^4\theta - 30\cos^2\theta + 3$

# Solid-State NMR: The Problem

- Typically, the width of lines in solid-state NMR spectra is greater than their separation.
- Peaks overlap and the signal is typically spread out over hundreds of ppm.



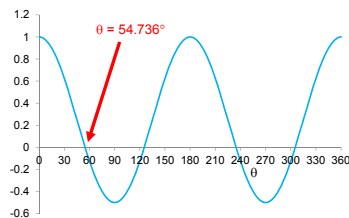
- The result is broad, featureless spectra that look like they contain no useful information.
- They actually contain too much information!
  - Chemistry, crystal and local symmetry, distances, bonds...

## 2. Improving Resolution and Sensitivity

### Magic Angle Spinning

- Remember that most anisotropic contributions are proportional to  $(3\cos^2\theta - 1) / 2$ .

- This is zero at the “magic” angle of  $54.736^\circ$ .



- If we could align all crystallites at the magic angle, we would get an isotropic spectrum.

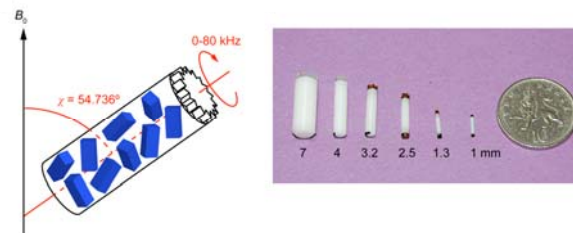
- This is not practical...

- If we could, instead, achieve an *average* crystallite orientation of the magic angle, we would still see the isotropic spectrum.

- Rapid isotropic tumbling is why solution state NMR spectra have such high resolution.

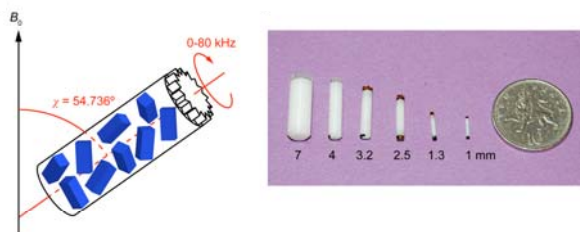
### Magic Angle Spinning

- In the magic angle spinning (MAS) experiment, the randomly oriented crystallites are packed into a rotor oriented at the magic angle.



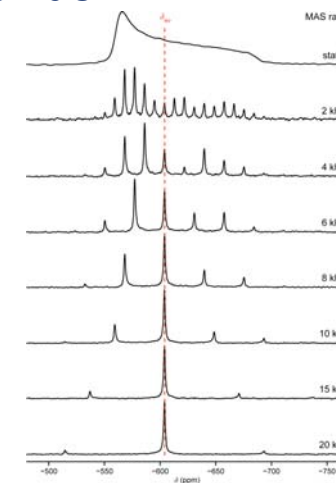
## Magic Angle Spinning

- Rapid rotation averages off-axis contributions to the crystallite orientation to zero, giving an orientation of  $54.736^\circ$ .
- The maximum rotation rate is limited by the speed of sound over the outer wall of the rotor.
- Smaller rotors can rotate faster, but hold less sample.
- Trade off between sensitivity (number of nuclei present) and resolution (MAS rate needed).



## Spinning Sidebands

- MAS works very well provided the rotation rate exceeds the broadening you are trying to remove.
- At “slow” MAS rates, spinning sidebands are observed.
- SSBs are still sharp and can provide information on anisotropic interactions (provided the manifolds from different resonances don't overlap).
- For some nuclei, (particularly  $^1\text{H}$  and  $^{19}\text{F}$ ), the homonuclear dipolar coupling still causes broad SSBs up to  $\sim 100$  kHz MAS.



## Decoupling

- As in solution NMR, decoupling can remove the effects of spin-spin interactions (dipolar and J).

$^1[^{13}\text{C}]$ -glycine

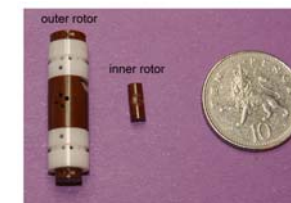
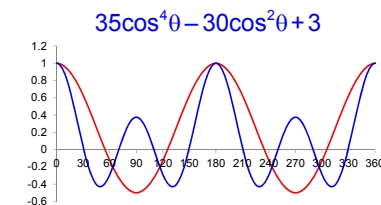
10.9 kHz

CSA is not removed  
(single-spin involved)

- Unlike solution-state NMR, 38 Hz counts as a narrow line!

## MAS and Quadrupolar Nuclei

- The second-order quadrupolar perturbation has an orientation dependence with roots at  $30.56^\circ$  and  $70.12^\circ$ .
- Reduced to  $\sim 1/3$  by MAS but not removed entirely.
- Could be removed by spinning at  $30.56^\circ$  (or  $70.12^\circ$ ).
- The Double Orientation Rotation (DOR) experiment spins the sample simultaneously at  $54.74^\circ$  and  $30.56^\circ$ .
- Specialist probe required, poor fill factor, top spinning rates  $\sim 2$  kHz (outer) and  $\sim 6$  kHz (inner) rotors...



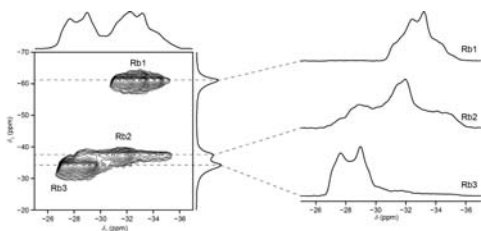
# The MQMAS Experiment

- Multiple-quantum (MQ) MAS has revolutionised high-resolution NMR of quadrupolar nuclei.

- 2D experiment that exploits the different A, B and C coefficients for different transitions.

$$v_Q = \frac{(v_Q^{PAS})^2}{v_0} [A + Bc_{00}^2(\theta) + Cd_{00}^4(\theta)]$$

- Correlates the isotropic MQ spectrum with the conventional MAS spectrum.



- Individual lineshapes can be extracted to provide  $\delta_{iso}$ ,  $C_Q$ ,  $\eta_Q$ .
- If this is not possible, the centre of gravity can still give  $\delta_{iso}$  and  $P_Q$ .

# Cross Polarisation

- Cross polarisation (CP) is a signal enhancement method that transfers magnetisation from a higher  $\gamma$ , more abundant spin I to a lower  $\gamma$ , less abundant spin S.

- Theoretical maximum enhancement of  $\gamma_I/\gamma_S$  is rarely achieved but improvements of 2-3 are common for  $^1H$ - $^{13}C$ .

4-9× time saving

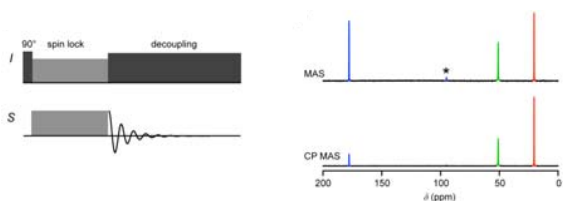
- Increased signal per unit time since higher- $\gamma$  nuclei typically relax faster (1 s for  $^1H$ , 120 s for  $^{13}C$  in  $CO_2H$ ).

10-100× time saving

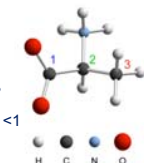
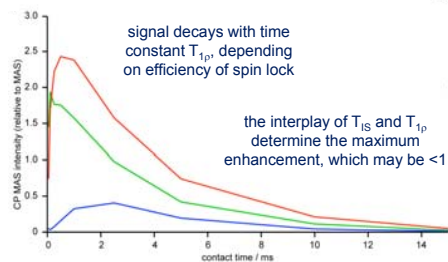
- A total time saving of a factor of ~hundreds is common.

- CP is used routinely for  $^{13}C$ , but the technique is not quantitative and care must be taken when comparing signals from  $C_{quat}$  and  $CH_3$  or  $Si(OSi)_3OH$  and  $Si(OSi)_4$ .

# Cross Polarisation

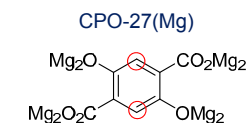
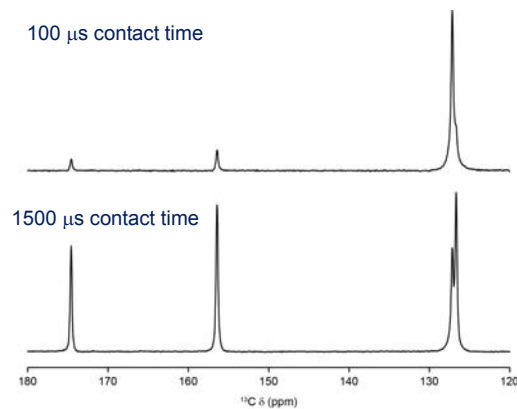


signal builds up with time constant  $T_{IS}$ , depending on I-S dipolar coupling



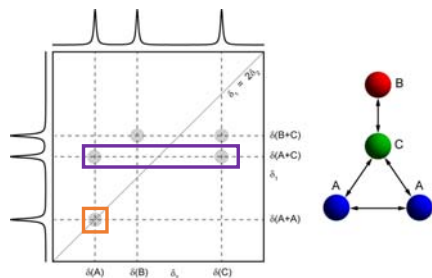
# Cross Polarisation

- The non-quantitative nature of CP can be used in "spectral editing" experiments, where a very short contact time is used to only show protonated species.



## Other Common Solids Experiments

- Double-quantum (DQ) MAS is the solid-state equivalent of COSY.
- Spectra look a bit different, since the experiment correlates DQ coherences with the MAS spectrum.

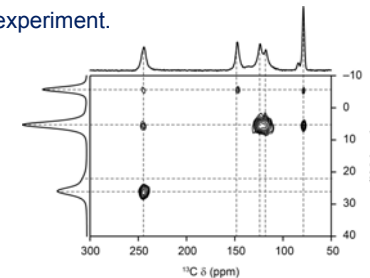
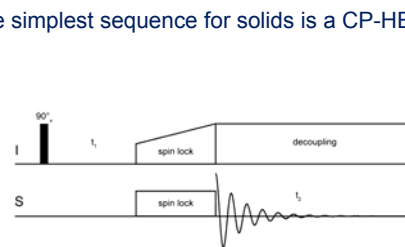


- Pairs of peaks with the same DQ shift correspond to spatially close nuclei.
- Signals on the 2:1 diagonal correspond to pairs of spins with the same shift.
- Isolated spins (e.g., O<sup>1</sup>H) may not be observed.

- Many known DQ excitation schemes: BABA, POST-C7, R and C sequences...

## Other Common Solids Experiments

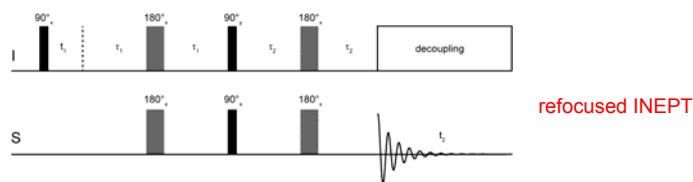
- HETCOR, or "HETernuclear CORrelation" covers a wide range of 2D experiments where chemical shift information from spin I is correlated with chemical shift information of spin S.
- The simplest sequence for solids is a CP-HETCOR experiment.



- A short contact time is normally used to show only spatially close pairs of nuclei (similar information to HSQC).

## Other Common Solids Experiments

- Other sequences such as INEPT and HMQC use the J coupling to transfer magnetisation.
- At least, in theory...



- In reality, there is generally still a contribution from the dipolar coupling and the delay,  $\tau$  corresponds to an effective coupling of  $\sim 100$ - $1000$  Hz.
- Active dipolar recoupling pulses can be applied during  $\tau$  to give a through-space version of the experiments ("D-HMQC" and "D-INEPT").

## 3. Summary



## Summary

- Interactions in NMR are anisotropic.
  - Molecules are always anisotropic, but rapid isotropic tumbling averages this in liquids.
- Sometimes anisotropic broadening is useful.
  - Point symmetry/geometry information.
- Most resonances in solids are broadened by multiple anisotropic interactions at once.
  - Broad, featureless, overlapping resonances are generally uninformative despite containing a lot of information!
- MAS can be used to improve resolution for  $I = 1/2$  nuclei but MQMAS is needed for  $I > 1/2$ .
- Decoupling can remove spin-spin interactions but can't remove CSA or quadrupolar broadening.
- Most liquids experiments have a solids analogue, but this might look or function a bit differently.

## Questions?

## Structure, Disorder and Dynamics - Applications of Solid-State NMR

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## Overview

- Structural information from ordered solids
- The effects of static disorder
- The effects of dynamics

# 1. Summary from this Morning

## Summary

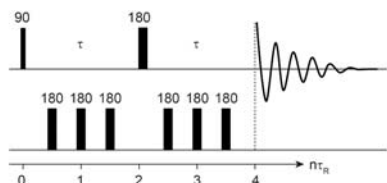
- Interactions in NMR are anisotropic.
  - Molecules are always anisotropic, but rapid isotropic tumbling averages this in liquids.
- A lot of solid-state NMR methodology is about improving resolution.
  - Solution-state spectra look nice and we'd like to mimic that!
- You already have experience of the information available in high-resolution spectra.
  - Chemistry, molecular symmetry, through-bond connectivity, stereochemistry (E/Z alkenes)...
- But anisotropy = information and more information is always good, right?
  - Can we measure anisotropic interactions?
  - Can they tell us anything?
  - Can we selectively observe just one at once?

## Anisotropic Interactions in NMR

Interaction	Size	Liquids	Solids
Zeeman	$10^7 - 10^9$ Hz	yes	yes
RF pulses	$10^3 - 10^5$ Hz	yes	yes
chemical shift	$10^4 - 10^5$ Hz	isotropic	anisotropic
J coupling	$1 - 10^3$ Hz	isotropic	anisotropic
dipolar coupling	$10^3 - 10^5$ Hz	no	anisotropic
quadrupolar coupling	$10^3 - 10^7$ Hz	no	anisotropic

## 2. Structural Information from Ordered Solids

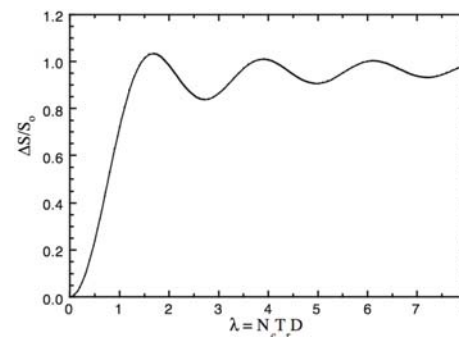
## Measuring Distances



- The Rotational Echo DOuble Resonance (REDOR) experiment is used to measure dipolar couplings.
- Requires isolated spin pairs (often through labelling).
- Two spectra are recorded, a spin echo and a spin echo with 180° pulses applied on the I spin every half rotor period to refocus the dipolar coupling, labelled S<sub>0</sub> and S, respectively.

## Measuring Distances

- A plot of  $\Delta S/S_0 = (S_0 - S_r)/S_0$  can be fitted to the “universal function”,  $\lambda$ , with the only unknown being the internuclear distance.



$$\lambda = N_c T_r D$$

$N_c$  = number of rotor periods

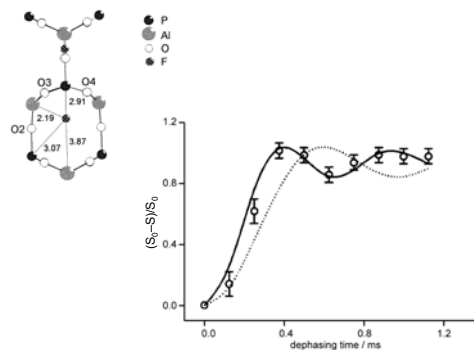
$T_r$  = rotor period

$D$  = dipolar coupling

$$\omega_D^{\text{PAS}} = -\frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi r_{IS}^3}$$

## Example: Crystal Structure of AIPO-5

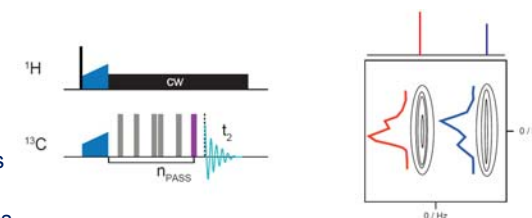
- Crystallographic refinement suggested an Al-F bond of 2.19 Å in AIPO-5 (prepared in fluoride medium).
- <sup>27</sup>Al-<sup>19</sup>F REDOR measurements provide a plot of  $(S_0 - S)/S_0$  that is more consistent with a bond length of 1.92 Å.
- REDOR can be used to refine structures, as in this case or, in cases where a crystal structure doesn't exist, structural constraints may be obtained from NMR.



*J. Phys. Chem B* 105, 2001, 12249.

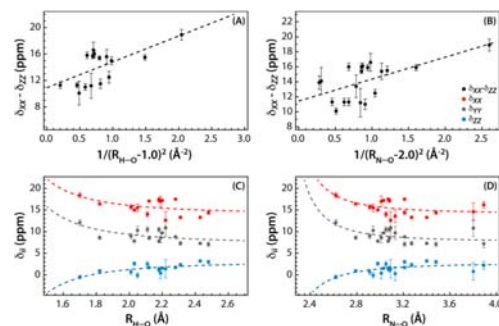
## Measuring CSAs

- The CSA can be reintroduced in the second dimension of a CSA-amplified Phase Adjusted Spinning Sidebands (PASS) experiment.
- Other methods are available!
- CSA doesn't always correlate directly with a single structural feature, but has been linked to hydrogen bond length in organics, Mg substitution in MgAPOs, axial Y-O bond length in Y<sub>2</sub>(Sn,Ti)<sub>2</sub>O<sub>7</sub>...
- CSA measurements often have a larger error than  $\delta_{\text{iso}}$ , so work better for large CSAs.



## Example: <sup>1</sup>H CSA in Hydrogen Bonds

- Proteins and other large biomolecules are one of the most challenging fields of structural determination.
- Measurement of <sup>1</sup>H CSAs in the CAP-Gly domain of mammalian dynactin shows that principal components of the shift tensor can be used to provide geometry constraints for hydrogen bonds.



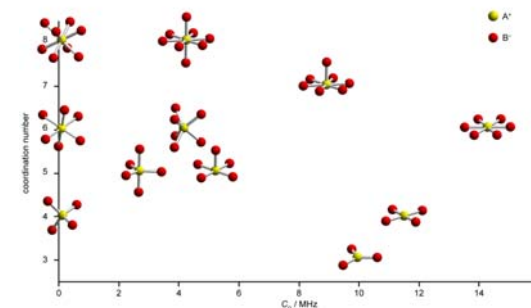
*J. Am. Chem. Soc.* 135, 2013, 1358.

## Measuring the Quadrupolar Interaction

- $C_Q$  and  $\eta_Q$  can be obtained from MAS or MQMAS experiments (sometimes at multiple fields).

$$\nu_Q = \frac{(v_Q^{PAS})^2}{v_0} [A + B d_{00}^2(\theta) + C d_{00}^4(\theta)]$$

- Provides information on bonding geometry...

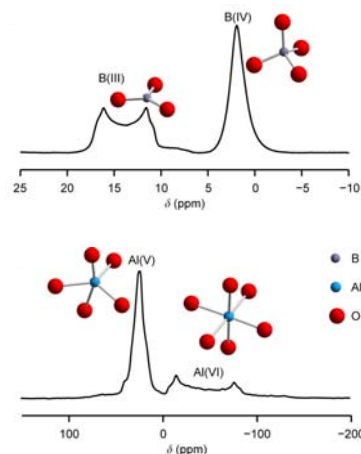


## Measuring the Quadrupolar Interaction

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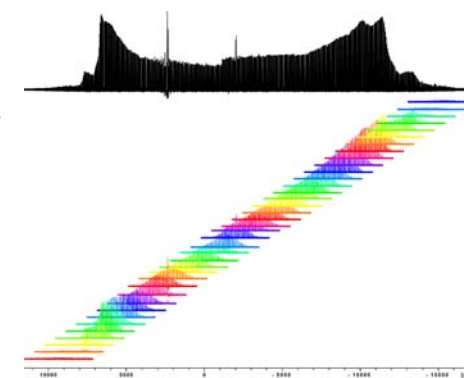
$$\nu_Q = \frac{(v_Q^{PAS})^2}{v_0} [A + B d_{00}^2(\theta) + C d_{00}^4(\theta)]$$

- ... and deviation from idealised geometry



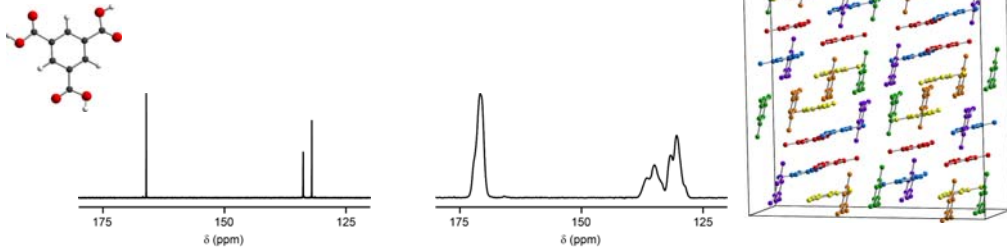
## Wideline NMR

- Sometimes  $C_Q$  is so large that MAS is not a practical option.
- Wideline methods such as broadband pulses (WURST, HS, etc.), sensitivity enhancement such as CPMG, and Variable-Offset-Cumulative Spectroscopy (VOCS) can be combined to record the whole spectrum.
- For example, <sup>63</sup>Cu in a Cu(I)CN/ methylthiourea metal-organic framework has  $C_Q \approx 82$  MHz
  - The CT signal is ~8 MHz wide at 20.0 T!



## More on the Chemical Shift

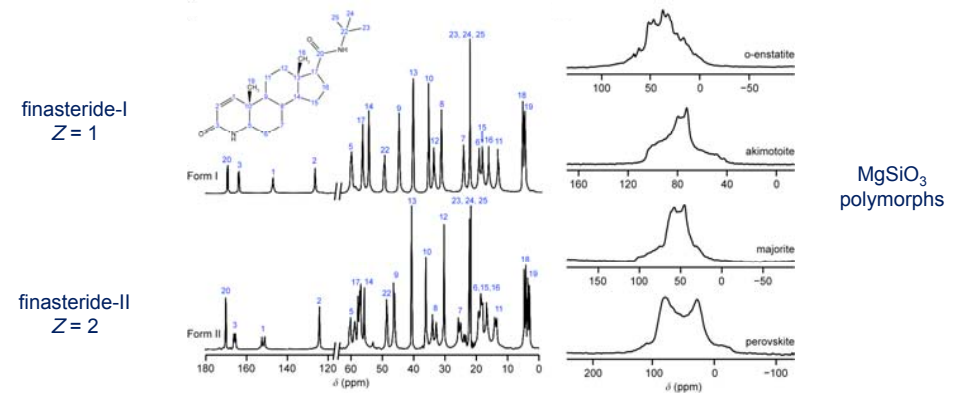
- In a dilute solution of molecules in a solvent, the molecules are indistinguishable by NMR.
- Solids are, of course, slightly more complicated...



- If two molecules are chemically equivalent but symmetrically inequivalent, they cannot be magnetically equivalent.

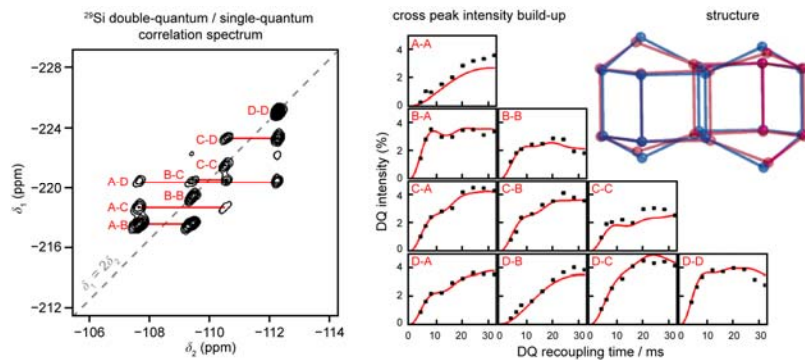
## More on the Chemical Shift

- Sensitivity to crystallographic inequivalence makes NMR a powerful probe of polymorphism.



## Example: Siliceous Zeolites

- In certain VERY favourable cases, it is even possible to solve a complete structure from NMR data.



*J. Am. Chem. Soc.* 127, 2005, 10365.

## 3. Static Disorder

## Types of Disorder

- Solid-state structure is characterised by long-range order or periodicity (fixed lattice points + motifs in an infinitely repeated unit cell).
- Many useful properties come from disorder, *i.e.*, some sort of variation in the ordered structure.
- Disorder can be classed loosely as:
  - Compositional: doping of different atoms or molecules onto lattice points (also includes vacancies).
  - Positional: spatial deviation of atoms or molecules from their lattice points.
  - Temporal: atomic/molecular positions vary with time.
- In addition, many useful materials are multi-component mixtures (bulk disorder).



ordered material



doped material  
compositional disorder



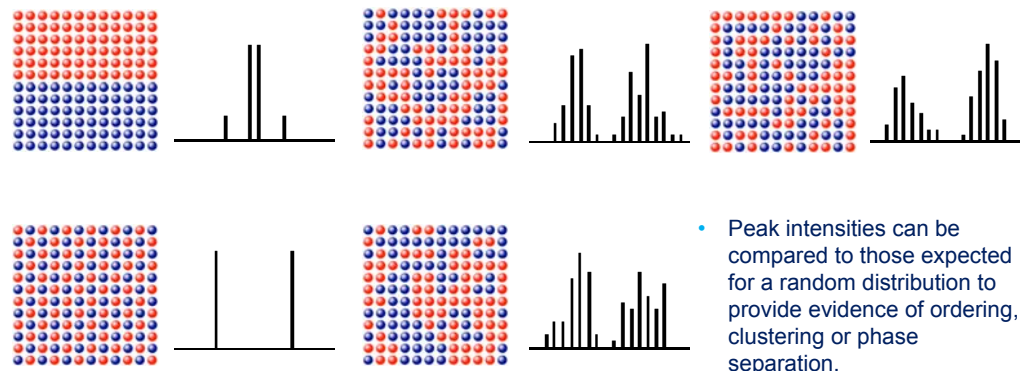
glassy material  
positional disorder



dynamics  
temporal disorder

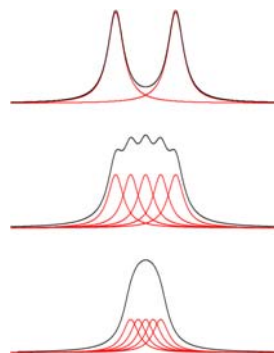
## Average and Local Structure

- NMR is more sensitive to the local than the long-range structure, which makes it an ideal probe of disorder.



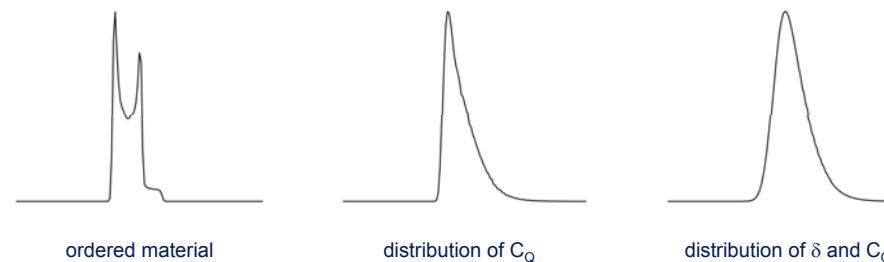
## The effects of disorder ( $I = 1/2$ )

- Variation in the local environment changes the chemical shift.
- Significant changes (*e.g.*, coordination number) lead to separate resonances.
- Smaller changes (*e.g.*, next-nearest neighbour occupancy) lead to smaller shift differences, often observed as splittings and shoulders.
- Smaller or longer-range changes may lead to a broadening rather than resolvable signals.
- Less discrete changes (*e.g.*, the continuous variation of bond angles in a glass) lead to a continuum of chemical shifts (*i.e.*, a broadening).
- Disorder-induced broadening cannot be removed by MAS since it results from a distribution of isotropic shifts!



## The Effects of Disorder ( $I > 1/2$ )

- Quadrupolar nuclei are affected by variation in the chemical shift and EFG tensors.
  - These often vary together, but not always!

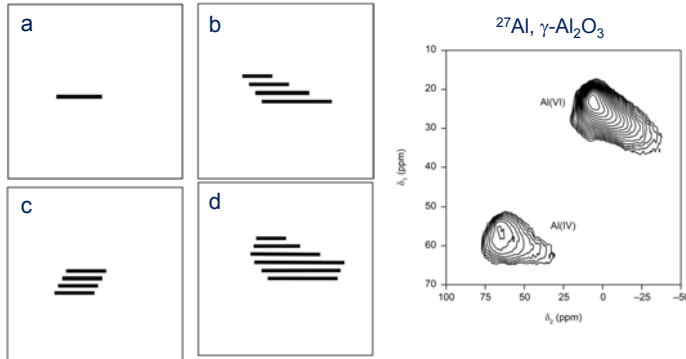


## The Effects of Disorder ( $I > 1/2$ )

- This variation also affects the appearance of MQMAS spectra

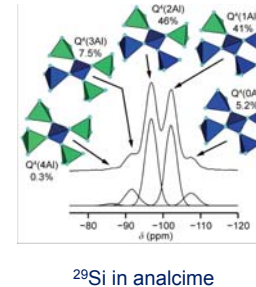
- a) ordered
- b) distribution of  $C_Q$
- c) distribution of  $\delta$
- d) distribution of  $\delta$  and  $C_Q$

- This can lead to complicated lineshapes in real materials!



## Example: Aluminosilicate Zeolites

- Crystallographic diffraction often can't tell the difference between, e.g., Al/Si, OH/F, OH/H<sub>2</sub>O, CH<sub>3</sub>/NH<sub>3</sub> when these have no long-range order.

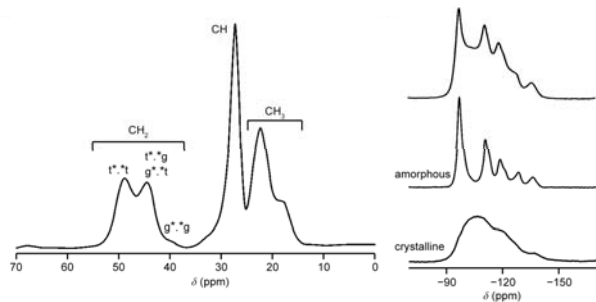


- Different signals for tetrahedrally-connected ( $Q^4$ ) Si depending on the number of Al neighbours ( $m$ ).
- <sup>29</sup>Si NMR is one of the most common ways to determine the Si/Al ratio of zeolites.

$$\frac{\text{Si}}{\text{Al}} = \frac{\sum_m I(Q^4(m))}{0.25 \sum_m m I(Q^4(m))}$$

## Example: Polymers

- Polymers are inherently difficult to study, but NMR can be used to characterise end groups, backbone conformation and amorphous and crystalline domains.



<sup>13</sup>C in atactic polypropylene

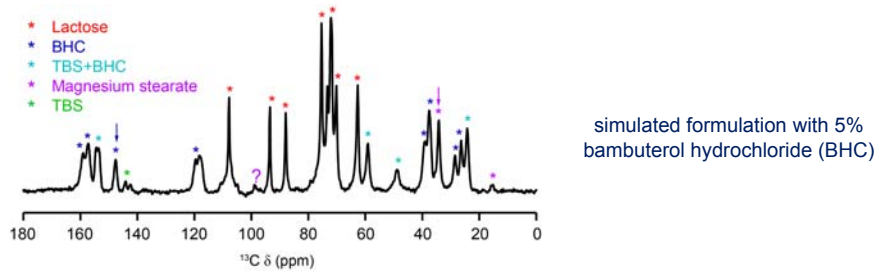
<sup>19</sup>F in vinylidene fluoride/  
trifluoroethylene copolymer

- Different domains have different spatial and temporal order so their signals can be separated by relaxation filters.
- Remember that liquids are amorphous and polymer chemists have low standards for "crystalline"!

## "Bulk Disorder"

- An extreme form of disorder occurs when one particle is completely different from the next.
  - a synthesis may produce multiple products
  - a molecule may crystallise in multiple polymorphs in the same batch
- Many useful and interesting materials are complex mixtures of complicated compounds.
  - bone, teeth, muscle tissue, wood, soil, car tyres, concrete, oil paintings, food, medicines...
- NMR is an excellent quantitative, non-destructive technique for characterising the whole sample at once, regardless of crystallinity.
- By combining the element-specificity of NMR with pulse sequences designed to filter signals for couplings, CSAs, relaxation, etc., it is possible to observe individual chemical components of even very complicated materials.
- The sensitivity of NMR is poor, so the limit of detection is quite high, especially for more complicated/insensitive pulse sequences and "difficult" nuclei.

# Example: Drug Forms in Tablets

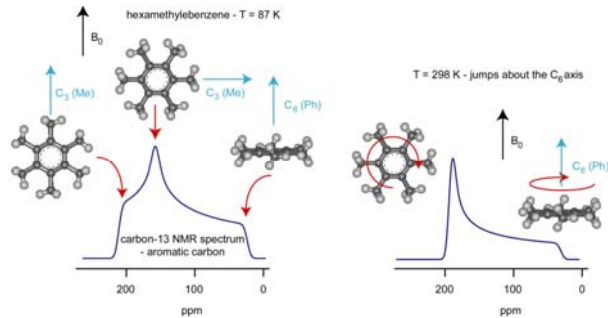


- By using pulse sequences designed to filter signals for couplings, CSAs, relaxation, etc., it may be possible to observe individual chemical components of even very complicated materials

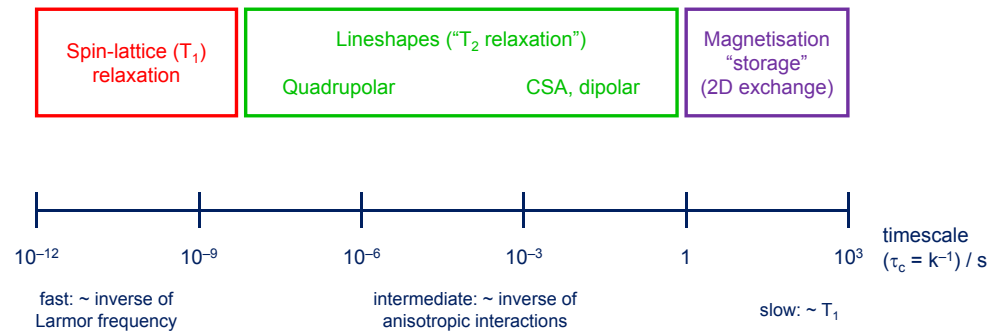
## 3. Dynamic Disorder

### Motion and NMR

- You may remember from this morning that motion is important for the appearance of NMR spectra!
- However, between “static” and “isotropic”, there are many other options...

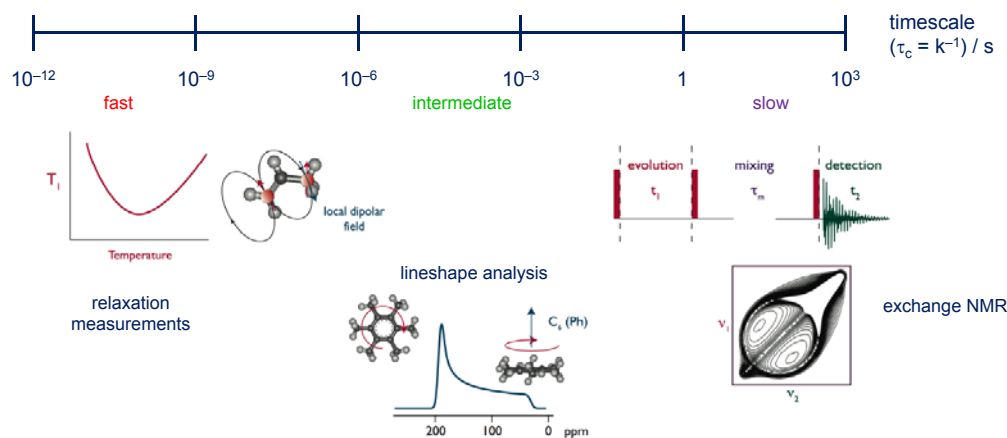


### The Effects of Motion



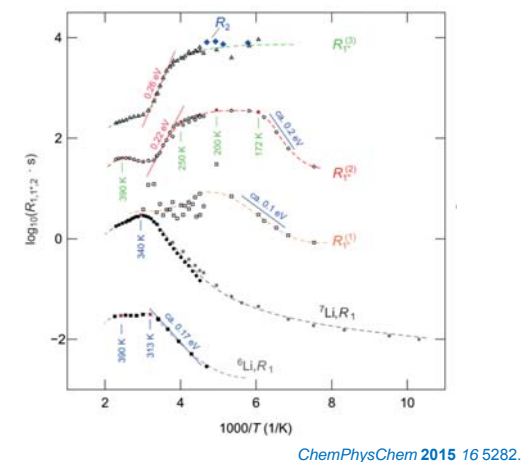


## Investigating Motion



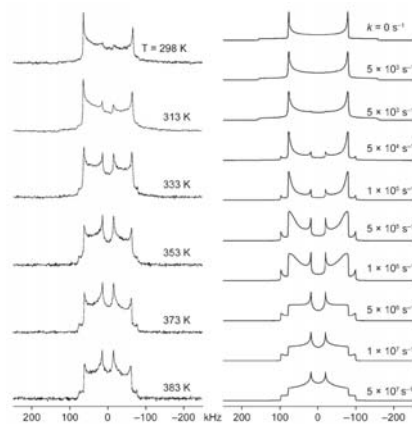
## Example: Fast Li Ion Motion

- Relaxation measurements for  $^6/7\text{Li}$  in Li ion conductors can be used to determine the activation energy for motional processes.
- These measurements can be used to determine whether the motion is local or bulk and, if bulk, the dimensionality of the pathway (linear, planar or 3D transport).
- Example shows complex local and long-range Li motion in  $\text{Li}_7\text{P}_3\text{S}_{11}$  glass ceramic.



## Example: $^2\text{H}$ Lineshapes

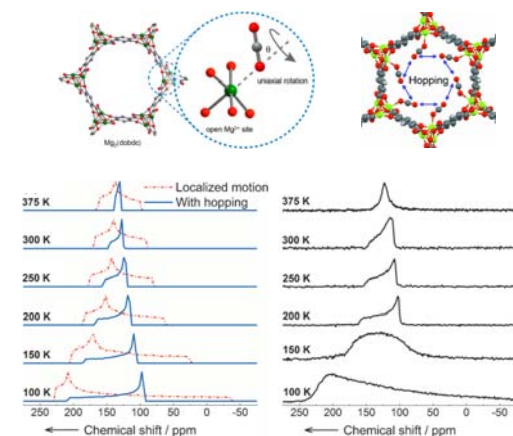
- Variation in the modulation of the  $^2\text{H}$  lineshape as a function of temperature is a common method of probing dynamics in the "intermediate" regime.
- Combination of experiment and simulation can extract rate constants and type of motion.
- For example, variable-temperature  $^2\text{H}$  NMR of perdeuterated  $\text{Sc}_2(\text{BDC})_3$  shows that the aromatic rings in the benzene-1,4-dicarboxylate undergo rapid  $180^\circ$  flipping at elevated temperatures.



*Inorg. Chem.* 2011 50 10844.

## Example: Guest Dynamics in MOF-74

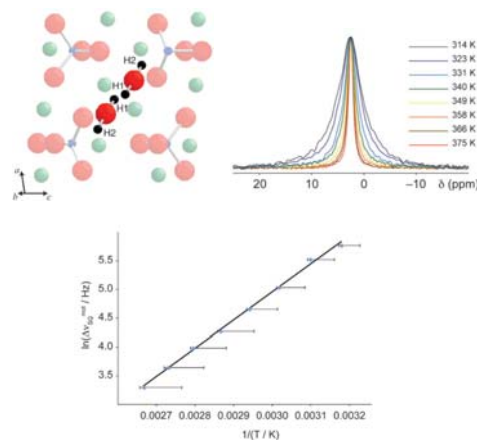
- Other anisotropic interactions can be used similarly.
- Two possible behaviours for  $\text{CO}_2$  in Mg-MOF-74:
  - Uniaxial rotation around Mg-O bond.
  - Hopping from one Mg site to another.
- $^{13}\text{C}$  CSA measurements, combined with modelling, show that only uniaxial rotation occurs at low temperatures, but hopping occurs simultaneously at elevated temperatures.



*Angew. Chem. Int. Ed.* 2013 52 4410.

## Example: $^2\text{H}$ in Humites

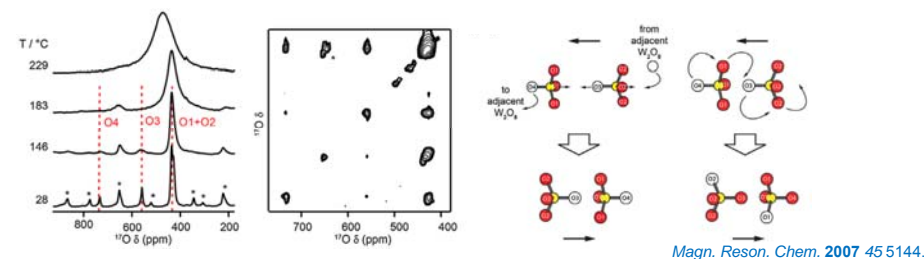
- In some cases, motion doesn't affect the anisotropic interaction very much.
- $\sim 180^\circ$  reorientation of O-D groups doesn't affect the  $^2\text{H}$  lineshape in clinohumite  $[\text{4Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{OH})_2]$ .
- Motion is still present and, by introducing MAS, the rotor frame axes are now reorienting on a timescale comparable to the motion.
- Arrhenius-type plot of  $\ln(\text{linebroadening})$  against  $1/T$  allows an activation energy of  $40 \pm 4 \text{ kJ mol}^{-1}$  to be determined.



*Phys. Chem. Chem. Phys.* **2010** 12 2989.

## Example: Slow Dynamics

- The EXSY experiment can be used to confirm the exchange of sites on a longer timescale.
- $^{17}\text{O}$  EXSY of  $\text{ZrW}_2^{17}\text{O}_8$  shows all four sites exchange at  $57^\circ\text{C}$ , confirming the presence of a "ratchet" mode of motion rather than a  $\text{S}_{\text{N}}2$ -like motion, which interconverts only two O types.
- At higher temperatures, all four O signals coalesce in the MAS spectrum, confirming rapid exchange.



*Magn. Reson. Chem.* **2007** 45 5144.

## Summary

- While anisotropic interactions in solids can confuse and complicate one-dimensional NMR spectra, this information can still be helpful if used correctly.
- Selective introduction of specific interactions by advanced pulse sequences allows us to extract valuable structural information.
- Solids are rarely ideal crystals!
- Solid-state NMR spectroscopy can almost always provide information to complement crystallographic measurements, since most of the interesting things in life aren't static or repetitive!

## Bibliography

- Many examples have been taken from the following reviews and references within
- S.E. Ashbrook, D.M. Dawson and J.M. Griffin, in *Local Structural Characterisation*, eds D.W. Bruce, D. O'Hare and R.I. Walton (Wiley, Chichester, 2014).
- S.E. Ashbrook and D.M. Dawson *Acc. Chem. Res.* **2013** 46 1964-1974.
- R.F. Moran, D.M. Dawson and S.E. Ashbrook *Int. Rev. Phys. Chem.* **2017** 36 39-115.