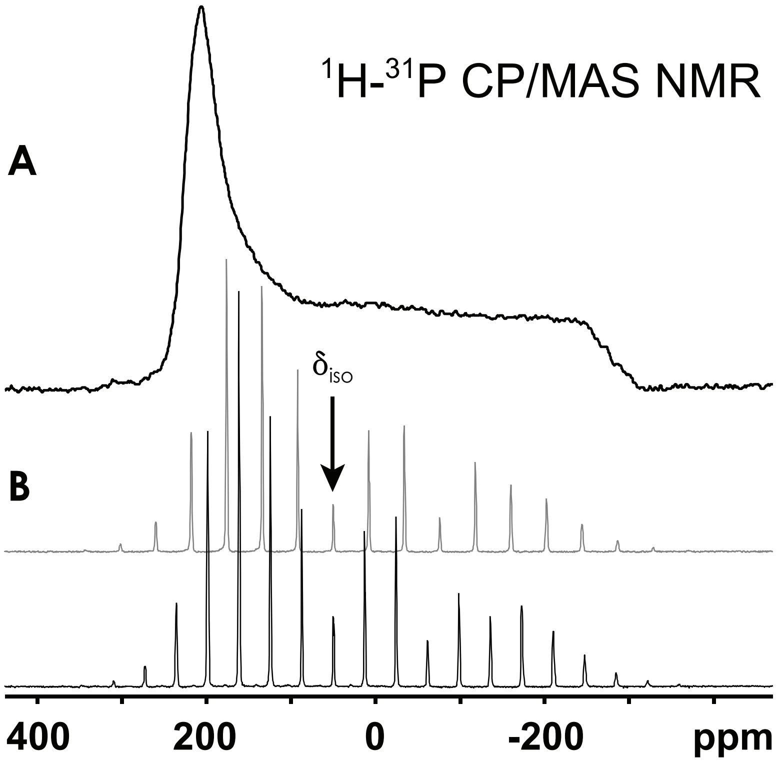
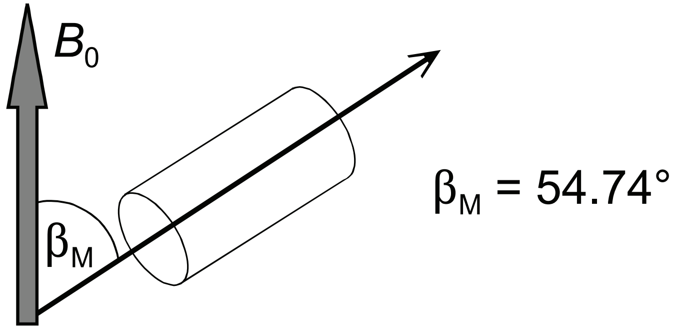
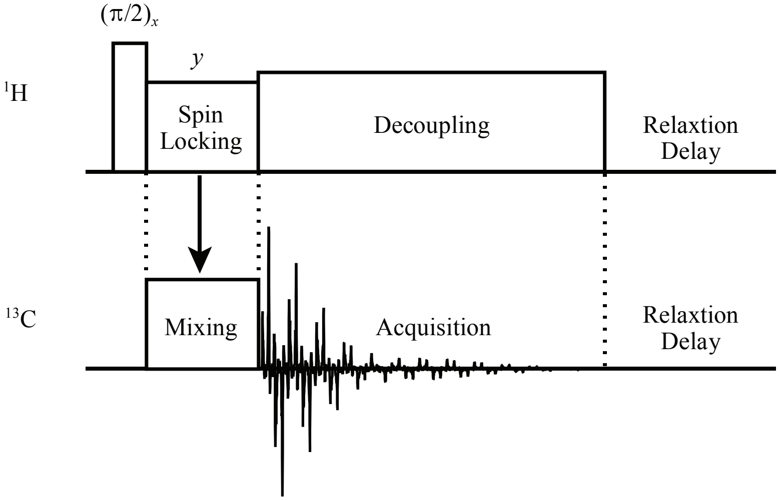
An Introduction to Solid-State NMR







NMR Workshop - June 24, 2010

R.W. Schurko
Department of Chemistry & Biochemistry, University of Windsor
http://www.uwindsor.ca/schurko

Outline

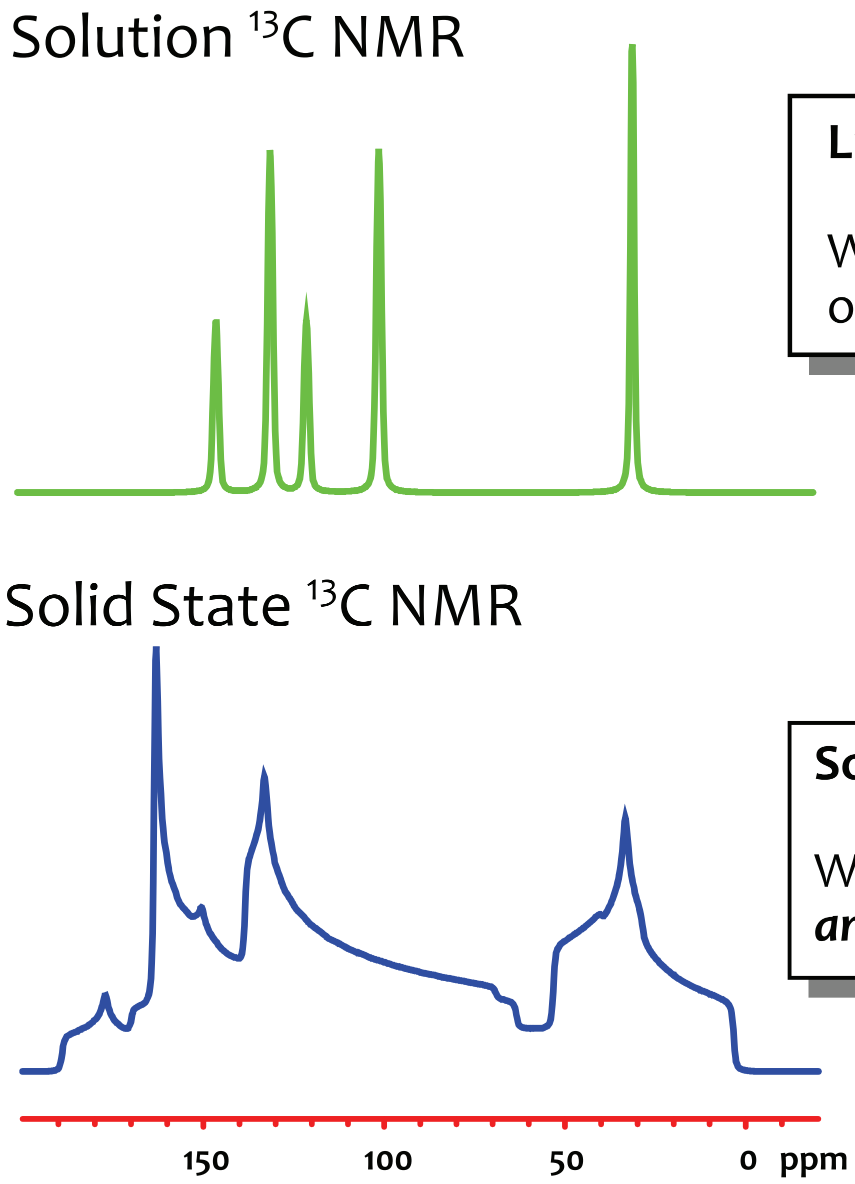
1. Solution vs. Solid-State NMR

2. Anisotropic NMR Interactions
    - Chemical Shielding
    - Spin-Spin Coupling: Dipolar vs. *J*-Coupling

3. Averaging Anisotropic NMR Interactions
    - Magic-Angle Spinning (MAS)
    - Setting the Magic Angle

4. Cross-Polarization (CP)

Solution vs. Solid-State NMR


Solution ^{13}C NMR

Solid State ^{13}C NMR

Liquids:

We observe the average, or ***isotropic*** values of NMR interactions

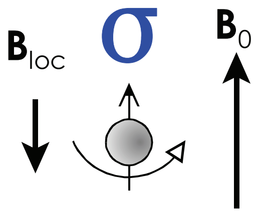
Solids:

We observe orientation dependence, or ***anisotropic*** features of NMR interactions

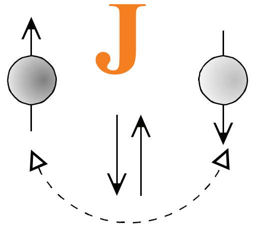
NMR Interactions

Small perturbative NMR interactions are what makes NMR a useful tool for probing molecular structure and dynamics

Important interactions in solution & the solid-state:

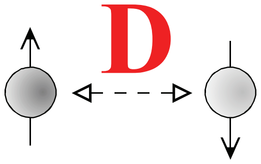


Chemical Shielding
- electronic environment
- nature of chemical bonding
- bond angles and lengths
- coordination numbers
- site differentiation



J-Coupling
- through-bond connectivities
- bond character
- dynamics

Also important in the solid-state:



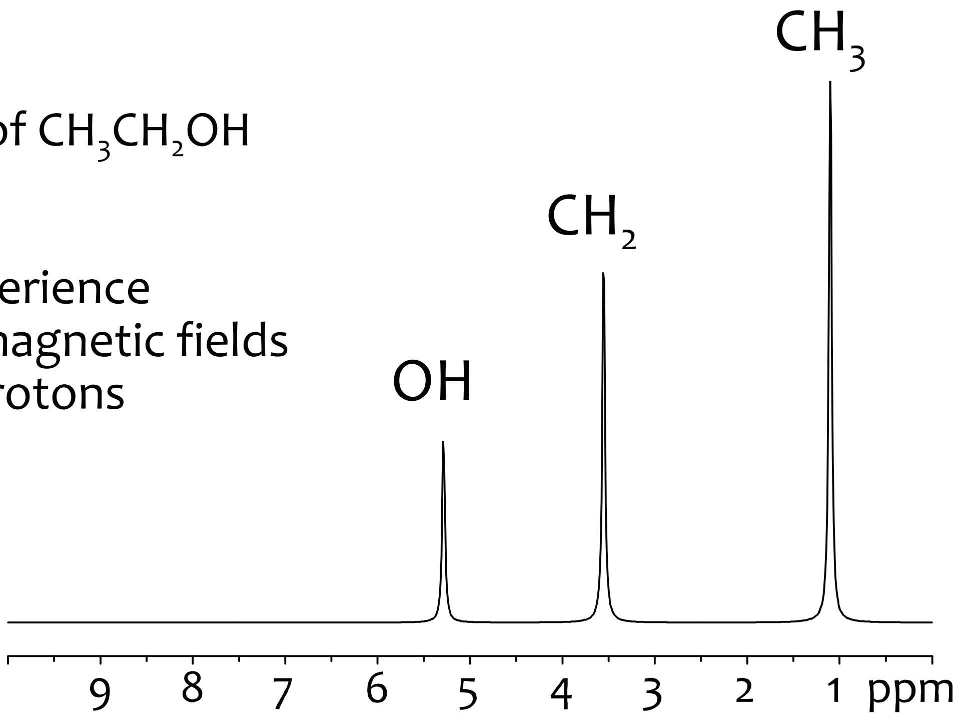
Dipolar Coupling
- through-space connectivities
- bond lengths
- dynamics
- diffusion
- primary source of relaxation!

Nuclear Magnetic Shielding

Electrons in molecules cause local magnetic fields to vary on a very small (but noticeable) scale. Magnetic fields experienced by nuclei at different sites in a molecule are different if the electronic environments are different. The effect is called **chemical shielding** or **nuclear magnetic shielding**:

^{1}H NMR spectrum of CH_3CH_2OH at 300 MHz

Protons of CH_3 experience different internal magnetic fields than CH_2 and OH protons

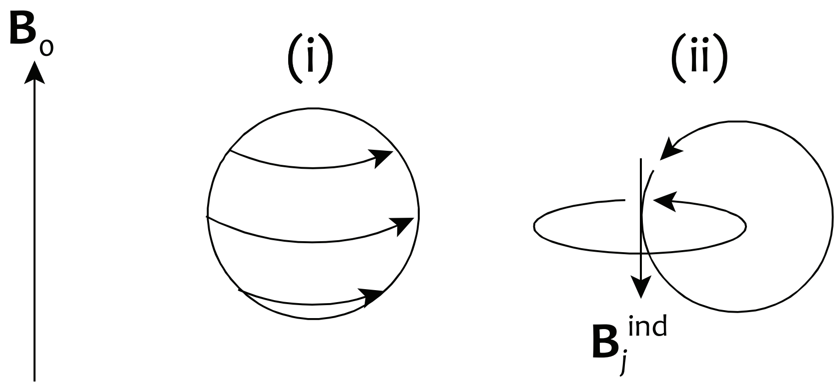


Each ppm is 1 millionth of the size of the applied magnetic field. So, for a 7.05 T (300 MHz) spectrometer, 1 ppm = 300 Hz for protons.

Nuclear Magnetic Shielding, 2

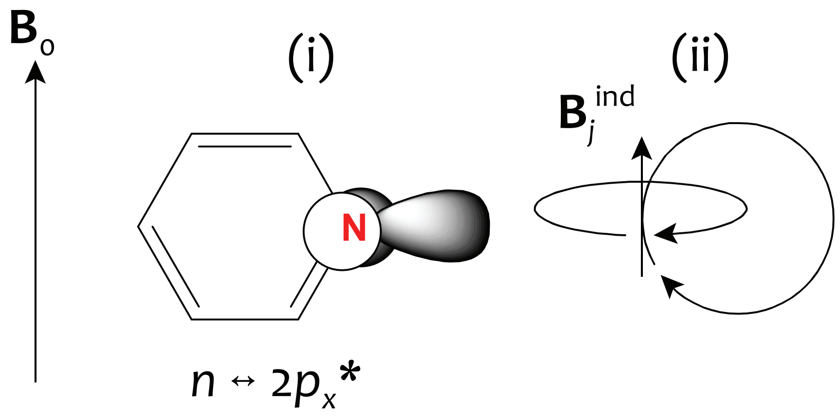
If the local magnetic fields produced by electron circulation oppose the applied magnetic field, B_o, the nucleus is said to be **shielded**; if the local magnetic fields add to B_o, the nucleus is said to be **deshielded**.

Shielding:
Usually arises from **diamagnetic** shielding (electron circulation)



The net Larmor frequency **decreases** in this case

Deshielding:
Arises from **paramagnetic** shielding (mixing of occupied and virtual orbitals):



The net Larmor frequency **increases** in this case

Chemical Shift vs. Shielding

Chemical shielding, σ (in ppm), is described by: $B_{\text{observed}} = B_0(1 - \sigma)$

The shielding scale of course is inconvenient as a reference, since we cannot measure the NMR spectrum of a bare nucleus. So, we choose to set a scale to an agreed upon reference:

$$\delta = \frac{\sigma_{\text{reference}} - \sigma}{1 - \sigma_{\text{reference}}} \times 10^{6} \approx \sigma_{\text{reference}} - \sigma$$

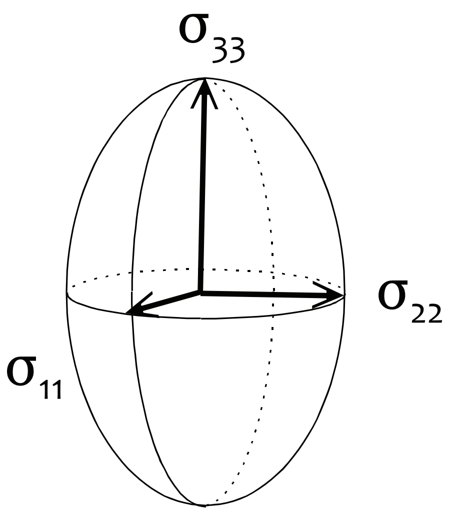
← Higher Frequency
Less Shielded
Downfield

Lower Frequency
More Shielded →
Upfield

	bare ^{13}C nucleus	species A	reference compound (TMS)
absolute frequency:	100.018543	100.010000	100.000000
σ scale:	0.00 ppm	85.41 ppm	185.40 ppm
δ scale:	185.43 ppm	100.00 ppm	0.00 ppm

Chemical Shielding Tensor

Chemical shielding is an anisotropic property, meaning that it depends on the orientation of the sample in the field.



$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

CS tensor in the molecular frame

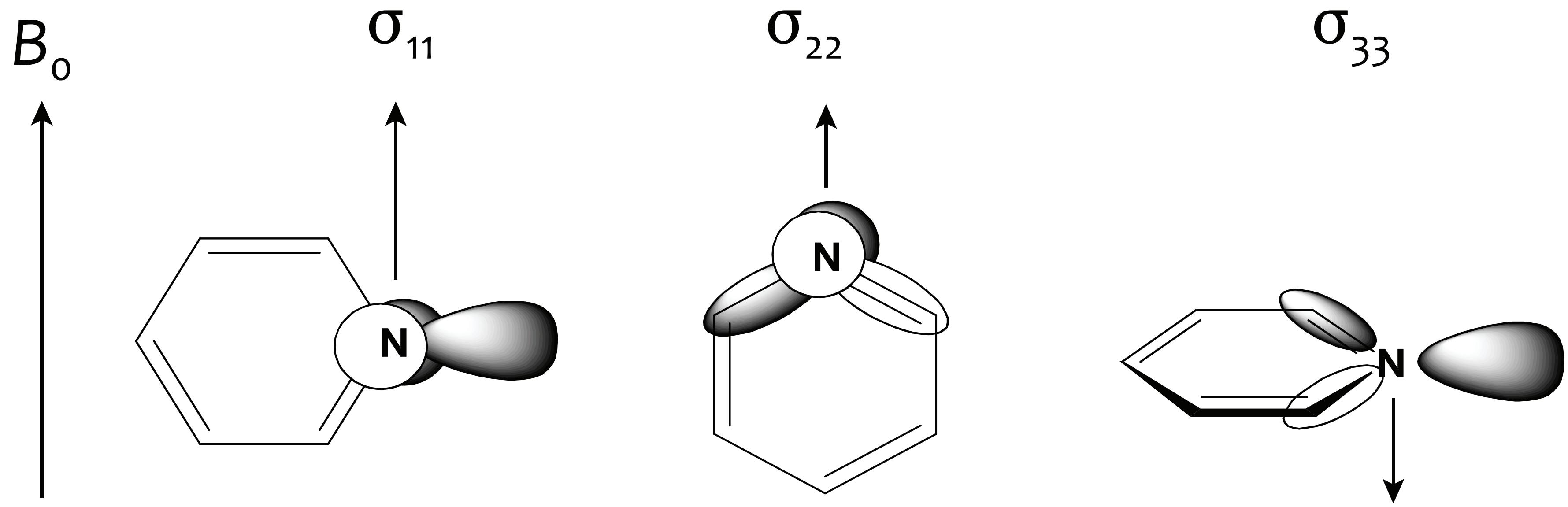
$$\sigma^{PAS} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

CS tensor in its own **principal axis system (PAS)**

The three-dimensional nature of chemical shielding can be described by a **second-rank tensor** with **three principal components**

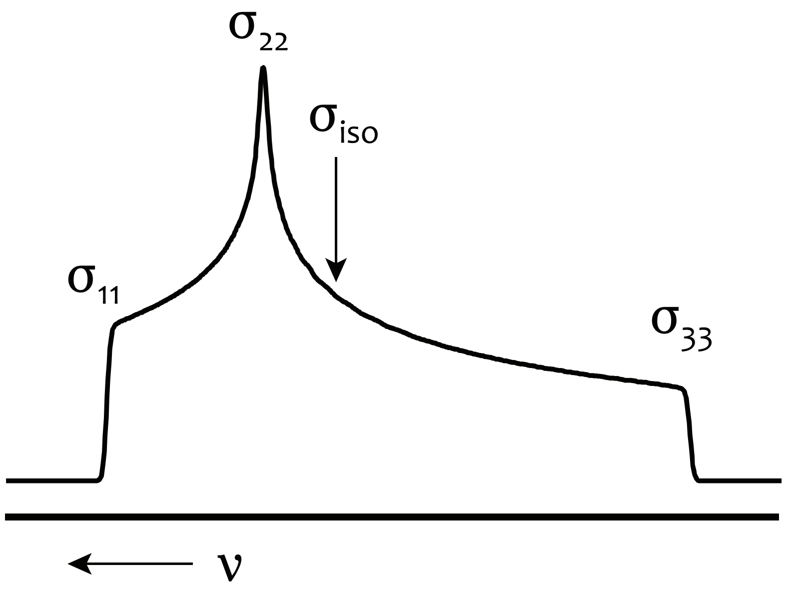
- **Magnetic interaction**: Circulation of electrons induces local fields at nuclei
- Magnetically induced mixing of **ground and excited** state MOs
- **Tensor is not traceless**, does not average to zero
- $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$
- $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; $\Omega = \sigma_{33} - \sigma_{11}$, $\kappa = 3(\sigma_{iso} - \sigma_{22})/\Omega$
- $\delta_{11} \leq \delta_{22} \leq \delta_{33}$
- $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$; $\Omega = \delta_{11} - \delta_{33}$, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$

Chemical Shift Anisotropy (CSA)



σ_{33}: Direction of highest shielding

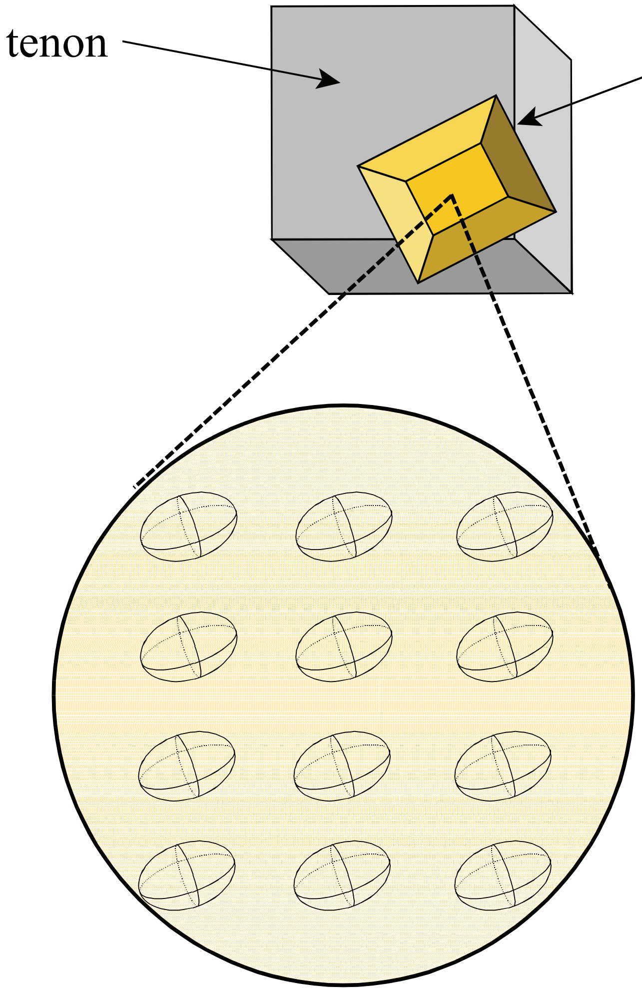
σ_{11}: Direction of lowest shielding



These orientations, and the many possible others, give rise to the solid-state NMR **powder pattern**

Chemical Shift Anisotropy (CSA), 2

Single-crystal NMR is NMR conducted using a single-crystal goniometer, and acquiring spectra for each orientation



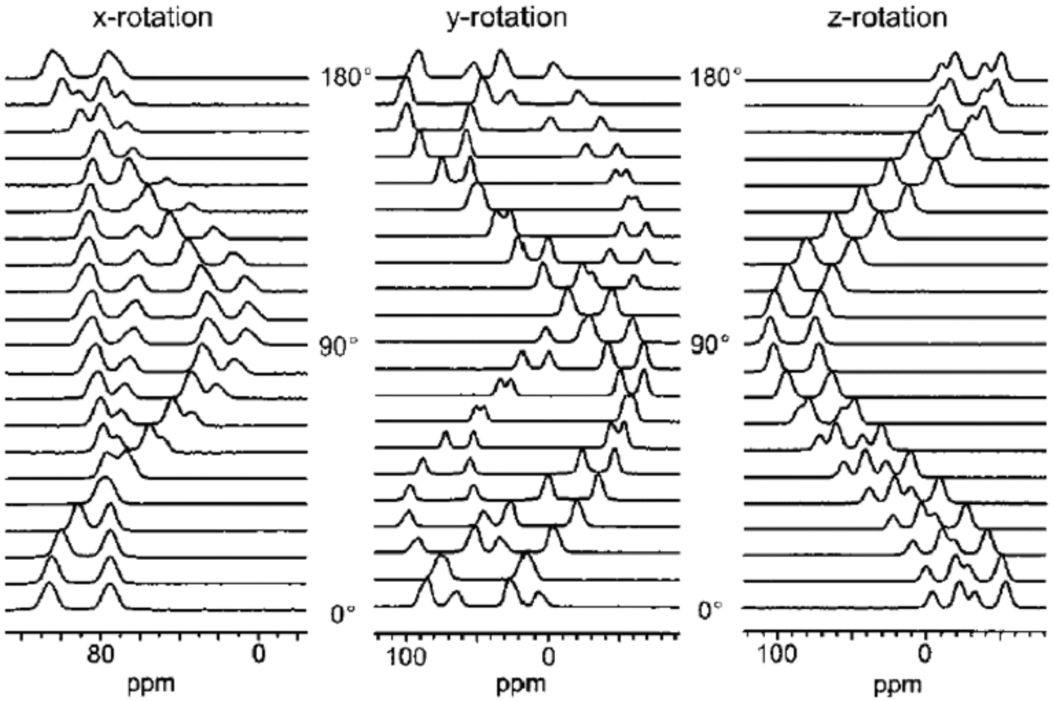
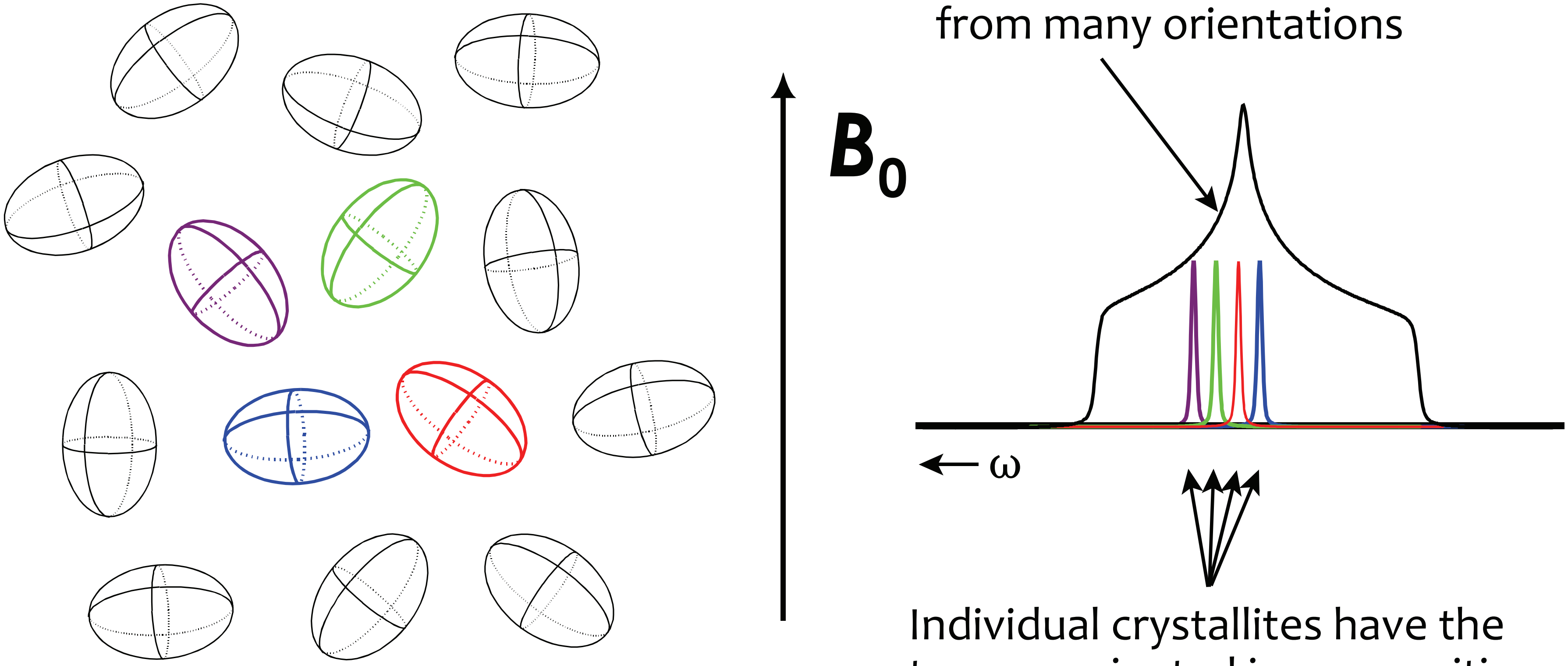


Figure 2. Phosphorus-31 CP NMR spectra of a single crystal of TMPS for rotations of the crystal holder about its *X*, *Y*, and *Z* axes, acquired at 4.7 T.

Chemical Shift Anisotropy (CSA), 3

Crystalline powder samples: tensors assume many different orientations due to random orientations of crystallites



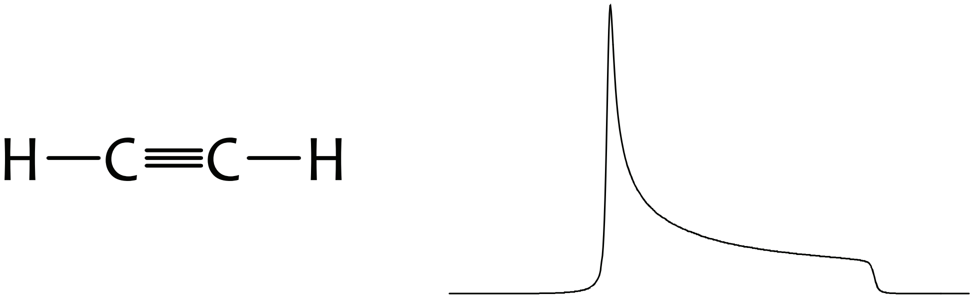
Overall powder pattern results from many orientations

Individual crystallites have the tensors oriented in one position w.r.t. B_0, and give rise to a discrete frequency

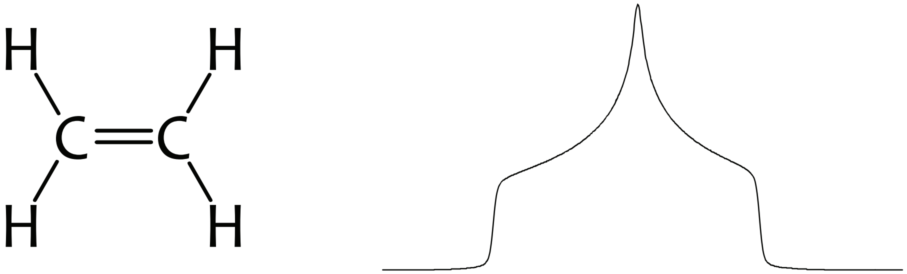
CSA: Structure and Symmetry

Aside from the fact that the CS tensor is the origin of isotropic chemical shifts that are observed in solution, there is also a rich connection between electronic structure, symmetry and CSA

Spherical symmetry: shielding is similar in all directions, very small CSA.



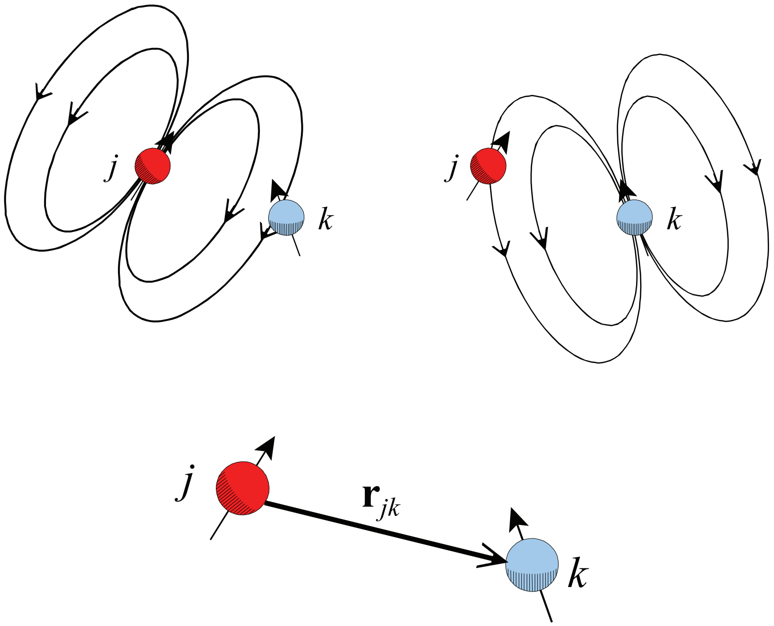
Axial symmetry: molecule is // to $\mathbf{B}_0$ maximum shielding; when molecule is ⊥ to $\mathbf{B}_0$ maximum deshielding



Non-axial symmetry: Shielding is different in three directions

Dipolar Coupling vs. J-Coupling

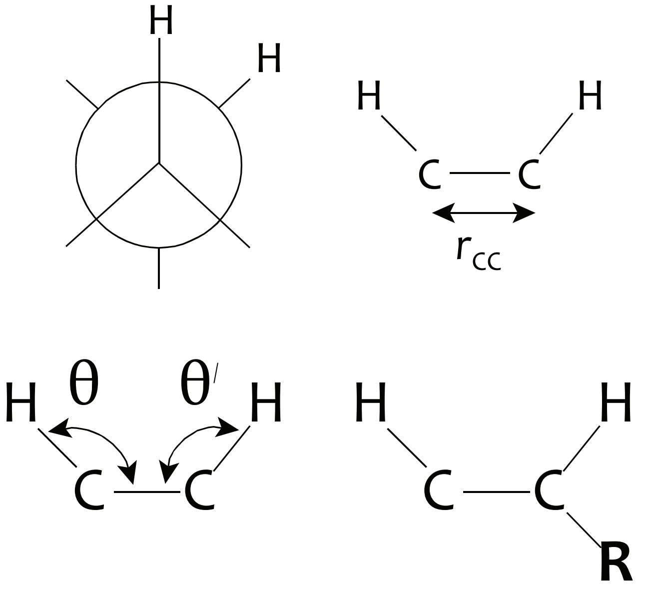
Dipolar coupling (direct spin-spin coupling): through space, independent of electronic structure



Depends only upon nuclear characteristics (size of γ) and internuclear distance. Simple to understand!

$$R_{jk}^{DD} = \frac{\mu_0}{4\pi}\frac{\gamma_j\gamma_k h}{\langle r_{jk}^3\rangle}$$

J-coupling (indirect spin-spin coupling): mediated by the electrons involved in bonding



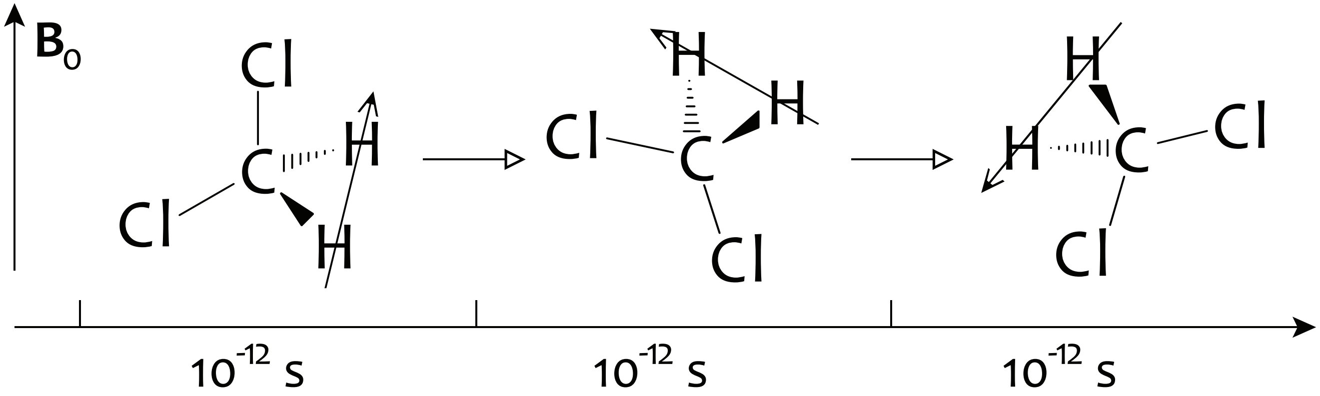
Depends upon nature of intervening bonds, distances, angles, substituents, etc. Complex mechanisms!

$${}^3J_{HH}^{iso} = A + B\cos\phi + C\cos 2\phi$$

Dipolar Coupling vs. J-Coupling, 2

Despite the very different origins of these two-spin mutual couplings, they can both be described by second-rank tensors which are *axially symmetric* (i.e., $J_{\parallel}$ is not the same as $J_{\perp}$; same for R_{DD})

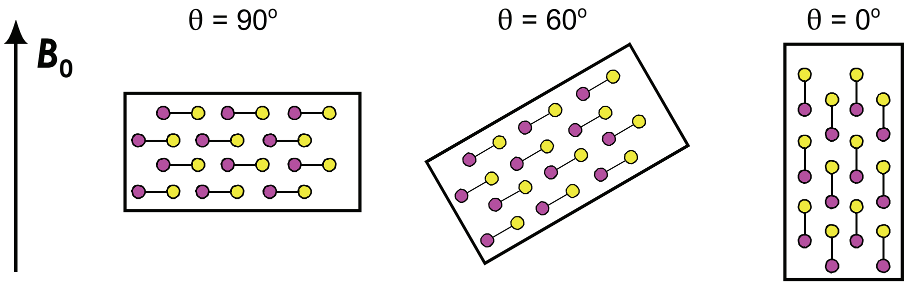
The major difference between these tensors is that the *J*-tensor is not traceless; this is what gives rise to the **isotropic J-coupling** we see in solution NMR spectra. The dipolar tensor is **traceless**; so, rapid tumbling averages the effects of the dipolar interaction in solution NMR.

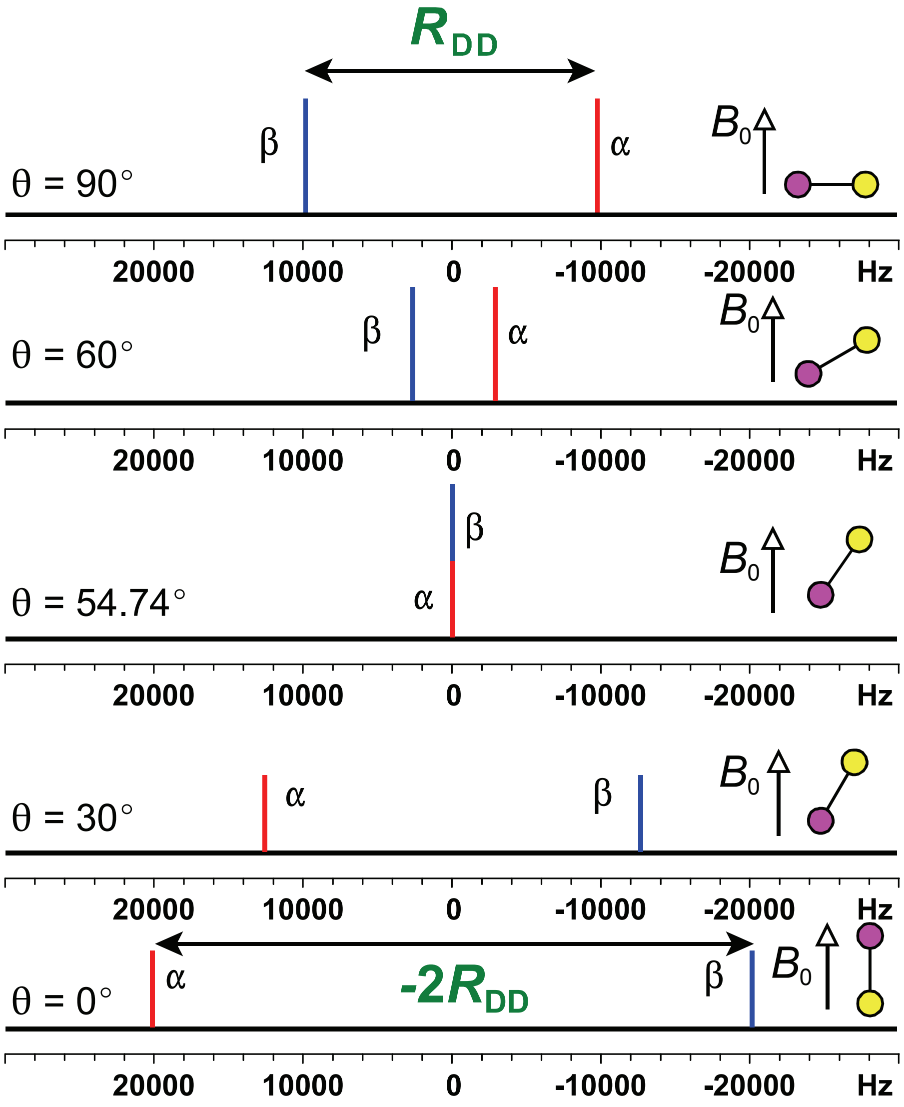


Fluctuating dipolar fields are the major reason for **relaxation phenomena** in both solution and solid-state NMR. This reorientation occurs so quickly, that the nuclear spins experience a **time average** of the angular part of the dipolar interaction $\langle 3\cos^2\theta - 1 \rangle$ over all possible orientations θ,ϕ.

Anisotropic Dipolar Interactions

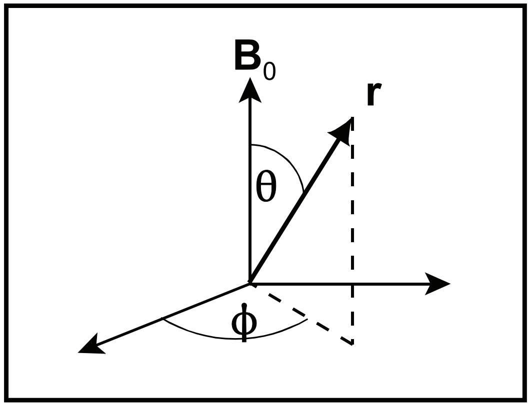
Imagine a single crystal in which all of the internuclear vectors are oriented in the same manner:





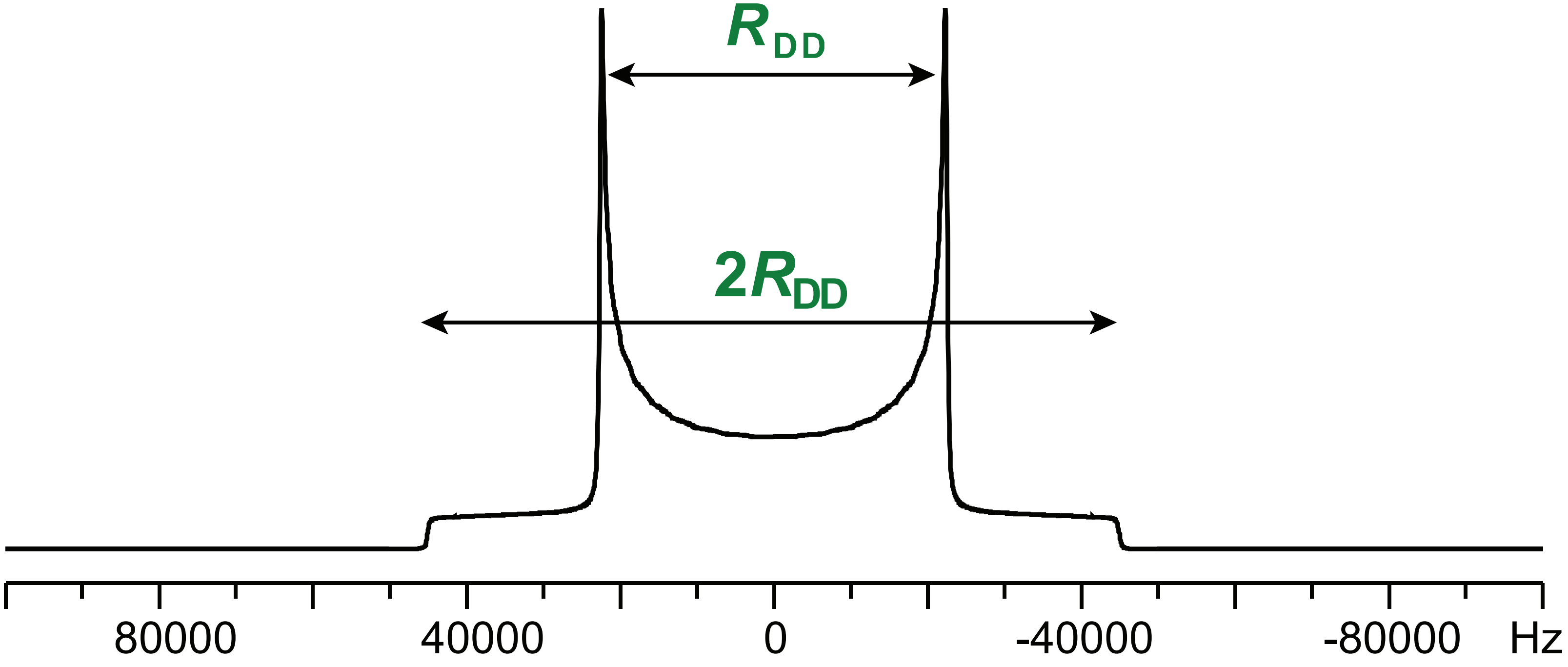
If we rotate the crystal with respect to B_0, we are able to see the orientation dependence of the dipolar coupling:

factor of $(1 - 3\cos^2\theta)$



Anisotropic Dipolar Interactions, 2

Just as for CSA, an isolated spin pair in a microcrystalline powder (e.g., two ^{1}H in $CaSO_4{\bullet}2H_2O$) gives rise to a **powder pattern** (called a Pake doublet).

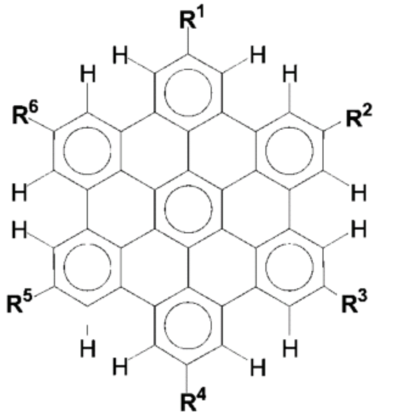


The pattern arises from the $(1 - 3\cos^2\theta)$ geometric dependence, and the size of the dipolar coupling constant, R_{DD}. It is comprised of two mirror image patterns (that resemble CSA patterns) which are superimposed.

Anisotropic Dipolar Interactions, 3

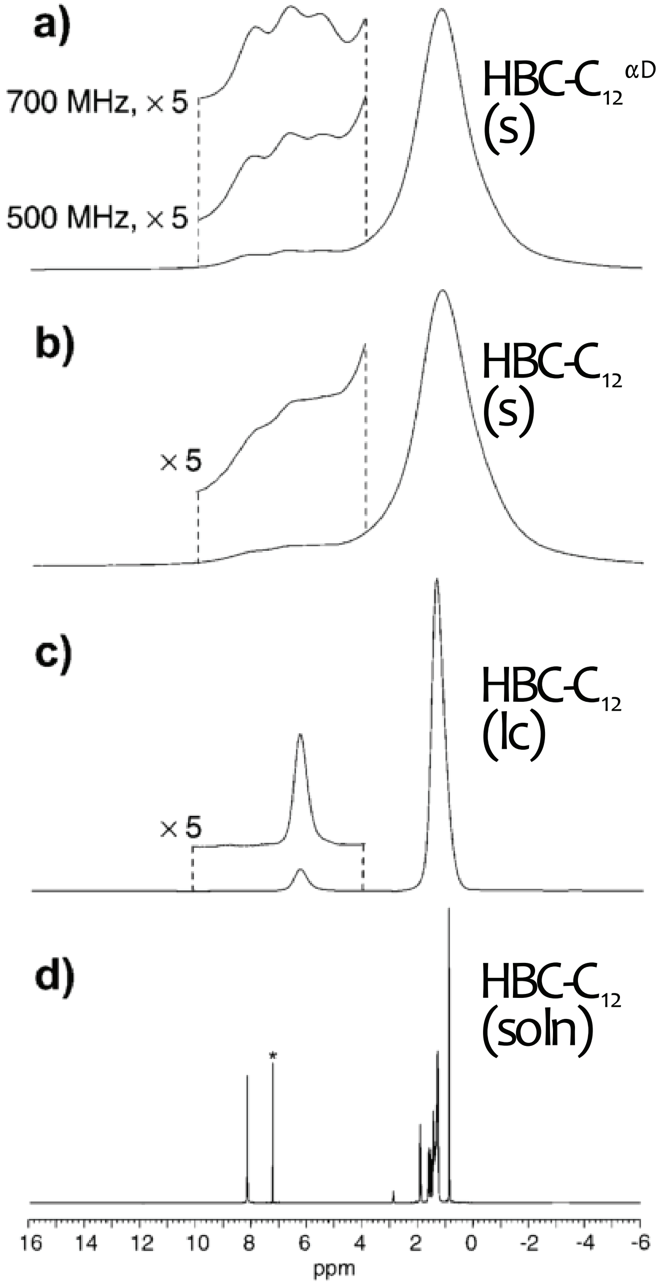
Dipolar interactions are typically much larger than *J*-couplings, and often dominate solid-state NMR spectra (in an unhelpful way!!)

For instance, a proton in an organic solid will have strong dipolar couplings to all of the surrounding protons, and its pattern will be extremely broad, overlapping with similarly broadened patterns of all of the other protons!



1: $R^n = -(CH_2)_{11}CH_3$
2: $R^n = -CD_2(CH_2)_{10}CH_3$
3: $R^n = -CH(CH_3)_2$
4: $R^n = -C(CH_3)_3$
5: $R^{1,2} = -C(CH_3)_3$
$R^{3\text{-}6} = -(CH_2)_{11}CH_3$

Schnell & Spiess, *J. Magn. Reson.* **2001**, *151*, 153–227.



As a result, ^1H NMR in the solid state is not particularly useful in comparison to solution ^1H NMR - though there are some tricks!

Averaging Anisotropic NMR Interactions

There are three common ways to average anisotropic NMR interactions, in order to extract information contained within the higher-resolution spectra:

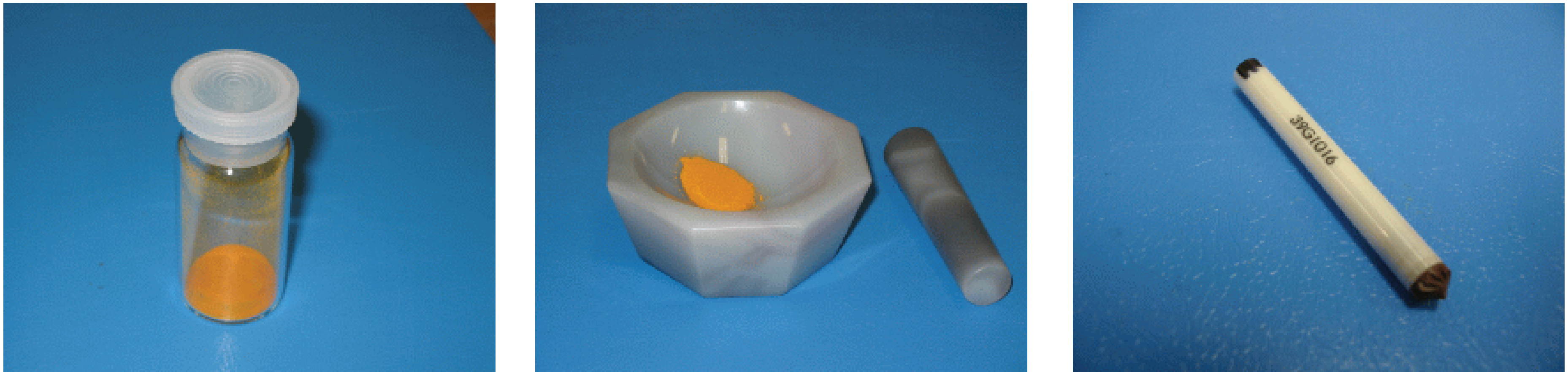
Magic-angle spinning (MAS):
Sample is rapidly spun in order to spatially average the anisotropic interactions (*we will focus on this aspect in this lecture*)

Specialized pulse sequences:
Sample (usually under MAS conditions) is subjected to a series of pulses with average the anisotropic interactions in "spin space"

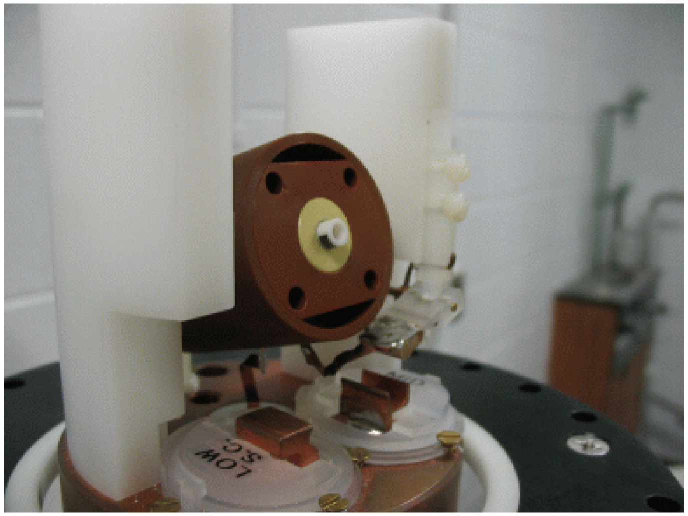
Two-dimensional NMR
Homonuclear (e.g., ^1H, ^1H) and heteronuclear (e.g., ^1H, ^{13}C) correlation experiments are utilized to improve resolution and develop correlations among nuclei at different sites in the system.

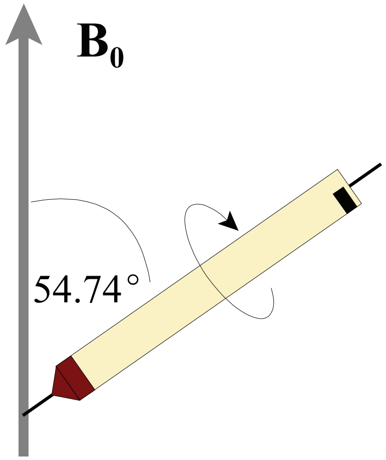
Magic-Angle Spinning (MAS): Preparation

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



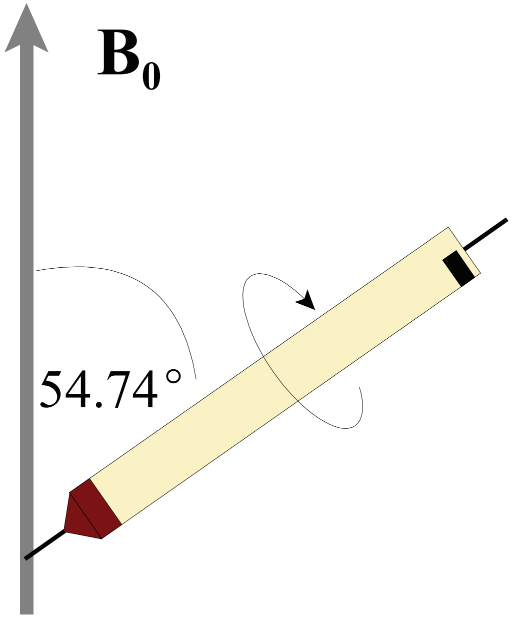
The rotor is inserted into the **stator** of the probe, and the probe is inserted into the magnet, such that the angle between the rotor axis and $\mathbf{B}_0$ is 54.74° (*magic angle*)





MAS: How it works

The rotor is spun rapidly about its axis at speeds ranging from 1 to 70 kHz (this depends on what probe you are using, and what sort of results you are hoping to achieve with your experiment).



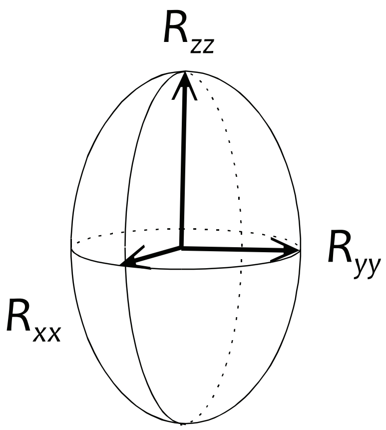
All of the NMR interactions (CS, J, DD) yield frequencies that are dependent upon the orientation of the interaction tensor in the magnetic field (or the coordinates of B_0 in the interaction frame)

The *Hamiltonians* describing these frequencies can be made **time dependent** when the sample is rotated in the magnetic field

By choosing the correct angle, it is possible to **coherently average** the anisotropic NMR interactions (i.e., all that is left is the **isotropic average**).

A simple case

Consider an NMR interaction tensor **R** which is *axially symmetric*. The unique component, R_{zz}, *which* determines the interaction frequency ω_{int}, is:

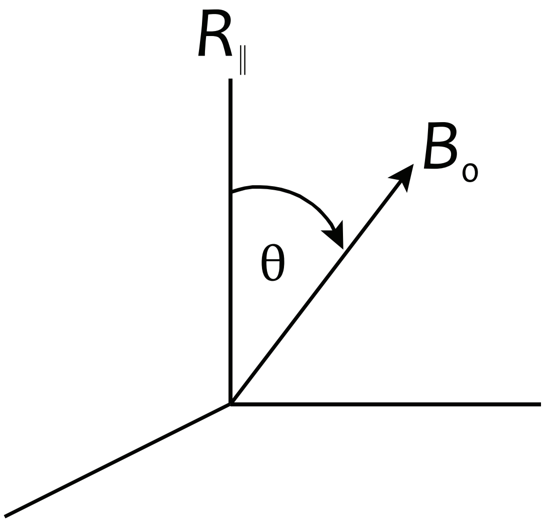


$R_{xx} = R_{yy}$

$$R_{zz}^{LAB} = R_{iso} + \underbrace{R_{\parallel}\left(\frac{3\cos^2\theta - 1}{2}\right)}_{\text{Anisotropic part}}$$

Consider the simplest system:

- single transition frequency, ω_{int}
- simple I_z operator (single spin)
- depends on one angle, θ
  (like in a single crystal)

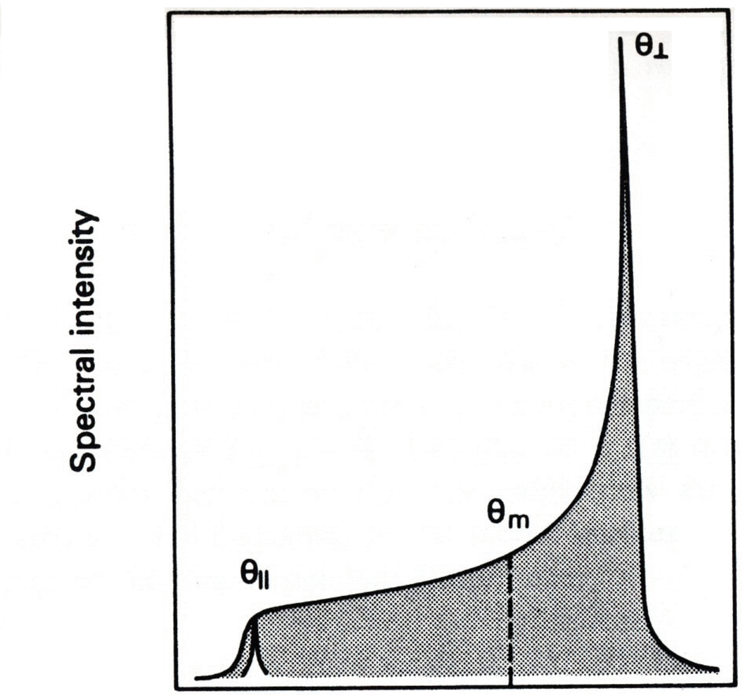


Then: $R_{zz}^{LAB} I_z \equiv \omega_{int} I_z$

Static powder pattern

If we make a single $\pi/2$ pulse on the system, we create the observable I_+ coherence (i.e., magnetization in the *xy*-plane). Then, the total observable signal averaged all possible angles θ is:

$$\langle I_+(t)\rangle = \int \exp[-i\omega_{int}(\theta)t]\ \underbrace{p(\theta)d\theta}_{\text{Probability of finding a crystallite with orientation } \theta}$$



Powder pattern

$\theta_\parallel = 0^o$, B$_o$ along unique axis, $\omega = R_{iso} + R_\parallel$

$\theta_\perp = 90^o$, B$_o$ along unique axis, $\omega = R_{iso} - R_\parallel/2$

$\theta_m = 54.74^o$, B$_o$ along unique axis, $\omega = R_{iso}$ [$\theta = \cos^{-1}(\sqrt{3}/3)$]

Rotating the sample

Rotate the sample at a frequency of ω_r inclined at some angle w.r.t. B_0:

(a) Over one rotational cycle, the average direction of $R_\parallel$ is along the rotational axis (regardless of original orientation)

(b) Now, imagine the fixed frame of the rotor. $R_\parallel$ is fixed in this frame with arbitrary angles α and β. B_0 would appear to *precess* about the *z* axis of this frame, fixed at the angle θ_m (magic angle), and sweeping a time-dependent *azimuthal angle* $\omega_r t$

An **instantaneous angle** $\theta(t)$ between $R_\parallel$ and B_0 is predicted by the *spherical law of cosines*:

$$\cos[\theta(t)] = \cos\theta_m \cos\beta + \sin\theta_m \sin\beta \cos(\alpha - \omega_r t)$$

(from θ_m-β to θ_m+β, and phase angle from 0 to 2π)

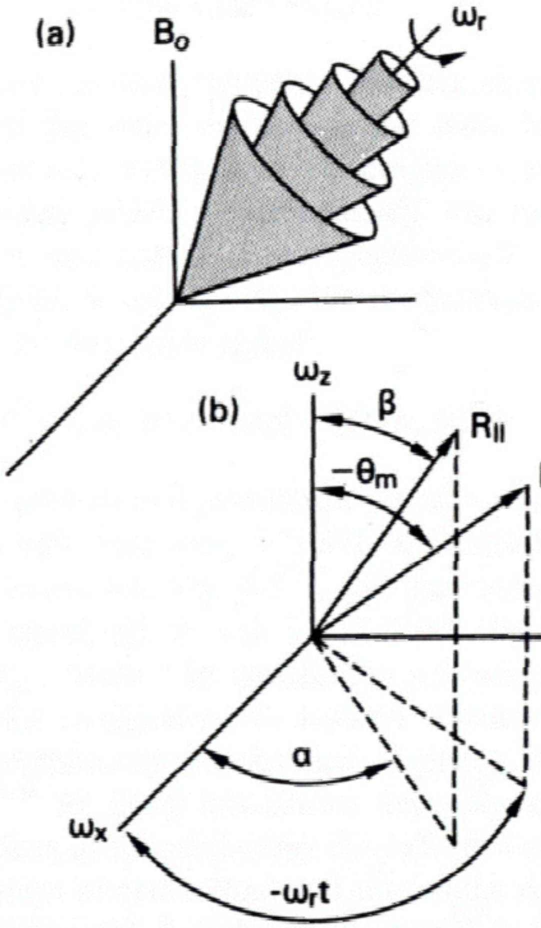


Figure 5.10. Magic-angle sample spinning. (*a*) The unique principal direction for each crystallite moves along a cone whose axis is always inclined at θ_m relative to B_0. (*b*) $R_\parallel$ and B_0 viewed in the rotor frame ω_x—ω_y—ω_z. Negative angles, ignored in [5–34], suggest only that the transformation is from LAB to rotor to PAS.

Time-dependent frequencies

So, if θ is time dependent, so is $\omega_{int}(\theta)$:

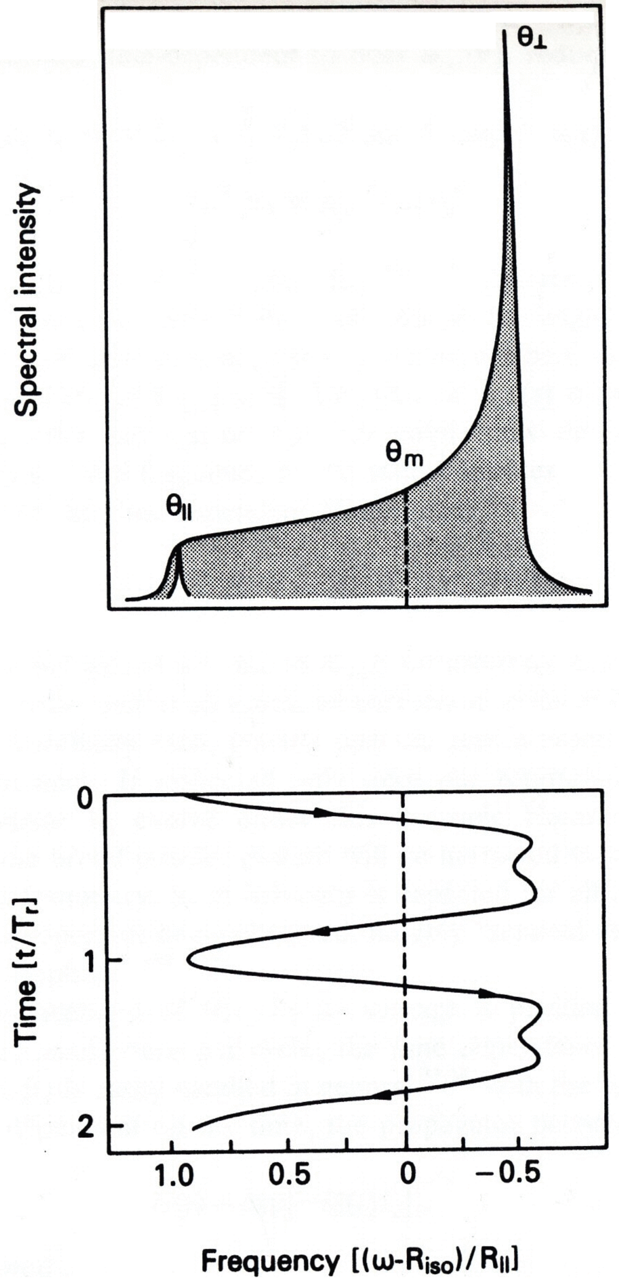
$$\omega_{int}(\theta) = R_{iso} + R_{\parallel}\left(\frac{3\cos^2\theta - 1}{2}\right)$$

$$= R_{iso} + \tfrac{1}{2}R_{\parallel}\,[\sqrt{2}\,\sin 2\beta\,\cos(\alpha - \omega_r t) + \sin^2\beta\,\cos\,2(\alpha - \omega_r t)]$$

This means that $\theta(t)$, $\cos(\theta)$ and $\omega_{int}(\theta)$ are all related non-linearly; there is a periodicity determined by the modulo ω_r, and a second one by $2\omega_r$

A plot of fraction of the rotational cycle, t/T_r, as a function of a dimensionless frequency parameter, $(\omega - R_{iso})/R_{\parallel}$, is shown for a single crystallite of orientation θ

In short, the average orientation dependence of the interaction is given by: $\langle 3\cos^2\theta\text{-}1\rangle = \tfrac{1}{2}(3\cos^2\theta_m\text{-}1)(3\cos^2\beta\text{-}1)$



Multiple rotor cycles

So, the time average for a single cycle is given by:

$H_{\mathrm{int}}(t,\alpha,\beta) = \omega_{\mathrm{int}}(t,\alpha,\beta)\, I_z = R_{\mathrm{iso}}\, I_z$ for any α, β combination

in other words, the system evolves only under the **isotropic Hamiltonian**

What if there are multiple cycles (which is always the case)??
Imagine now that we have time-dependent frequencies, described by a function $\xi(t)$:

$$\xi(t) = \omega(t')dt'$$

Then, over multiple rotor periods, we have a function dependent upon the isotropic parameter, R_{iso}, and a time-dependent anisotropic function:

$$\xi(t,\alpha,\beta) = \frac{R_{\parallel}}{2\omega_r}\left(\sqrt{2}\,\sin 2\beta[\sin\alpha - \sin(\alpha - \omega_r t)]\right.$$
$$\left. + \tfrac{1}{2}\sin^2\beta[\sin 2\alpha - \sin 2(\alpha - \omega_r t)]\right) + R_{\mathrm{iso}}\, t$$

Fast vs. slow spinning

The important portion of the equation is the ratio of the anisotropic term and the rotation frequency, $R_{\|}/\omega_r$:

If $R_{\|}/\omega_r \rightarrow 0$ (i.e., ω_r much larger than $R_{\|}$, infinitely fast spinning)
- We get a single isotropic peak, and the anisotropic term disappears

If $R_{\|}/\omega_r \rightarrow \infty$ (i.e., ω_r much smaller than $R_{\|}$, sample not rotating)
- We get the "static" powder pattern pictured on the previous page

If $R_{\|} \approx \omega_r$ (this is the most common case!)
- The basic pattern is repeated in each revolution of the rotor

$$\langle I_+(t,\alpha,\beta)\rangle = \int \exp[-i\xi(t,\alpha,\beta)]$$

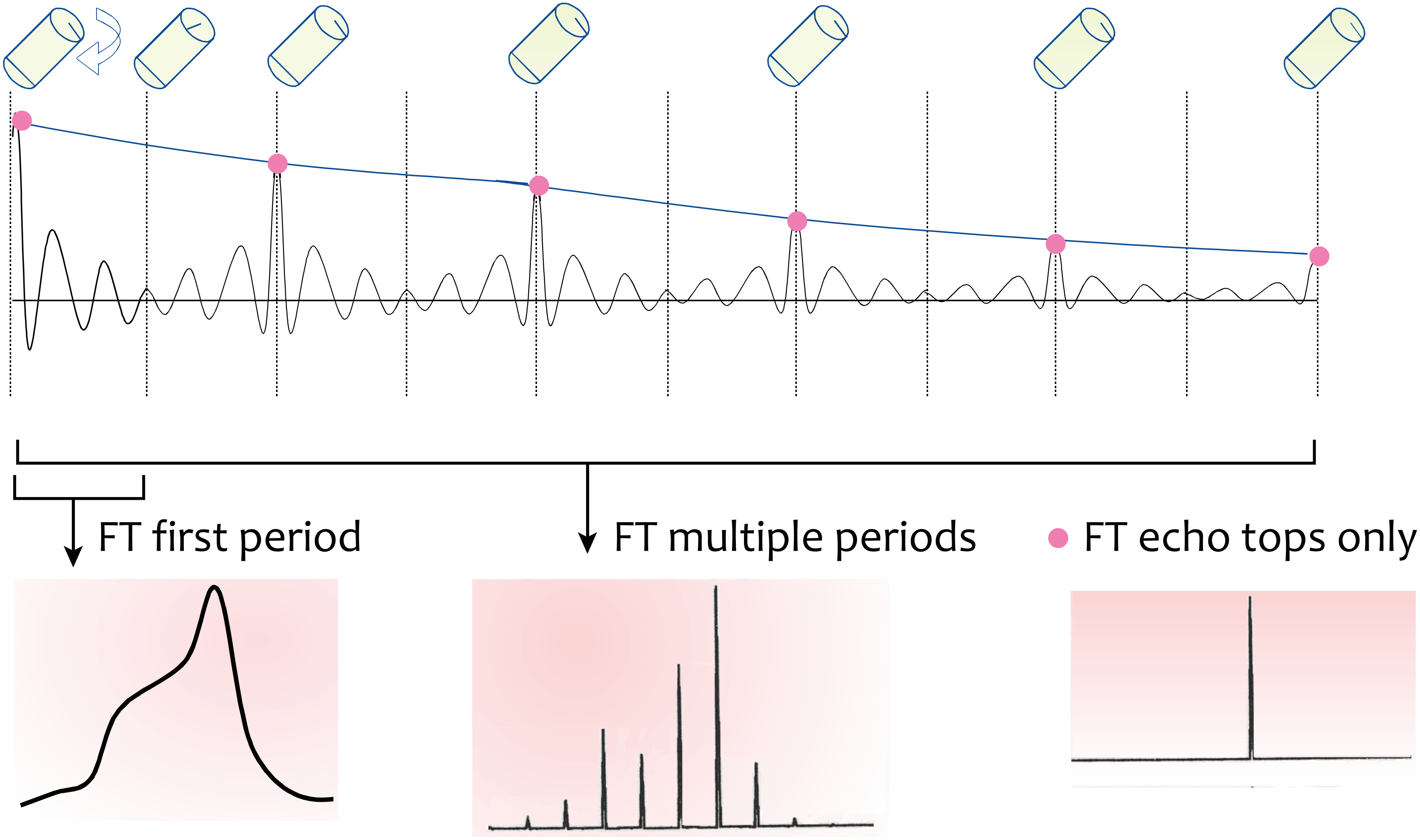
In other words, the $\omega_{\text{int}}(t,\alpha,\beta)$ and FID (free induction decay) are affected: **rotational echoes** appear in the FID (in the time domain).

This means that the FT of the FID will yield a frequency pattern:

- centred at $\omega = R_{\text{iso}}$ (irregardless of spinning speed)
- composed of **spinning sidebands** at multiples of ω_r from the centreband
- intensities of all peaks depend on $R_{\|}$, ω_r, α and β

Rotational Echoes

Refocusing of the magnetization occurs each time the rotor completes a cycle (and the crystallites return to their initial positions). In the FID, this leads to the formation of **rotational echoes**.



FT first period

FT multiple periods

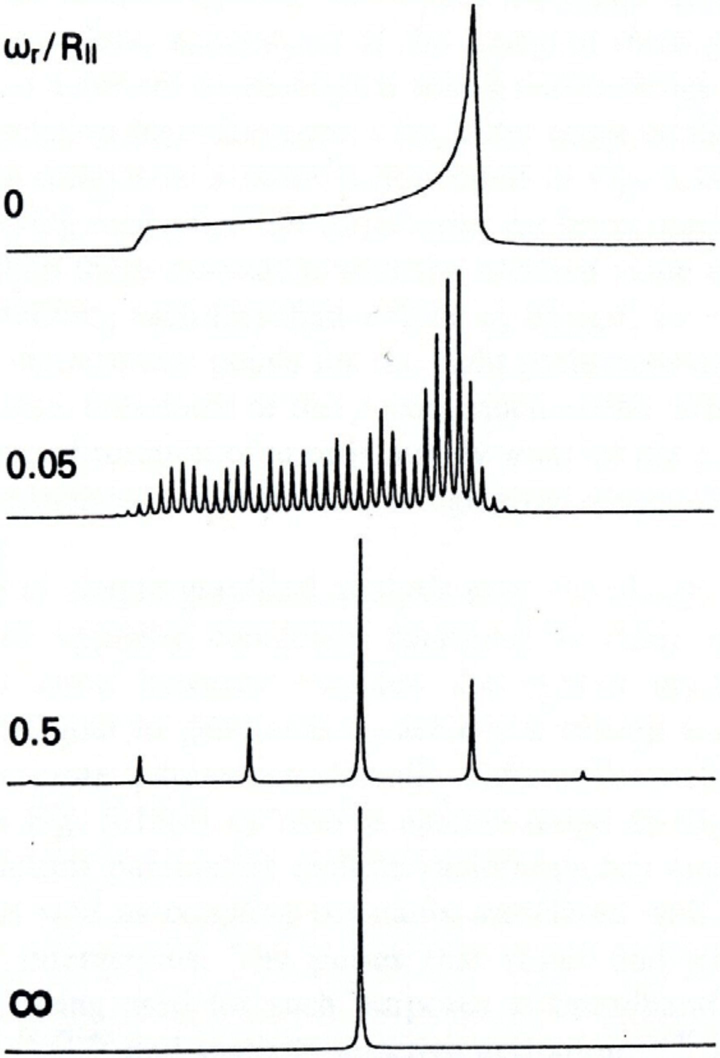
● FT echo tops only

Spinning sidebands

Consider these CSA patterns:

- The isotropic centreband always remains in the same position, and indicates the same isotropic shift as in solution.
- At slower spinning rates, many ssbs can be seen - they are actually useful, in that they may be analyzed to obtain the CSA
- At infinite spinning speeds (or when $R_{\|}/\omega_r \rightarrow 0$), all of the ssbs disappear, and only the isotropic centreband remains

Most importantly:
MAS gives a huge boost in **signal-to-noise**, since the *integrated signal intensity* is the same in all of these spectra

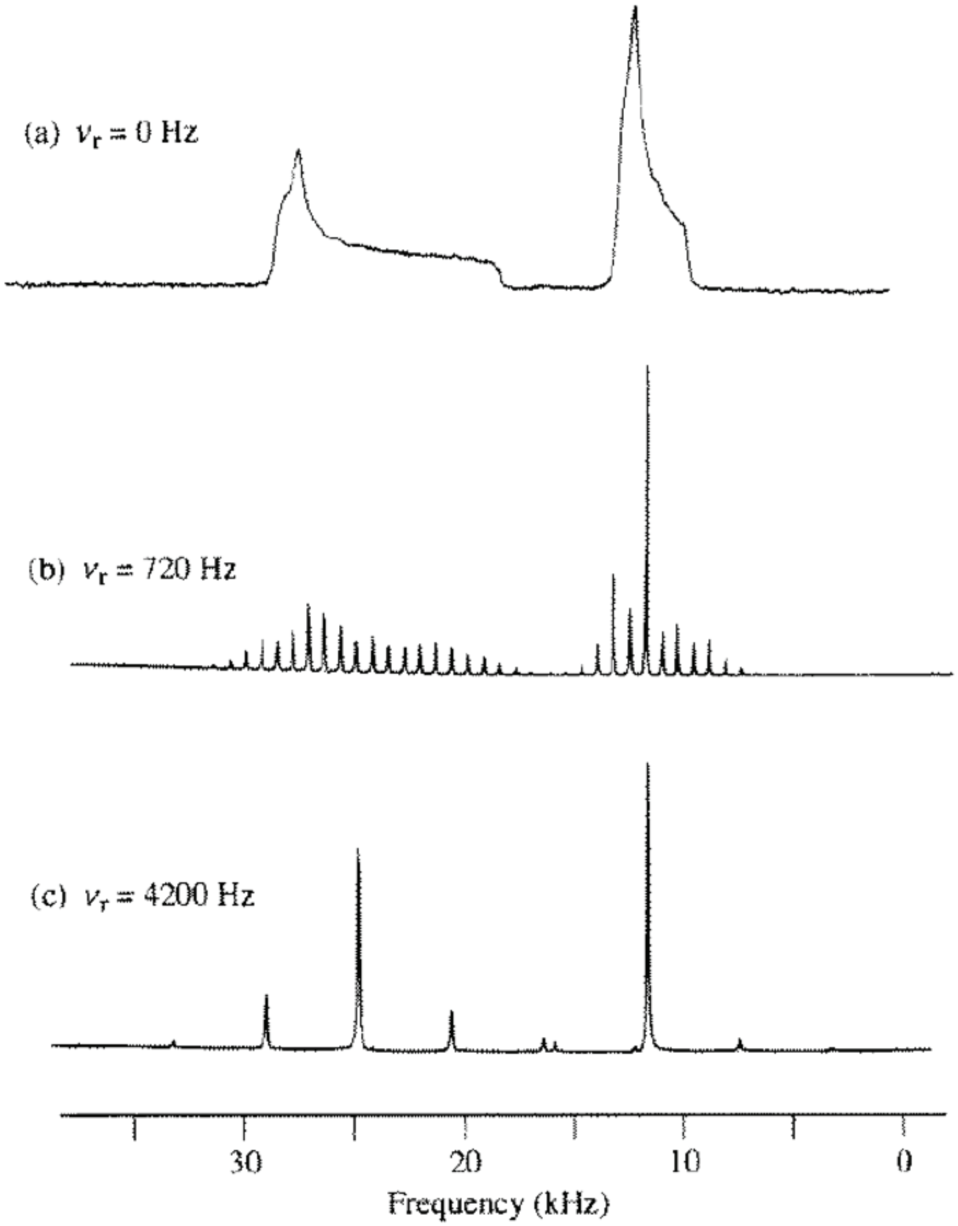


Sideband patterns over the full range of rotational rates

Example of ^{13}C MAS NMR Spectra

Pictured to the right are ^{13}C (a) static and (b,c) MAS NMR of zinc acetate, which has CO_2^- and CH_3 resonances.

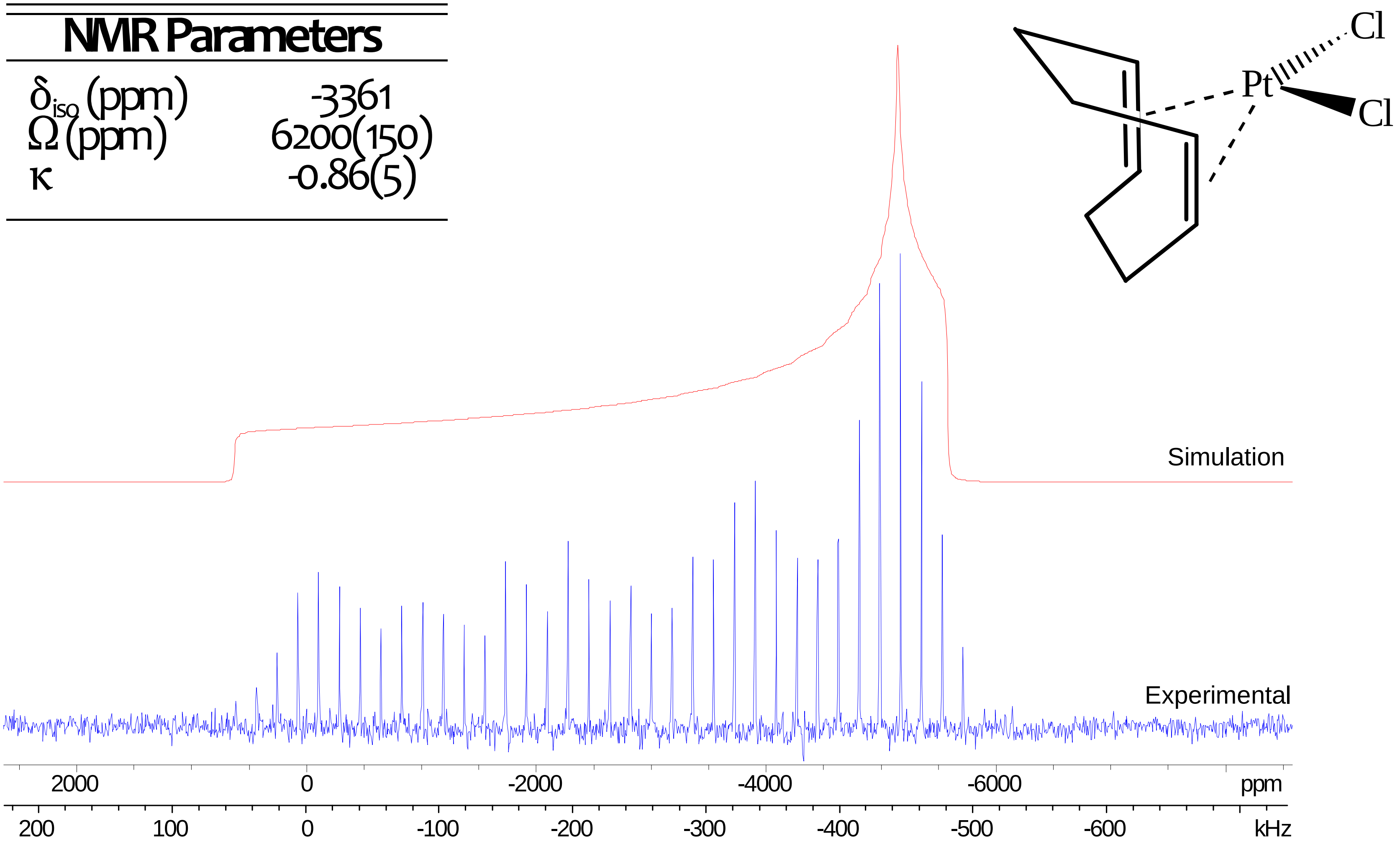
Note that at moderate MAS speeds (i.e., around 5 kHz or higher) it is possible to attentuate most SSBs in general ^{13}C NMR spectra.



Example of ^{195}Pt MAS NMR Spectrum

On the other hand, heavy metals nuclides like ^{195}Pt have enormous CSAs, and patterns can span hundreds of kHz to several MHz:

NMR Parameters	
δ_{iso} (ppm)	-3361
Ω (ppm)	6200(150)
κ	-0.86(5)

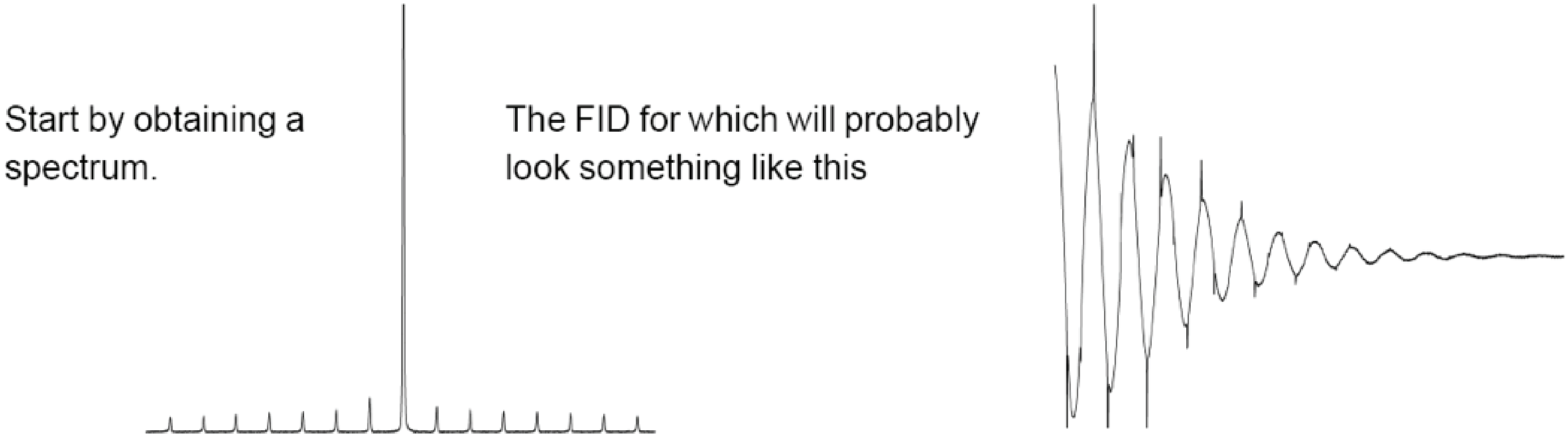


Setting the Magic Angle, 1

Setting the magic angle in crucial for obtaining high-resolution SSNMR spectra. If improperly set, lines can be broad or split, and you lose both resolution and signal to noise!

Running ^{79}Br NMR of KBr can be useful for setting the magic angle:

1. Run a test spectrum



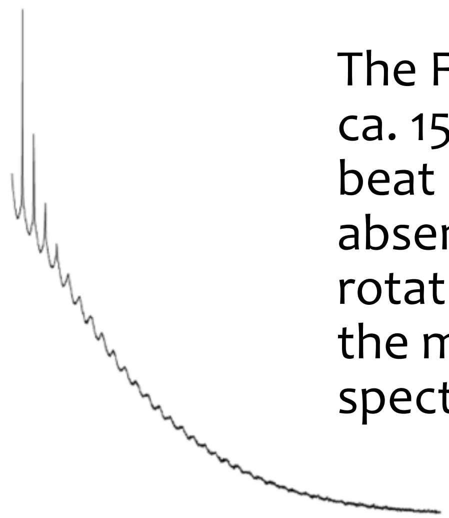
Start by obtaining a spectrum.

The FID for which will probably look something like this

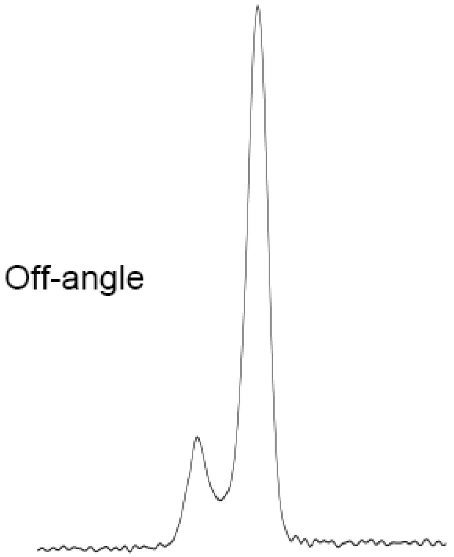
Ideally, you would like to position the transmitter frequency dead centre on the isotropic centreband.

Setting the Magic Angle, 2

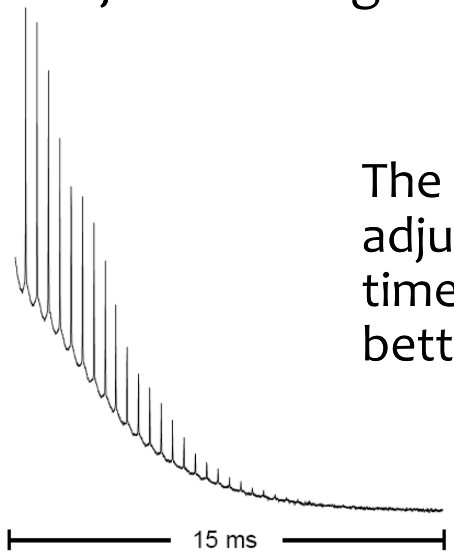
2. Set the transmitter on-resonance, and run it again!



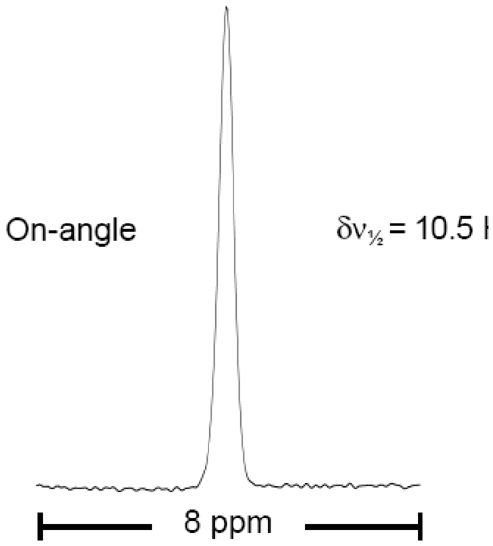
The FID on the right covers a time period of ca. 15 ms. Since you are on-resonance, the beat pattern from being off resonance is absent, and only a clear decay topped by rotational echoes is observed. In this case, the magic angle is slightly off. FT leads to a spectrum which clearly indicates the misset.



3. Adjust the angle and reacquire!

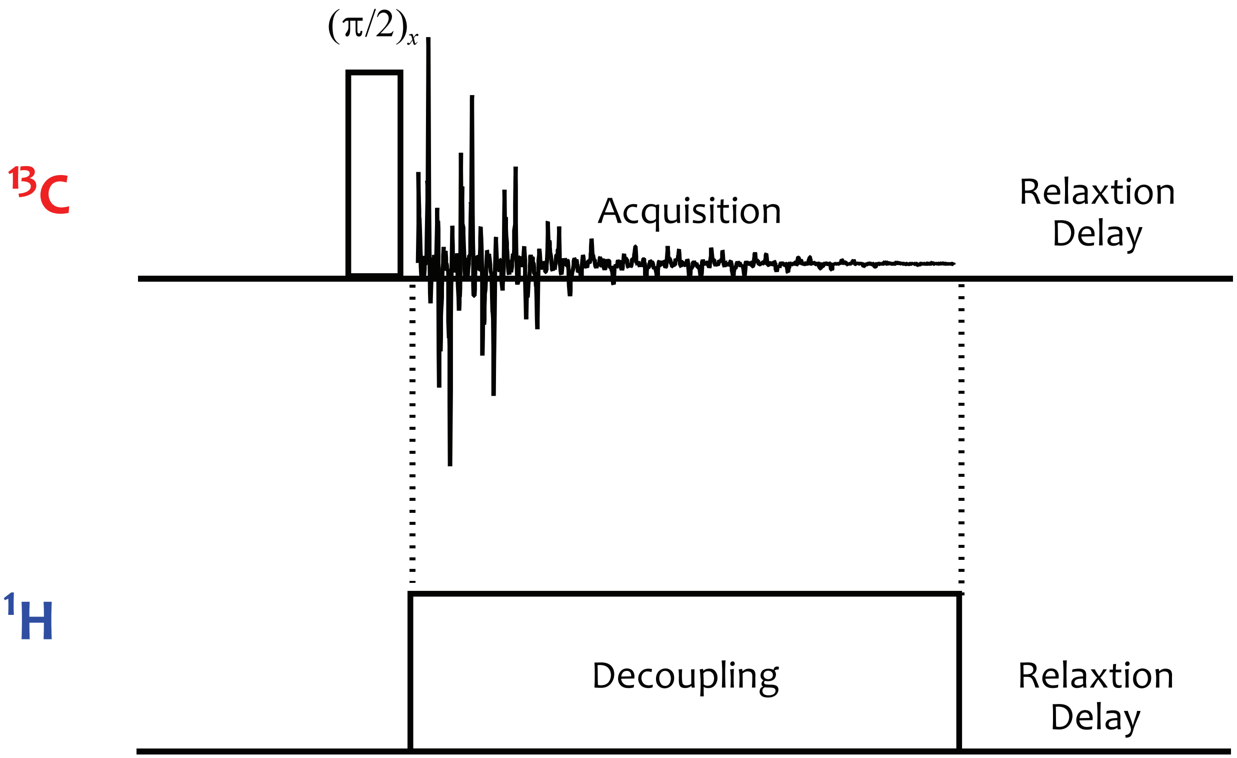


The rotational echoes increase in intensity; adjust until the echoes stretch out as far in time as possible (the more intensity, the better). FT leads to a nice sharp line!



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.

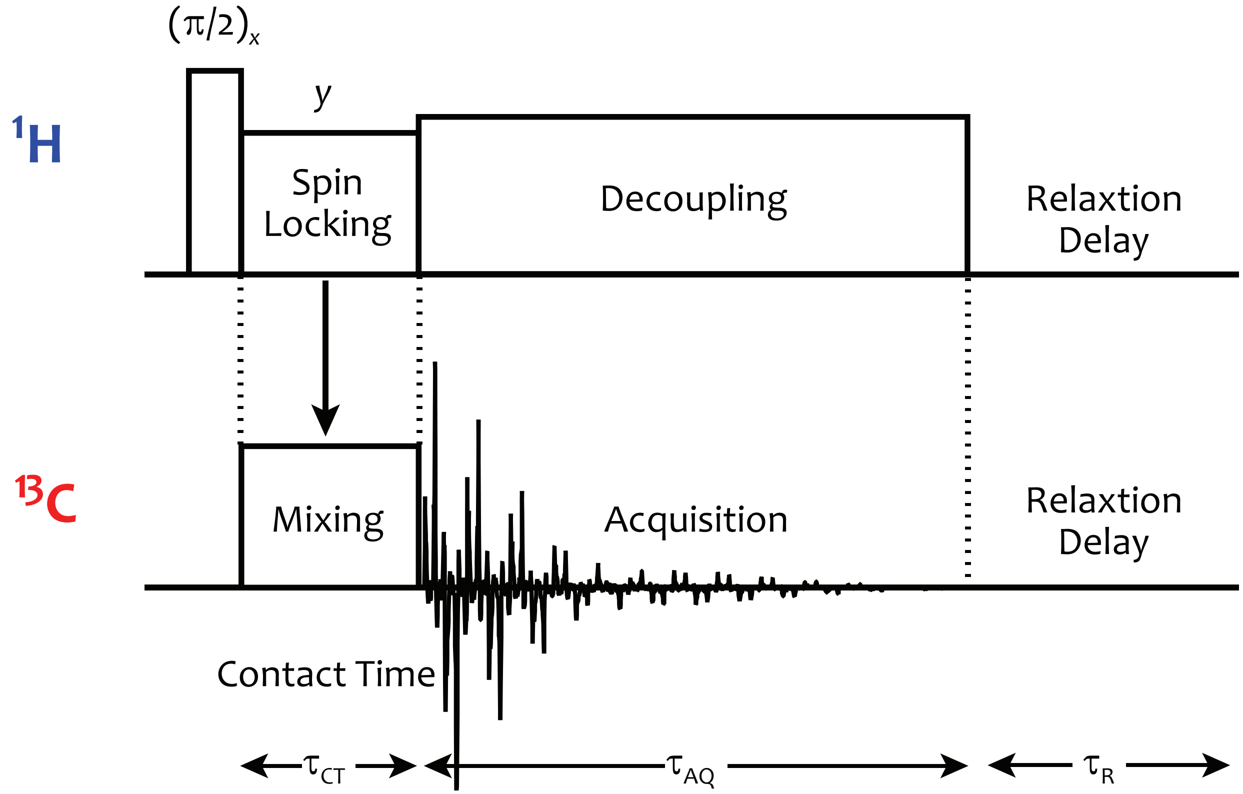


Typically, for organic molecules, this experiment is accompanied by **high-power proton decoupling** in order to resolve sharp ^{13}C resonances, and to eliminate dipolar and *J*-couplings between ^{13}C and ^{1}H.

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

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., ^{1}H) to **dilute spins** (e.g., ^{13}C) which are **dipolar coupled**.



Advantages:

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

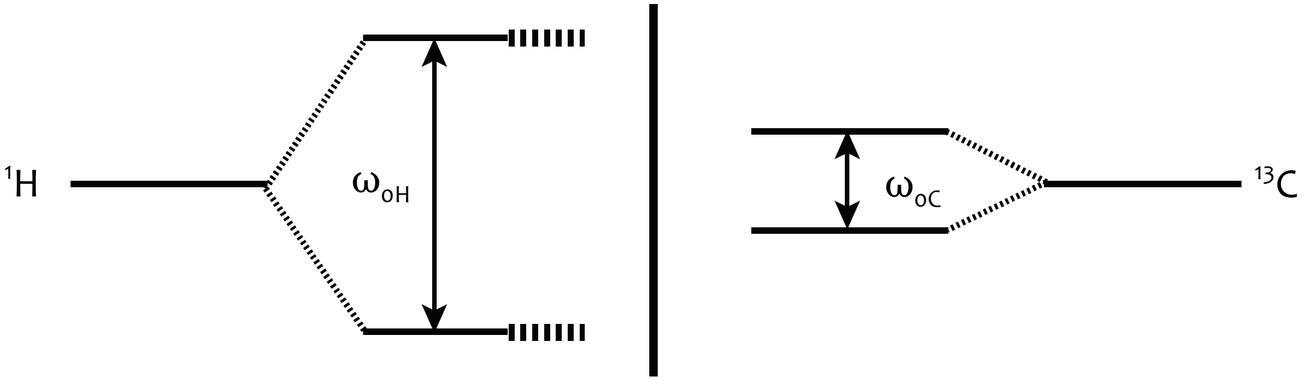
Hartmann-Hahn Matching

In order for CP to work, it is necessary to tune the B_1 fields for the ^{1}H and ^{13}C nuclei. The best way to picture this is as two separate rotating frames, each nutating at distinct frequencies, $\omega_1(^{13}\mathrm{C})$ and $\omega_1(^{1}\mathrm{H})$, that must be matched:

$$\omega_1(^{13}\mathrm{C}) = \gamma(^{13}\mathrm{C})B_1(^{13}\mathrm{C}) = \omega_1(^{1}\mathrm{H}) = \gamma(^{1}\mathrm{H})B_1(^{1}\mathrm{H})$$

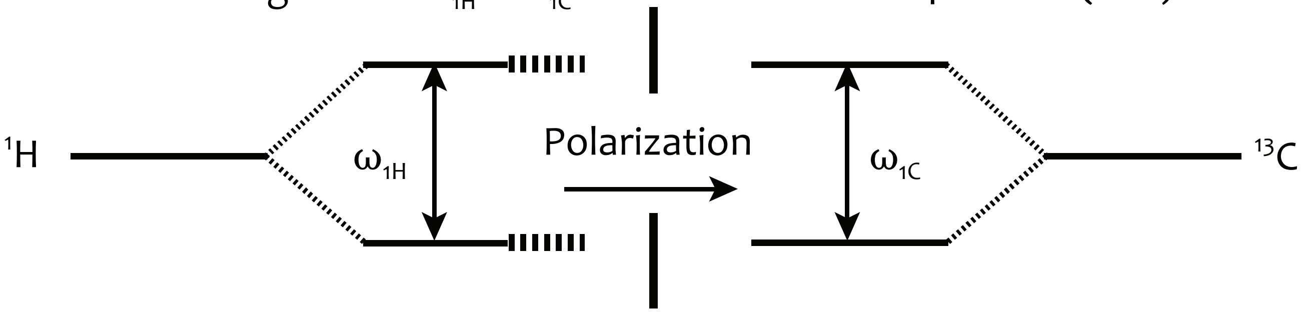
Lab frame: $\omega_{oH} > \omega_{oC}$

Extremely different frequencies (MHz)



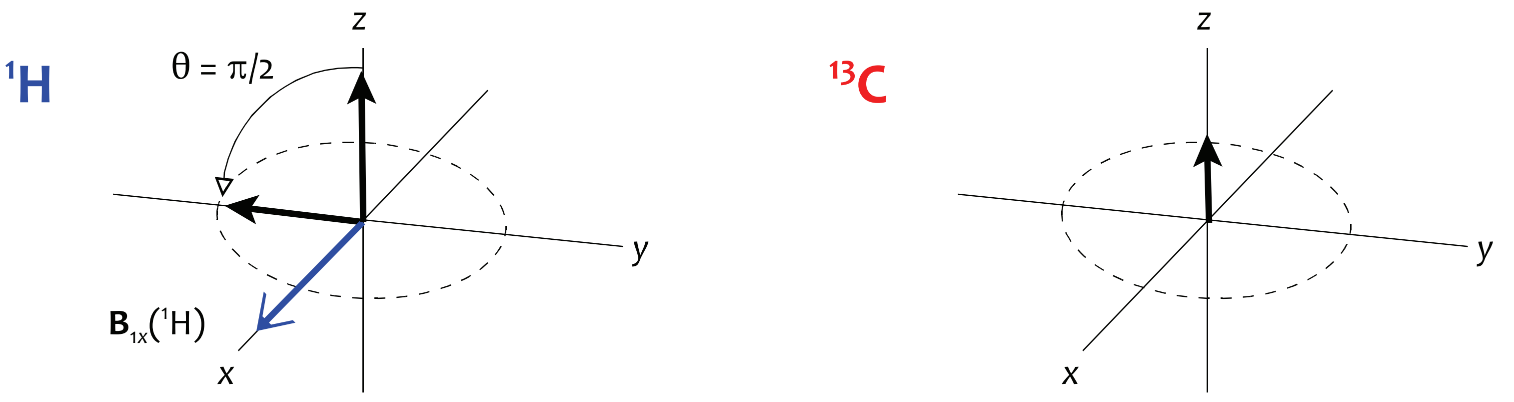
Rf rotating frame: $\omega_{1H} \simeq \omega_{1C}$

Matched frequencies (kHz)

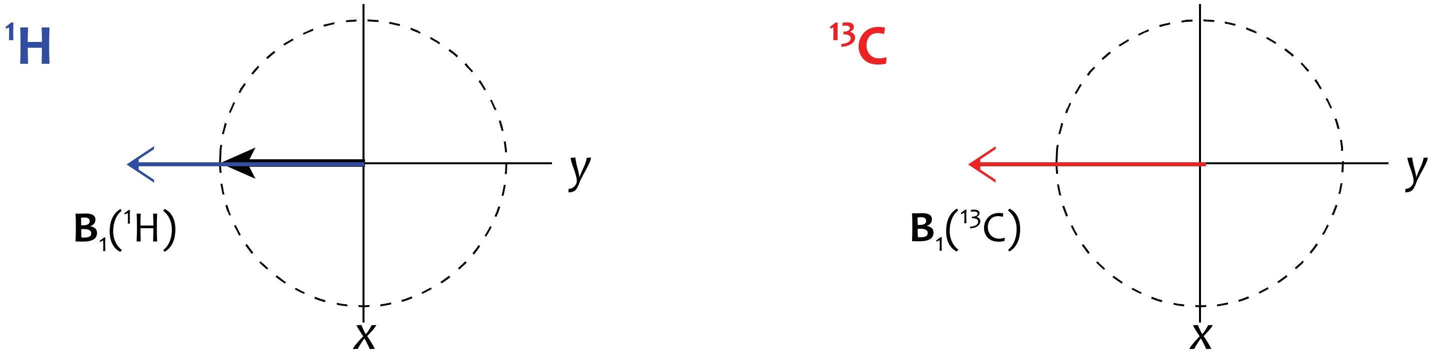


How CP Works

1. First, make a $\pi/2(^1H)$ pulse to get things started. Nothing is initially done on the ^{13}C channel.

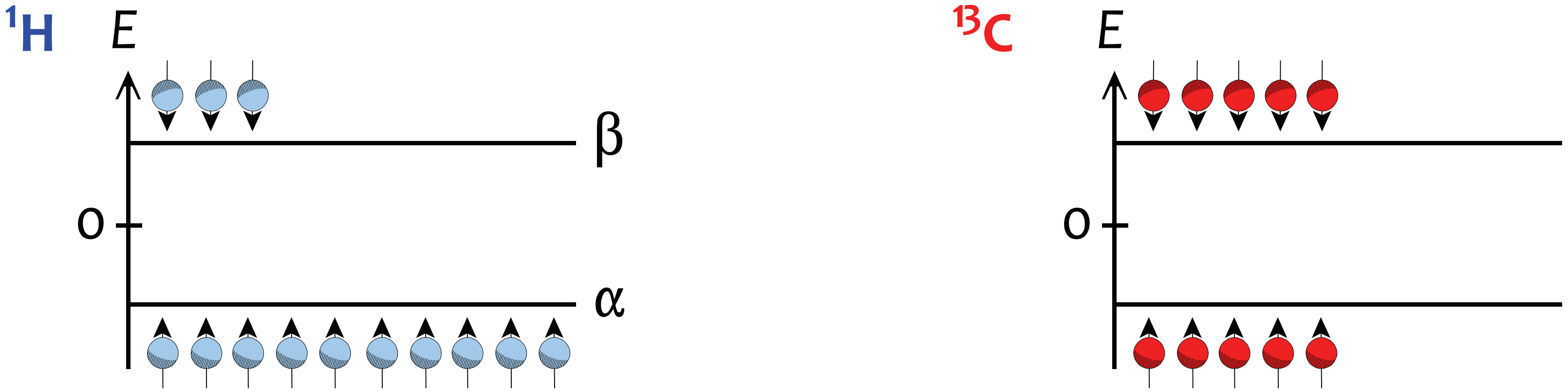


2. Now, let's look at the *xy*-plane in each of the rotating frames. We will apply B_1 fields known as **spin-locking fields** along with -*y* axis. In addition, we insure that they have the same nutation frequencies (this means that the frames rotate at the same frequencies)



How CP Works, 2

3. Think about the difference between these frames. The ^{1}H frame has a small B_1 field, but a massive magnetization created by B_0 precessing about the *y* axis. The ^{13}C frame has no magnetization at all along the *y* axis.



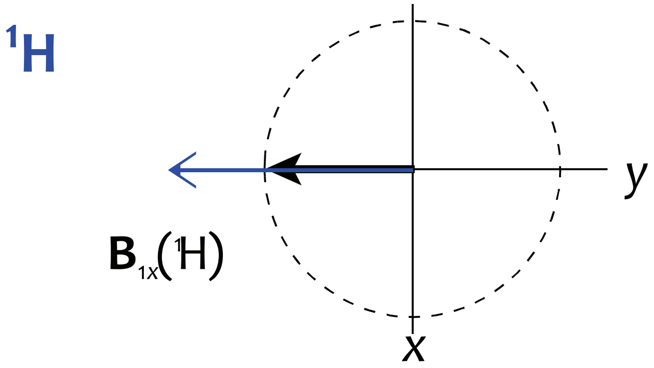
$$\frac{N_\beta}{N_\alpha} = \frac{e^{-E_\beta/kT}}{e^{-E_\alpha/kT}} = e^{-(E_\beta - E_\alpha)/kT}$$

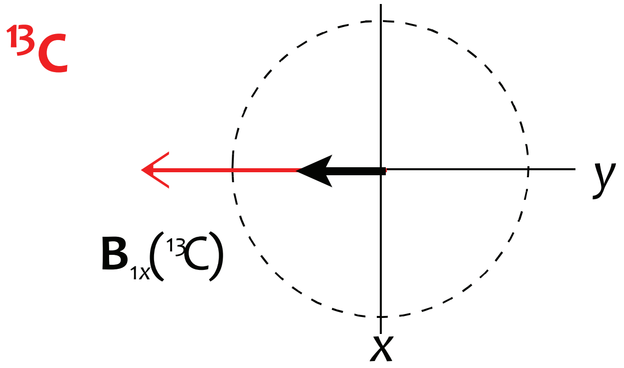
$$= e^{\hbar\omega_0/kT} \approx 1 + \frac{\hbar\omega_0}{kT}$$

According to the *Boltzmann distribution*, which tells us about the populations of these levels, the **spin temperature** of ^{1}H along the *y* axis is **very cold** (big population difference, low temperature), and that of ^{13}C is **very hot** (no population difference, high temperature)

How CP Works, 3

4. If the Hartmann-Hahn match is in place, the frames have very similar energies, but very different temperatures. They are said to be in **thermal contact** with one another. Hence, polarization is transferred from the abundant protons to the dilute ^{13}C nuclei as long as the **spin locking fields** are left on. This is known as the **contact time** (usually milliseconds). ^{13}C polarization builds along the -*y* axis.



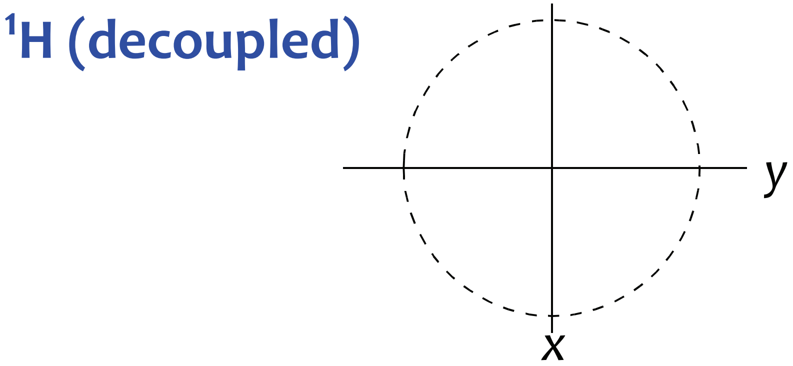


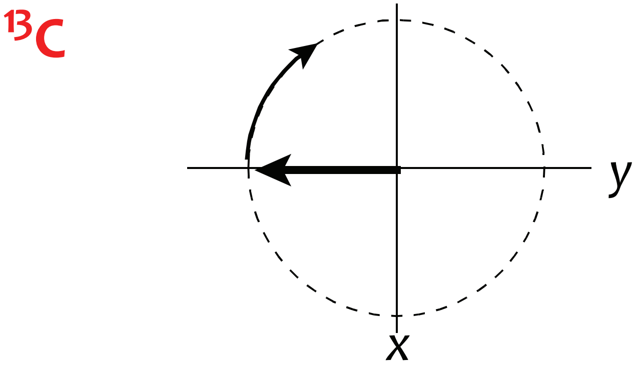
The best contact time for achieving optimum transfer of polarization is highly dependent upon the relaxation characteristics of the ^{1}H and ^{13}C nuclei; notably, cross relaxation can influence the setting of this time period.

In addition: the ^{1}H and ^{13}C nuclei must be **dipolar coupled** to one another for CP to work; otherwise, thermal contact between these frames cannot be established.

How CP Works, 4

5. Finally, the spin locking fields are shut off, and the receiver is opened on the ^{13}C channel. Normally, one applies **high power ^{1}H decoupling** to ensure that the ^{13}C NMR spectrum is sharp and of high S/N!



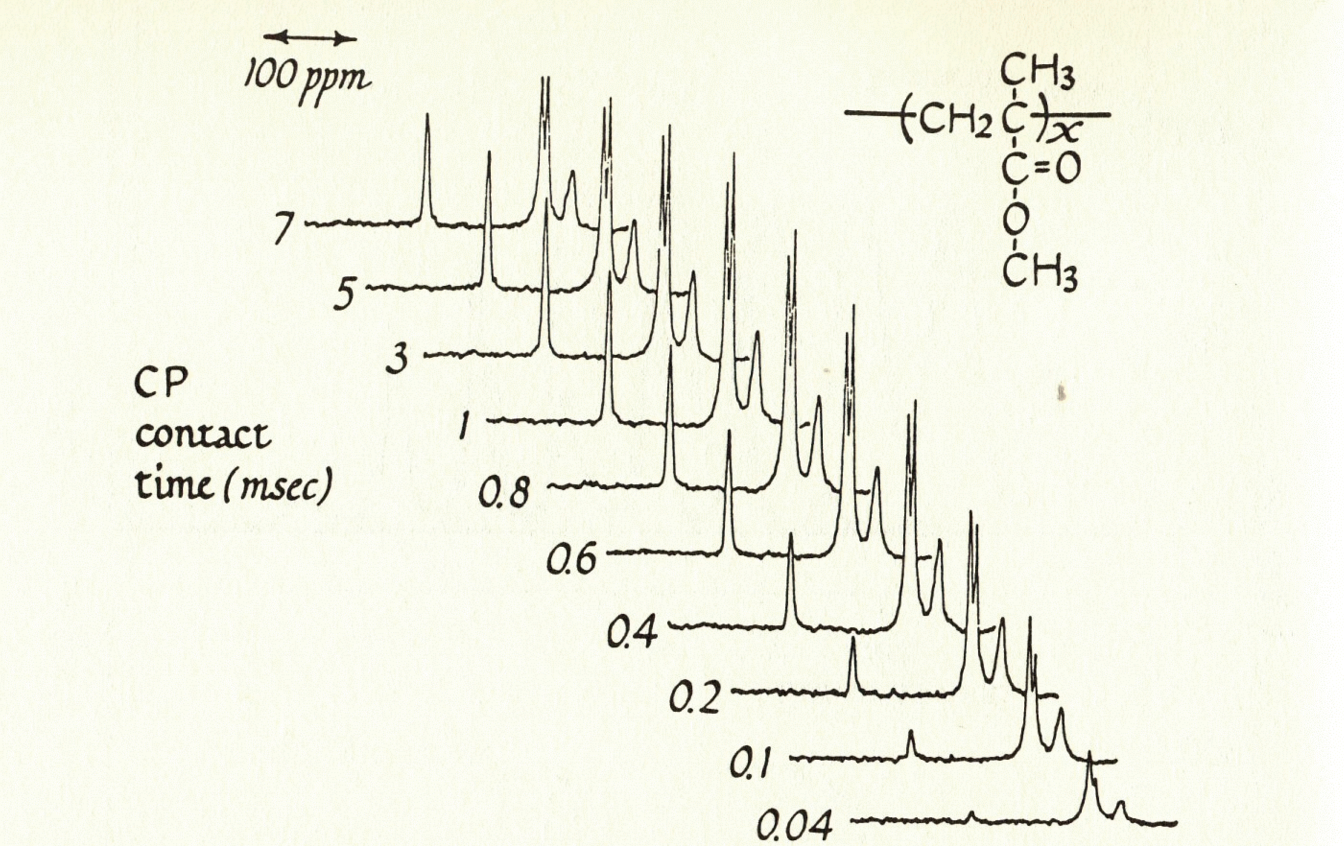


6. One must wait for the ^{1}H magnetization to recover to thermal equilibrium before starting the sequence again - this is the **relaxation delay**. For common organic molecules with at least one methyl group, the RD is ca. 4 to 6 seconds long.

Compare this to some ^{13}C RDs, which may be many seconds to minutes in length. The situation for heavy metals can be even worse: some have RDs on the order of hours or days!

Variable Contact Time Experiments

Different structural motifs for carbon have distinct responses to variation in contact times - which can be very useful for structural assignment, but challenging for quantitation via CP/MAS.



The CO resonance (leftmost) builds up more slowly (wrt CT) than the protonated carbons; the proximity of protons in the latter case facilitates efficient polarization transfer compared to the unprotonated CO carbon.

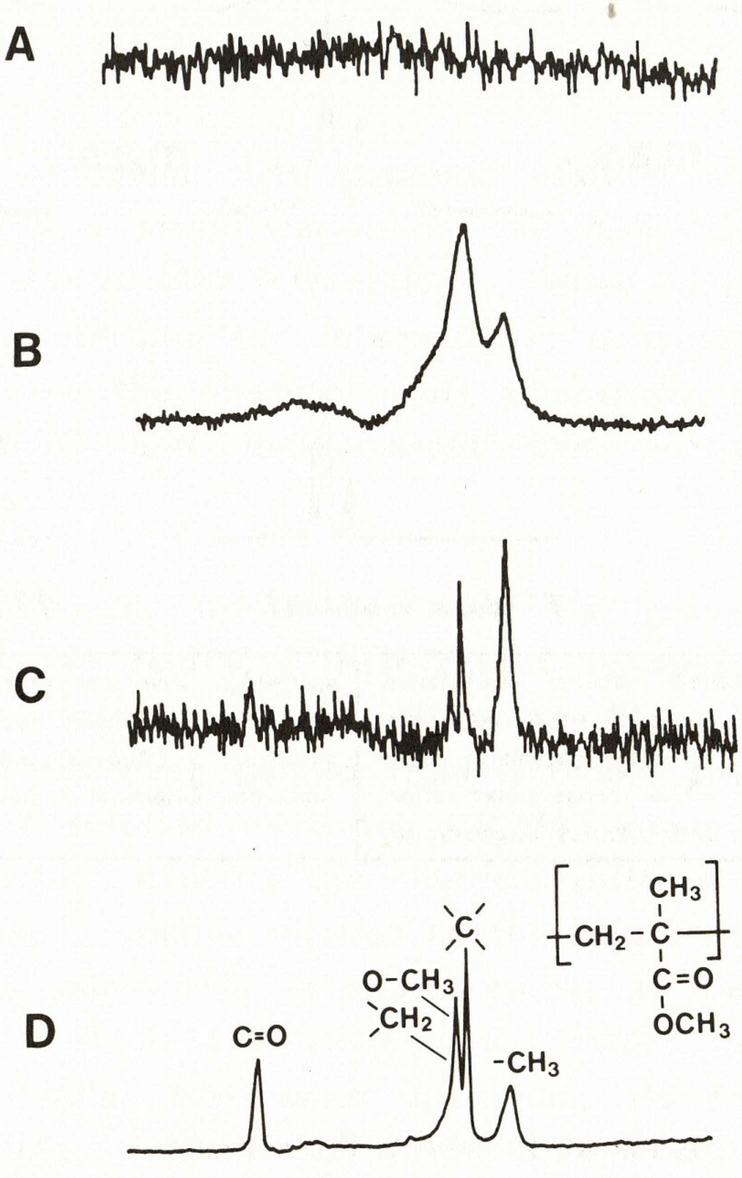
^{13}C SSNMR of poly(methylmethacrylate)

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



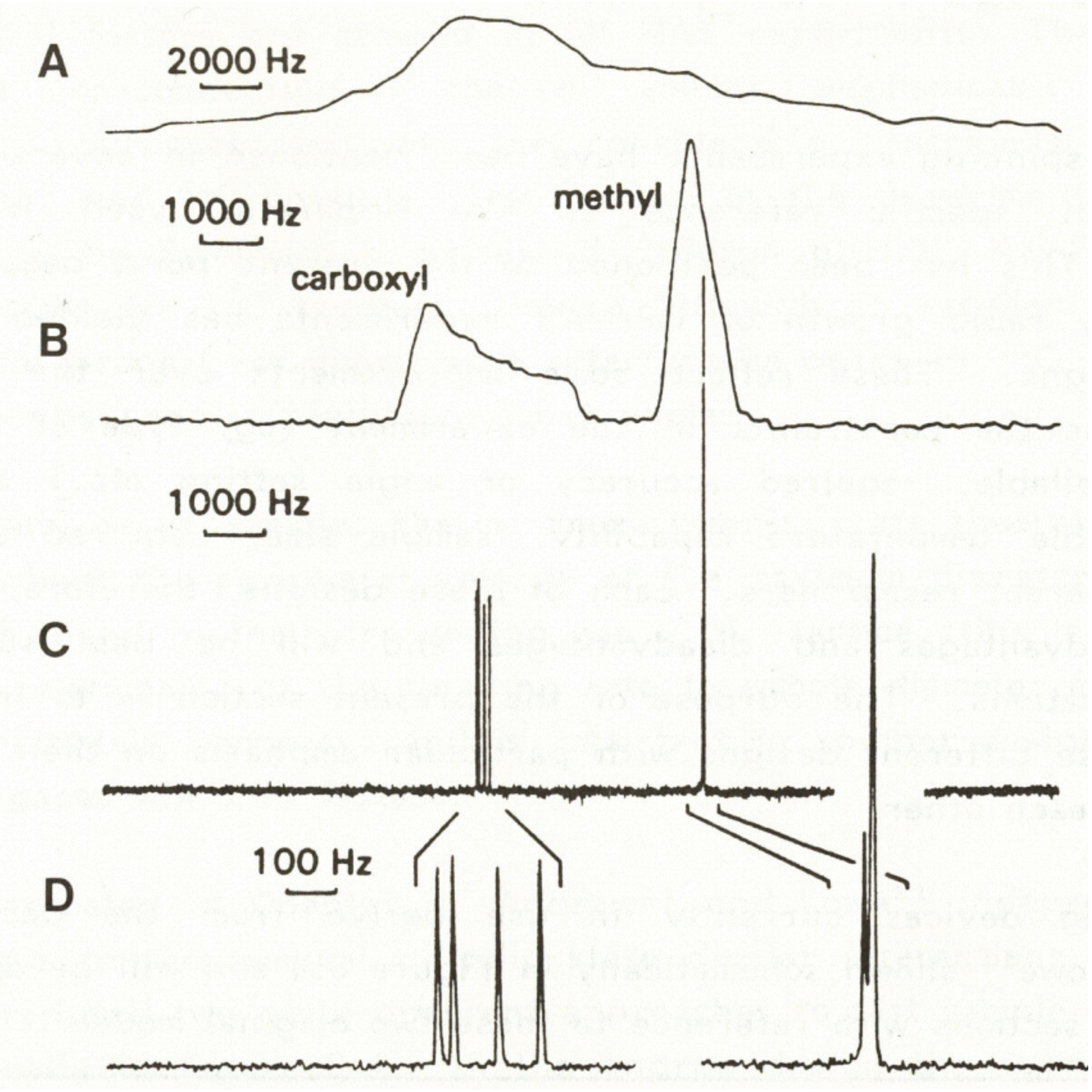
^{13}C SSNMR of calcium acetate hemihydrate

A: Static
No ^{1}H decoupling

B: Static
High-power decoupling

C: MAS
High-power decoupling

D: Different sites observed resulting from crystallographically inequivalent sites: $2Ca(CH_3COO)_2 \cdot H_2O$



Conclusions

We have just scratched the surface of what solid-state NMR is capable of doing....

You can put almost anything solid (or even semi-solid) inside of an NMR spectrometer's superconducting magnet

You can access most of the elements in the periodic table

You can measure internuclear distances, with greater precision than X-ray diffraction in many instances

You can investigate structure and dynamics in small molecules, alloys, tissues, membranes, proteins, polymers, chunks of wood or ice, minerals, semiconductors, pharmaceuticals, inorganic complexes, catalysts, porous solids, amorphous solids, glasses, etc. etc. etc.