Chemistry Solid State NMR
PAUL BENDER CHEMICAL INSTRUMENTATION CENTER

An Introduction to Solid State NMR from a Materials/Chemistry Perspective

Materials Seminar

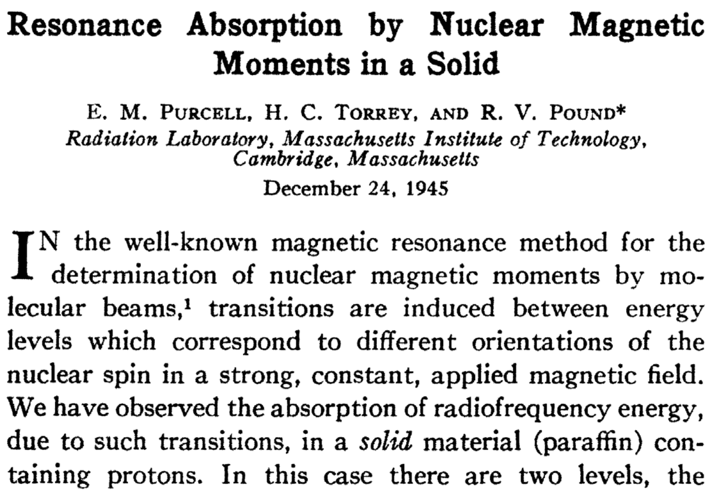
03/11/2021

Dr. Cathy Clewett

Outline

- History/Uses
- A little theory
- Challenges – Solutions
- Practical Implementations
- Chemistry Facility
  - Probes
  - Policies

History: 1946

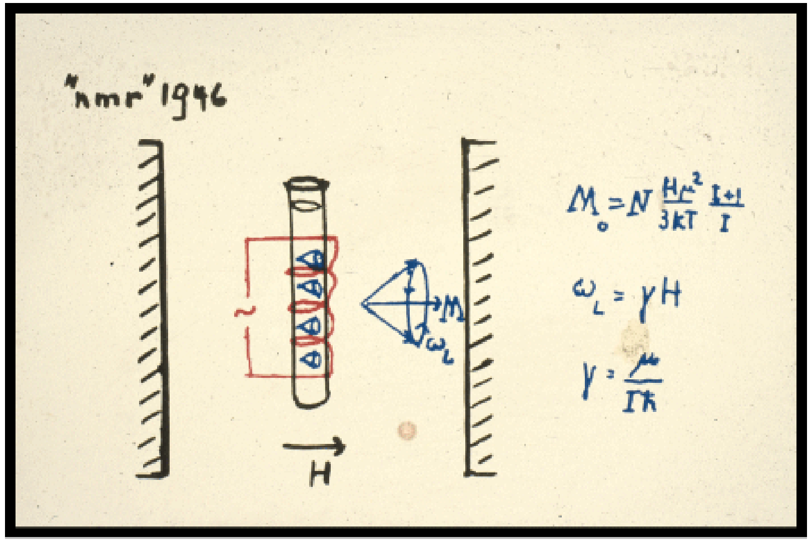


Resonance Absorption by Nuclear Magnetic Moments in a Solid

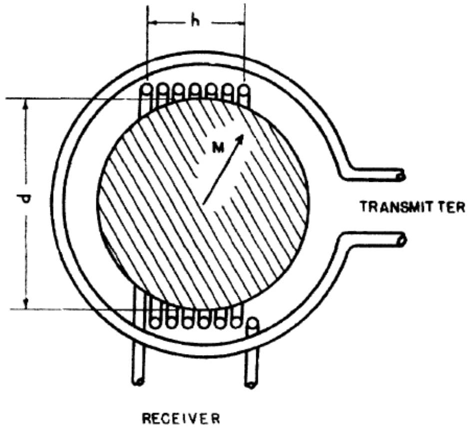
E. M. Purcell, H. C. Torrey, and R. V. Pound*
Radiation Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts

December 24, 1945

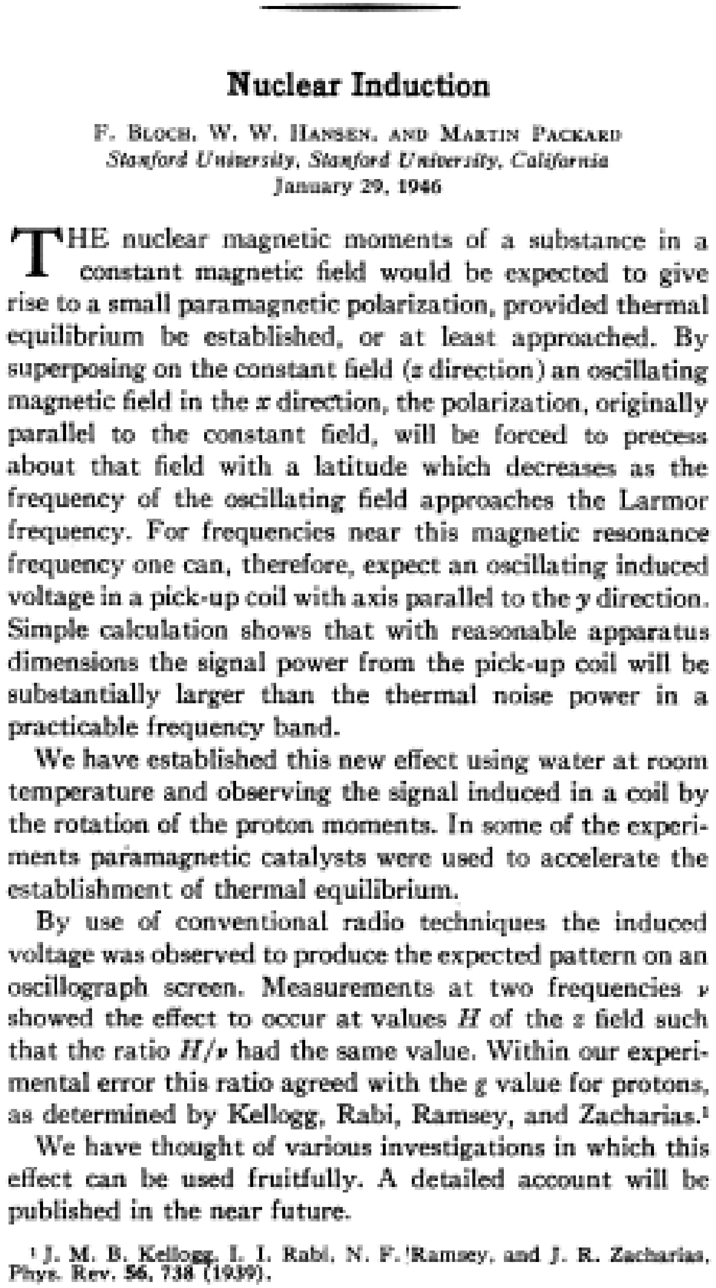
In the well-known magnetic resonance method for the determination of nuclear magnetic moments by molecular beams,[1] transitions are induced between energy levels which correspond to different orientations of the nuclear spin in a strong, constant, applied magnetic field. We have observed the absorption of radiofrequency energy, due to such transitions, in a *solid* material (paraffin) containing protons. In this case there are two levels, the



Page from Bloch's notebook showing the theory behind his famous experiment. Note coffee stains.



Bloch's apparatus. The water sample (hatched circle) is surrounded by transmitter and receiver loops. The main magnetic field (perpendicular to the plane) is not shown.



Nuclear Induction

F. Bloch, W. W. Hansen, and Martin Packard
Stanford University, Stanford University, California

January 29, 1946

The nuclear magnetic moments of a substance in a constant magnetic field would be expected to give rise to a small paramagnetic polarization, provided thermal equilibrium be established, or at least approached. By superposing on the constant field (z direction) an oscillating magnetic field in the x direction, the polarization, originally parallel to the constant field, will be forced to precess about that field with a latitude which decreases as the frequency of the oscillating field approaches the Larmor frequency. For frequencies near this magnetic resonance frequency one can, therefore, expect an oscillating induced voltage in a pick-up coil with axis parallel to the y direction. Simple calculation shows that with reasonable apparatus dimensions the signal power from the pick-up coil will be substantially larger than the thermal noise power in a practicable frequency band.

We have established this new effect using water at room temperature and observing the signal induced in a coil by the rotation of the proton moments. In some of the experiments paramagnetic catalysts were used to accelerate the establishment of thermal equilibrium.

By use of conventional radio techniques the induced voltage was observed to produce the expected pattern on an oscillograph screen. Measurements at two frequencies ν showed the effect to occur at values H of the z field such that the ratio H/ν had the same value. Within our experimental error this ratio agreed with the g value for protons, as determined by Kellogg, Rabi, Ramsey, and Zacharias.[1]

We have thought of various investigations in which this effect can be used fruitfully. A detailed account will be published in the near future.

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[1] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, and J. R. Zacharias, Phys. Rev. 56, 738 (1939).

http://mriquestions.com/who-discovered-nmr.html, PhysRev 69:37, PhysRev 69:127

Differences between solution and solid state spectra

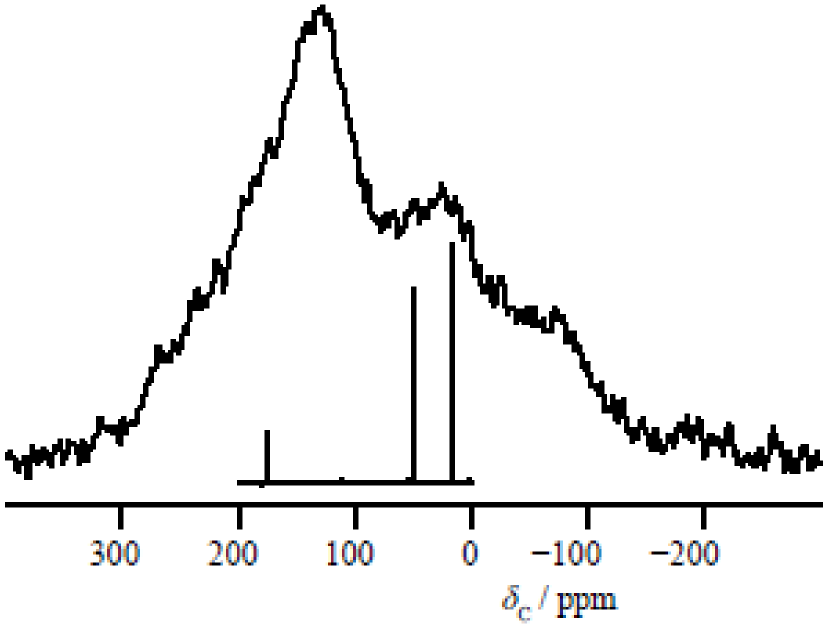


Figure 1.1. Carbon-13 spectra of alanine in the solid state (upper trace) and in solution (lower trace). The latter was obtained using proton decoupling, as is usual for solutions. The former involved no special techniques.

(Apperley, 2012)

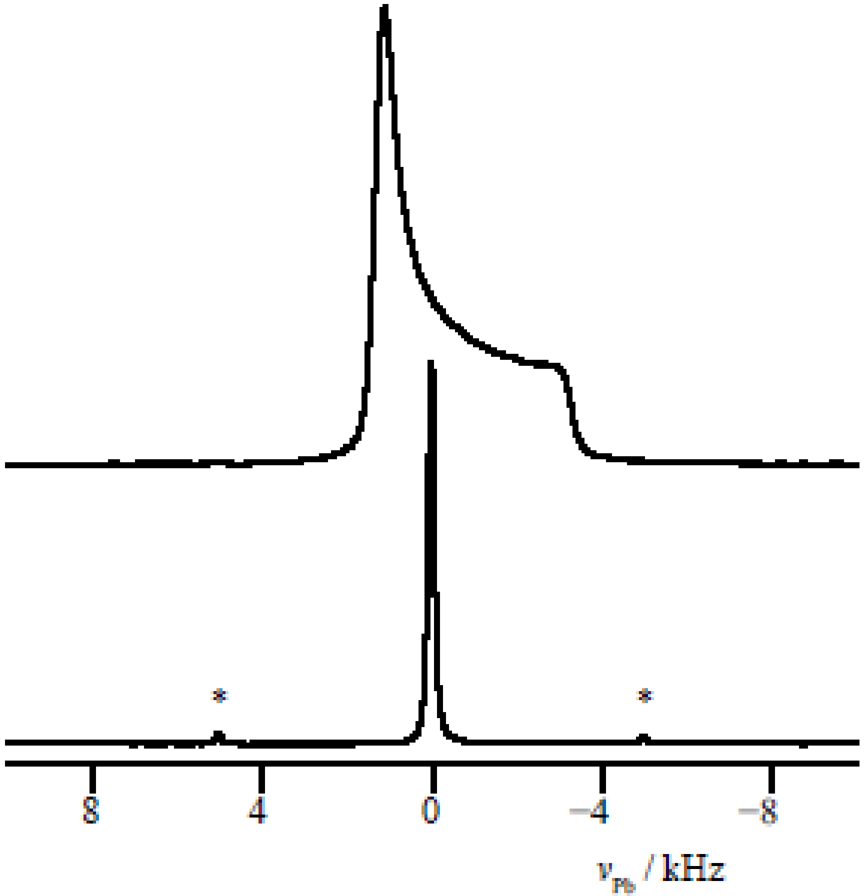


Figure 1.2. Lead-207 NMR spectra of microcrystalline lead nitrate under static (upper trace) and magic-angle spinning (lower trace) conditions. The former is an example of a powder pattern. The latter is discussed in section 1.5. Magic-angle spinning (including spinning sidebands, indicated in this figure by asterisks) is discussed in section 2.7.

When would you use solid state NMR?

- The experimental sample is contained in media with little or no mobility (such as, a crystalline or powder state, membrane-bound system or aligned solution).
- Capable of looking at a variety of materials. It does not require crystalline materials like diffraction techniques, and can still determine local molecular environments.
- A huge variety of solid state NMR experiments are available for measurement of
  - internuclear distances (dipolar recoupling)
  - deconvolution of quadrupolar/dipolar influenced spectra
  - probing site symmetry and chemistry
  - observing solid state dynamics, etc.

Solid state NMR has been applied to:

- organic complexes
- inorganic complexes
- zeolites
- polymers
- surfaces
- mesoporous solids
- microporous solids
- aluminosilicates/phosphates
- glasses
- food products
- wood/cellulose/lignin
- ceramics
- bones
- semiconductors
- metals and alloys
- archaeological specimens
- resins
- minerals
- biological molecules
- cements

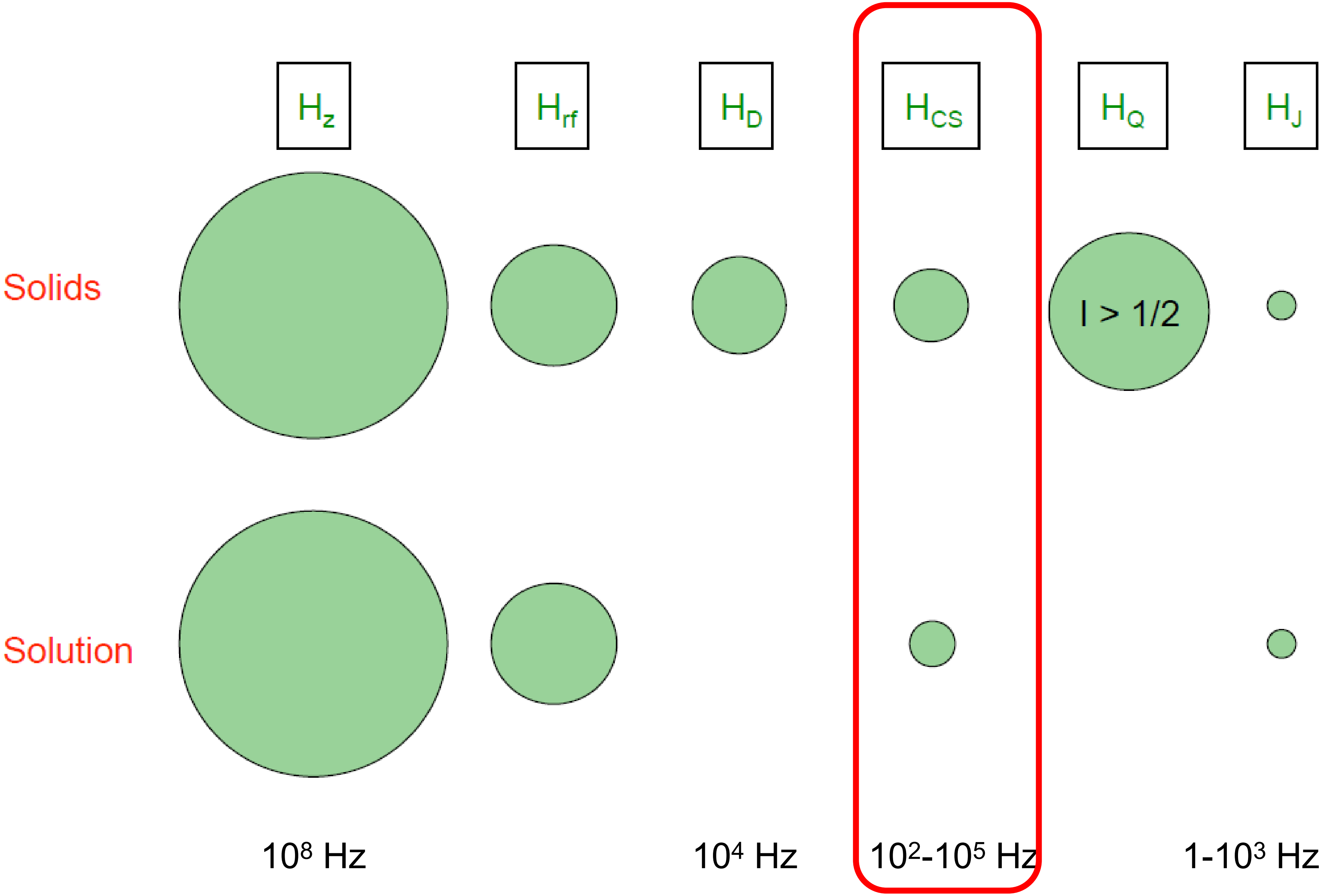
Total Energy of interaction

$$E_{NMR} = E_z + E_{RF} + \underbrace{E_S + E_J + E_D + E_Q}_{\text{Internal interactions, depend on orientation, anisotropic *}} + E_P$$

- $E_Z = \left(\frac{\gamma_j}{2\pi}\right) h m_j B_0$ Zeeman
- E_{RF} magnetic fields from RF irradiation causes transitions
- E_P paramagnetic interactions
- * in solution, each of these are motionally averaged to the isotropic component.

(Apperley, 2012)

Interactions in NMR



H_z H_{rf} H_D H_{CS} H_Q H_J

Solids

I > 1/2

Solution

10^8 Hz

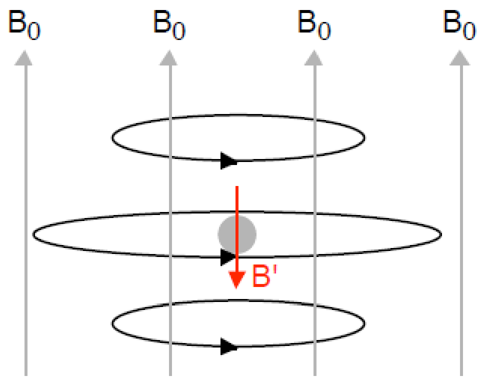
10^4 Hz

10^2-10^5 Hz

1-10^3 Hz

(Ashbrook, 2009)

Chemical shift



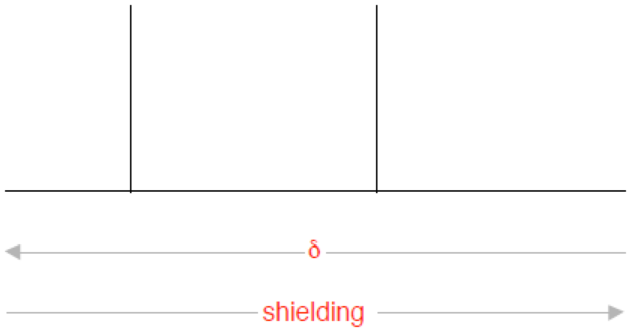
- The magnetic field a nucleus sees, B, is usually not equal to B_0
- In an atom, the surrounding electrons generate a small magnetic field which opposes B_0
- The nucleus is “shielded” from B_0, with

$$B = B_0 - B' = B_0 (1 - \sigma)$$

$$|\omega| = \gamma B_0 (1 - \sigma)$$

- In molecules the motion of the electrons is more complicated and depends on the bonded atoms and local neighbouring groups of atoms
- Can augment or oppose the field
- This “chemical shift” defines the local environment
- Defined (ppm) relative to a reference

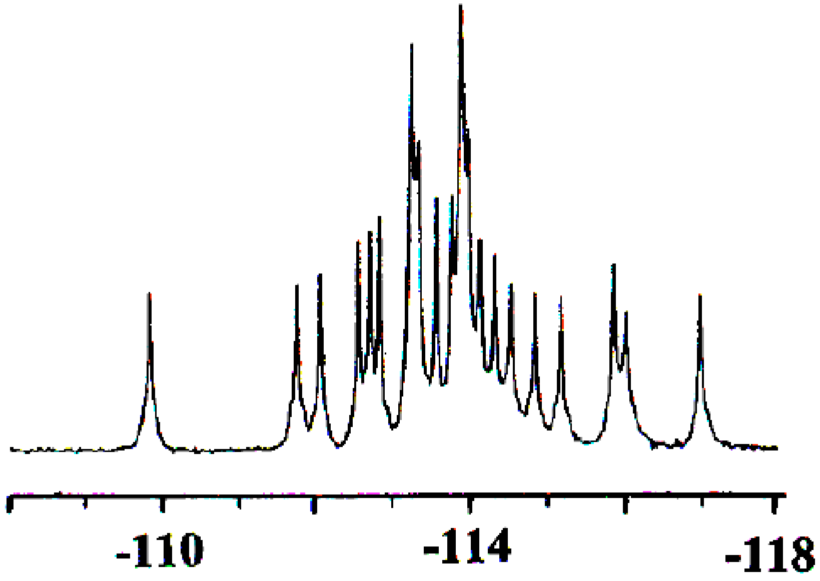
$$\delta = 10^6 (\nu - \nu_{ref}) / \nu_{ref}$$

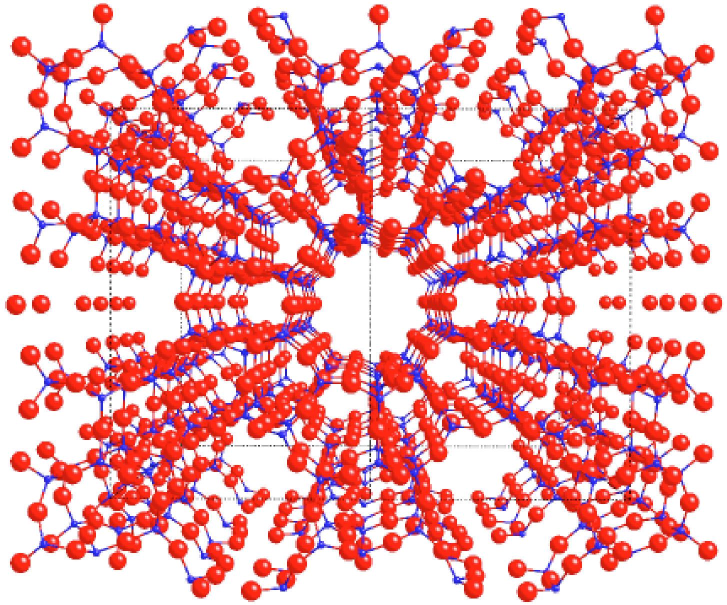


(Ashbrook, 2009)

Chemical shift

^{29}Si NMR spectrum of zeolite ZSM-5
(28 different Si species)

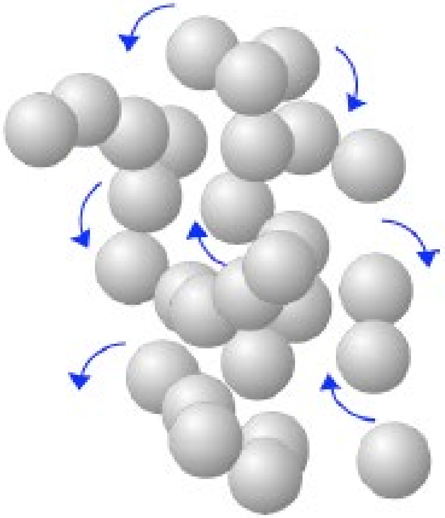


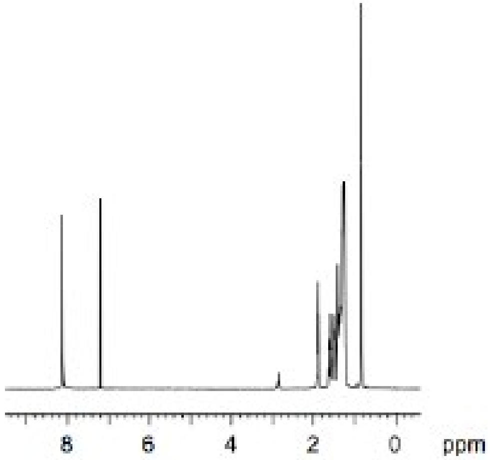


(Ashbrook, 2009)

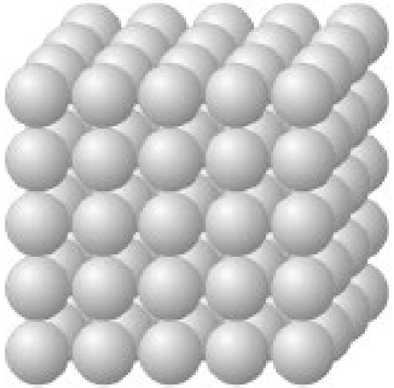
Averaging of interactions

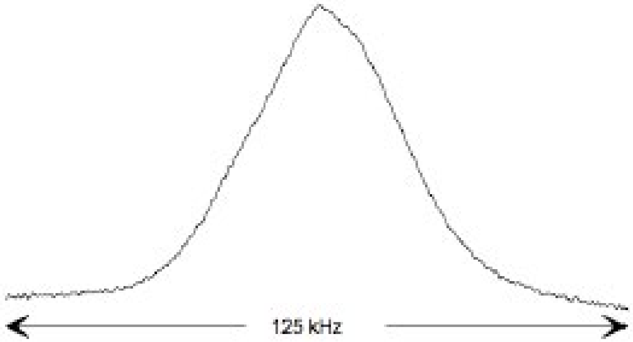
Liquids





Solids





(Ashbrook, 2009)

Chemical shift anisotropy

- The shielding of the nucleus is anisotropic (orientationally dependent)
- Although averaged in liquids to an isotropic value, in solids, the chemical shift anisotropy (CSA) becomes important

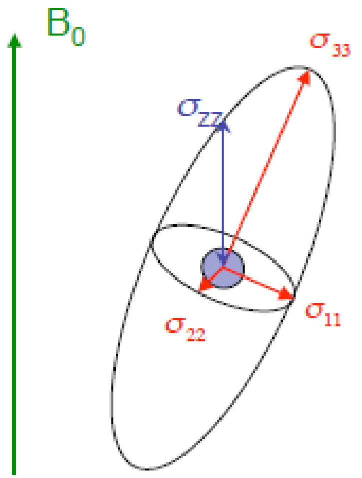
$H_{CS} = \mathbf{I} \cdot \sigma \cdot \gamma \mathbf{B_0}$ secular approximation $H_{CS} = \gamma B_0 \sigma_{zz} I_z$

Principal axis system (PAS)

$$\sigma = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

$\sigma_{iso} = (1/3)(\sigma_{11} + \sigma_{22} + \sigma_{33})$
$\Delta\sigma_{CS} = (\sigma_{33} - \sigma_{iso})$
$\eta_{CS} = (\sigma_{11} - \sigma_{22}) / (\sigma_{33} - \sigma_{iso})$ $0 < \eta_{CS} < 1$

Alternative convention
$\Delta\sigma_{CS}' = \sigma_{33} - (\sigma_{22} + \sigma_{11})/2 = 3\,\Delta\sigma_{CS} / 2$



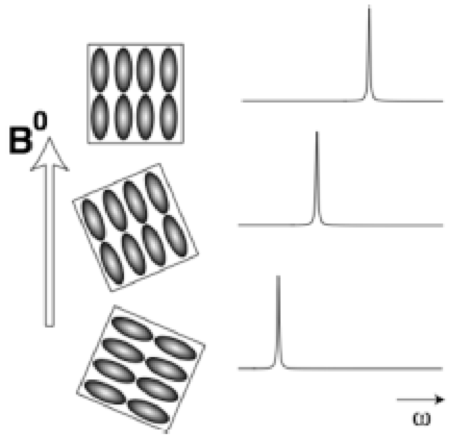
(Ashbrook, 2009)

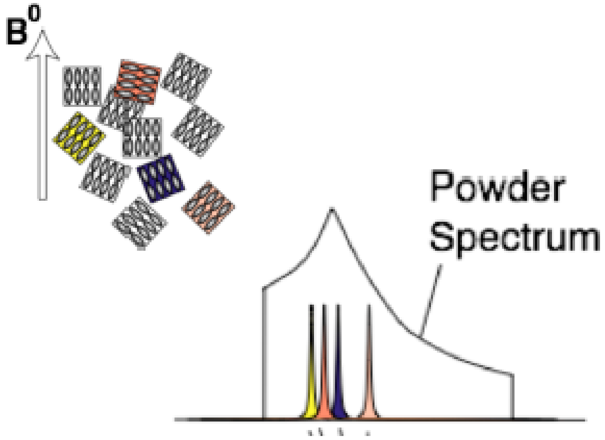
Chemical shift anisotropy

- We rotate to convert between the PAS and lab frame, which reveals the angular dependence of the shielding

$$\sigma_{zz} = \sigma_{iso} + (\Delta\sigma_{CS}/2)\,[(3\cos^2\theta_i - 1) + \eta_{CS}(\sin^2\theta\cos 2\phi)]$$

- In a single crystal all molecules have the same orientation with respect to B_0
- Different single crystals will have a different orientation with respect to B_0 and so a different chemical shift

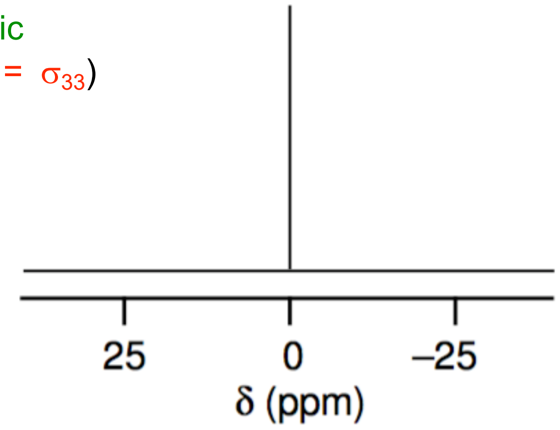




- Powder samples are composed of millions of single crystals all with different orientations
- This results in a broad powder-pattern lineshape with characteristic features
- Typical magnitude 10^2-10^5 Hz

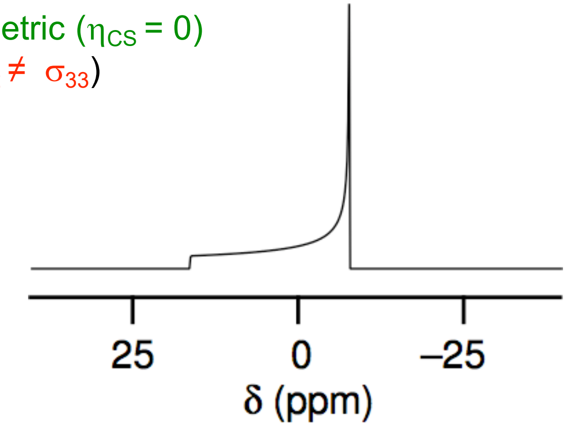
(Ashbrook, 2009)

Chemical shift anisotropy



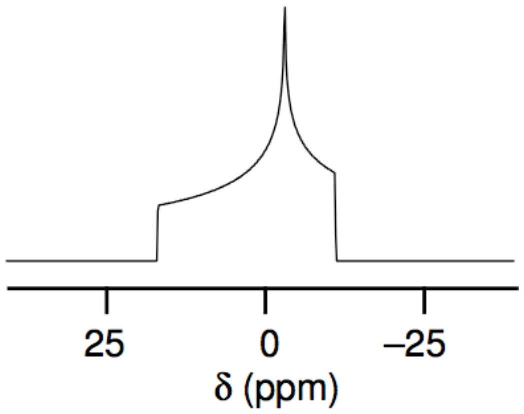
Cubic

$(\sigma_{11} = \sigma_{22} = \sigma_{33})$



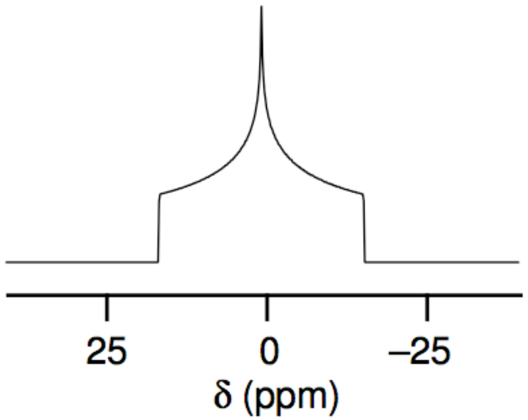
Axially symmetric ($\eta_{CS} = 0$)

$(\sigma_{11} = \sigma_{22} \neq \sigma_{33})$



Axially asymmetric ($\eta_{CS} = 0.5$)

$(\sigma_{11} \neq \sigma_{22} \neq \sigma_{33})$

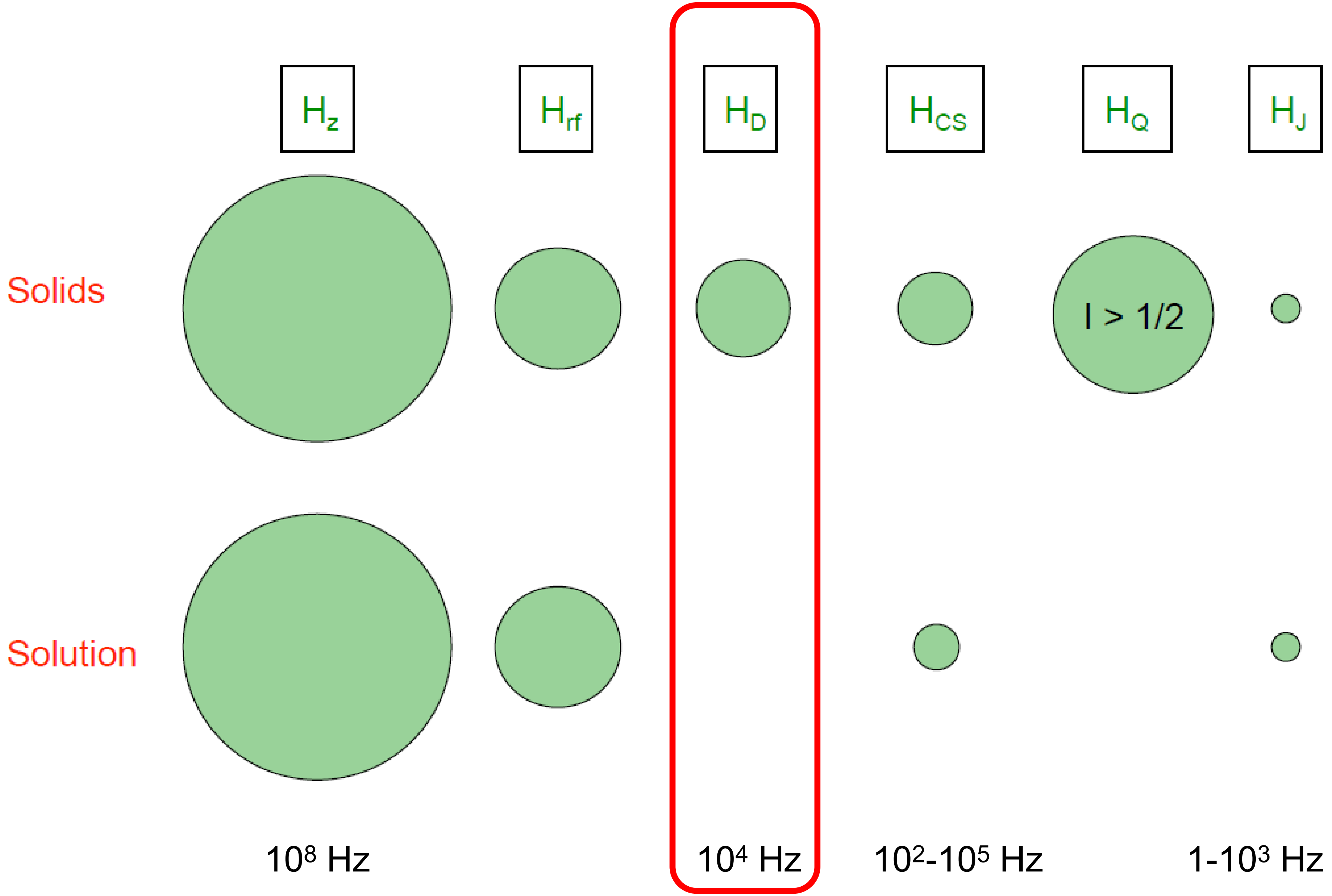


Axially asymmetric ($\eta_{CS} = 1$)

$(\sigma_{11} \neq \sigma_{22} \neq \sigma_{33})$

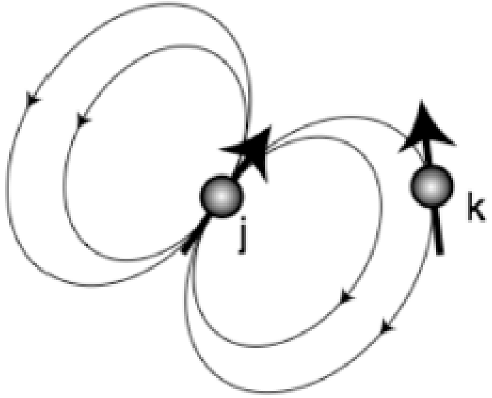
(Ashbrook, 2009)

Interactions in NMR

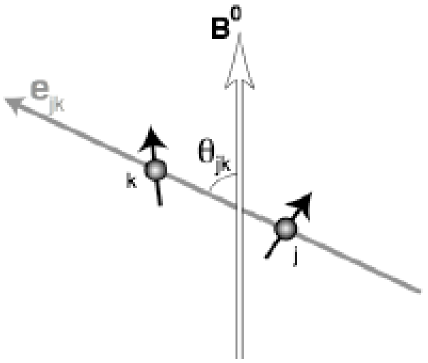


(Ashbrook, 2009)

Dipolar interactions



- The nuclear magnetic dipole moments possess small localized fields which interact with the dipole moments of nearby nuclei
- This dipolar interaction is a through-space interaction
- It is averaged to zero in rapidly tumbling liquids



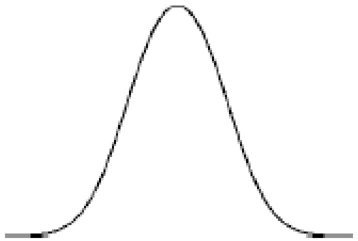
- The dipolar interaction between two spins k and j is given by

$$\omega_D = \omega_D^{PAS}(3\cos^2\theta_{jk} - 1)/2$$

where ω_D^{PAS} is the dipolar coupling constant

$$\omega_D^{PAS} = -(\mu_0/4\pi)(\gamma_k\,\gamma_j\,\hbar/r_{jk}^3)$$

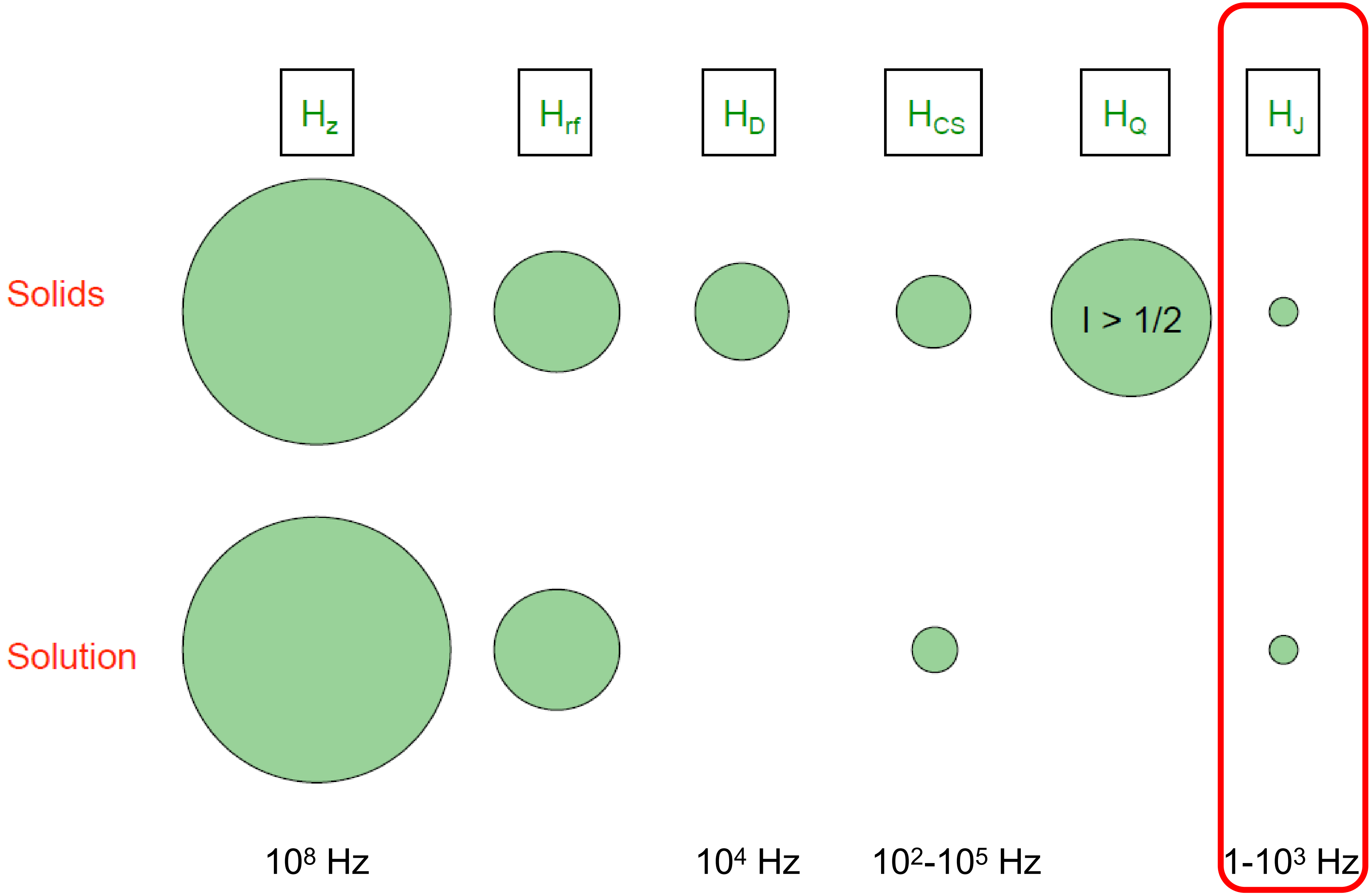
- For ^1H / ^{13}C separated by 100 pm ≈ 30 kHz



- In solids many atoms at many different distances and at many angles leads to substantial broadening

(Ashbrook, 2009)

Interactions in NMR



(Ashbrook, 2009)

J coupling

- Indirect coupling between nuclear spin mediated by the bonding electrons
- Termed J/scalar/spin-spin/indirect dipolar coupling
- “Spectral manifestation of a chemical bond”

$$H_J = 2\pi \, \mathbf{I}_J \cdot \mathbf{J} \cdot \mathbf{I}_k$$

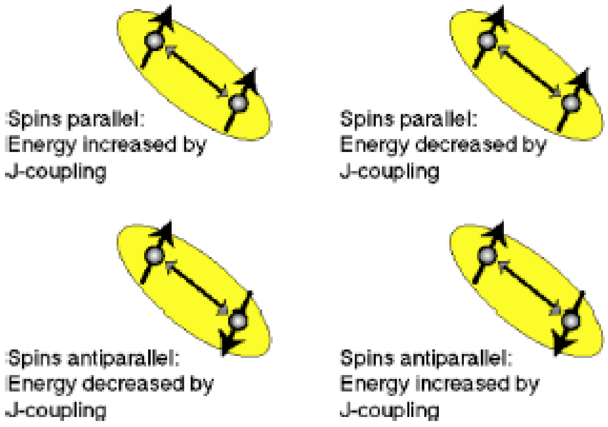
Principal axis system (PAS)

Isotropic J coupling $J_{iso} = (1/3)(J_{xx} + J_{yy} + J_{zz})$

Anisotropic J coupling often small and difficult to distinguish from dipolar coupling

- The sign of J indicates whether the spin-spin contribution lowers or raises the energy of the system
- Typically observed for 1-3 bond interactions and typical magnitudes 1-1000 Hz (e.g., $^{1}H/^{13}C$ ~135 Hz)

$J_{jk} > 0$ $J_{jk} < 0$



Spins parallel: Energy increased by J-coupling

Spins parallel: Energy decreased by J-coupling

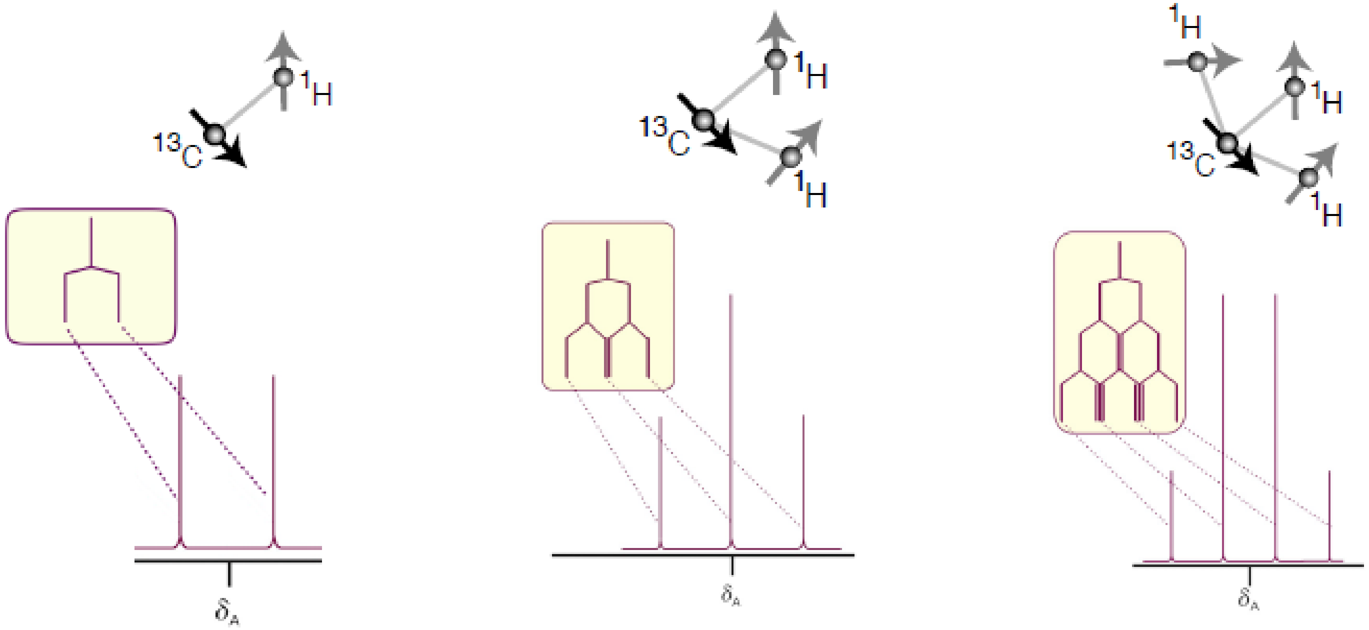
Spins antiparallel: Energy decreased by J-coupling

Spins antiparallel: Energy increased by J-coupling

(Ashbrook, 2009)

J coupling

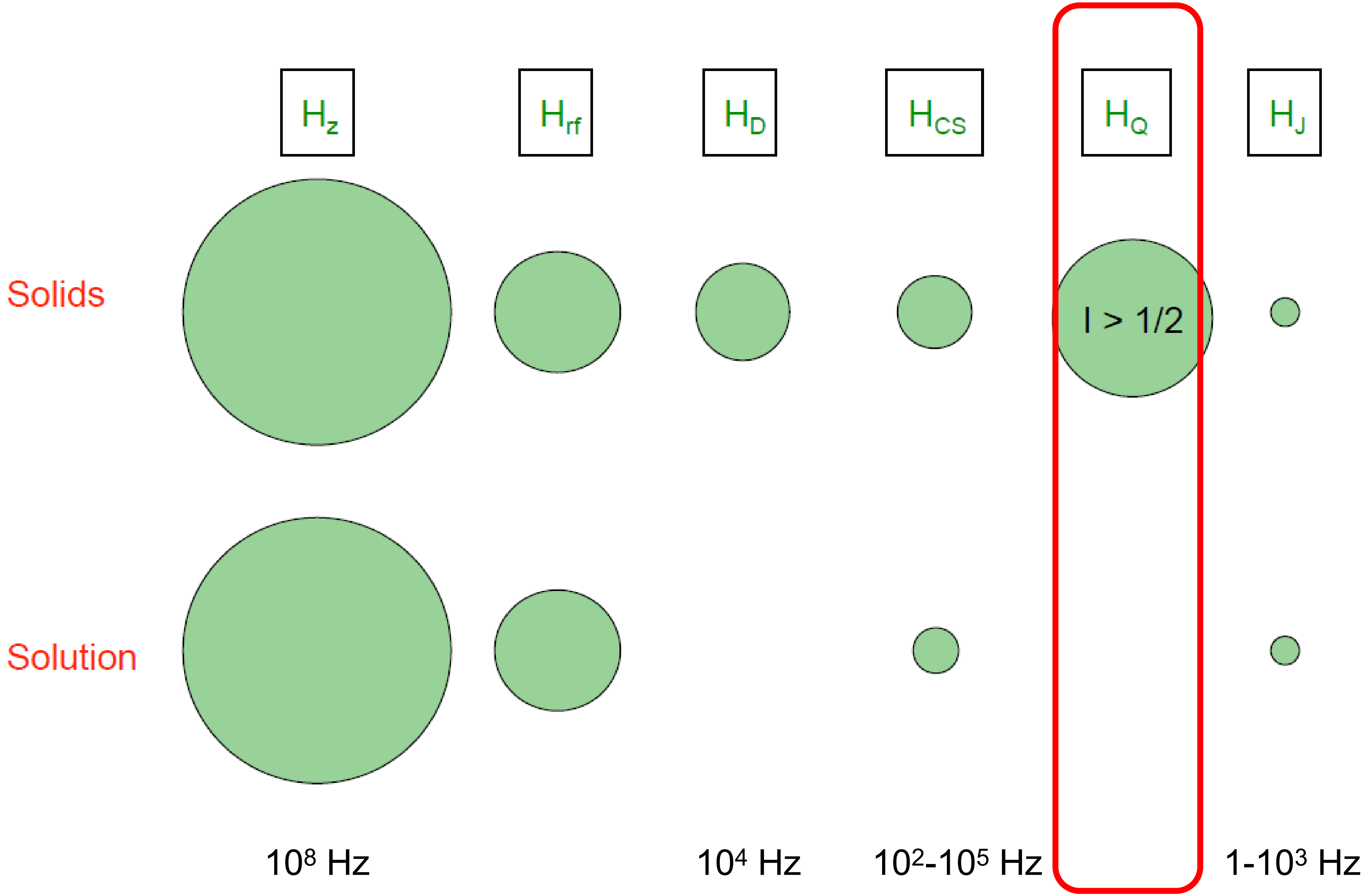
- In solution-state NMR spectra many resonances exhibit complicated splitting patterns, resulting from scalar or J coupling
- The multiplet patterns depend upon the number of nuclei to which a spin is coupled



- For solids, the J coupling is usually much smaller than many other interactions and so multiplet structures are rarely resolved
- The coupling can still be used for the transfer of magnetization

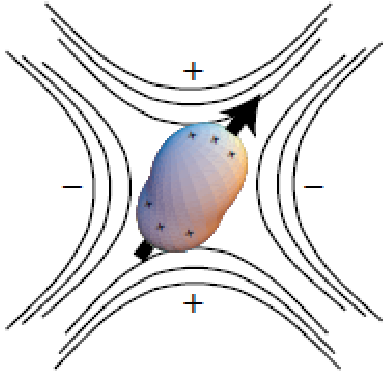
(Ashbrook, 2009)

Interactions in NMR



(Ashbrook, 2009)

Quadrupolar nuclei



- Over 75% of nuclides in the Periodic Table have I > 1/2 (^{2}H, $^{6/7}$Li, ^{11}B, ^{14}N, ^{17}O, ^{23}Na, ^{25}Mg, ^{27}Al, ^{35}Cl, ^{39}K, ^{45}Sc, ^{51}V, ^{59}Co, ^{71}Ga, ^{87}Rb, ^{93}Nb, …)
- Spectra broadened by interaction between the nuclear electric quadrupole moment (eQ) and the electric field gradient (EFG)
- Broadening can be very large (often ~MHz)

$$H_Q = \frac{eQ}{2I\,(2I-1)\hbar}\,\mathbf{I}.\mathbf{V}.\mathbf{I}$$

Principal axis system (PAS)

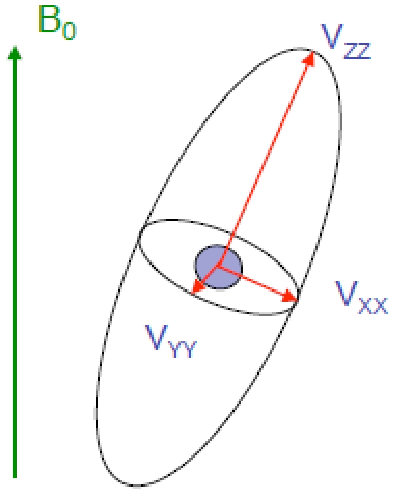
$$\begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix}$$

$C_Q = eQV_{zz} / h$

$\eta_Q = (V_{xx} - V_{yy}) / V\mathbf{zz}$ $\qquad 0 < \eta_Q < 1$

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

$\omega_Q{}^{PAS} = 3\,C_Q / 4I\,(2I-1)$ $\qquad$ (or $3\,C_Q / 2I\,(2I-1)$)



(Ashbrook, 2009)

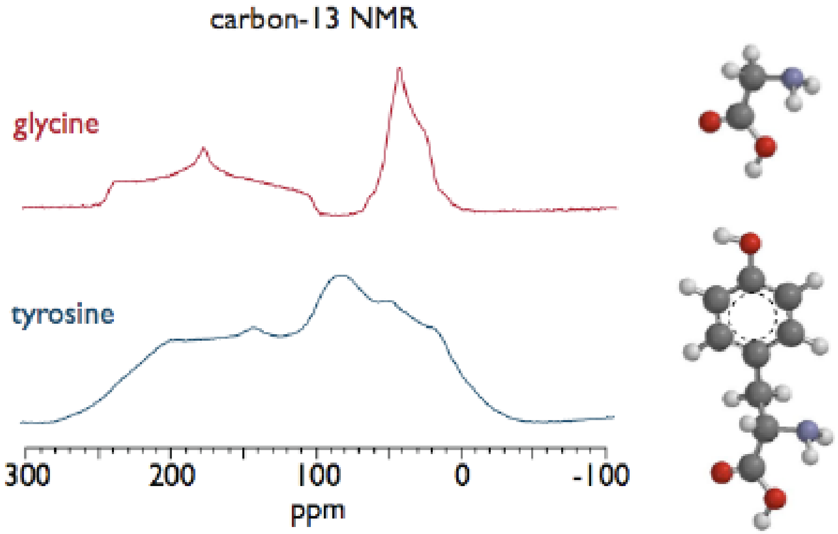
Solid-state NMR challenges

Resolution

- Anisotropic interactions result in powder lineshapes
- Lineshapes from inequivalent sites overlap
- Multiple interactions result in broad featureless lineshapes

Sensitivity

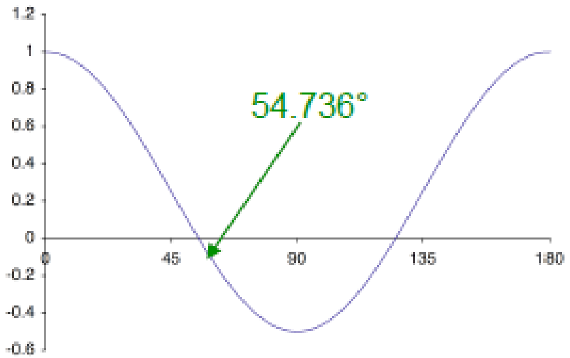
- NMR is inherently insensitive
- Many useful nuclei have low natural abundance (^{13}C, ^{15}N)
- Inefficient relaxation results in long experiment times



(Ashbrook, 2009)

Magic-angle spinning (MAS)

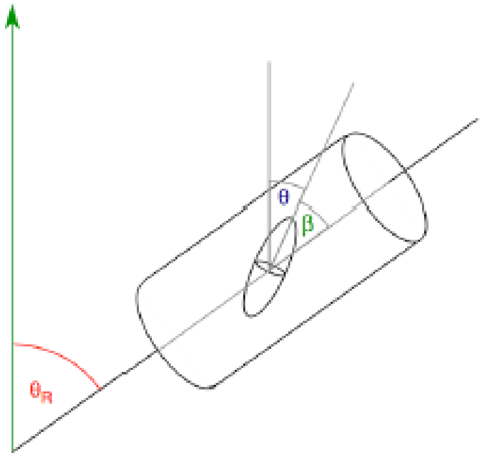
- Magic-angle spinning (MAS) mimics the tumbling motion in solution by rotation of the sample around an axis inclined at an angle θ_R to the external magnetic field
- Introduced by Raymond Andrew in 1958



- When θ = 54.736°(the "magic angle") the magnitude of interactions which depend upon $(3\cos^2\theta - 1)$ is zero
- To remove the broadening in a powdered sample all the crystallites would have to have this orientation simultaneously

- MAS involves rotation of the sample around an angle of θ_R = 54.736° to the magnetic field
- If spinning is sufficiently rapid the "average" orientation of all crystallites is 54.736°
- Anisotropic interactions are then averaged to zero but isotropic terms are retained

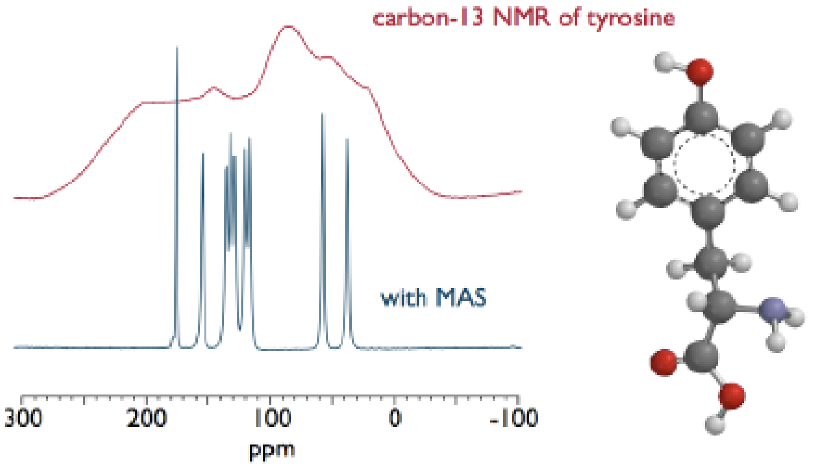
$$\langle 3\cos^2\theta - 1\rangle \propto (3\cos^2\theta_R - 1)(3\cos^2\beta - 1)$$

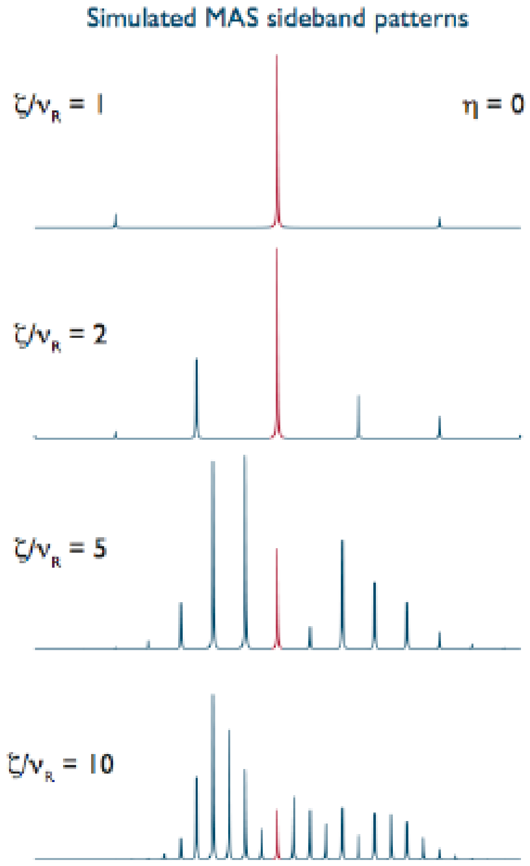


(Ashbrook, 2009)

Magic-angle spinning (MAS)

- MAS improves both the resolution and sensitivity of the spectrum


carbon-13 NMR of tyrosine


Simulated MAS sideband patterns

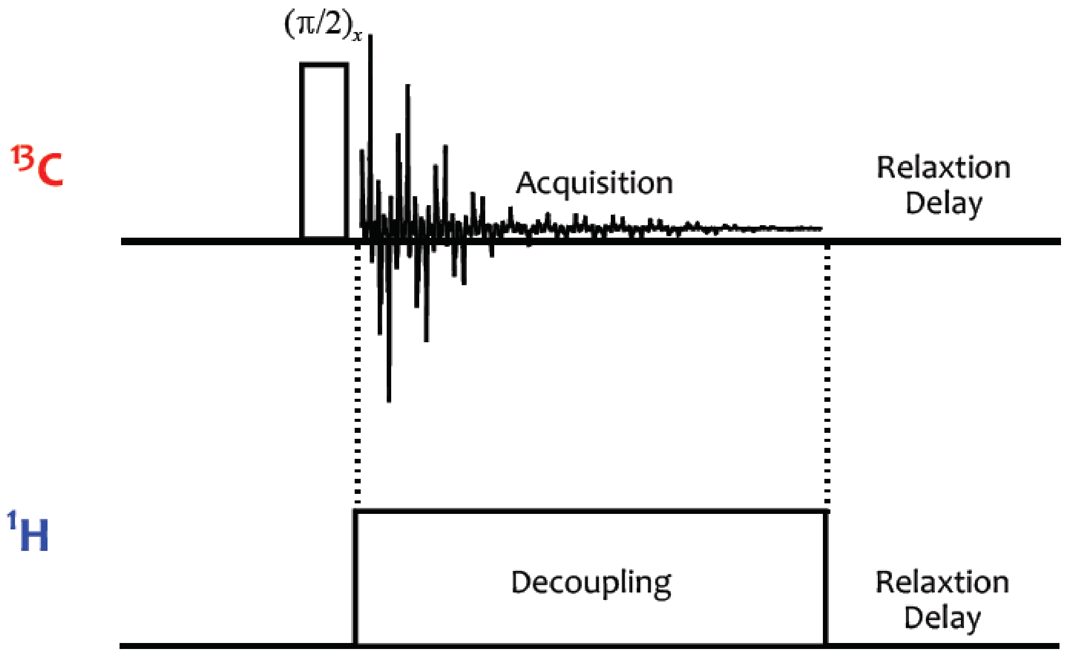
- If spinning is not sufficiently rapid the averaging is not complete

- At slower rates the lineshape breaks up into spinning sidebands (separated by the ω_R)

(Ashbrook, 2009)

Bloch Decay

The simplest NMR experiment is the **single pulse** or **Bloch decay** experiment, where a single π/2 pulse is followed by an acquisition period.



Typically, for organic molecules, this experiment is accompanied by **high-power proton decoupling** in order to resolve sharp ^{13}C resonances, and to eliminate dipolar and *J*-couplings between ^{13}C and ^{1}H.

Disadvantage: the **relaxation delay** for most spin-1/2 nuclei is quite long!

(Schurko, 2010)

Summary: I = 1/2 NMR

- NMR spectra are affected by CSA, dipolar and scalar couplings

- MAS

  removes CSA (δ_{CSA}, η_{CS})
  retains δ_{iso}

  removes heteronuclear dipolar couplings
  removes homonuclear dipolar couplings (fast MAS)

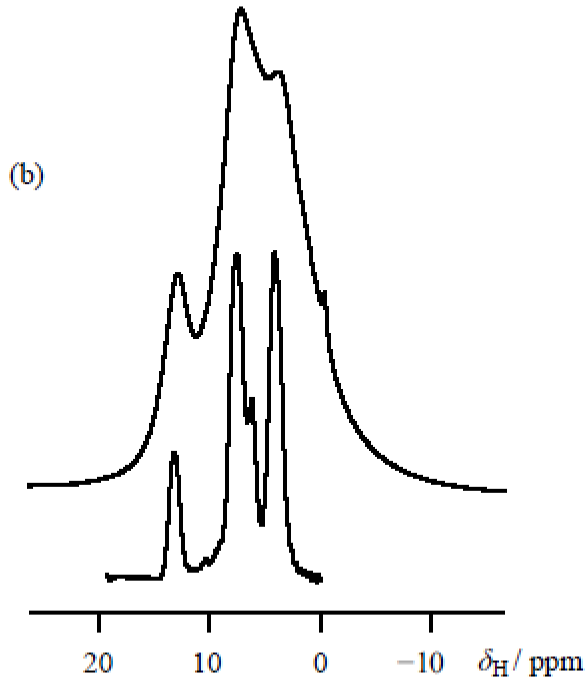
  removes J_{aniso}
  retains J_{iso}

- Decoupling

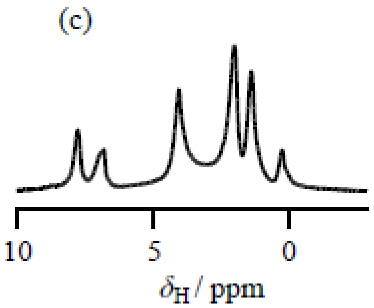
  removes heteronuclear dipolar couplings
  removes homonuclear dipolar couplings

  removes J_{aniso} *and* J_{iso}

(Ashbrook, 2009)

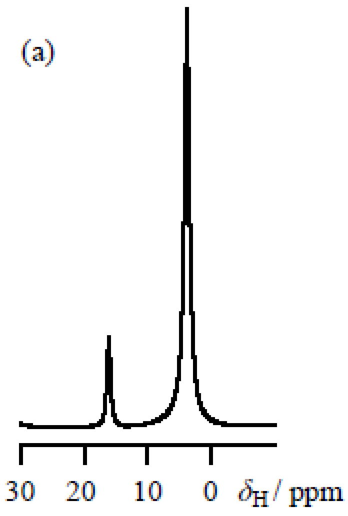


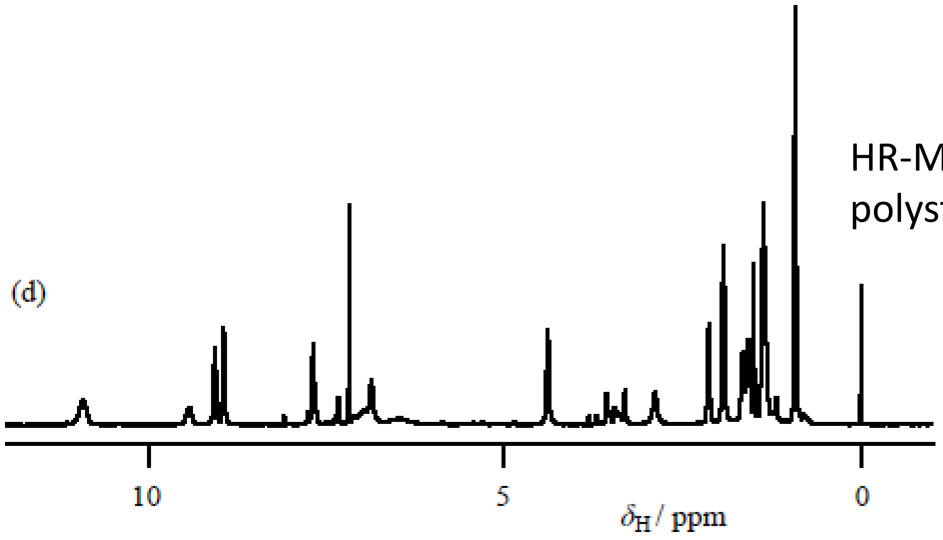
1H spectrum from
3- Methoxybenzoic acid
Upper: 15 kHz no decoupling
Lower: with LG decoupling, 10 kHz



Organic compound in Si matrix 60 kHz, 800 MHz 1H

5 KHz, naturally resolved
From mineral octosilicate





HR-MAS organic compound on
polystyrene bead

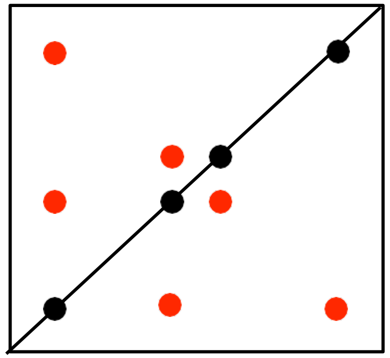
(from Apperley, 2012)

Advanced approaches

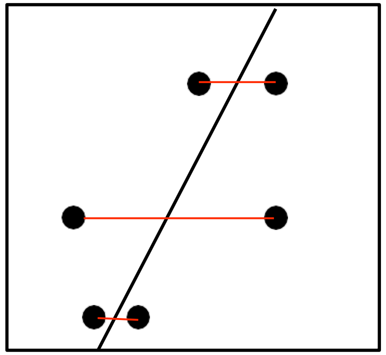
- NMR parameters provide information on structure and symmetry but much of this information is removed in the quest for higher resolution

- Recoupling *Reintroduction of interactions into NMR spectra in a controlled manner*
  Measurement of dipolar couplings and distances
  Measurement of CSA parameters

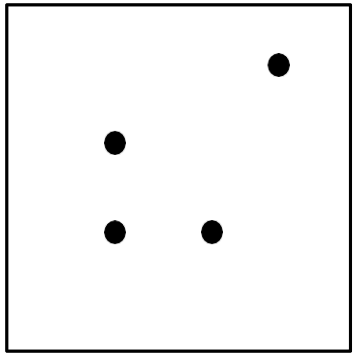
- 2D NMR *Separation of different interactions in different dimensions*
  Magnetization transfer by dipolar coupling giving through-space connectivity Magnetization transfer by J coupling giving through-bond connectivity



Homonuclear: COSY like



Homonuclear: DQ experiments

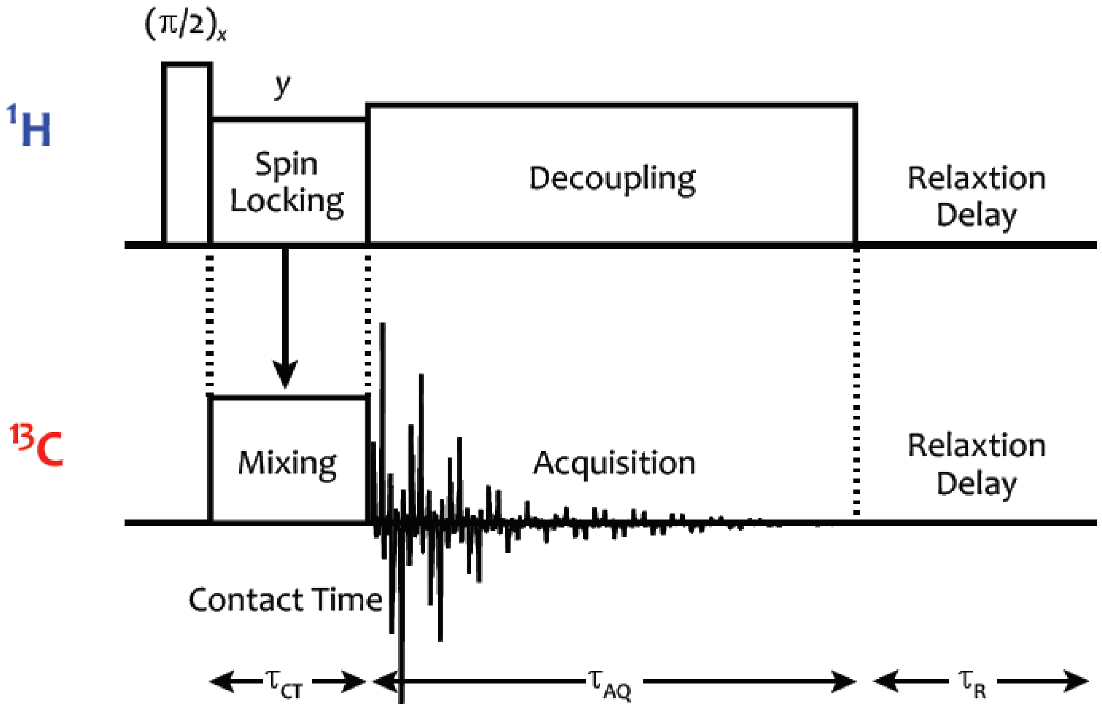


Heteronuclear

(Ashbrook, 2009)

Cross Polarization (CP)

CP is one of the most commonly used techniques in SSNMR, and is often coupled with MAS (i.e., CP/MAS). It involves transferring **spin polarization** from **abundant spins** (e.g., ^1H) to **dilute spins** (e.g., ^{13}C) which are **dipolar coupled**.



Advantages:

- Enhancement of signal by a ratio of γ_H/γ_X (for $^1H/^{13}C$, this is ca. 4x)
- No $\pi/2$ pulse on ^{13}C means the relaxation delay is dependent upon the ^1H longitudinal relaxation time (T_1), which is typically very short!

(Schurko, 2010)

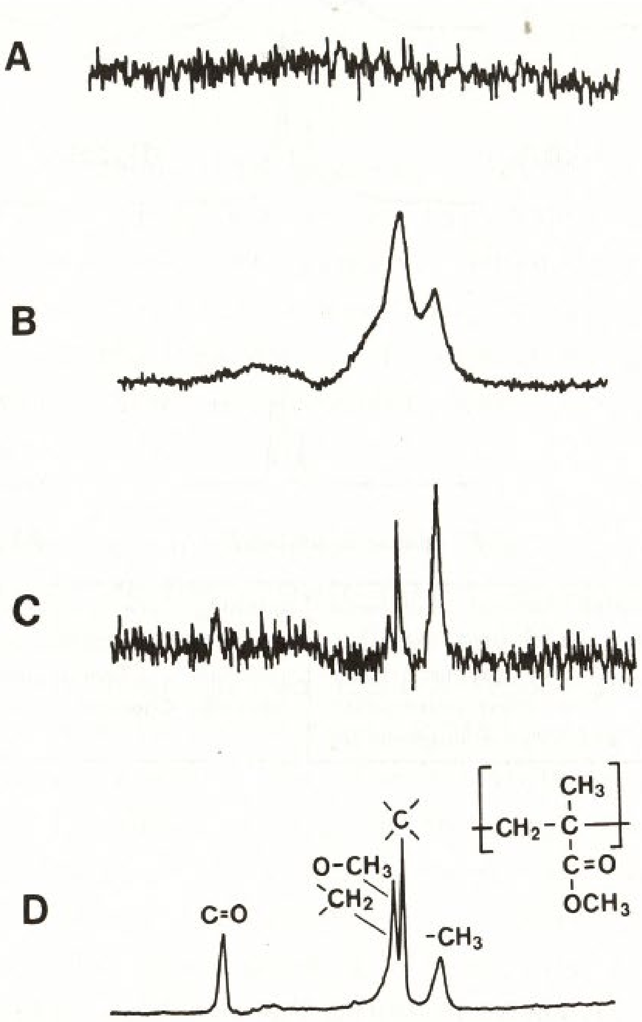
^{13}C SSNMR of poly(methylmethacrylate)

A: No spinning (static)
No CP
Low-power decoupling

B: No spinning (static)
^{1}H-^{13}C CP
High-power decoupling

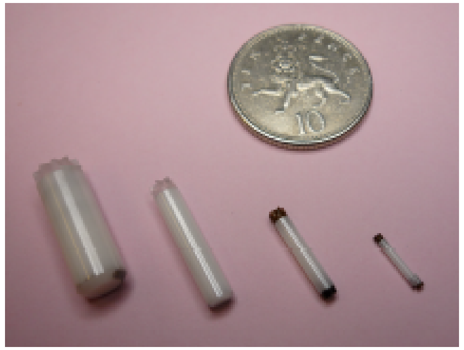
C: Magic-angle spinning
No CP
High-power decoupling

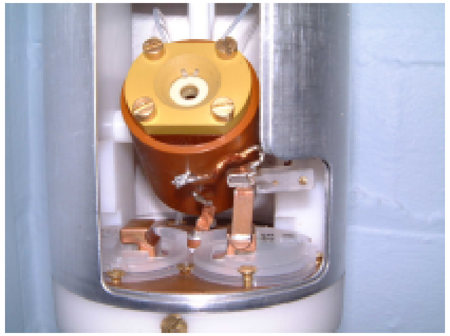
D: Magic-angle spinning
^{1}H-^{13}C CP
High-power decoupling

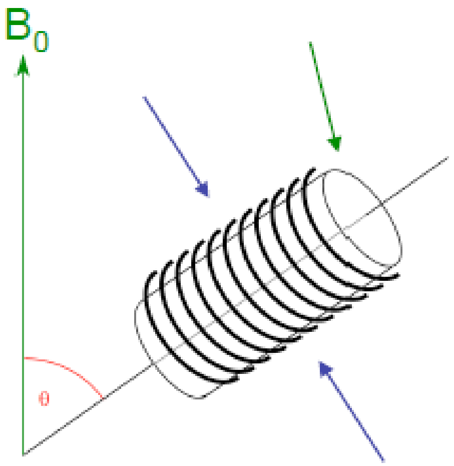


(Schurko, 2010)

Practical implementation







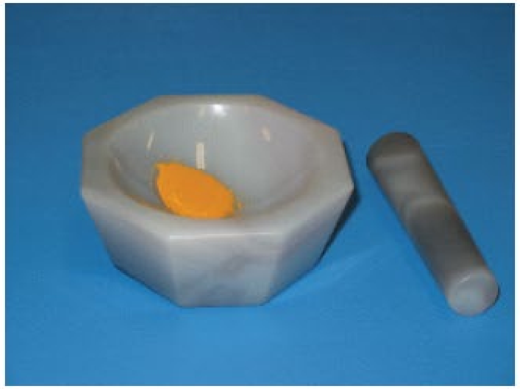
Diameter / mm	Rate / kHz	Sample volume / µl
14	5	1000-3000
7	7	300-500
4	15	50-90
2.5	35	~11
1.3	70	~2

1. Bearing gas reduces friction
2. Drive gas rotates turbines

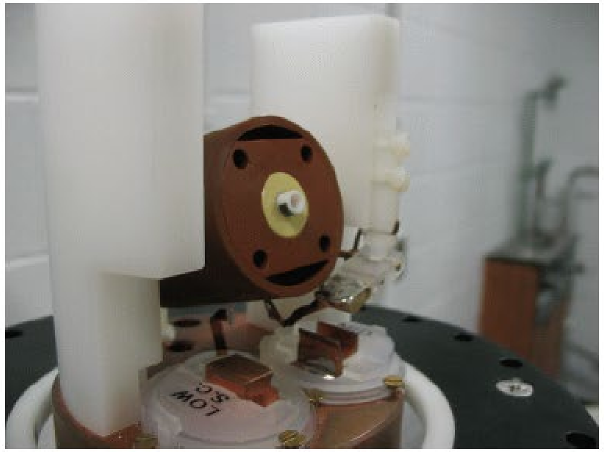
(Ashbrook, 2009)

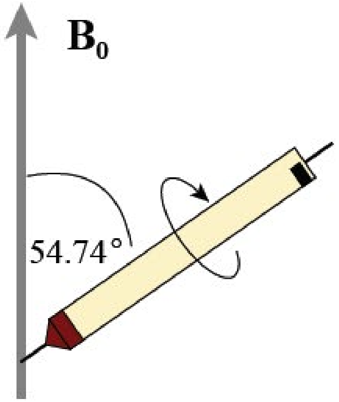
Magic-Angle Spinning (MAS): Preparation

The solid-sample is taken (either on the benchtop or in a glovebox) and ground into a fine powder, and packed into a **rotor**.

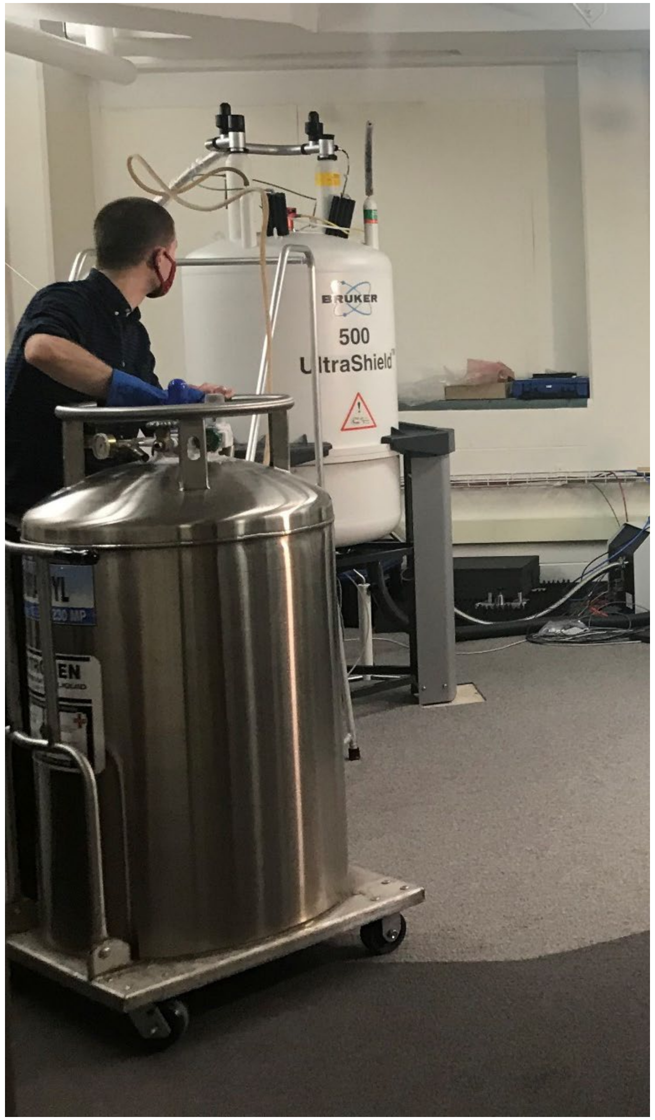


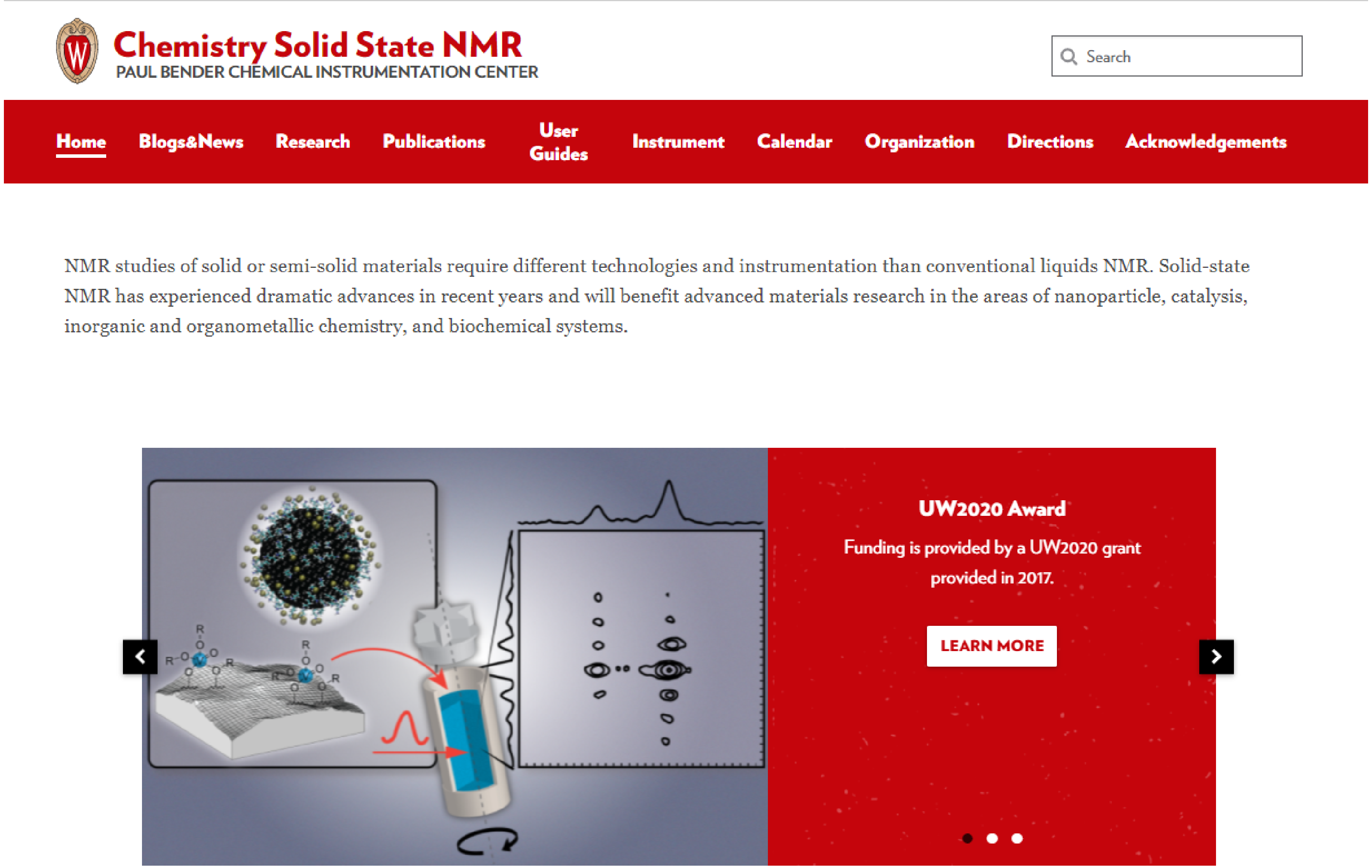
The rotor is inserted into the **stator** of the probe, and the probe is inserted into the magnet, such that the angle between the rotor axis and $\mathbf{B}_0$ is 54.74° (*magic angle*)





(Schurko, 2010)





Chemistry Solid State NMR
PAUL BENDER CHEMICAL INSTRUMENTATION CENTER

NMR studies of solid or semi-solid materials require different technologies and instrumentation than conventional liquids NMR. Solid-state NMR has experienced dramatic advances in recent years and will benefit advanced materials research in the areas of nanoparticle, catalysis, inorganic and organometallic chemistry, and biochemical systems.

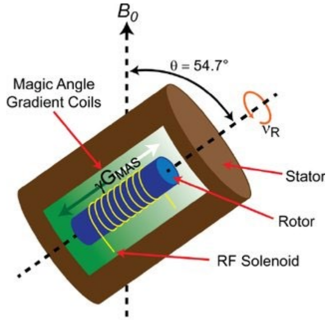
UW2020 Award

Funding is provided by a UW2020 grant provided in 2017.

https://ssnmr.chem.wisc.edu/

Bruker 4mm CP-MAS Probe: Good starting point for most solids work --easy to use probe for routine spectra of most nuclei including ^{1}H, ^{19}F, ^{13}C and ^{27}Al

Bruker 4mm HR-MAS Probe: High resolution NMR of samples containing solutions, gels, swellable solids, polymers and membranes



Phoenix 1.2mm CP/MAS Probe: Very fast 60kHz spinning enables the ^{1}H-assisted detection of other nuclei.

Doty 4mm B_{max} Probe: Solids, semi-solids, and solutions can be studied. Any nucleus, quantitative data, slow diffusion, and high sensitivity are unique characteristics of this probe.

Bruker 3.2 mm EF MAS Probe: Solid peptides, proteins, or carbon based materials. Good for paramagnetic samples Optimized to avoid RF heating

Chemistry NMR Facility

Paul Bender Chemistry Instrumentation Center

- Primarily a student-run operation
  - Samples run by students
  - Groups provide consumables
- Access obtained via training and coursework
  - provided by facility staff
- Detailed Users Guides to assist in the use of equipment
- Facility staff can give expert advice on
  - Experiment selection
  - Manuscript preparation

Resources

- R.W. Schurko**, An Introduction to Solid-State NMR**, NMR Workshop - June 24, 2010, Department of Chemistry & Biochemistry, University of Windsor, http://schurko.cs.uwindsor.ca/resources/ssnmr_workshop_cpmas-schurko.pdf
- Sharon Ashbrook, **The Power of Solid-State NMR**, CASTEP Workshop Oxford, August 2009 http://www.tcm.phy.cam.ac.uk/castep/oxford/power_nmr.pdf
- M. J. Duer, **Solid-State NMR Spectroscopy Principles and Applications**, Blackwell Science, Ltd, Online ISBN:9780470999394, 2002
- D.C. Apperley, R.K. Harris, P. Hodgkinson, **Solid State NMR: Basic Principles and Practice**, Momentum Press, NY, 2012 (e-copy available)