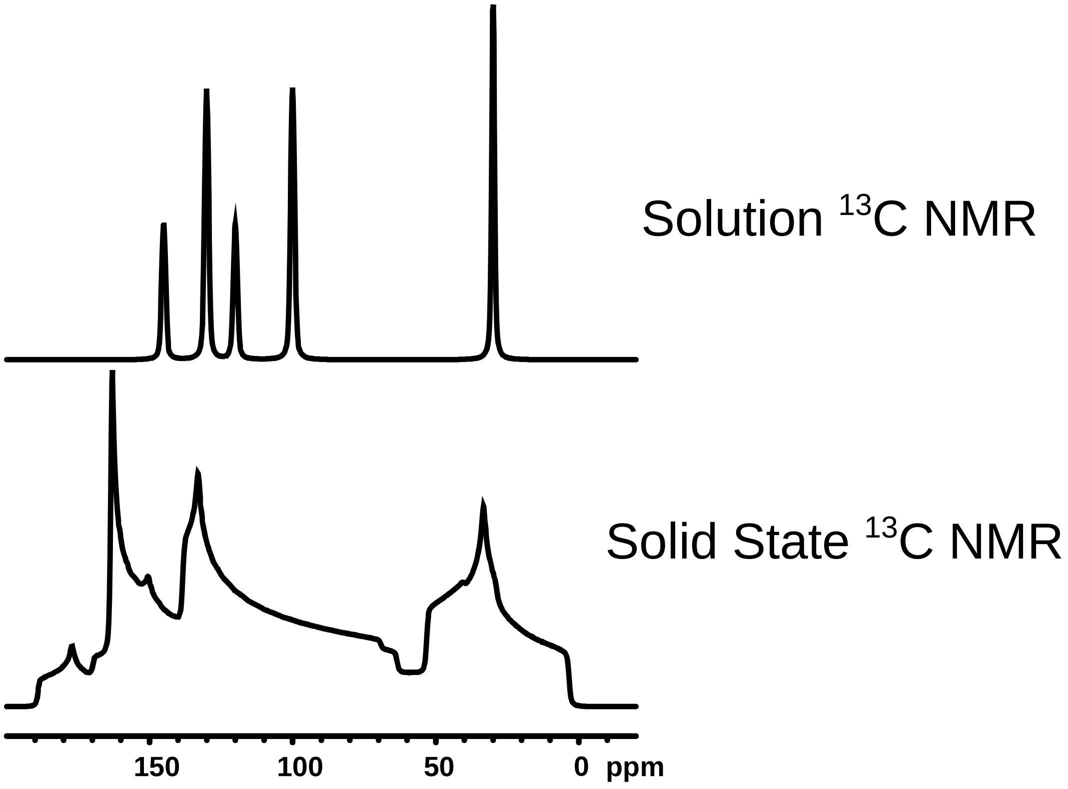
Introduction to Solid State NMR

In solution NMR, spectra consist of a series of very sharp transitions, due to averaging of **anisotropic NMR interactions** by rapid random tumbling.

By contrast, solid-state NMR spectra are very broad, as the full effects of anisotropic or **orientation-dependent** interactions are observed in the spectrum.

High-resolution NMR spectra can provide the same type of information that is available from corresponding solution NMR spectra, but a number of special techniques/equipment are needed, including magic-angle spinning, cross polarization, special 2D experiments, enhanced probe electronics, etc.

The presence of broad NMR lineshapes, once thought to be a hindrance, actually provides much information on chemistry, structure and dynamics in the solid state.

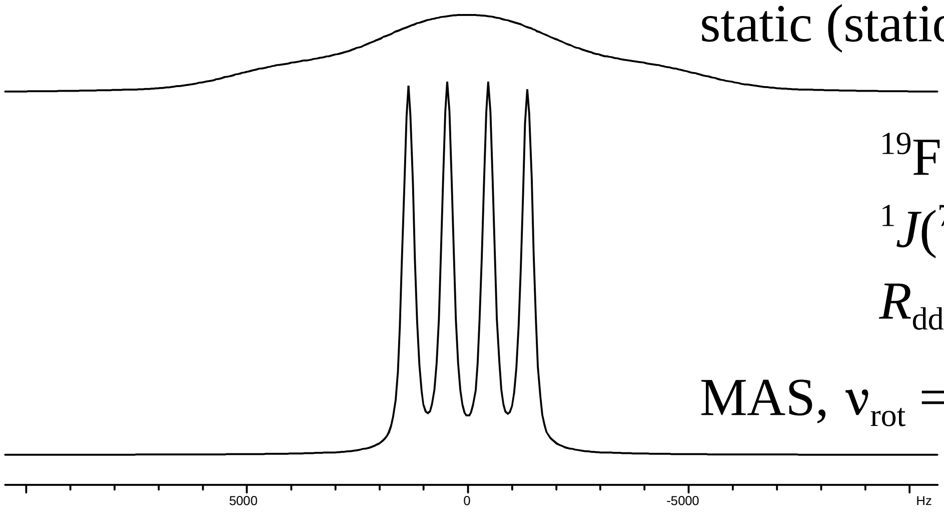


Origins of Solid-State NMR

Original NMR experiments focused on ^{1}H and ^{19}F NMR, for reasons of sensitivity. However, anisotropies in the local fields of the protons broadened the ^{1}H NMR spectra such that no spectral lines could be resolved. The only cases where useful spectra could be obtained was for isolated homonuclear spin pairs (e.g., in H_2O), or for fast moving methyl groups.

Much of the original solid state NMR in the literature focuses only upon the measurement of ^{1}H spin-lattice relaxation times as a function of temperature in order to investigate methyl group rotations or motion in solid polymer chains.

The situation changed when it was shown by E.R. Andrew and I.J. Lowe that anisotropic dipolar interactions could be supressed by introducing artificial motions on the solid - this technique involved rotating the sample about an axis oriented at 54.74° with respect to the external magnetic field. This became known as **magic-angle spinning** (**MAS**).



static (stationary sample)

^{19}F NMR of $KAsF_6$

$^1J(^{75}As,^{19}F) = 905$ Hz

$R_{dd}(^{75}As,^{19}F) = 2228$ Hz

MAS, $\nu_{rot} = 5.5$ kHz

In order for the MAS method to be successful, spinning has to occur at a rate equal to or greater than the dipolar linewidth (which can be many kHz wide). On older NMR probe designs, it was not possible to spin with any stability over 1 kHz!

High-Resolution Solid-State NMR

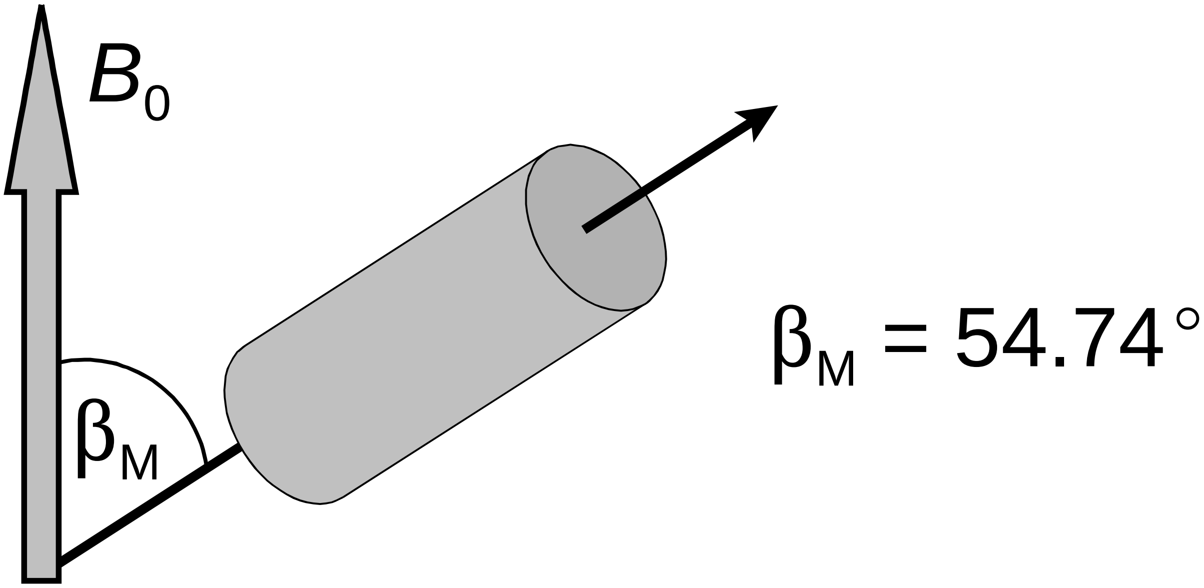
A number of methods have been developed and considered in order to minimize large anisotropic NMR interactions between nuclei and increase S/N in rare spin (e.g., ^{13}C, ^{15}N) NMR spectra:

- **Magic-angle spinning**: rapidly spinning the sample at the magic angle w.r.t. B_0, still of limited use for "high-gamma" nuclei like protons and fluorine, which can have dipolar couplings in excess of 100 kHz (at this time, standard MAS probes spin from 7 to 35 kHz, with some exceptions)
- **Dilution**: This occurs naturally for many nuclei in the periodic table, as the NMR active isotope may have a low natural abundance (e.g., ^{13}C, 1.108% n.a.), and the dipolar interactions scales with r^{-3}. However, this only leads to "high-resolution" spectra if there are no heteronuclear dipolar interactions (i.e., with protons, fluorine)!Also, large anisotropic chemical shielding effects can also severely broaden the spectra!
- **Multiple-Pulse Sequences**: Pulse sequences can impose artifical motion on the spin operators (leaving the spatial operators, *vide infra*) intact. Multipulse sequences are used for both heteronuclear (very commong) and homonuclear (less common) decoupling -^{1}H NMR spectra are still difficult to acquire, and use very complex, electronically demanding pulse sequences such as CRAMPS (combined rotation and multiple pulse spectroscopy). Important 2D NMR experiments as well!
- **Cross Polarization**: When combined with MAS, polarization from abundant nuclei like ^{1}H, ^{19}F and ^{31}P can be transferred to dilute or rare nuclei like ^{13}C, ^{15}N, ^{29}Si in order to enhance signal to noise and reduc waiting time between successive experiments.

Magic-Angle Spinning

Notice that the dipolar and chemical shielding interactions both contain ($3\cos^2\theta-1$) terms. In solution, rapid isotropic tumbling averages this spatial component to zero (integrate over $\sin\theta d\theta$).

Magic-angle spinning introduces artificial motion by placing the axis of the sample **rotor** at the magic angle (54.74°) with respect to $\mathbf{B}_0$ - the term $3\cos^2\theta - 1 = 0$ when $\theta = 54.74°$. The rate of MAS must be greater than or equal to the magnitude of the anisotropic interaction to average it to zero.



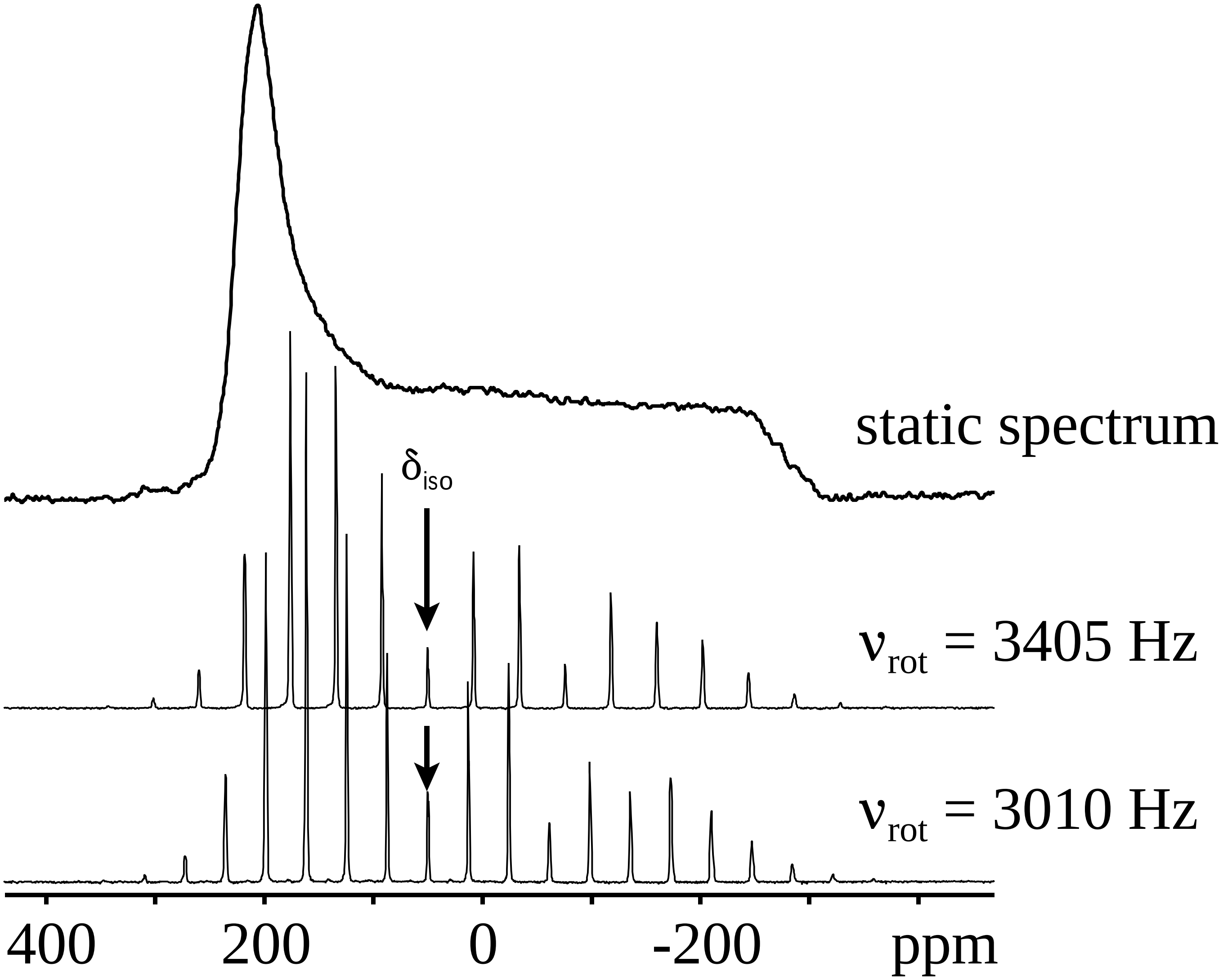
Samples are finely powdered and packed tightly into rotors, which are then spun at rates from 1 to 35 kHz, depending on the rotor size and type of experiment being conducted.

If the sample is spun at a rate less than the magnitude of the anisotropic interaction, a manifold of spinning sidebands becomes visible, which are separated by the rate of spinning (in Hz).

Magic-Angle Spinning

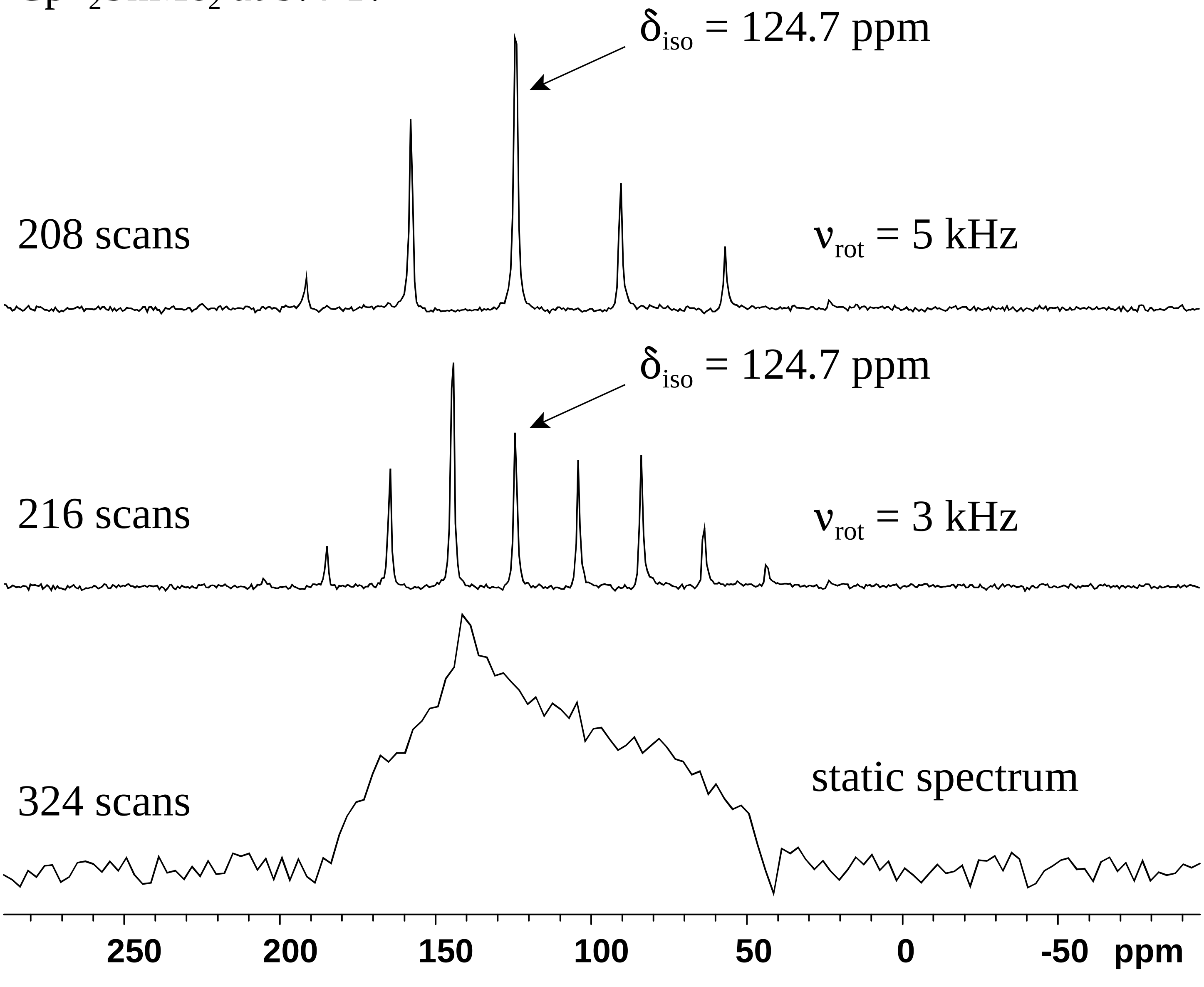
Here is an example of MAS applied in a ^{31}P CPMAS NMR experiment:

The span of this spectrum is $\Omega \approx 500$ ppm, corresponding to a breadth of about 40000 Hz (^{31}P at 4.7 T). The isotropic centreband can be identified since it remains in the same position at different spinning rates.



Magic-Angle Spinning

Here is an example of a ^{119}Sn CPMAS NMR spectrum of $Cp^*_2SnMe_2$ at 9.4 T:



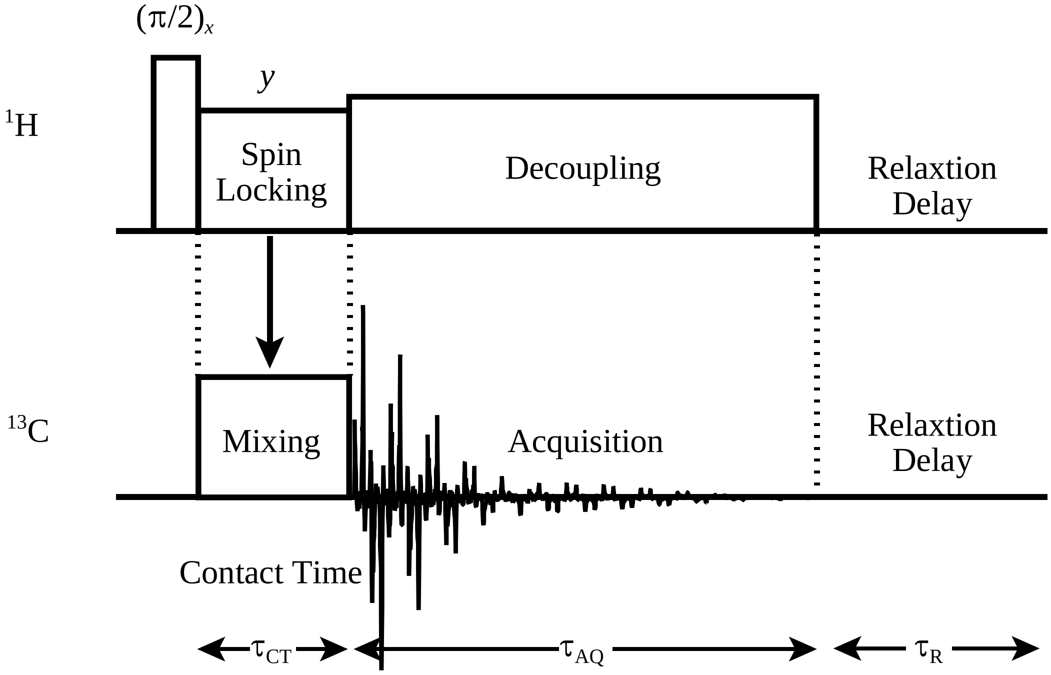
Even with MAS slower than the breadth of the anisotropic interaction, signal becomes localized under the spinning sidebands, rather than spread over the entire breadth as in the case of the static NMR spectrum. Notice the excellent signal to noise in the MAS spectra, and poor signal to noise in the static spectrum, despite the increased number of scans.

Cross Polarization

Cross polarization is one of the most important techniques in solid state NMR. In this technique, polarization from abundant spins such as ^{1}H or ^{19}F is transferred to dilute spins such as ^{13}C or ^{15}N. The overall effect is to enhance S/N:

1. Cross polarization enhances signal from dilute spins potentially by a factor of γ_I/γ_S, where *I* is the abundant spin and *S* is the dilute spin.
2. Since abundant spins are strongly dipolar coupled, they are therefore subject to large fluctuating magnetic fields resulting from motion. This induces rapid spin-lattice relaxation at the abundant nuclei. The end result is that one does not have to wait for slowly relaxing dilute nuclei to relax, rather, the recycle delay is dependent upon the T_1 of protons, fluorine, etc.

Polarization is transferred during the spin locking period, (the **contact time**) and a π/2 pulse is only made on protons:



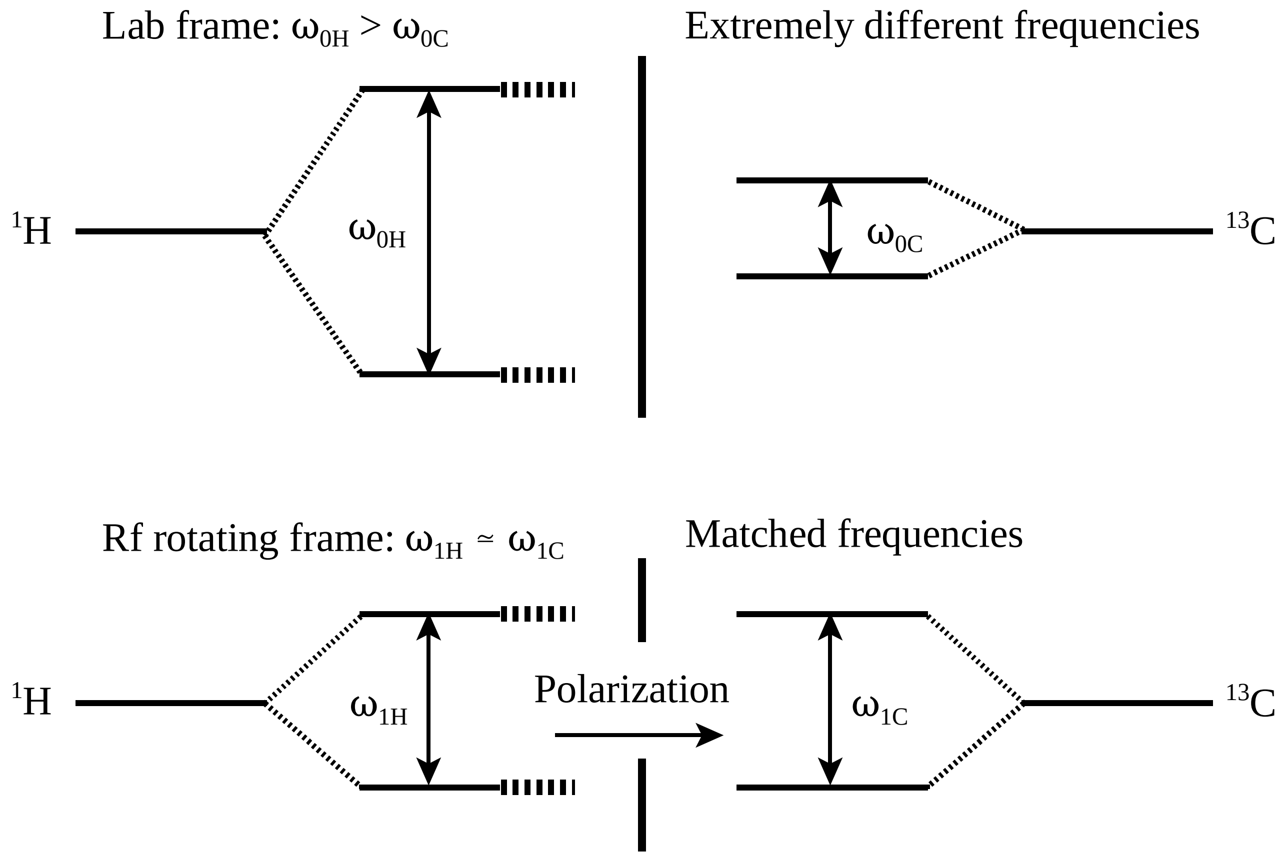
Cross Polarization

Cross polarization requires that nuclei are dipolar coupled to one another, and surprisingly, it even works while samples are being spun rapidly at the magic angle (though not if the spinning rate is greater than the anisotropic interaction). Hence the acronym CPMAS NMR (Cross Polarization Magic-Angle Spinning NMR)

The key to obtaining efficient cross polarization is setting the **Hartmann-Hahn match** properly. In this case, the rf fields of the dilute spin (e.g., $\omega_{1C\text{-}13}$) is set equal to that of the abundant spin (e.g., $\omega_{1H\text{-}1}$) by adjusting the power on each of the channels:

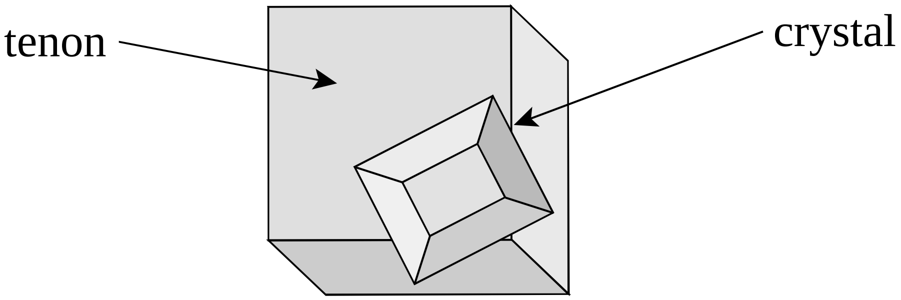
$$\gamma_{C\text{-}13}B_{C\text{-}13} = \gamma_{H\text{-}1}B_{H\text{-}1}$$

If these are set properly, the proton and carbon magnetization precess in the rotating frame at the same rate, allowing for transfer of the abundant spin polarization to carbon:



Single Crystal NMR

It is possible to conduct solid-state NMR experiments on single crystals, in a similar manner to X-ray diffraction experiments. A large crystal is mounted on a **tenon**, which is mounted on a goniometer head. If the orientation of the unit cell is known with respect to the tenon, then it is possible to determine the orientation of the NMR interaction tensors with respect to the molecular frame.



Here is a case of single crystal ^{31}P NMR of tetra-methyl diphosphine sulfide (TMPS); anisotropic NMR chemical shielding tensors can be extracted.

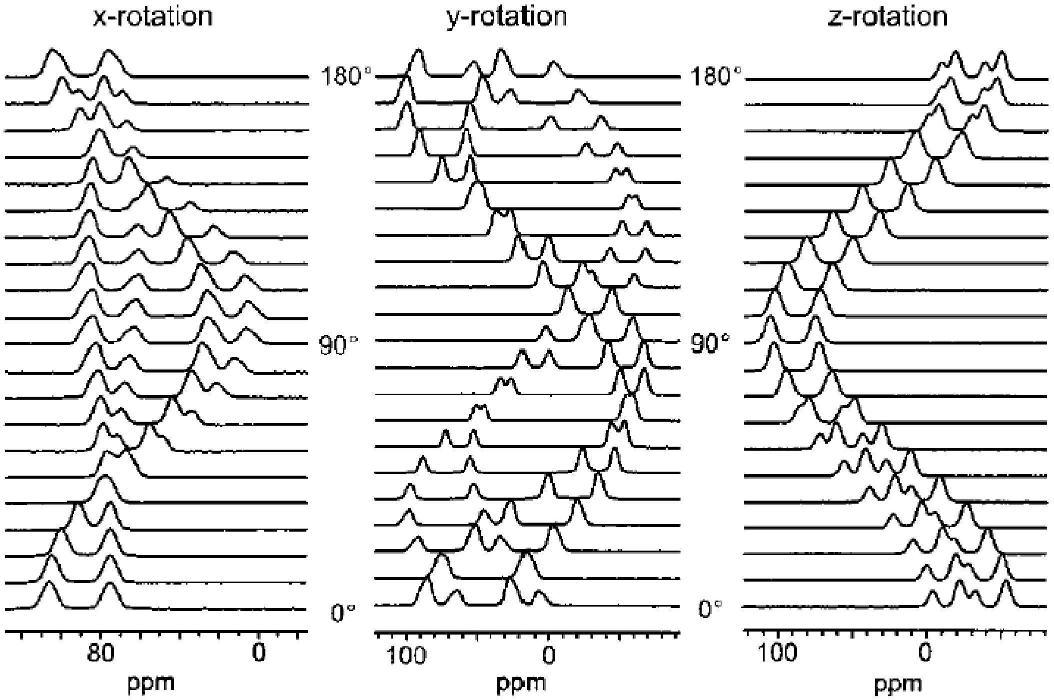
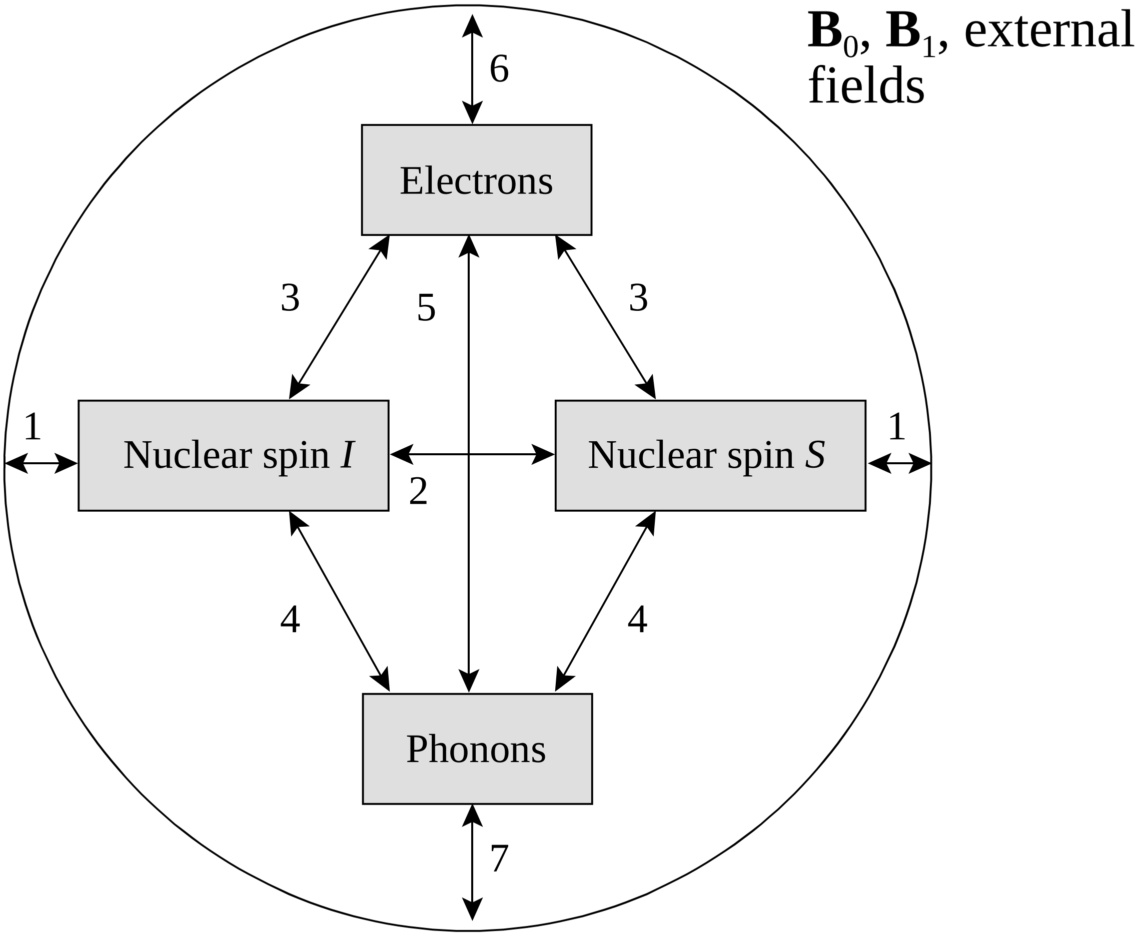


Figure 2. Phosphorus-31 CP NMR spectra of a single crystal of TMPS for rotations of the crystal holder about its *X*, *Y*, and *Z* axes, acquired at 4.7 T.

NMR Interactions in the Solid State

In the solid-state, there are seven ways for a nuclear spin to communicate with its surroundings:



1: Zeeman interaction of nuclear spins
2: Direct dipolar spin interaction
3: Indirect spin-spin coupling (*J*-coupling), nuclear-electron spin coupling (paramagnetic), coupling of nuclear spins with molecular electric field gradients (quadrupolar interaction)
4: Direct spin-lattice interactions
3-5: Indirect spin-lattice interaction via electrons
3-6: Chemical shielding and polarization of nuclear spins by electrons
4-7: Coupling of nuclear spins to sound fields

NMR Interactions in the Solid State

Nuclear spin interactions are distinguished on the basis of whether they are external or internal:

$$\mathcal{H} = \mathcal{H}_{\mathrm{ext}} + \mathcal{H}_{\mathrm{int}}$$
$$\mathcal{H}_{\mathrm{ext}} = \mathcal{H}_{0} + \mathcal{H}_{1}$$

Interactions with external fields $\mathbf{B}_0$ and $\mathbf{B}_1$

The “size” of these external interactions is larger than $\mathcal{H}_{\mathrm{int}}$:

$$||\mathcal{H}|| = [\mathrm{Tr}\{\mathcal{H}^2\}]^{1/2}$$

The hamiltonian describing internal spin interactions:

$$\mathcal{H}_{\mathrm{int}} = \mathcal{H}_{II} + \mathcal{H}_{SS} + \mathcal{H}_{IS} + \mathcal{H}_{\mathrm{Q}} + \mathcal{H}_{\mathrm{CS}} + \mathcal{H}_{\mathrm{L}}$$

$\mathcal{H}_{II}$ and $\mathcal{H}_{SS}$: homonuclear direct dipolar and indirect spin-spin coupling interactions

$\mathcal{H}_{IS}$: heteronuclear direct dipolar and indirect spin-spin coupling interactions

$\mathcal{H}_{\mathrm{Q}}$: quadrupolar interactions for *I* and *S* spins

$\mathcal{H}_{\mathrm{CS}}$: chemical shielding interactions for *I* and *S*

$\mathcal{H}_{\mathrm{L}}$: interactions of spins *I* and *S* with the lattice

In the solid state, all of these interactions can make secular contributions. Spin state energies are shifted resulting in direct manifestation of these interactions in the NMR spectra.

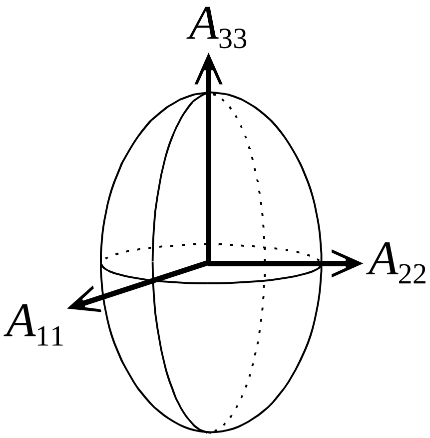
For most cases, we can assume the **high-field approximation**; that is, the Zeeman interaction and other external magnetic fields are much greater than internal NMR interactions. Correspondingly, these internal interactions can be treated as perturbations on the Zeeman hamiltonian.

NMR Interaction Tensors

All NMR interactions are anisotropic - their three dimensional nature can be described by **second-rank Cartesian tensors**, which are 3 × 3 matrices.

$$\mathcal{H} = \mathbf{I}\cdot\overline{\overline{\mathbf{A}}}\cdot\mathbf{S} = [I_x,\ I_y,\ I_z]\begin{bmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{bmatrix}\begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$$

The NMR interaction tensor describes the orientation of an NMR interaction with respect to the cartesian axis system of the molecule. These tensors can be **diagonalized** to yield tensors that have three **principal components** which describe the interaction in its own **principal axis system** (**PAS**):



$$\mathcal{H}_{\text{PAS}} = \begin{bmatrix} A_{11} & 0 & 0 \\ 0 & A_{22} & 0 \\ 0 & 0 & A_{33} \end{bmatrix}$$

Such interaction tensors are commonly pictured as ellipsoids or ovaloids, with the A_{33} component assigned to the largest principal component.

Nuclear spins are coupled to external magnetic fields via these tensors:

$$\mathcal{H} = \mathbf{I}\cdot\overline{\overline{\mathbf{Z}}}\cdot\mathbf{B}_0,\ \mathcal{H} = \mathbf{I}\cdot\overline{\overline{\mathbf{Z}}}\cdot\mathbf{B}_1,$$

$$\mathbf{B}_0 = [B_{0x},\ B_{0y},\ B_{0z}] = [0,0,\ B_0],$$

$$\mathbf{B}_1 = 2[B_{1x},\ B_{1y},\ B_{1z}]\cos\omega t$$

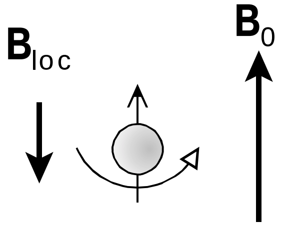
$$\overline{\overline{\mathbf{Z}}} = -\gamma_I\overline{\overline{\mathbf{1}}}, \qquad \overline{\overline{\mathbf{1}}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

NMR Interaction Tensors

Using Cartesian tensors, the spin part of the Hamiltonian (which is the same as in solution NMR) is separated from the spatial anisotropic dependence, which is described by the second-rank Cartesian tensor.

$$\mathcal{H}_{\mathrm{CS}} = \gamma \mathbf{I}\cdot\overline{\overline{\boldsymbol{\sigma}}}\cdot\mathbf{B}_{\mathbf{0}}$$

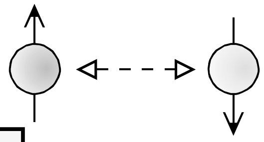
chemical shielding



$$\mathcal{H}_{\mathrm{DD}} = \sum_{i<j}\hbar\gamma_i\gamma_j r_{ij}^{-3}\left(\mathbf{I}_i\cdot\mathbf{I}_j - \frac{3(\mathbf{I}_i\cdot\mathbf{r}_{ij})(\mathbf{I}_j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\right)$$

$$= \sum_{i=j}\mathbf{I}_i\cdot\overline{\overline{\mathbf{D}}}\cdot\mathbf{I}_j$$

dipolar interaction

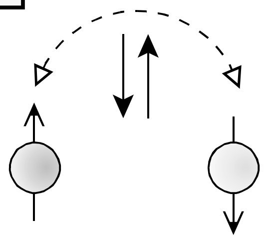


$$D_{\alpha,\beta} = \hbar\gamma_i\gamma_j r_{ij}^{-3}(\delta_{\alpha\beta} - 3e_\alpha e_\beta),$$

$\alpha,\beta = x,y,z;\ e_\alpha$: α−component of unit vector along r_{ij}

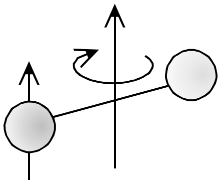
$$\mathcal{H}_{\mathrm{J}} = \sum_{i\neq j}\mathbf{I}_i\cdot\overline{\overline{\mathbf{J}}}\cdot\mathbf{I}_j$$

indirect spin-spin (*J*)
coupling



$$\mathcal{H}_{\mathrm{CR}} = \sum_{i}\mathbf{I}_i\cdot\overline{\overline{\mathbf{C}}}_i\cdot\mathbf{J}$$

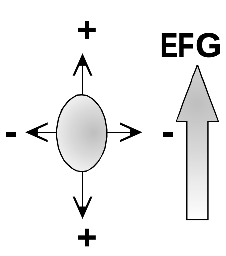
spin-rotation coupling



$$\mathcal{H}_{\mathrm{Q}} = \frac{eQ}{2I(2I-1)\hbar}\sum_{i}\mathbf{I}\cdot\overline{\overline{\mathbf{V}}}\cdot\mathbf{I}$$

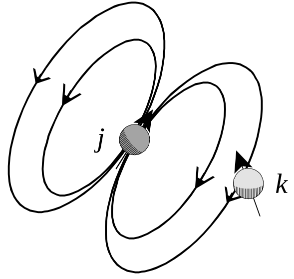
quadrupolar coupling

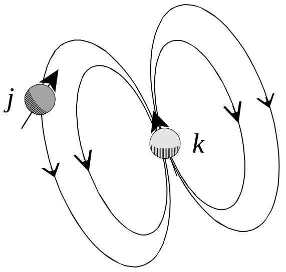
$$\overline{\overline{\mathbf{V}}} = \{V_\alpha, V_\beta\};\ \alpha,\beta = x,y,z$$



Dipolar Interaction

The dipolar interaction results from interaction of one nuclear spin with a magnetic field generated by another nuclear spin, and vice versa. This is a direct through space interaction which is dependent upon the γ of each nucleus, as well as r_{jk}^{-3}:





Dipolar coupling constant:

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

Nuclear Pair	**Internuclear Distance**	R^{DD} **(Hz)**
^{1}H, ^{1}H	10 Å	120 kHz
^{1}H, ^{13}C	1 Å	30 kHz
^{1}H, ^{13}C	2 Å	3.8 kHz

Recall that the dipolar hamiltonian can be expanded into the **dipolar alphabet**, which has both spin operators and spatially dependent terms. Only term *A* makes a secular contribution for heteronuclear spin pairs, and *A* and *B* (flip flop) both make contributions for homonuclear spin pairs:

$$A = R_{jk}^{DD}(1-3\cos^2\theta)I_{jz}I_{kz}$$

$$B = -\frac{R_{jk}^{DD}}{4}(1-3\cos^2\theta)(I_{j+}I_{k-}+I_{j-}I_{k+})$$

$$C = -\frac{3R_{jk}^{DD}}{2}\sin\theta\cos\theta\exp(-i\varphi)(I_{j+}I_{kz}+I_{k+}I_{jz})$$

$$D = C^*$$

$$E = -\frac{3R_{jk}^{DD}}{4}\sin^2\theta\exp(-2i\varphi)(I_{j+}S_{k+})$$

$$F = E^*$$

$$\text{where } (I_{j+})^* = I_{j-}\ ,\ (I_{k+})^* = I_{k-}$$

In a **solid-state** powder sample, every magnetic spin is coupled to every other magnetic spin; dipolar couplings serve to severely broaden NMR spectra.

In **solution**, molecules reorient quickly; nuclear spins feel a **time average** of the spatial part of the dipolar interaction $\langle 3\cos^2\theta - 1\rangle$ over all orientations θ,ϕ.

Dipolar Interaction

The dipolar interaction tensor is **symmetric** and **traceless**, meaning that the interaction is symmetric between the two nuclei, and there is no **isotropic dipolar coupling**:

$$\mathrm{Tr}\{\overline{\overline{\mathbf{D}}}\} = 0$$

For a heteronuclear spin pair in the solid state, the $(3\cos^2\theta - 1)$ term is not averaged by random isotropic tumbling: the spatial term will have an effect on the spectrum!

$$\begin{aligned} h^{-1}\mathcal{H} &= -(\nu_A I_{Az} + \nu_X I_{Xz}) + h^{-1}\mathcal{H}_{\mathrm{DD}} \\ &= -(\nu_A I_{Az} + \nu_X I_{Xz}) + R^{\mathrm{DD}} I_{Az} I_{Xz} (3\cos^2\theta - 1) \end{aligned}$$

So, for an NMR spectrum influenced only by the Zeeman and AX dipolar interaction, the frequencies for A can be calculated as:

$$\nu = \nu_A \pm \frac{1}{2} R^{\mathrm{DD}} (3\cos^2\theta - 1)$$

For a homonuclear spin pair, the flip flop term (*B*) is also important:

$$h^{-1}\mathcal{H} = -\nu_0(I_{1z} + I_{2z}) - R^{\mathrm{DD}}(3\cos^2\theta - 1)[I_{1z}I_{2z} - \frac{1}{4}(I_{1+}I_{2-} + I_{1-}I_{2+})]$$

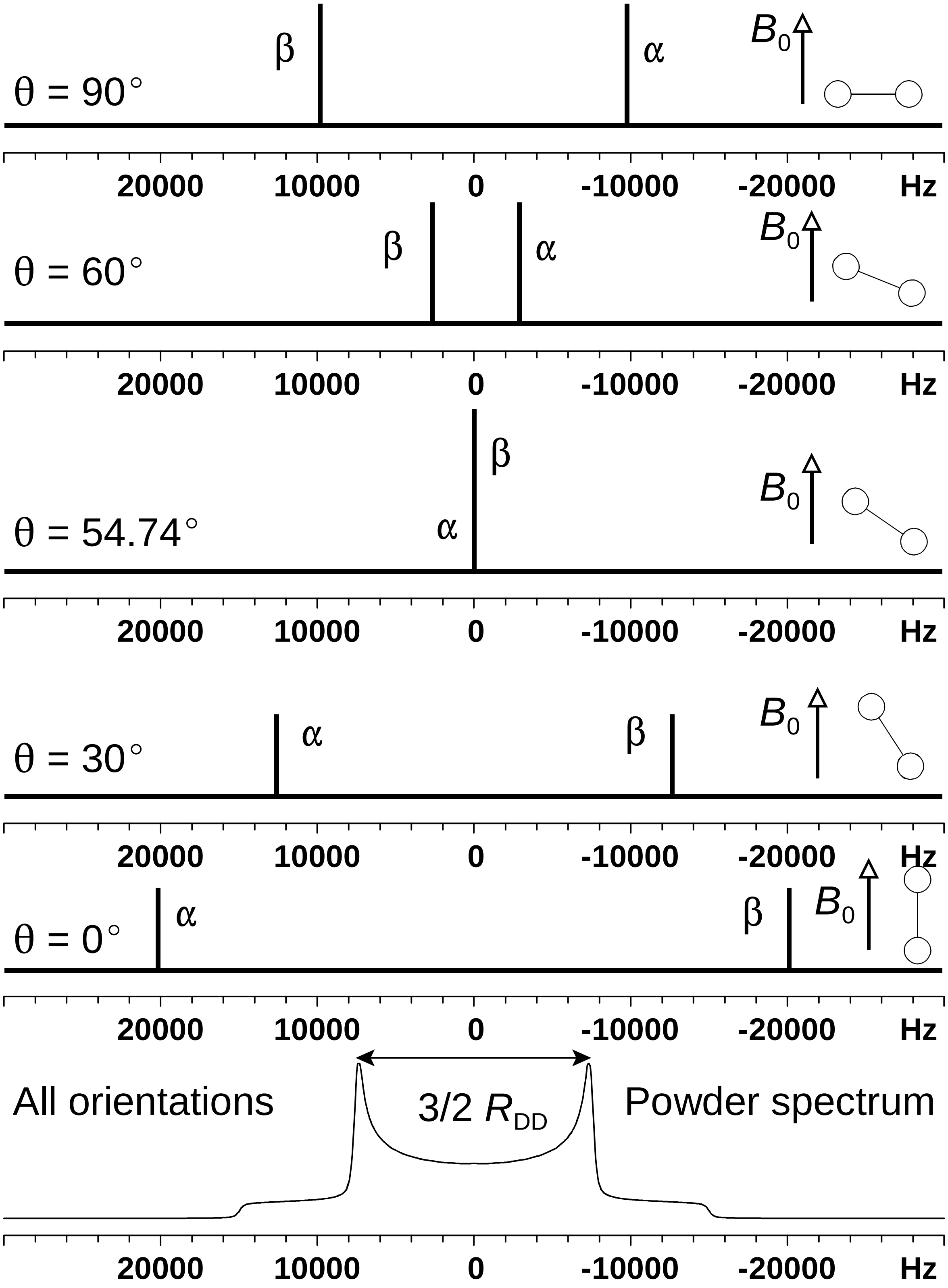
So the frequencies of the transitions can be calculated as:

$$\nu = \nu_0 \pm \frac{3}{4} R^{\mathrm{DD}} (3\cos^2\theta - 1)$$

In a **single crystal** with one orientation of dipolar vectors, a single set of peaks would be observed; in a **powder**, the spectra take on the famous shape known as the **Pake doublet** (see following slides).

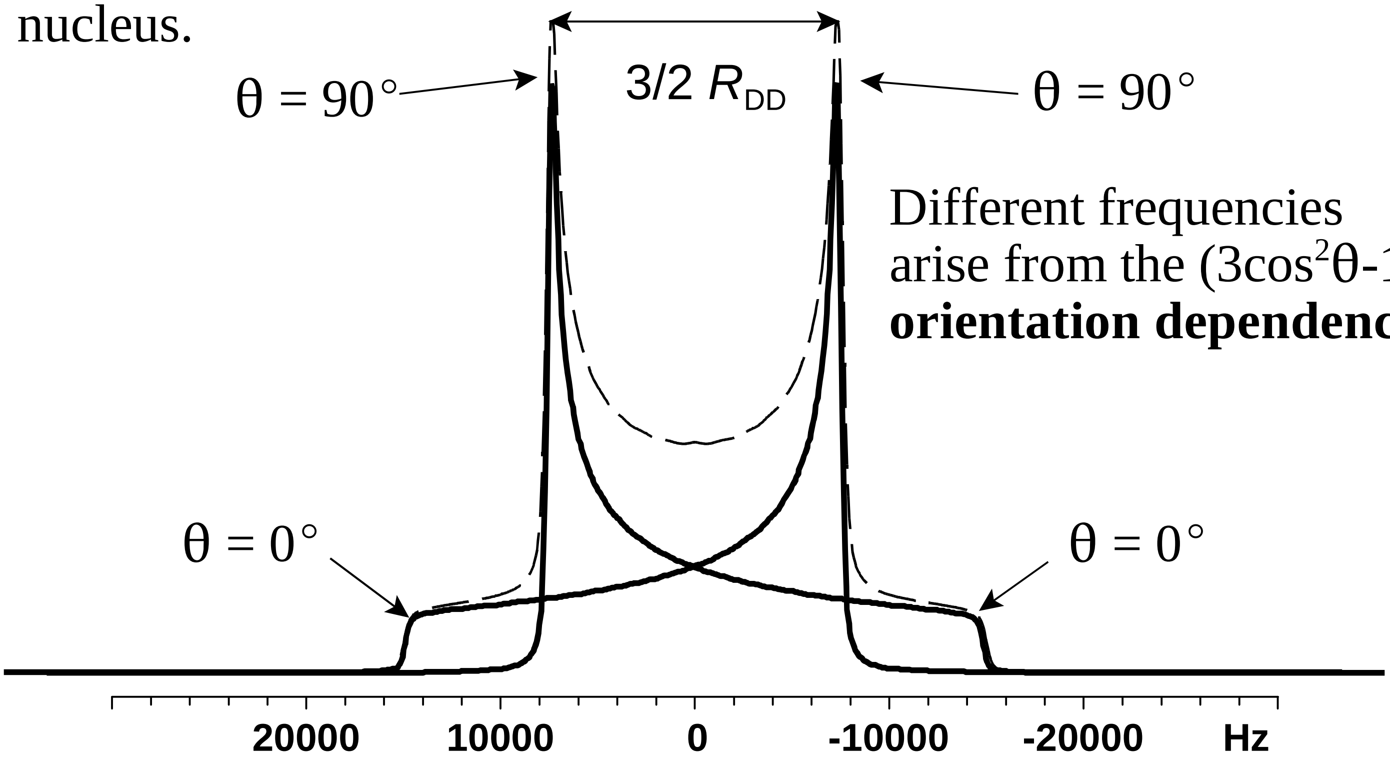
Dipolar Interaction

For single crystal spectra of a homonuclear spin pair, with R^{DD} = 6667 Hz (powder spectrum, all orientations, is at the bottom)



Dipolar Interaction

The Pake doublet was first observed in the ^{1}H NMR spectrum of solid $CaSO_4 \cdot H_2O$. The Pake doublet is composed of two subspectra resulting from the α and β spin states of the coupled nucleus.



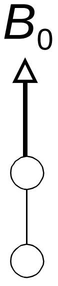
Different frequencies arise from the $(3\cos^2\theta\text{-}1)$ **orientation dependence**

The intensities of these peaks result from sinθ weighting of the spectrum (from integration over a sphere):

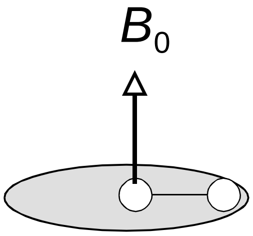
$$\langle \mathcal{H}^{DD} \rangle = R^{DD} \cdot \langle 3\cos^2\theta - 1 \rangle \cdot (\text{spin part})$$

$$\propto \int_0^{2\pi} \left[\int_0^{\pi} (1 - 3\cos^2\theta)\sin\theta \, d\theta \right] d\varphi = 0$$

For θ = 0°, there is only one possible orientation of the dipolar vector, and it is weighted as sinθ = 0



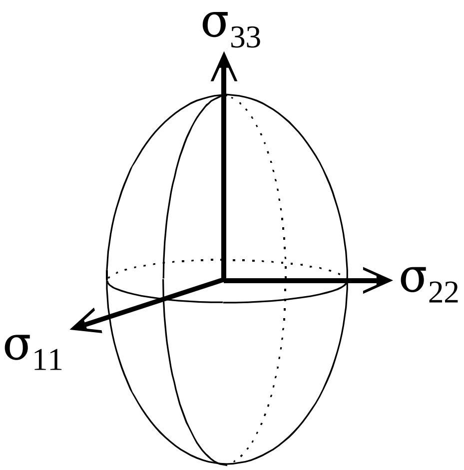
For θ = 90°, there are many orientations about a plane perpendicular to B_0. this is weighted as sinθ = 1



Chemical Shielding Anisotropy

Chemical shielding is an anisotropic interaction characterized by a shielding tensor σ, which can also be diagonalized to yield a tensor with **three principal components**.

$$\boldsymbol{\sigma}^{\text{molecule}} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \qquad \boldsymbol{\sigma}^{\text{PAS}} = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$



$$\sigma_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$$

$$\Omega = \sigma_{33} - \sigma_{11}$$

$$\kappa = \frac{\sigma_{\text{iso}} - \sigma_{22}}{\Omega}$$

The principal components are assigned such that $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$ (i.e., σ_{11} is the least shielded component and σ_{33} is the most shielded component).

σ_{iso} is the **isotropic chemical shielding** (measured in solution as a result of averaging by isotropic tumbling). The trace of the chemical shielding tensor is non-zero!

Ω is the **span**, which measures in ppm the breadth of the CSA powder pattern

κ is the **skew**, which measures the asymmetry of the powder pattern.

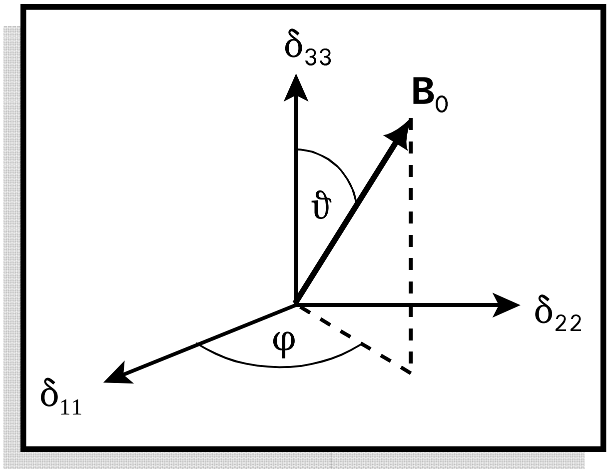
Keep in mind, these expressions can be also written for ***chemical shift*** *(see Lecture 12 for comparison of shielding and shift)*

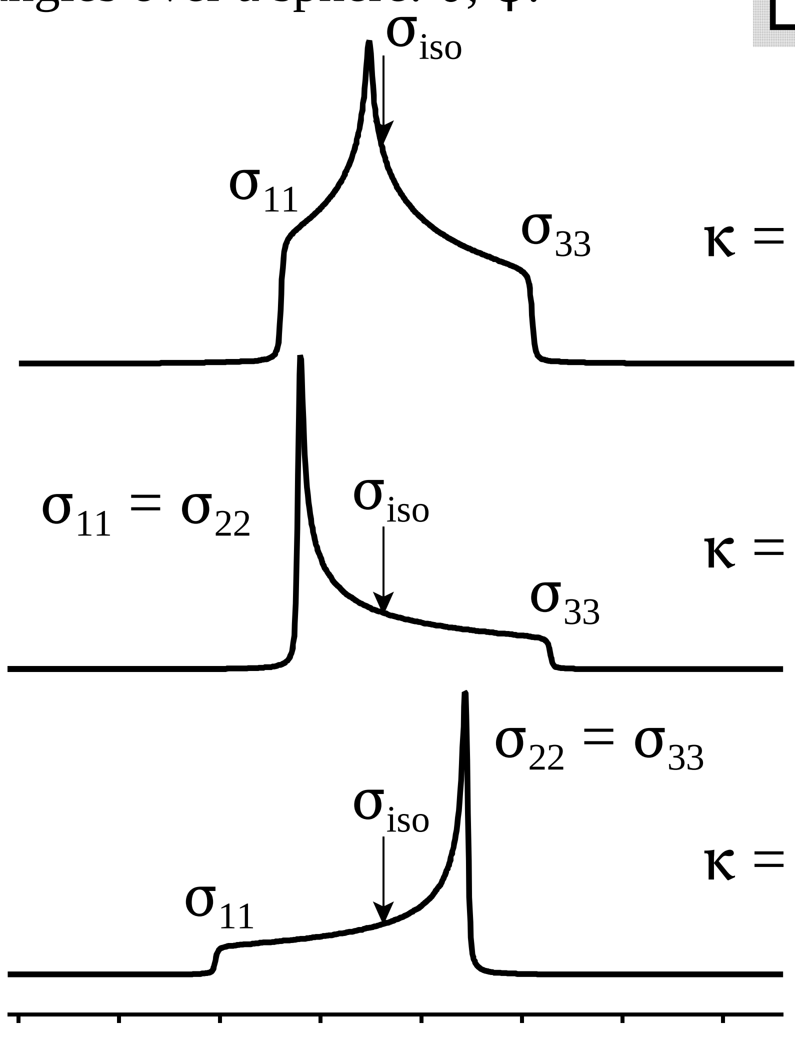
Chemical Shielding Anisotropy

It can be shown that chemical shielding anisotropy gives rise to frequency shifts with the following orientation dependence:

$$\nu_{CS} = \nu_0 \left(\sigma_{11}\sin^2\theta\cos^2\varphi + \sigma_{22}\sin^2\theta\sin^2\varphi + \sigma_{33}\cos^2\theta\right) .$$

In order to calculate powder patterns (for any anisotropic NMR interaction), one must calculate frequencies for a large number of orientations of the interaction tensor with respect to the magnetic field - many polar angles over a sphere: θ, ϕ.





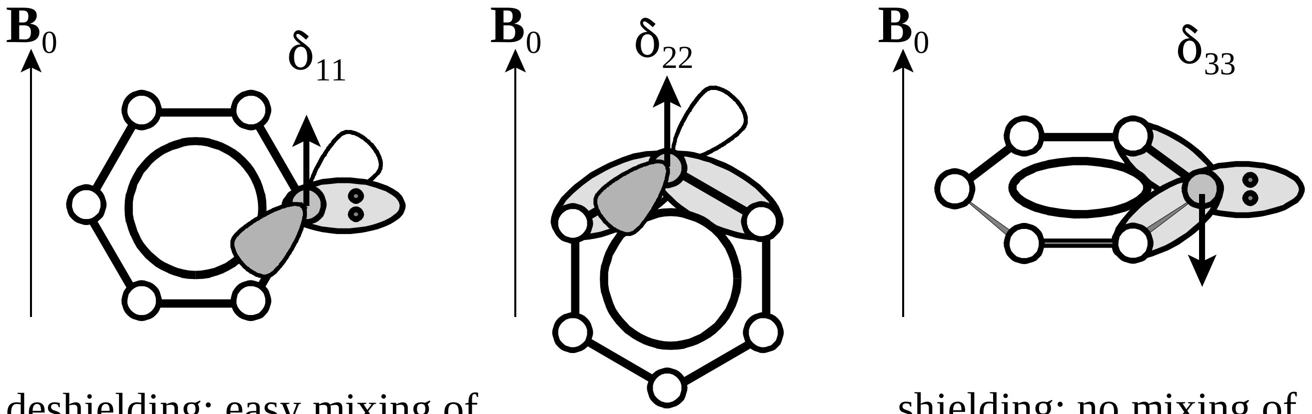
κ = +0.3 non-axial CSA tensor

κ = +1.0 axial symmetry

κ = -1.0 axial symmetry

Chemical Shielding Anisotropy

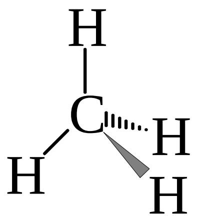
Why is the chemical shift orientation dependent? Molecules have definite 3D shapes, and certain electronic circulations (which induced the local magnetic fields) are preferred over others. Molecular orbitals and crystallographic symmetry dictate the orientation and magnitude of chemical shielding tensors.

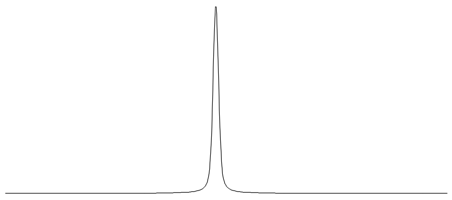


deshielding: easy mixing of ground and excited states

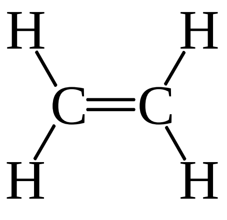
shielding: no mixing of ground and excited states

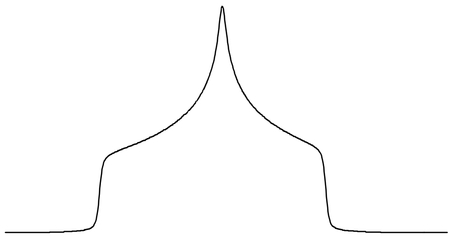
Consider ^{13}C shielding tensors in a few simple organic molecules:





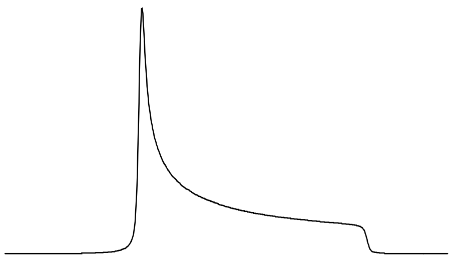
Spherical symmetry: shielding is similar in all directions, very small CSA.





Non-axial symmetry: Shielding is different in three directions

$H-C\equiv C-H$

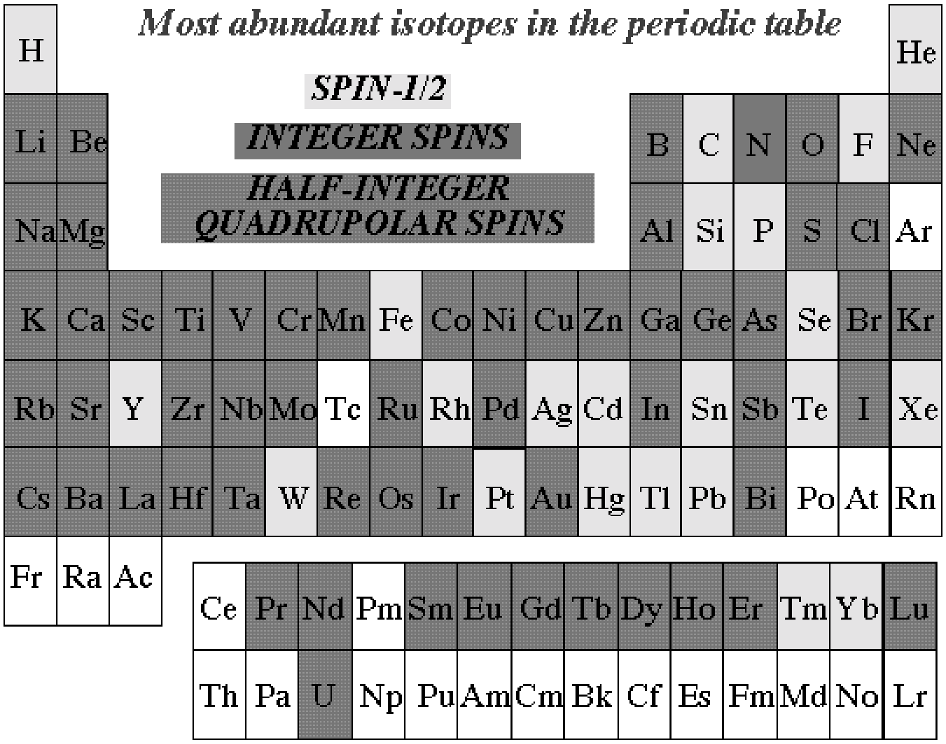


Axial symmetry: molecule is // to $\mathbf{B}_0$ maximum shielding; when molecule is ⊥ to $\mathbf{B}_0$ maximum deshielding

Solid-State NMR of Quadrupolar Nuclei

As discussed earlier in the course, solution NMR of quadrupolar nuclei is often wrought with complications, mainly because of the rapid relaxation of the quadrupolar nucleus due to the large quadrupolar interaction (which may be on the order of MHz). At best, very broad peaks are observed.

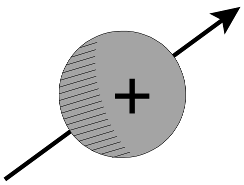
Recent technological advancements and new pulse sequences have opened up the periodic table (73% of NMR active nuclei are quadrupolar nuclei) to solid-state NMR. The strange broadening effects of quadrupolar nuclei, once viewed as a hindrance to performing such experiments in the solid state, are now exploited to provide invaluable information on solid state chemistry, structure and dynamics.

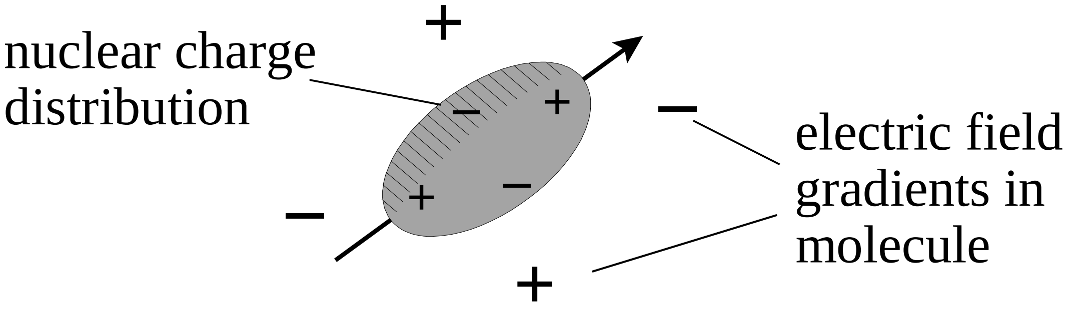


Notably, NMR of **half-integer quadrupolar nuclei** has become quite commonplace, and allowed investigation of a broad array of materials. The only integer quadrupolar nuclei investigated regularly are ^{2}H (very common) and ^{14}N (less common).

Solid-State NMR of Quadrupolar Nuclei

Quadrupolar nuclei have a spin > 1/2, and an asymmetric distribution of nucleons giving rise to a non-spherical positive electric charge distribution; this is in contrast to spin-1/2 nuclei, which have a spherical distribution of positive electric charge.

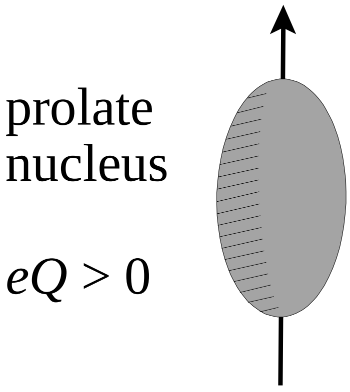


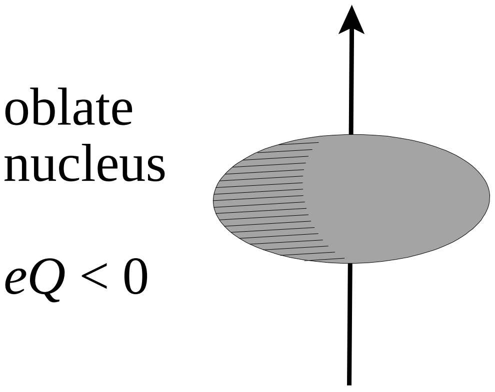


Spin-1/2 Nucleus

Quadrupolar Nucleus

The asymmetric charge distribution in the nucleus is described by the nuclear electric quadrupole moment, *eQ*, which is measured in barn (which is ca. 10^{-28} m^2). *eQ* is an instrinsic property of the nucleus, and is the same regardless of the environment.

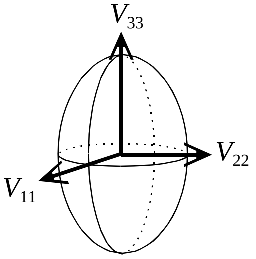




Quadrupolar nuclei interact with electric field gradients (EFGs) in the molecule: EFGs are spatial changes in electric field in the molecule. Like the dipolar interaction, the quadrupolar interaction is a ground state interaction, but is dependent upon the distribution of electric point charges in the molecule and resulting EFGs.

Solid-State NMR of Quadrupolar Nuclei

The EFGs at the quadrupolar nucleus can be described by a symmetric traceless tensor, which can also be diagonalized:



$$\mathbf{V} = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix} \qquad \mathbf{V}^{\mathrm{PAS}} = \begin{bmatrix} V_{11} & 0 & 0 \\ 0 & V_{22} & 0 \\ 0 & 0 & V_{33} \end{bmatrix}$$

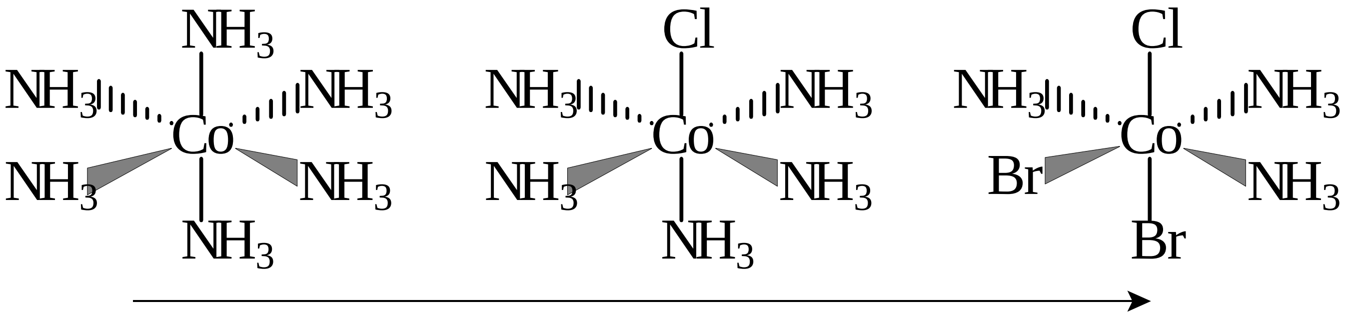
The principal components of the EFG tensor are defined such that $|V_{11}| \leq |V_{22}| \leq |\mathrm{V}_{33}|$. Since the EFG tensor is traceless, isotropic tumbling in solution averages it to zero (unlike *J* and σ).

The magnitude of the quadrupolar interaction is given by the **nuclear quadrupole coupling constant**:

$$C_{\mathrm{Q}} = eQ \cdot V_{33}/h \text{ (in kHz or MHz)}$$

The asymmetry of the quadrupolar interaction is given by the **asymmetry parameter**, $\eta = (V_{11} - V_{22})/V_{33}$, where $0 \leq \eta \leq 1$.
If $\eta = 0$, the EFG tensor is **axially symmetric**.

For a quadrupolar nucleus in the centre of a spherically symmetric molecule, the EFGs cancel one another resulting in very small EFGs at the quadrupolar nucleus. As the spherical symmetry breaks down, the EFGs at the quadrupolar nucleus grow in magnitude:



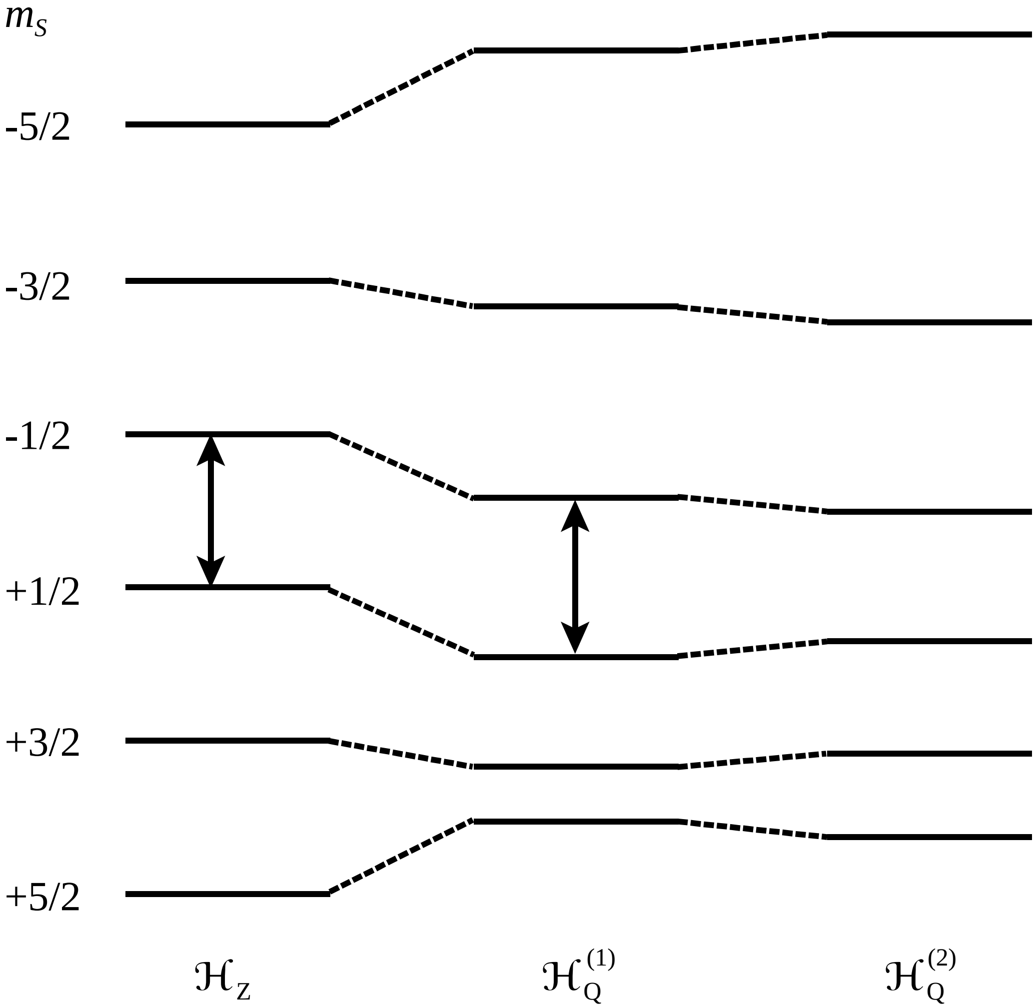
Increasing EFGs, increasing quadrupolar interaction

Solid-State NMR of Quadrupolar Nuclei

The quadrupolar interaction, unlike all of the other anisotropic NMR interactions, can be written as a sum of first and second order interactions:

$$\mathcal{H}_Q = \mathcal{H}_Q^{(1)} + \mathcal{H}_Q^{(2)}$$

Below, the effects of the first- and second-order interactions on the energy levels of a spin-5/2 nucleus are shown:



The first order interaction is proportional to C_Q, and the second-order interaction is proportional to C_Q^2/ν_0, and is much smaller (shifts in energy levels above are exaggerated). Notice that the first-order interaction does not affect the **central transition**.

Solid-State NMR of Quadrupolar Nuclei

The first-order quadrupolar interaction is described by the hamiltonian (where θ and ϕ are polar angles):

$$\mathcal{H}_{\mathrm{Q}}^{(1)} = \frac{1}{2} Q^{\prime}(\theta,\varphi)\ [I_z^2 - I(I+1)/3]$$

where

$$Q^{\prime}(\theta,\varphi) = (\omega_{\mathrm{Q}}/2)\ [3\cos^2\theta - 1 - \eta\sin^2\theta\cos 2\varphi]$$

$$\omega_{\mathrm{Q}} = 3e^2qQ/[2I(2I-1)\hbar]$$

quadrupole frequency, where $eq = V_{33}$

If the quadrupolar interaction becomes larger as the result of increasing EFGs, the quadrupolar interaction can no longer be treated as a perturbation on the Zeeman hamiltonian. Rather, the eigenstates are expressed as linear combinations of the pure Zeeman eigenstates (which are no longer quantized along the direction of $\mathbf{B}_0$. The full hamiltonian is required:

$$\mathcal{H}_{\mathrm{Q}}^{(2)} = \frac{1}{6}\omega_{\mathrm{Q}}[3I_z^2 - I(I+1) + \eta(I_x^2 + I_y^2)]$$

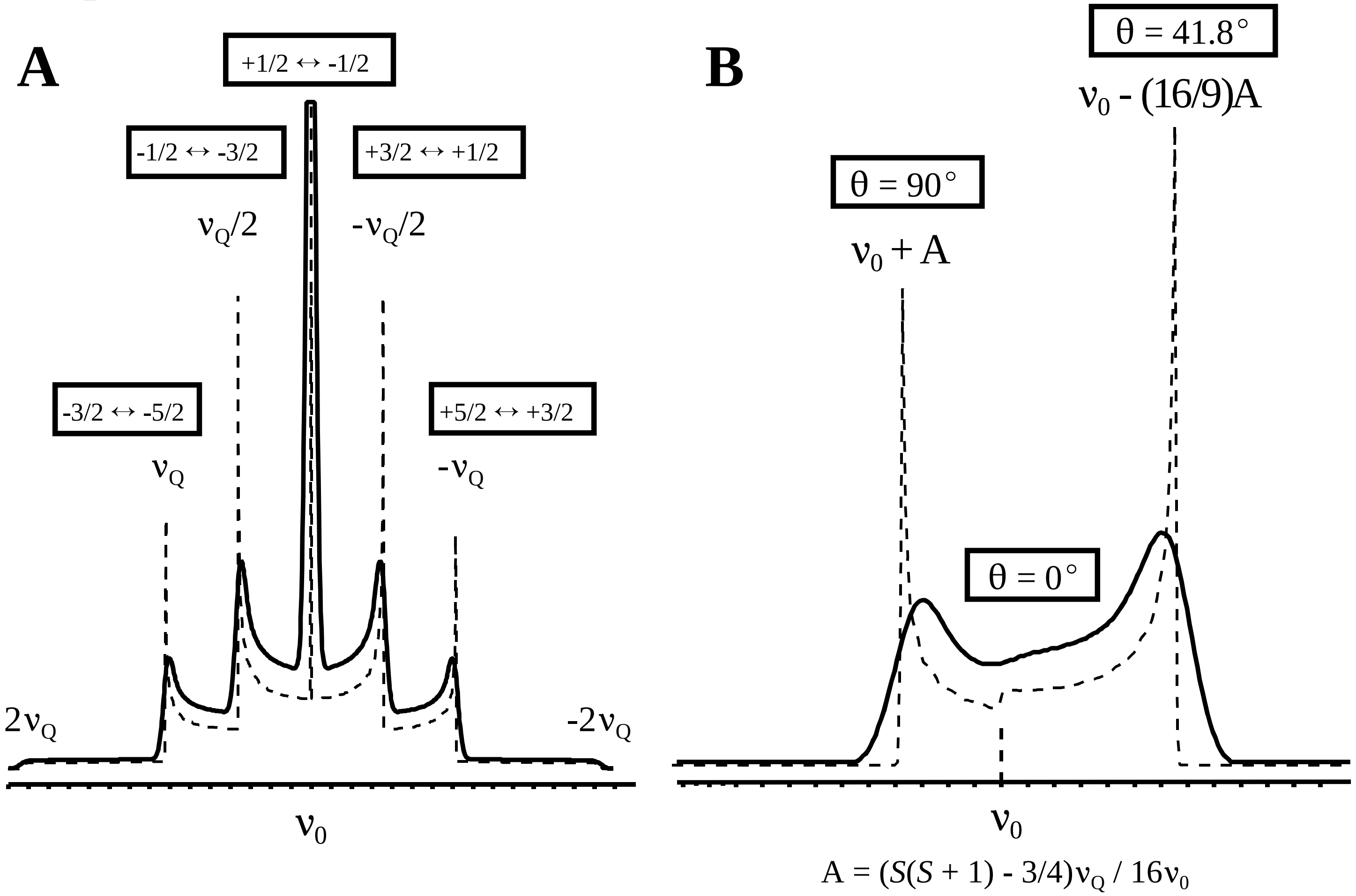
Perturbation theory can be used to calculate the second-order shifts in energy levels (note that this decreases at higher fields)

$$\omega_{\mathrm{Q}}^{(2)} = -\frac{\omega_{\mathrm{Q}}^2}{16\omega_0}\left(I(I+1) - \frac{3}{4}\right)(1-\cos^2\theta)(9\cos^2\theta - 1)$$

when η = 0.

Solid-State NMR of Quadrupolar Nuclei

Static spectra of quadrupolar nuclei are shown below for the case of spin 5/2:



In A, only the first-order quadrupolar interaction is visible, with a sharp central transition, and various satellite transitions that have shapes resembling axial CSA patterns.

In B, the value of C_Q is much larger. The satellite transitions broaden anddisappear and only the central transition spectrum is left (which is unaffected by first-order interactions). It still has a strange shape due to the orientation dependence of the second-order quadrupolar frequency.

MAS NMR of Quadrupolar Nuclei

Unlike first-order interactions, the second-order term is no longer a second-rank tensor, and is not averaged to zero by MAS. The second-order quadrupolar frequency can be expressed in terms of zeroth-, second- and fourth-order Legendre polynomials: $P_n(\cos\theta)$, where $P_0(\cos\theta) = 1$, and

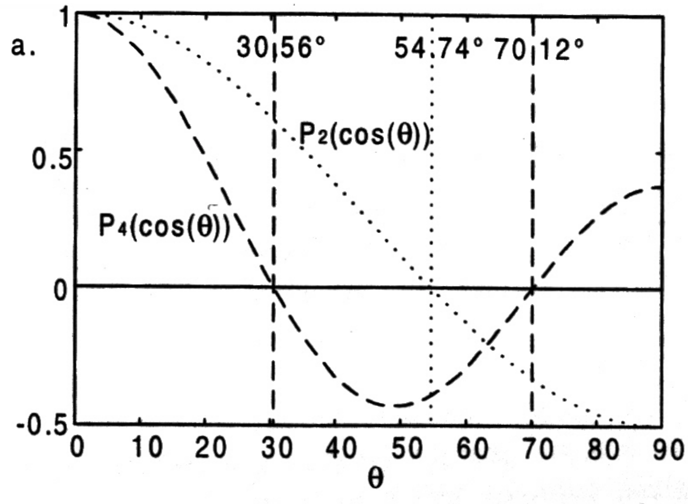
$$P_2(\cos\theta) = (3\cos^2\theta - 1)$$

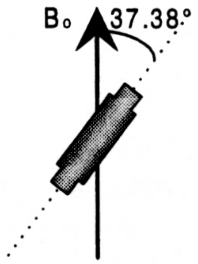
$$P_4(\cos\theta) = (35\cos^4\theta - 30\cos^2\theta + 3)$$

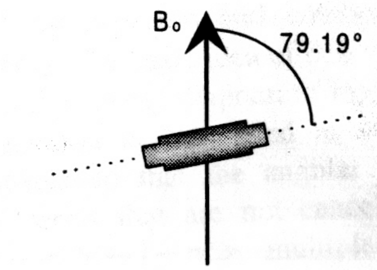
The averaged value of $\omega_Q^{(2)}$ under fast MAS is written as

$$\langle\omega_Q^{(2)}\rangle_{rot} = A_0 + A_2 P_2(\cos\beta) + A_4 P_4(\cos\beta)$$

where A_2 and A_4 are functions of ω_Q, ω_0 and η as well as the orientation of the EFG tensor w.r.t. the rotor axis, and β is the angle between the rotor axis and the magnetic field.





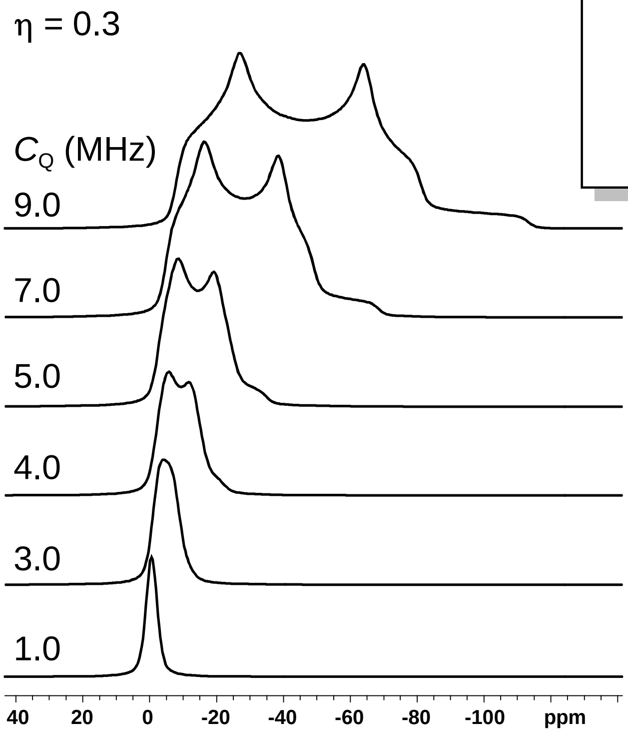


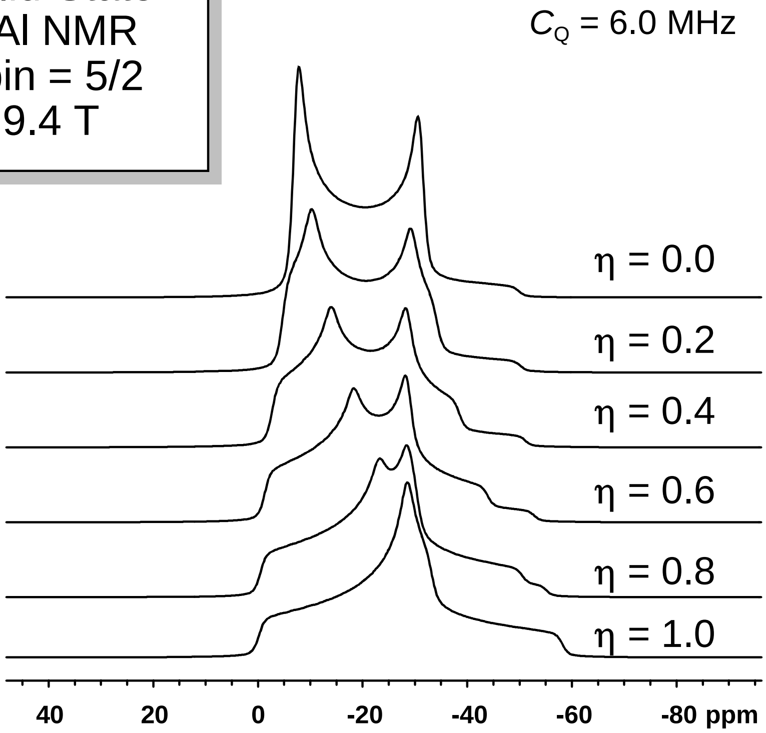
So the second-order quadrupolar interaction cannot be completely averaged unless the rotor is spun about two axes simultaneously - at $\beta = 30.55°$ and $70.12°$. There are experiments called DOR (double rotation - actual special probe that does this) and DAS (dynamic angle spinning - another special probe).

MAS NMR of Quadrupolar Nuclei

MAS lineshapes of the central transition of half-integer quadrupolar nuclei look like this, and are very sensitive to changes in both C_Q and η:

Solid-State
^{27}Al NMR
spin = 5/2
9.4 T



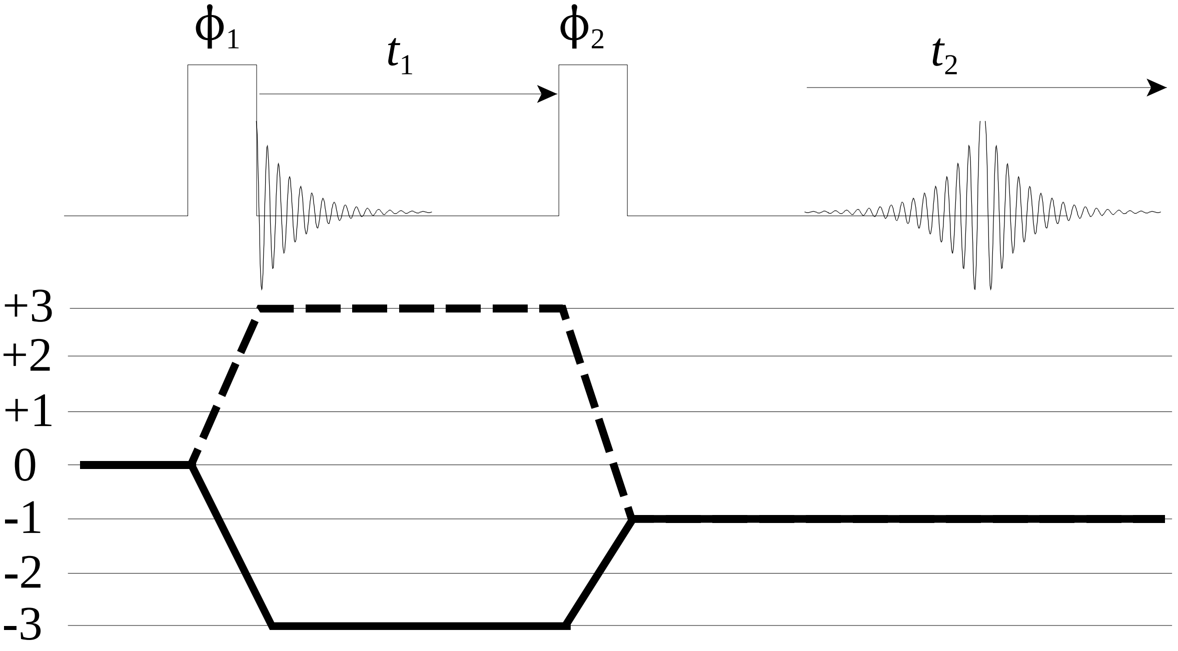


However, in the presence of overlapping quadrupolar resonances from several sites, the spectra can be very difficult to deconvolute, especially in the case of disordered solids where lineshapes are not well defined!

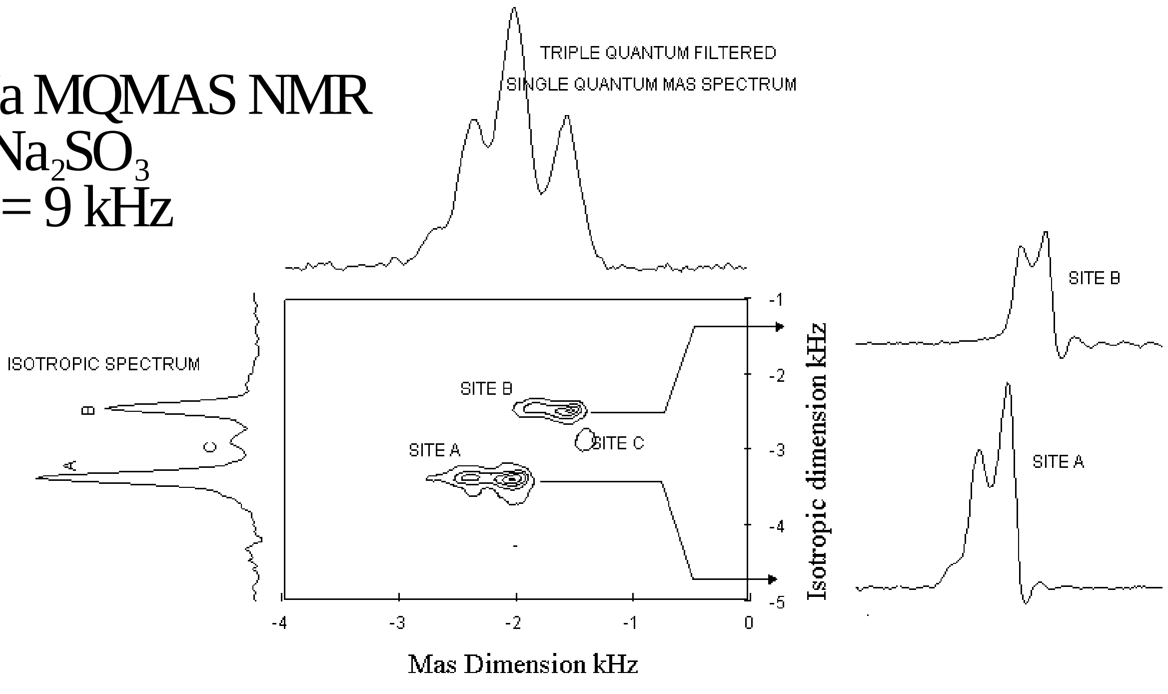
One can use DOR or DAS techniques, but this requires expensive specialized probes. Fortunately a technique has been developed which can be run on most solid state NMR probes, known as **MQMAS (multiple quantum magic-angle spinning) NMR**.

MQMAS NMR

MQMAS NMR is used to obtain high-resolution NMR spectra of quadrupolar nuclei. It involves creating a triple-quantum (or 5Q) coherence. During the 3Q evolution, the second-order quadrupolar interaction is averaged; however, since we cannot directly observe the 3Q coherence, it must be converted to a 1Q coherence for direct observation.



^{23}Na MQMAS NMR
of Na_2SO_3
rot = 9 kHz



Solid State NMR: Summary

Solid state NMR is clearly a very powerful technique 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
zeolites
microporous solids
minerals
glasses
food products
ceramics
semiconductors
archaelogical specimens
resins
inorganic complexes
mesoporous solids
aluminosilicates/phosphates
biological molecules
cements
wood
bones
metals and alloys
polymers
surfaces

Most of the NMR active nuclei in the periodic table are available for investigation by solids NMR, due to higher magnetic fields, innovative pulse sequences, and improved electronics, computer and probe technology.