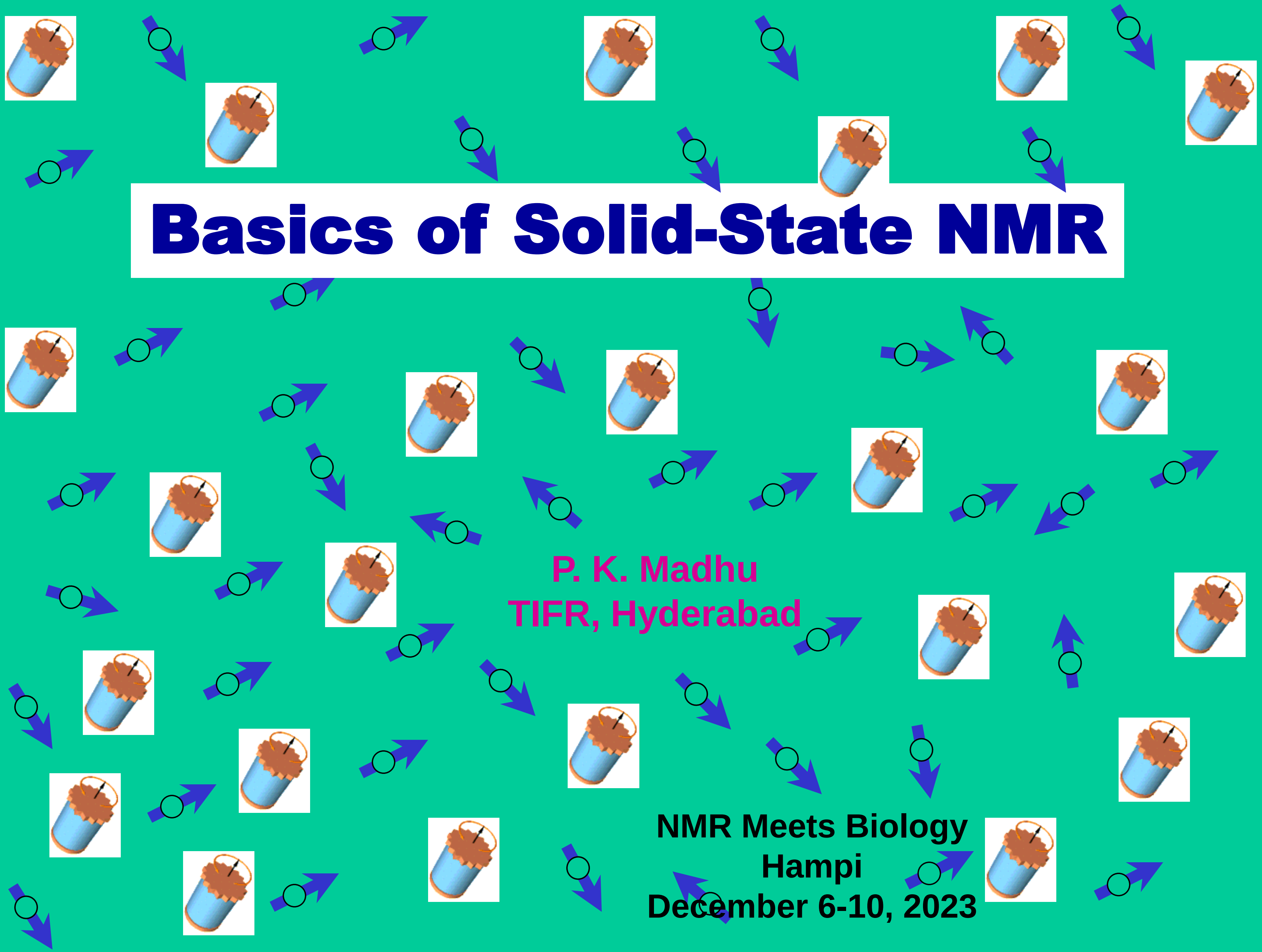

Basics of Solid-State NMR

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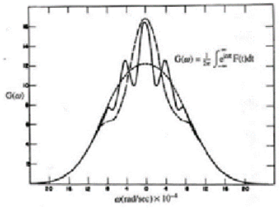
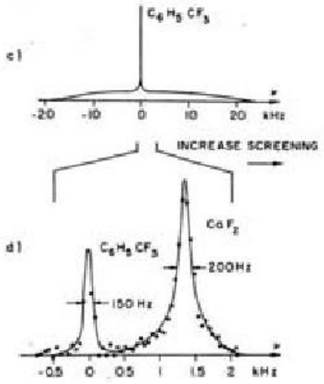
TIFR, Hyderabad

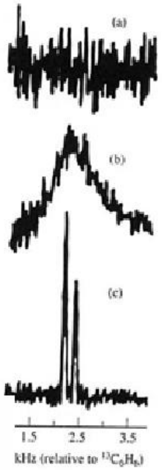
NMR Meets Biology
Hampi
December 6-10, 2023

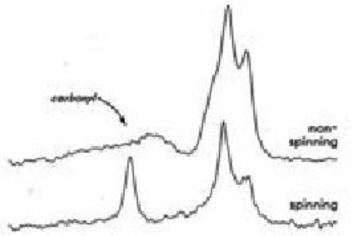
Time Line of Solid-State NMR

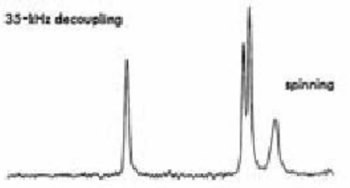
- **NMR in solid paraffin, 1946 (Purcell, Torrey, Pound)**
- **Magic-angle spinning, 1959 (Andrew, Lowe)**
- **Lee-Goldburg sequence in spin space, 1965 (Lee, Goldburg)**
- **WAHUHA sequence (Waugh, Huber, Haeberlen)**
- **CP concept, 1962 (Hartmann, Hahn)**
- **Direct observation of dilute spins, 1972 (Pines, Gibby, Waugh)**
- **Return of the MAS: CPMAS, 1976 (Schaefer, Stejskal)**
- **High-resolution for Quadrupolar nuclei, 1988, 1995 (Virlet, Llor, Samoson, Frydman)**
- **Efficient heteronuclear dipolar decoupling, 1995 (TPPM, SPINAL,……)**
- **Efficient homonuclear dipolar decoupling, 1999 (PMLG, DUMBO,……)**
- **Biomolecular applications (Oschkinat, Baldus, McDermott, Reinstra….)**

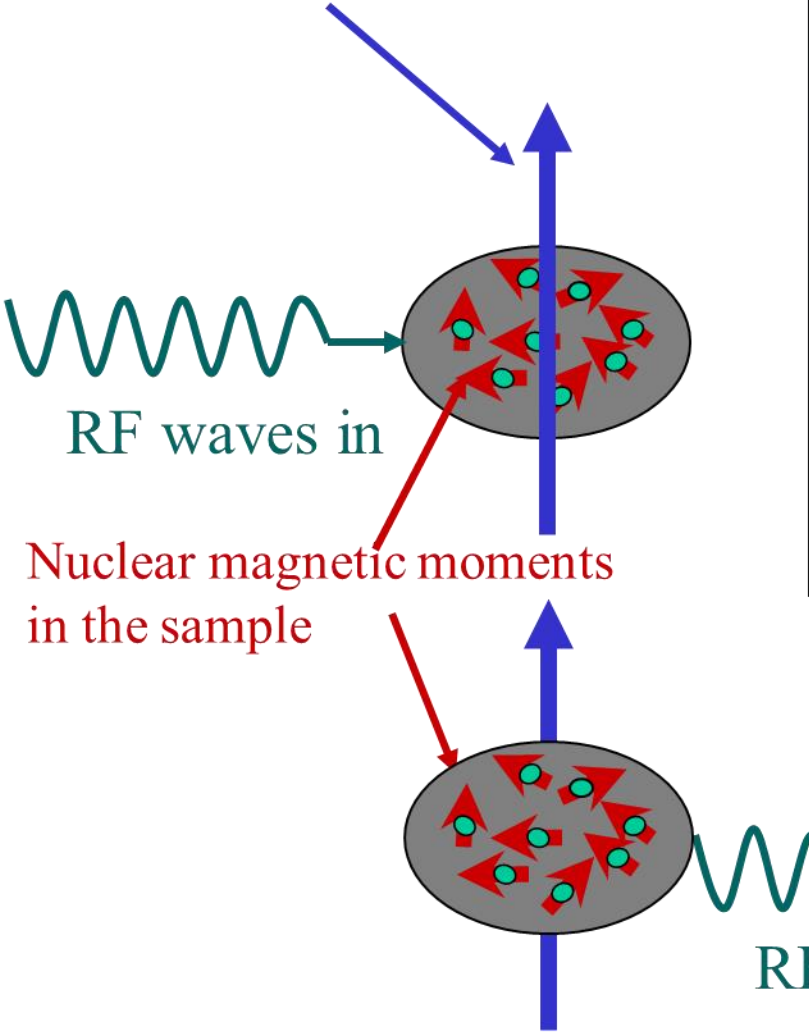










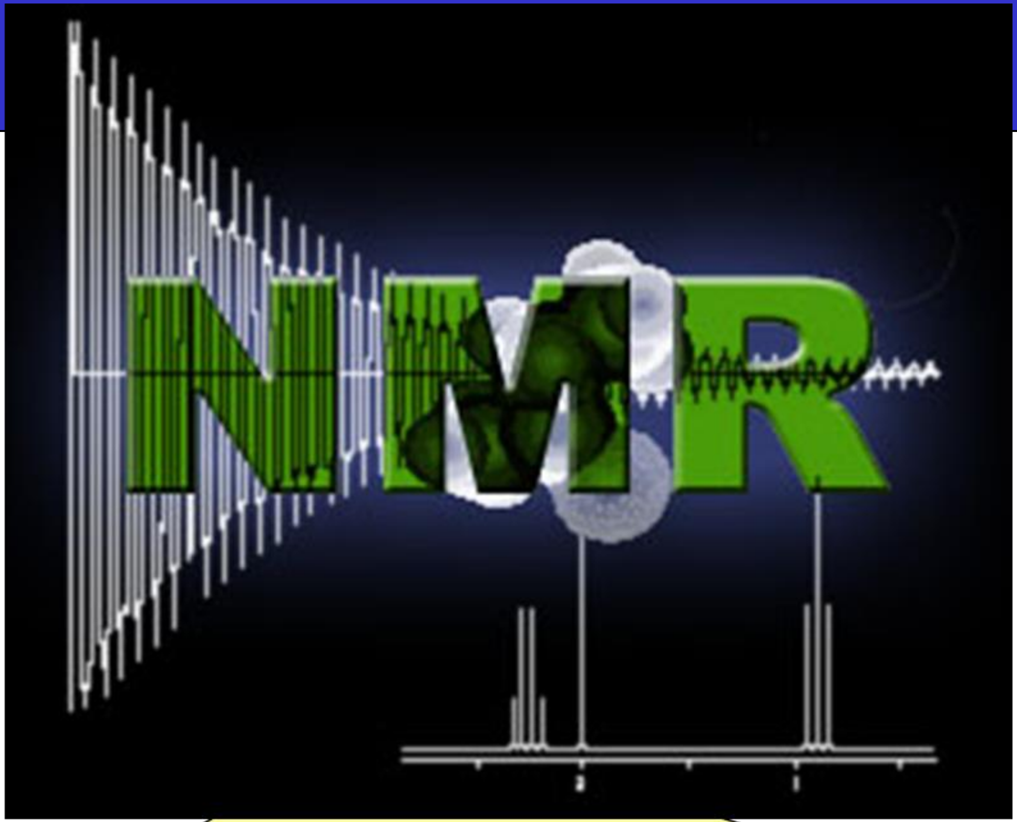


B_0, External magnetic field

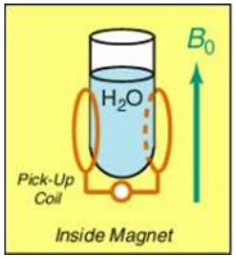
RF waves in

Nuclear magnetic moments in the sample

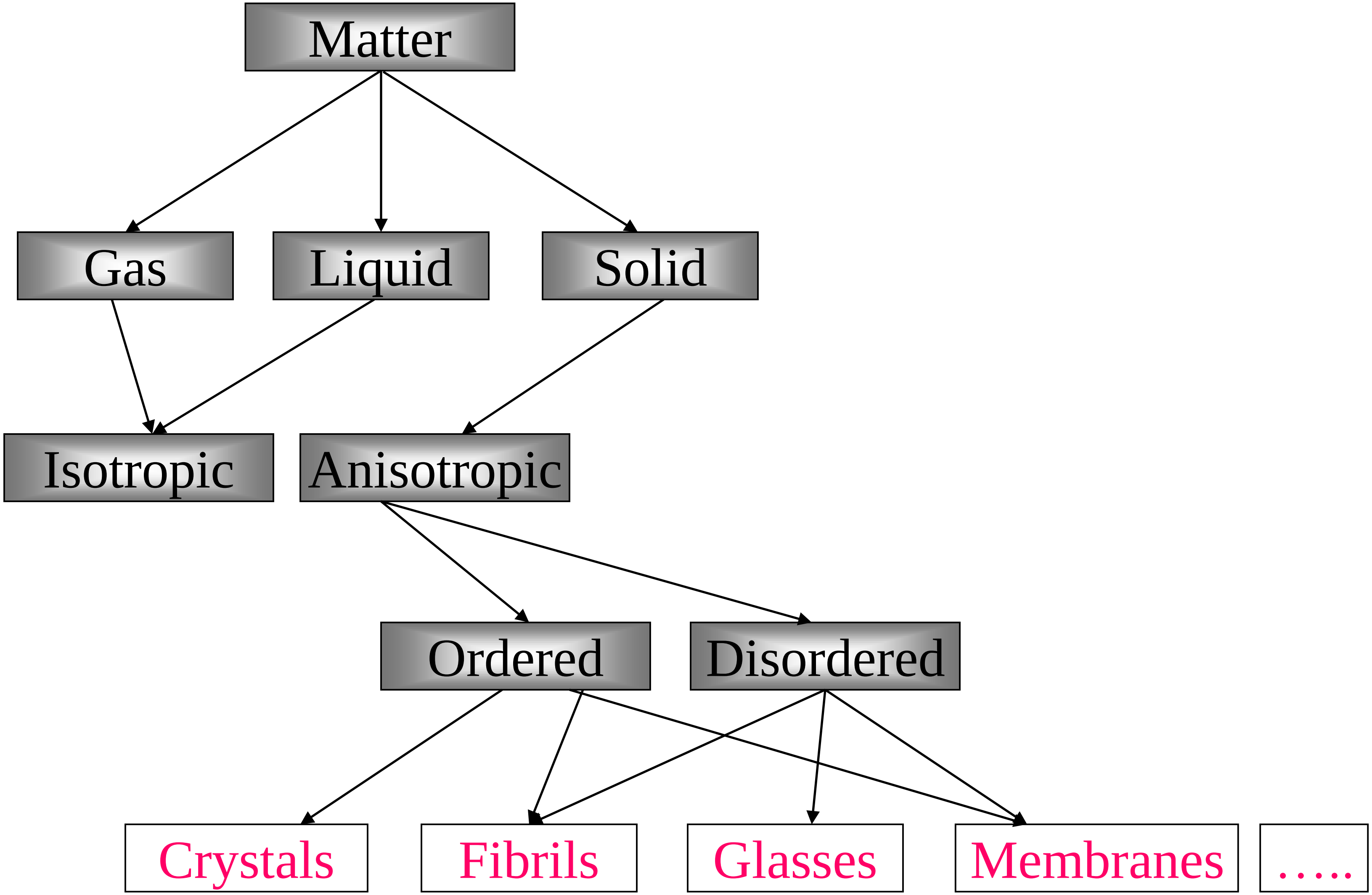
RF waves out



The frequency of emitted RF waves reveals information about the magnetic environment of atomic nuclei



Matter: NMR Classification



Matter

Gas

Liquid

Solid

Isotropic

Anisotropic

Ordered

Disordered

Crystals

Fibrils

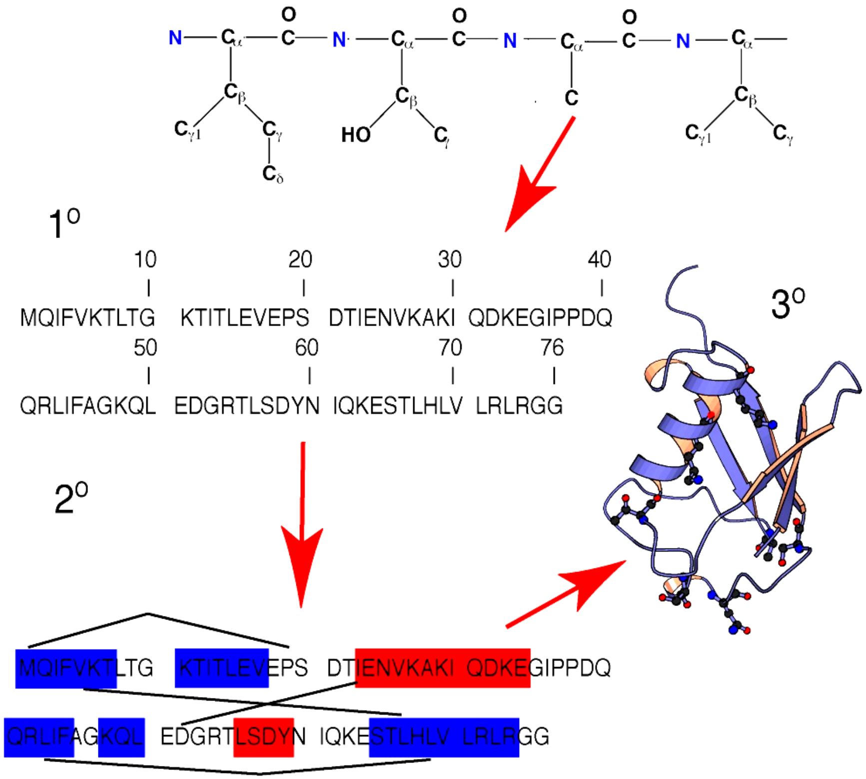
Glasses

Membranes

…..

Solution-State NMR: General Protocol

1. **Isotopically label protein (^{15}N, ^{13}C)**
2. **Assign the chemical shifts**
3. **Collect restraints**
4. **Calculate structure**
5. **Refine (repeat)**



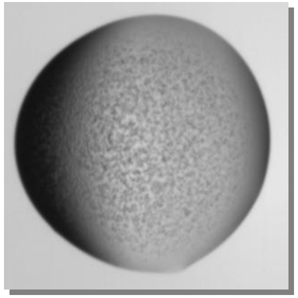
This has been done over 5,000 times in solution!

(http://www.pdb.org/pdb/statistics/holdings.do)

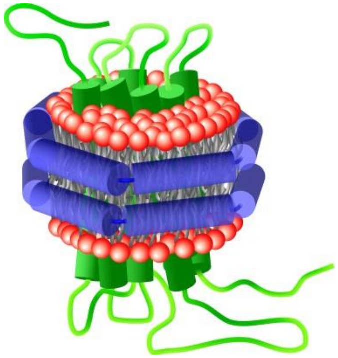
Kumar, A.; Ernst, R.R.; Wüthrich, K. Biochem. Biophys. Res. Comm. 1980, 95, 1–6.
Williamson, M.P.; Havel, T.F.; Wüthrich, K., J. Mol. Biol. 1985, 182, 295–315.

Solid-State NMR in Structural Biology

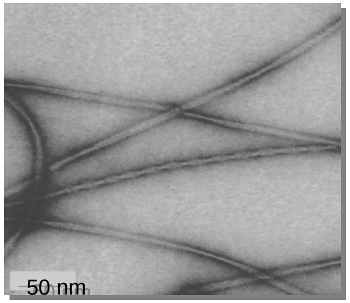
Many proteins cannot be studied by the traditional structural methods (X-ray crystallography or solution NMR)



Nano/microcrystalline globular proteins

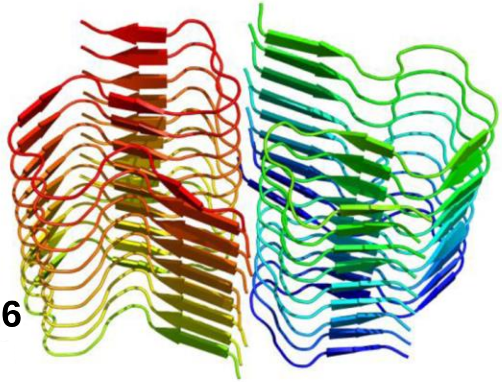


Membrane proteins



Fibrils

Aβ_{42} Fibrils



Bob Griffin and coworkers, 2016

Solution- and Solid-State NMR

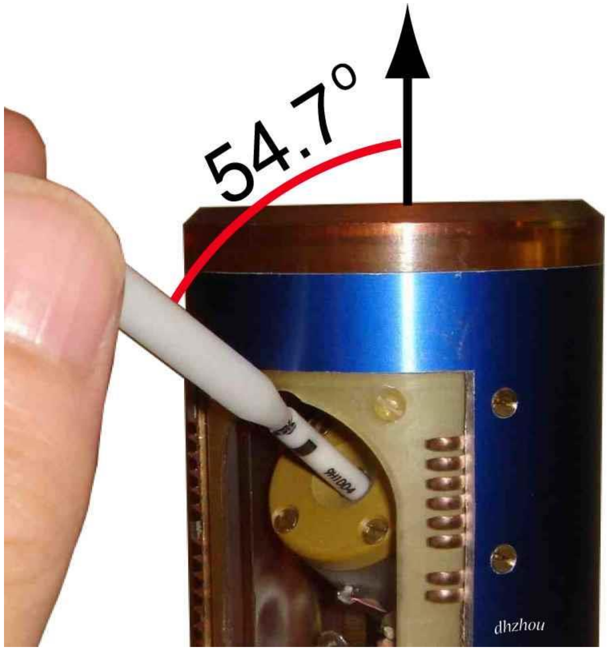
Solution NMR:

- size limitation
- very narrow resonances

Solid-state NMR:

- no size limit on samples
- broader resonances

Solution NMR sample tube



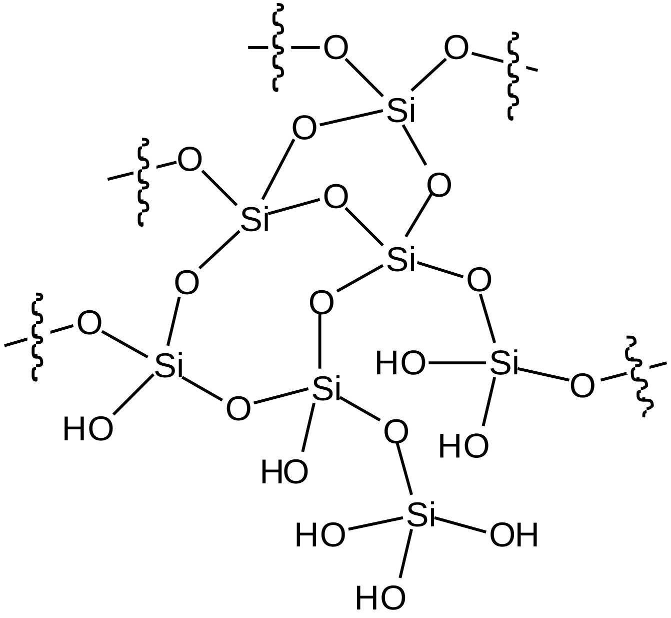
Solid-state NMR probe

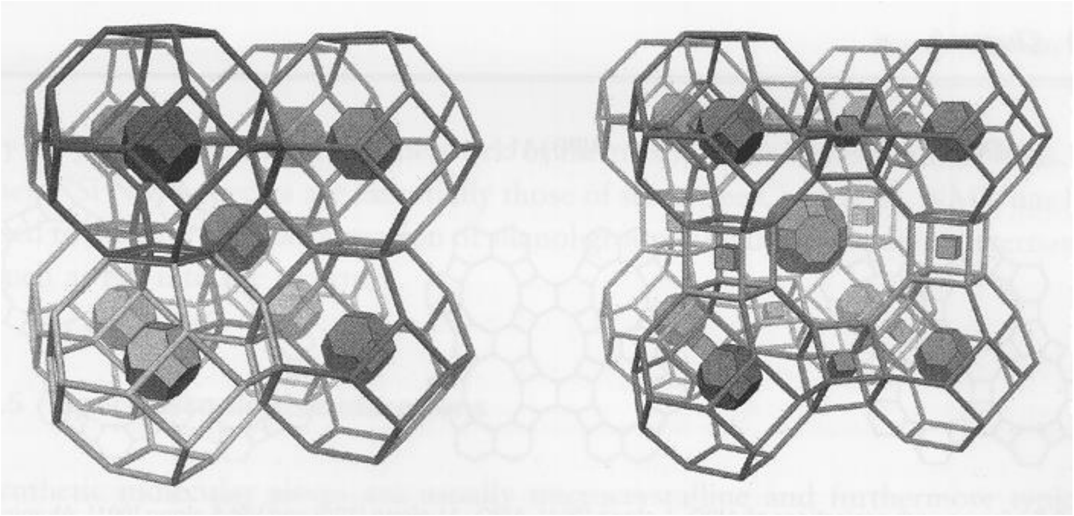
Targets for SSNMR: Biology

- Lipid bilayers
- Membranes reconstituted with different additives such as cholesterol, drugs or peptides
- Structure analysis of membrane-active peptides, ion channels, and receptors
- Amyloid fibrils
- Globular proteins, IDP’s
- ………………..

Targets for SSNMR

Polymers, Zeolites, Glasses, ………...





Reality

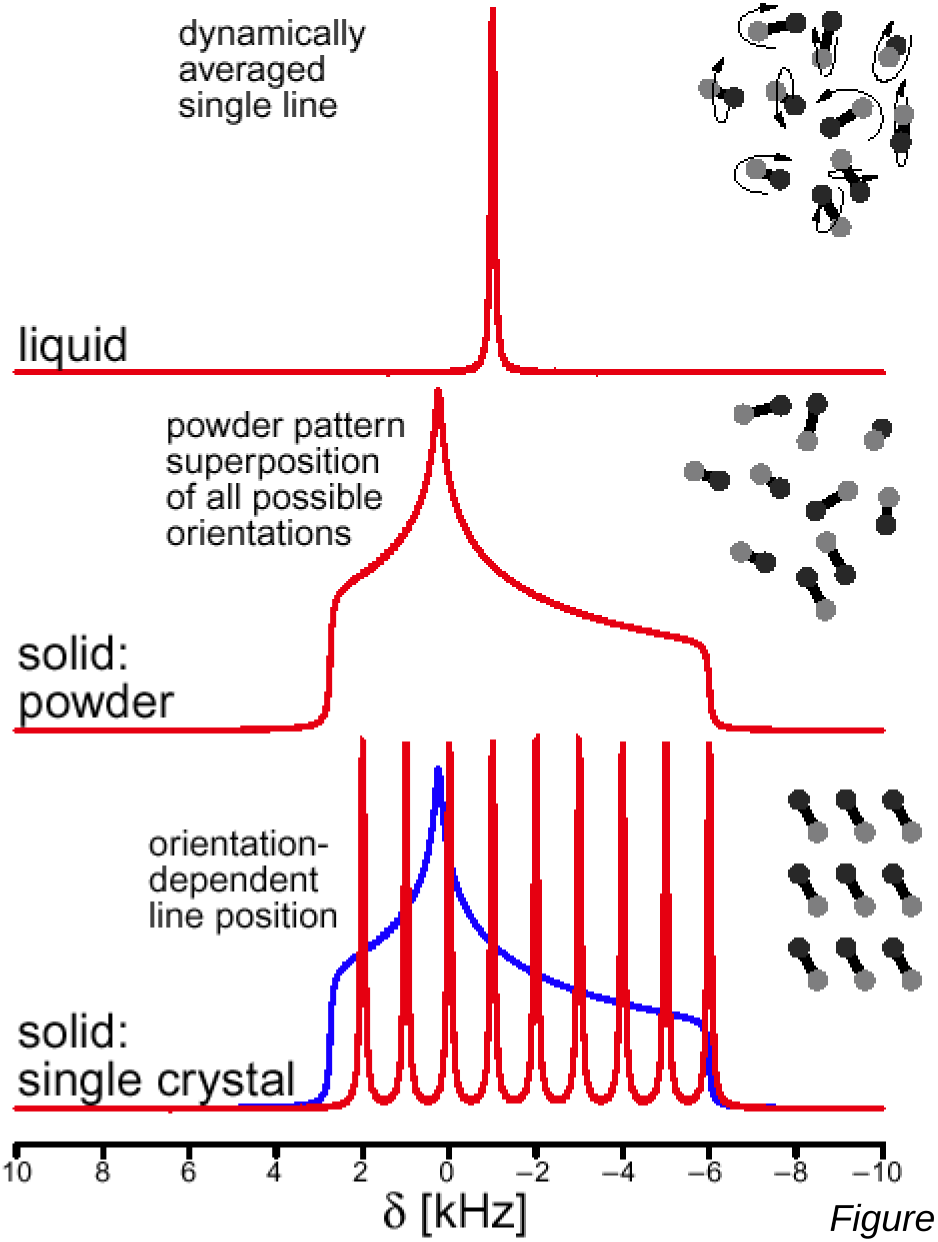
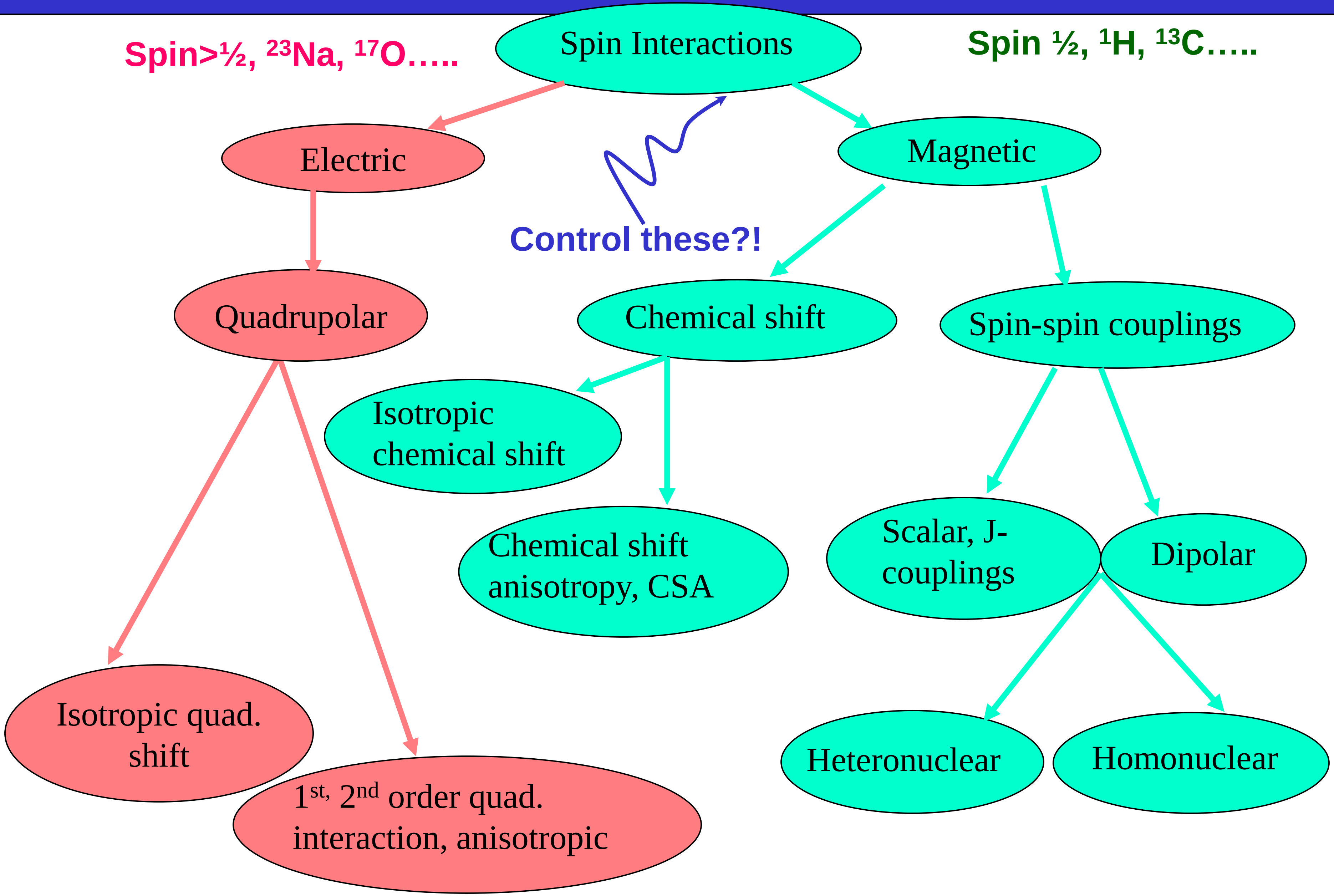


Figure courtesy: Matthias Ernst

Nuclear Spin Interactions



Spin>½, ^{23}Na, ^{17}O…..

Spin Interactions

Spin ½, ^{1}H, ^{13}C…..

Electric

Magnetic

Control these?!

Quadrupolar

Chemical shift

Spin-spin couplings

Isotropic chemical shift

Chemical shift anisotropy, CSA

Scalar, J-couplings

Dipolar

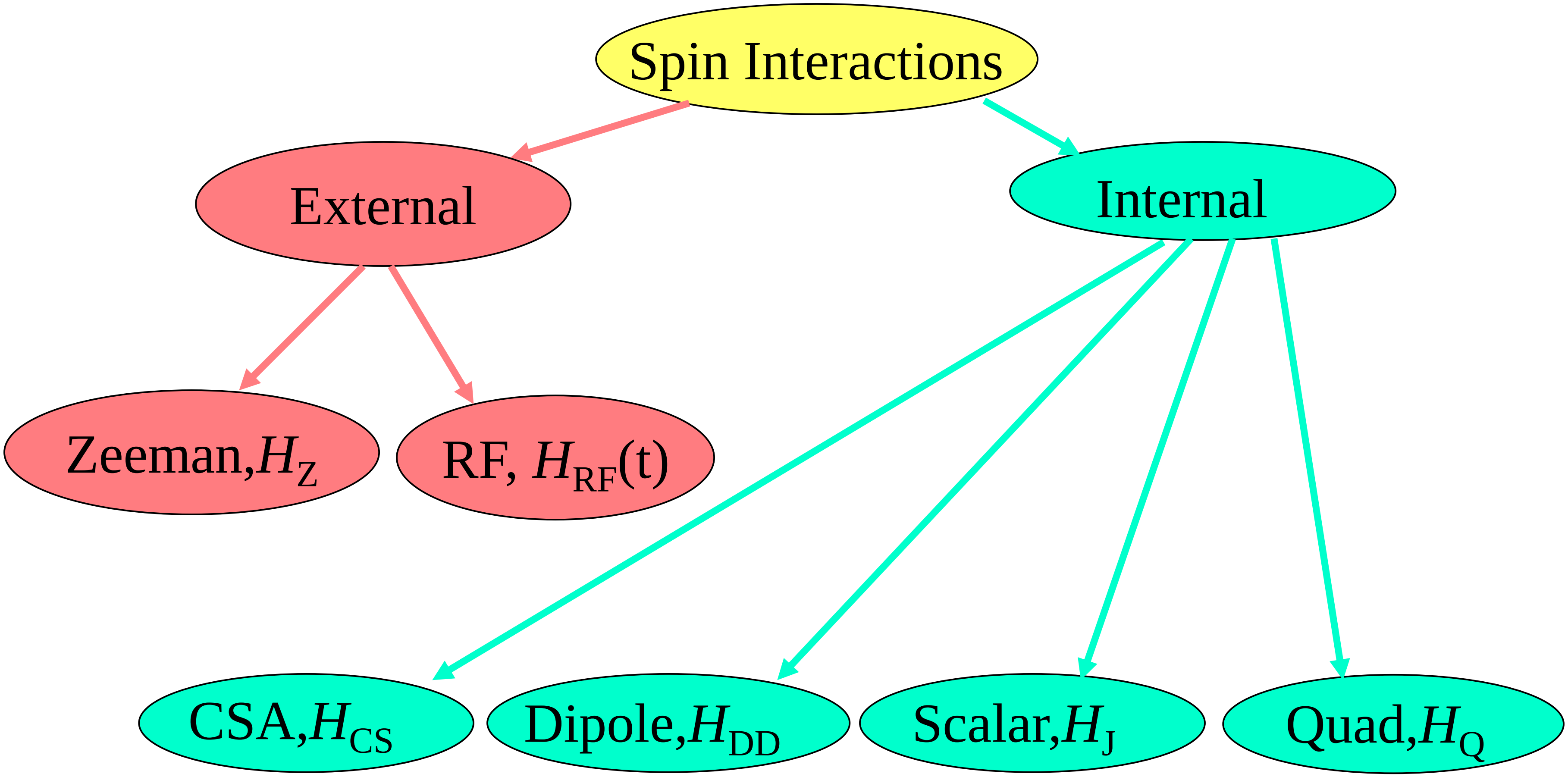
Isotropic quad. shift

1st, 2nd order quad. interaction, anisotropic

Heteronuclear

Homonuclear

Nuclear Spin Interactions



Spin Interactions

External

Internal

Zeeman,H_Z

RF, $H_{RF}(t)$

CSA,H_{CS}

Dipole,H_{DD}

Scalar,H_J

Quad,H_Q

Only the isotropic parts manifest in solution-state.

Spin: Some History

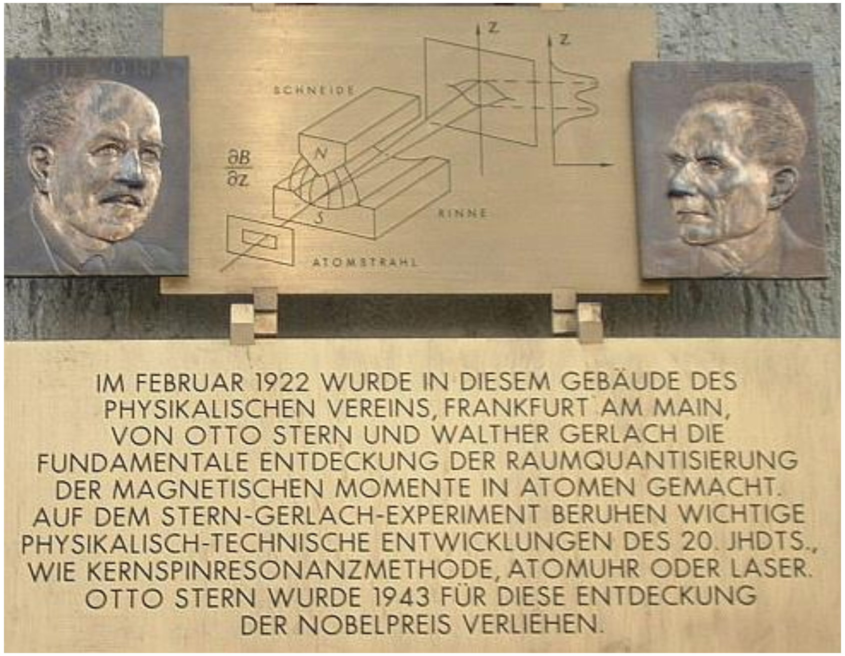
- **Uhlenbeck and Goudsmit**: particles have “spin”, corresponding to rotation of a particle spinning around its own axis
- Spin of the electron is ½: two states +½=“spin-up” and –½=“spin-down”
- This is not fully consistent from what people knew before. However, this is appropriate because spin is a quantum notion (we do not know why!)
- Stern-Gerlach experiment

✓ The beam of atoms is deflected by inhomogeneous field

✓ Reason: intrinsic magnetic moment (spin) of particles

✓ The distribution of the μ-vector is not continuous!

✓ Spin is quantised!!!



IM FEBRUAR 1922 WURDE IN DIESEM GEBÄUDE DES
PHYSIKALISCHEN VEREINS, FRANKFURT AM MAIN,
VON OTTO STERN UND WALTHER GERLACH DIE
FUNDAMENTALE ENTDECKUNG DER RAUMQUANTISIERUNG
DER MAGNETISCHEN MOMENTE IN ATOMEN GEMACHT.
AUF DEM STERN-GERLACH-EXPERIMENT BERUHEN WICHTIGE
PHYSIKALISCH-TECHNISCHE ENTWICKLUNGEN DES 20. JHDTS.,
WIE KERNSPINRESONANZMETHODE, ATOMUHR ODER LASER.
OTTO STERN WURDE 1943 FÜR DIESE ENTDECKUNG
DER NOBELPREIS VERLIEHEN.

Spin

- Spin of a particle is its intrinsic angular momentum (as if the particle rotates). Honestly, nobody knows where spin comes from.
- Spin is a very fundamental concept, which also affects the symmetry of the w.f. of a system of identical particles. Example: Pauli principle.
- Spin is a quantum notion: it vanishes if we tend $\hbar \to 0$!

- Spin operators are introduced in the same way as those for the angular momentum:
  - Eigen-states are $\left| S, S_z \right\rangle$; $S^2 = S(S+1)$, S_z varies from $-S$ to S.
  - Commutation rules are

$$[\hat{S}_y, \hat{S}_z] = i\hat{S}_x,\ [\hat{S}_z, \hat{S}_x] = i\hat{S}_y,\ [\hat{S}_x, \hat{S}_y] = i\hat{S}_z$$

- An important difference from angular momentum: spin can be half-integer
- Spin operators are $(2S+1)*(2S+1)$ matrices
- For $S=1/2$ such matrices are related to the Pauli matrices

Spin-½

- Spin operator can be written as

$$\hat{\vec{S}} = \frac{1}{2}\hat{\vec{\sigma}}, \quad \hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Basis

$$\boxed{\begin{matrix} |\alpha\rangle = |\uparrow\rangle \\ |\beta\rangle = |\downarrow\rangle \end{matrix}}$$

- Useful relations of the Pauli matrices:

$$\hat{\sigma}_x^2 = \hat{\sigma}_y^2 = \hat{\sigma}_z^2 = \hat{e}, \quad \hat{\sigma}_y\hat{\sigma}_z = i\hat{\sigma}_x, \quad \hat{\sigma}_z\hat{\sigma}_x = i\hat{\sigma}_y, \quad \hat{\sigma}_x\hat{\sigma}_y = i\hat{\sigma}_z$$

$$\hat{\sigma}_i\hat{\sigma}_k + \hat{\sigma}_k\hat{\sigma}_i = 2\delta_{ik}, \quad \left[\hat{\sigma}_i, \hat{\sigma}_j\right] = 2i\varepsilon_{ijk}\hat{\sigma}_k, \quad \mathrm{Tr}\{\hat{\sigma}_i\} = 0$$

- Every 2*2 Hermitian matrix is a linear combination of the unity matrix and the Pauli matrices

Spin-1/2 Angular Momentum Operators

- Spin-1/2 nuclei have two Zeeman eigenstates:

$$|\alpha\rangle = |\frac{1}{2}, \frac{+1}{2}\rangle$$

$$|\beta\rangle = |\frac{1}{2}, \frac{-1}{2}\rangle$$

$$\boxed{\begin{aligned} |\alpha\rangle &= |\uparrow\rangle \\ |\beta\rangle &= |\downarrow\rangle \end{aligned}}$$

- Angular momentum spin operators in the Zeeman eigenbasis:

$$I_x = \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad I_y = \tfrac{1}{2i}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \qquad I_z = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- Action of spin operators on the Zeeman eigenstates:

$$I_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle \qquad I^+|\alpha\rangle = 0 \qquad I^-|\alpha\rangle = |\beta\rangle$$

$$I_z|\beta\rangle = \frac{-1}{2}|\beta\rangle \qquad I^+|\beta\rangle = |\alpha\rangle \qquad I^-|\beta\rangle = 0$$

Spin-1/2 Rotation Operators

- Rotation operators:

$$R_x(\beta) = \exp(-i\beta I_x)$$
$$R_y(\beta) = \exp(-i\beta I_y)$$
$$R_z(\beta) = \exp(-i\beta I_z)$$

- Evaluation of rotation: $R_x(\beta) I_y R_x(-\beta) = I_y \cos\beta + [I_x, I_y] \sin\beta$

- Spin-1/2 rotation operators:

$$R_x(\beta) = \begin{pmatrix} \cos\frac{1}{2}\beta & -i\sin\frac{1}{2}\beta \\ -i\sin\frac{1}{2}\beta & -\cos\frac{1}{2}\beta \end{pmatrix} \qquad R_y(\beta) = \begin{pmatrix} \cos\frac{1}{2}\beta & -\sin\frac{1}{2}\beta \\ \sin\frac{1}{2}\beta & \cos\frac{1}{2}\beta \end{pmatrix}$$

$$R_z(\beta) = \begin{pmatrix} \exp\{-i\frac{1}{2}\beta\} & 0 \\ 0 & \exp\{i\frac{1}{2}\beta\} \end{pmatrix}$$

Spin ½: rotations

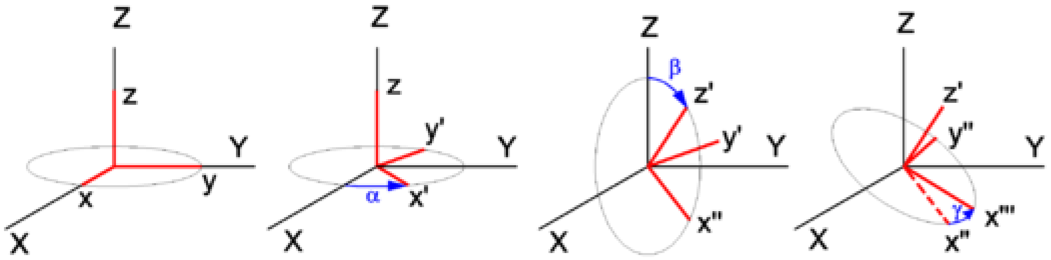
- Generally, the rotation operator is

$$\hat{U}(\vec{n},\varphi)=\exp\left[-i\varphi\left(\vec{n}\cdot\hat{\vec{\sigma}}\right)/2\right]=\cos\frac{\varphi}{2}-i\left(\vec{n}\cdot\hat{\vec{\sigma}}\right)\sin\frac{\varphi}{2}$$

- Explicitly, rotations about *X*,*Y*,*Z*

$$\hat{U}_x(\varphi)=\begin{pmatrix}\cos\frac{\varphi}{2} & \sin\frac{\varphi}{2}\\ \sin\frac{\varphi}{2} & \cos\frac{\varphi}{2}\end{pmatrix},\quad \hat{U}_y(\varphi)=\begin{pmatrix}\cos\frac{\varphi}{2} & i\sin\frac{\varphi}{2}\\ -i\sin\frac{\varphi}{2} & \cos\frac{\varphi}{2}\end{pmatrix},\quad \hat{U}_z(\varphi)=\begin{pmatrix}e^{i\varphi/2} & 0\\ 0 & e^{-i\varphi/2}\end{pmatrix},$$

- Euler rotations
  transition from any reference frame to a new frame can be achieved by three elemental rotations



- We go from an old *x*,*y*,*z* to new *x*,*y*,*z* : *zyz*-rotation by *α*,*β*,*γ*
- The rotation operator is

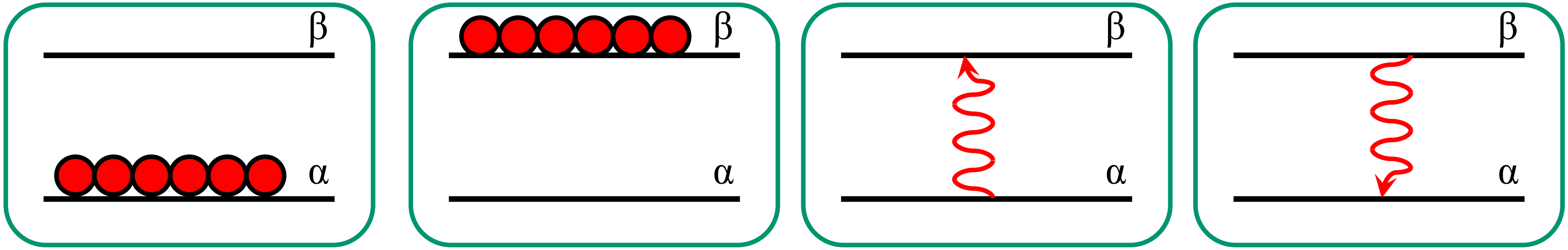
$$\hat{R}=\hat{R}(\alpha,\beta,\gamma)=\hat{R}_{z''}(\gamma)\hat{R}_y(\beta)\hat{R}_z(\alpha)$$

Density Matrix of a Spin-½ Particle

- D.m. of a spin ½ particle:

$$\rho = \begin{pmatrix} \rho_{\alpha\alpha} & -\rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix}$$

$$\rho = \overline{|\psi\rangle\langle\psi|} \implies \rho^2 = \rho$$



$\rho_{\alpha\alpha}$ $\rho_{\beta\beta}$ $\rho_{-} = \rho_{\alpha\beta}$ $\rho_{+} = \rho_{\beta\alpha}$

- Physical meaning of the elements:

  Diagonal elements are populations

  Off-diagonal elements are coherences ρ_{mn}

  The trace of the d.m. is equal to 1

- The d.m. is a Hermitian matrix: $(N^2 - 1)$ independent parameters

- The equilibrium density matrix becomes:

$$\rho^{eq} = \begin{pmatrix} \frac{1}{2} + \frac{1}{4}B & 0 \\ 0 & \frac{1}{2} - \frac{1}{4}B \end{pmatrix}$$

$$B = \frac{\hbar\omega_o}{k_B T}$$

Two or More Spins ½

- The d.m. for two spins can be expressed in terms of product operators

$$\{\hat{E},\hat{S}_x,\hat{S}_y,\hat{S}_z\}\otimes\{\hat{E},\hat{I}_x,\hat{I}_y,\hat{I}_z\}=\left\{\begin{matrix}\hat{E};\hat{S}_x,\hat{S}_y,\hat{S}_z;\hat{I}_x,\hat{I}_y,\hat{I}_z;\hat{S}_x\hat{I}_x,\hat{S}_y\hat{I}_x,\hat{S}_z\hat{I}_x,\\ \hat{S}_x\hat{I}_y,\hat{S}_y\hat{I}_y,\hat{S}_z\hat{I}_y,\hat{S}_x\hat{I}_z,\hat{S}_y\hat{I}_z,\hat{S}_z\hat{I}_z\end{matrix}\right\}$$

- Each product operator is now a 4*4 matrix; likewise, the Hamiltonian is a 4*4 matrix and it is expressed via the product operators
- What is the direct product (Kronecker product)?

$$\hat{A}\otimes\hat{B}=\begin{pmatrix}a_{11} & a_{12}\\ a_{21} & a_{22}\end{pmatrix}\otimes\begin{pmatrix}b_{11} & b_{12}\\ b_{21} & b_{22}\end{pmatrix}=\begin{pmatrix}a_{11}\hat{B} & a_{12}\hat{B}\\ a_{21}\hat{B} & a_{22}\hat{B}\end{pmatrix}=\begin{pmatrix}a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12}\\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22}\\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12}\\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22}\end{pmatrix}$$

- Example with 2 spins:

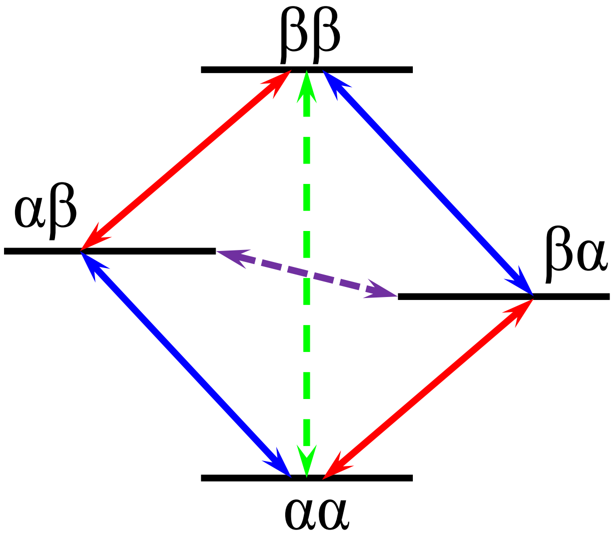
$$\hat{S}_x=\hat{S}_x\otimes\hat{E}=\begin{pmatrix}0 & 1/2\\ 1/2 & 0\end{pmatrix}\otimes\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}=\frac{1}{2}\begin{pmatrix}0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\end{pmatrix}$$

- Other operators can be constructed in the same way. More spins: use direct products of spin operators

Two Spins-½

- Relation between populations/coherences and d.m. elements

Energy level diagram



Density matrix

	αα	**αβ**	**βα**	**ββ**
αα	$p_{\alpha\alpha}$	**SQC**	**SQC**	**DQC**
αβ	**SQC**	$p_{\alpha\beta}$	**ZQC**	**SQC**
βα	**SQC**	**ZQC**	$p_{\beta\alpha}$	**SQC**
ββ	**DQC**	**SQC**	**SQC**	$p_{\beta\beta}$

- SQCs are given by S_x, S_y, S_xI_z, S_yI_z, I_x, I_y, S_zI_x, S_zI_y
- DQCs and ZQCs are given by combinations of S_xI_x, S_yI_y, S_xI_y, S_yI_x
- We can directly measure only transverse magnetization S_x, S_y, I_x, I_y
- Other operators cannot be observed directly, but they affect the signal
- Coherence order for ρ_{mn}: $p_{mn} = M(|m\rangle) - M(|n\rangle)$

Evolution of the Density Matrix

- The S.e. in the bra and ket representations is

$$\frac{\partial}{\partial t}\left|\Psi\right\rangle = -\frac{i}{\hbar}\hat{H}\left|\Psi\right\rangle, \qquad \frac{\partial}{\partial t}\left\langle\Psi\right| = \frac{i}{\hbar}\left\langle\Psi\right|\hat{H}$$

- The equation for the d.m. is as follows:

$$\frac{\partial}{\partial t}\hat{\rho} = \frac{\partial}{\partial t}\left\{\left|\Psi\right\rangle\left\langle\Psi\right|\right\} = \left\{\frac{\partial}{\partial t}\left|\Psi\right\rangle\right\}\left\langle\Psi\right| + \left|\Psi\right\rangle\left\{\frac{\partial}{\partial t}\left\langle\Psi\right|\right\} = -\frac{i}{\hbar}\left[\hat{H},\hat{\rho}\right]$$

Liouville-von Neumann equation:

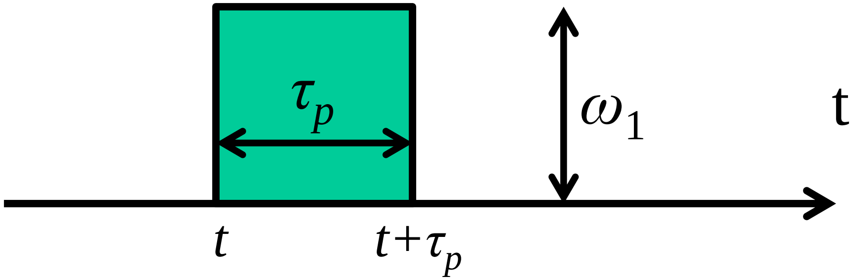
$$\rho(t) = \exp(-\tfrac{i}{\hbar}Ht)\rho_0 \exp(\tfrac{i}{\hbar}Ht)$$

$$\rho(t) = U(t)\rho(0)U^{-1}t$$

- U is the propagator, time dependent, and unitary
- The solution is simple for a time-independent Hamiltonian:
- For a time-dependent Hamiltonian we solve the equation numerically in small time steps or use some tricks

RF-Pulses

- What happens to the d.m. (magnetization) when we apply a pulse?



the phase is ϕ_p
the flip angle is $\varphi=\omega_1\tau_p$

- The w.f. and d.m. after the pulse

$$\left|\Psi_{after}\right\rangle = \hat{R}_{\phi_p}(\varphi)\left|\Psi_{before}\right\rangle, \qquad \left\langle\Psi_{after}\right| = \left\langle\Psi_{before}\right|\hat{R}_{\phi_p}(-\varphi)$$

$$\hat{\rho}_{after} = \hat{R}_{\phi_p}(\varphi)\hat{\rho}_{before}\hat{R}_{\phi_p}(-\varphi)$$

- The action of a strong pulse is equivalent to a rotation (we assume that only the B_1-term is relevant)

$$\hat{R}_{\phi_p}(\varphi) = \exp\left[-i\omega_1\tau_p\left(\cos\phi_p\hat{S}_x + \sin\phi_p\hat{S}_y\right)\right] = \exp\left[-i\varphi\left(\cos\phi_p\hat{S}_x + \sin\phi_p\hat{S}_y\right)\right]$$

- A π/2-pulse generates a coherence, a π-pulse inverts the populations

$$\hat{R}_{\phi_p}(\pi/2)\hat{S}_z\hat{R}_{\phi_p}(-\pi/2) = -\hat{S}_y, \qquad \hat{R}_{\phi_p}(\pi)\hat{S}_z\hat{R}_{\phi_p}(-\pi) = -\hat{S}_z$$

“Sandwich relationships”

- Is there a simple way to calculate the effect of pulses?
- Three cyclically commuting operators:

$$\left[\hat{A},\hat{B}\right]=i\hat{C},\quad \left[\hat{C},\hat{A}\right]=i\hat{B},\quad \left[\hat{B},\hat{C}\right]=i\hat{A}$$

- Example:

$$[\hat{S}_y,\hat{S}_z]=i\hat{S}_x,\ [\hat{S}_z,\hat{S}_x]=i\hat{S}_y,\ [\hat{S}_x,\hat{S}_y]=i\hat{S}_z$$

- The following relation is then true:

$$\exp\left[-i\theta\hat{A}\right]\hat{B}\exp\left[i\theta\hat{A}\right]=\cos\theta\,\hat{B}+\sin\theta\,\hat{C}$$

- A, B, C are like the axis of our 3D-space; we “rotate” *B* “around” A by the angle θ. Cyclic permutations provide two more relations

$$\exp\left[-i\theta\hat{B}\right]\hat{C}\exp\left[i\theta\hat{B}\right]=\cos\theta\,\hat{C}+\sin\theta\,\hat{A}$$
$$\exp\left[-i\theta\hat{C}\right]\hat{A}\exp\left[i\theta\hat{C}\right]=\cos\theta\,\hat{A}+\sin\theta\,\hat{B}$$

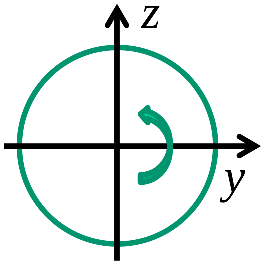
- Of course, these rules apply to the spin operators
- RF-pulses give *x* and *y*-rotations. Free precession gives a *z*-rotation by a time-dependent angle ωt

See M. H. Levitt, “Spin Dynamics”, cyclic commutation

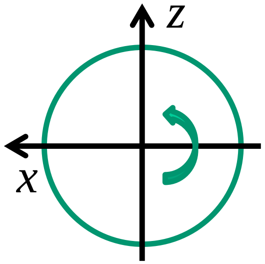
Phase of the Pulse

- Different phases

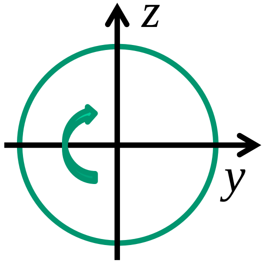
x-pulse, $\phi_p=0$



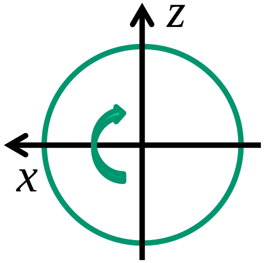
y-pulse, $\phi_p=\pi/2$



–*x*-pulse, $\phi_p=\pi$



–*y*-pulse, $\phi_p=2\pi/2$

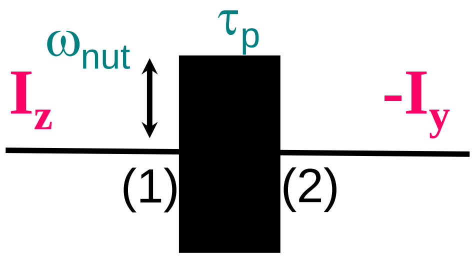


- Pulse of a general phase is a combination of three rotations

$$\hat{R}_{\phi_p}(\varphi)=\exp\left[-i\varphi\left(\cos\phi_p\hat{S}_x+\sin\phi_p\hat{S}_y\right)\right]=\hat{R}_z\left(\phi_p\right)\hat{R}_x(\varphi)\hat{R}_z\left(-\phi_p\right)$$

- Rotation about z turns the {x,y} axes; then a pulse is turning the spins around the new x; finally, we return to the original frame
- Free precession is just a *z*-rotation

Representation of *x*-Pulse



Assume ϕ_p=0

Pulse characteristics:

Frequency, w_{ref}
Phase, f_p
Amplitude, w_{nut}
Flip angle of the pulse: $\beta_p = \omega_{nut}\tau_p$

- Pulse and density matrix: $\rho^{eq} = \begin{pmatrix} \frac{1}{2}+\frac{1}{4}B & 0 \\ 0 & \frac{1}{2}-\frac{1}{4}B \end{pmatrix}$

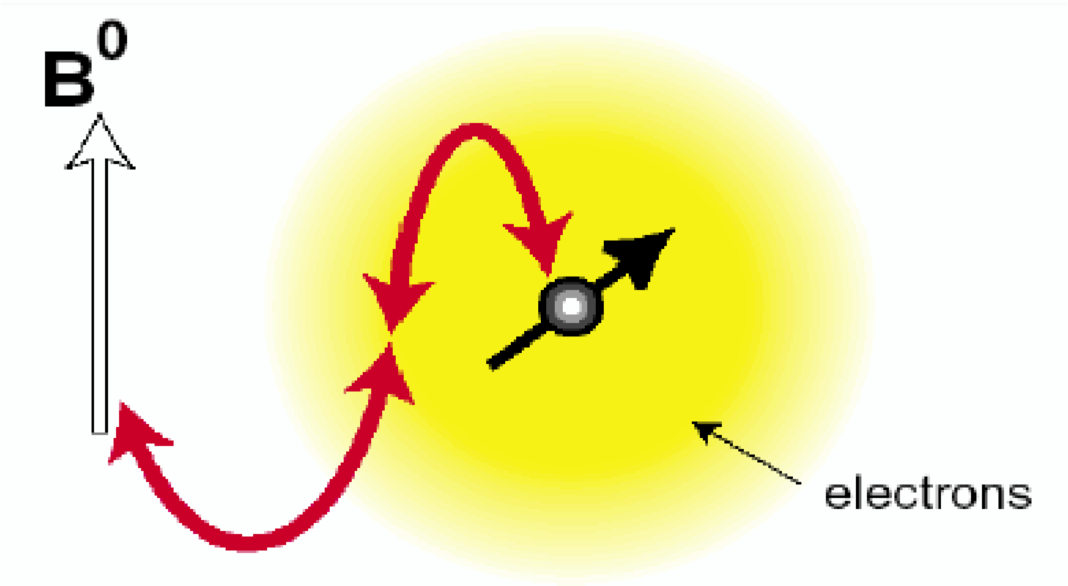
$$\Big\downarrow \quad R_x\left(\frac{\pi}{2}\right)$$

$$\rho = \begin{pmatrix} \frac{1}{2} & -\frac{B}{4} \\ \frac{B}{4} & \frac{1}{2} \end{pmatrix}$$

- Pulse equalises the populations of the two states
- Pulse converts the population difference into coherences

Some Hamiltonians and Their Representations

Chemical-Shift Anisotropy Hamiltonian



CSA interaction: Indirect magnetic interaction between the external field and the nuclear spins through the electron cloud at each nuclear spin site

Information about the local environment of the nuclear spins

Chemical-Shift Anisotropy Hamiltonian

$$\boldsymbol{B}^{j}_{local} = \boldsymbol{B}_0 + \boldsymbol{B}^{j}_{induced}$$

$$\boldsymbol{B}^{j}_{induced} = \boldsymbol{\delta}^{j} . \boldsymbol{B}_0$$

$\boldsymbol{\delta}^{j}$ is the CSA tensor at the nuclear spin site j

$$\delta^{j} = \begin{pmatrix} \delta^{j}_{xx} & \delta^{j}_{xy} & \boxed{\delta^{j}_{xz}} \\ \delta^{j}_{yx} & \delta^{j}_{yy} & \boxed{\delta^{j}_{yz}} \\ \delta^{j}_{zx} & \delta^{j}_{zy} & \boxed{\delta^{j}_{zz}} \end{pmatrix}$$

The chemical-shift tensor

Induced field is not always parallel to the Zeeman field

Only terms relevant, since the static field is along the z direction

Chemical-Shift Anisotropy Hamiltonian

$$\boldsymbol{B}^{j}_{induced} = \delta^{j}.\boldsymbol{B}_{0}$$

The CS Hamiltonian is, hence, orientation dependent

$$H^{j}_{CS} = -\mu_{j}.\boldsymbol{B}^{j}_{induced}$$

$$= -\gamma_{j}\delta^{j}_{xz}(\Theta)B_{0}I_{jx} - \gamma_{j}\delta^{j}_{yz}(\Theta)B_{0}I_{jy} - \gamma_{j}\delta^{j}_{zz}(\Theta)B_{0}I_{jz}$$

Orientation of the molecule with respect to B_0 and
the position of the nuclear spin within the molecule

Secular approximation:

$$H^{j}_{CS} = -\gamma_{j}\delta^{j}_{zz}(\Theta)B_{0}I_{jz}$$

Chemical-Shift Anisotropy Hamiltonian

$$H_{CS}^{j} = -\gamma_j \delta_{zz}^{j}(\Theta) B_0 I_{jz}$$

In liquids, perform an orientational average:

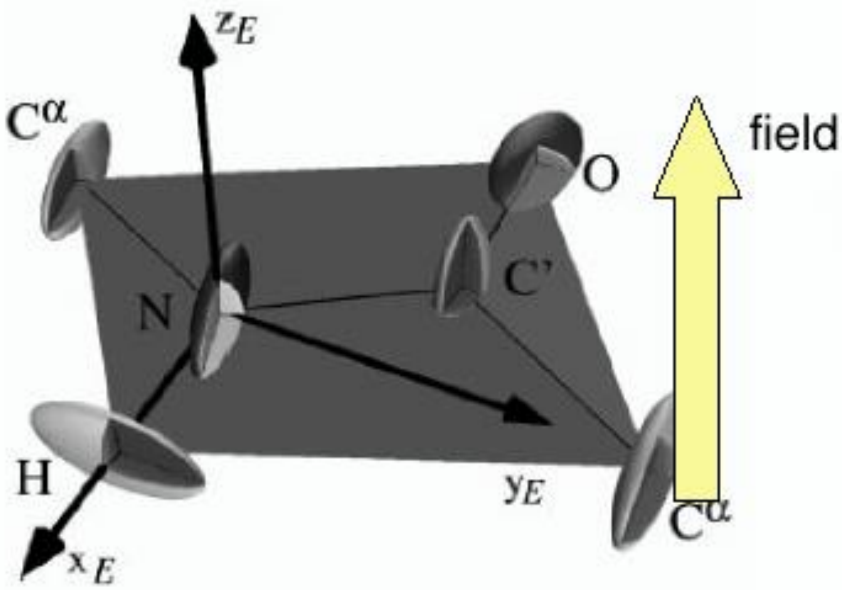
$$H_0^j = H_{static}^j + H_{iso-CS}^j = \omega_0^j I_{jz}$$

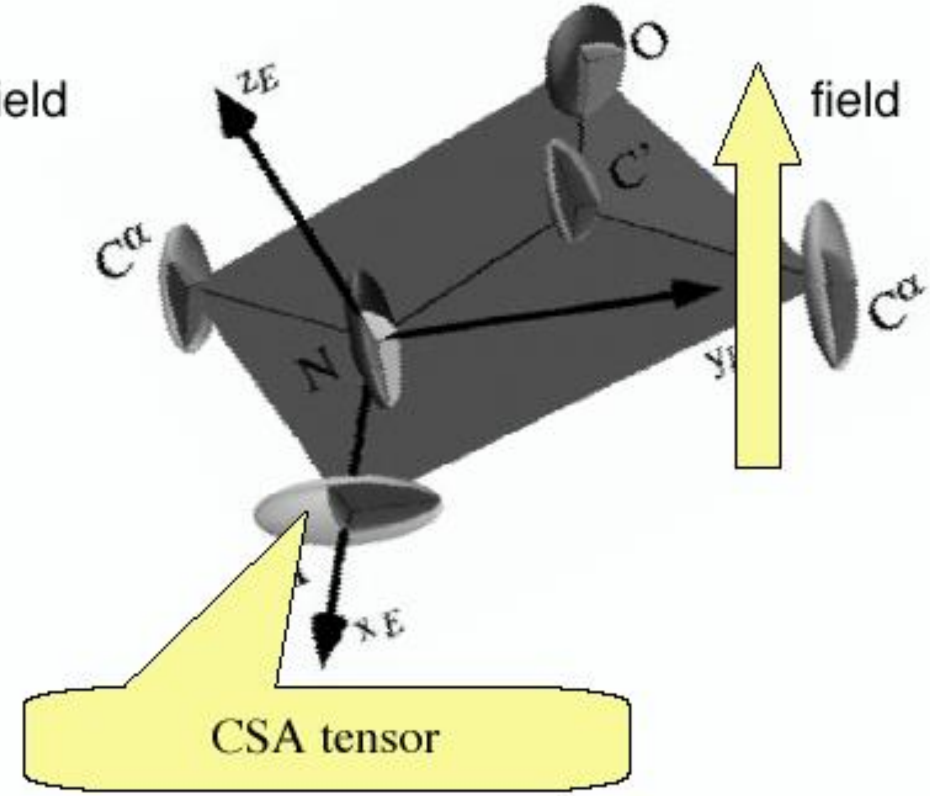
The chemically-shifted Larmor frequency $\omega_0^j = -\gamma_j B_0 \, (1 + \delta_{iso-CS}^j)$

In liquids crystals, the resonance position depends upon the orientation (or phase transition which can shift the peak):

$$\overline{\delta_{zz}^{j}(\Theta)} \neq \delta_j^{iso}$$

Chemical-Shift Anisotropy Tensor





CSA tensor

Chemical shift depends on molecular orientation with respect to the field

Chemical-Shift Anisotropy Tensor

Irreducible components of a tensor

$$\delta = \delta_{iso}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} + \begin{pmatrix}0 & \alpha_{xy} & \alpha_{xz}\\ \alpha_{yx} & 0 & \alpha_{yz}\\ \alpha_{zx} & \alpha_{zy} & 0\end{pmatrix} + \begin{pmatrix}\beta_{xx} & \beta_{xy} & \beta_{xz}\\ \beta_{yx} & \beta_{yy} & \beta_{yz}\\ \beta_{zx} & \beta_{zy} & \beta_{zz}\end{pmatrix}$$

rank 0

rank 1
antisymmetric

rank 2
symmetric

$$\delta_{iso} = \frac{1}{3} Tr\delta$$

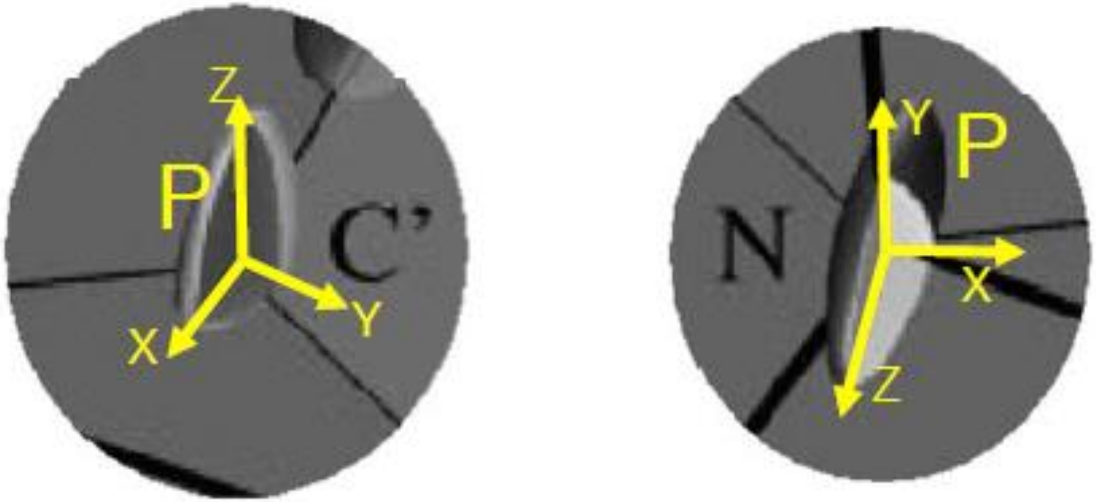
$$\alpha_{\mu\nu} = \frac{1}{2}(\delta_{\mu\nu} - \delta_{\nu\mu})$$

$$\beta_{\mu\nu} = \frac{1}{2}(\delta_{\mu\nu} + \delta_{\nu\mu} - 2\delta_{iso}\delta^{\mu}_{\nu})$$

$$\alpha_{ij} = -\alpha_{ji}$$
$$\beta_{ij} = \beta_{ji}$$

Principal Axes

There are three special directions in which the induced field is parallel to the applied field. These are called the principal axes of the tensor (CSA here), denoted as X, Y, and Z. The principal axes are in general different for various chemical sites.



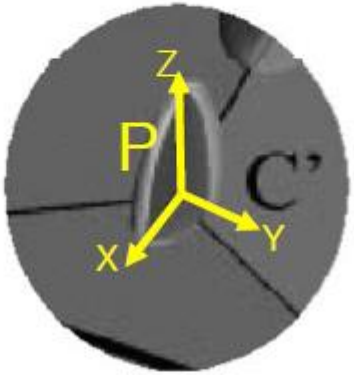
Principal Values

When the applied field is along a principal axis, the induced field is proportional and parallel to the applied field, multiplied by a number, which is called the principal value of the tensor, here, the CSA tensor.

$$B^{j}_{induced}(\text{along X}) = \delta^{j}_{XX} B_{applied}\ \ (\text{along X})$$

$$B^{j}_{induced}(\text{along Y}) = \delta^{j}_{YY} B_{applied}\ \ (\text{along Y})$$

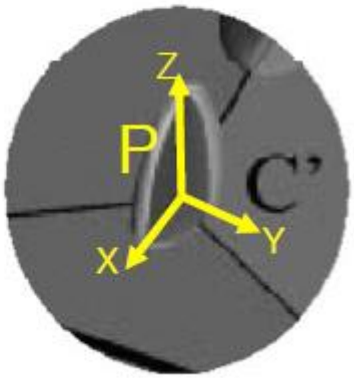
$$B^{j}_{induced}(\text{along Z}) = \delta^{j}_{ZZ} B_{applied}\ \ (\text{along Z})$$



Principal values of the chemical shift tensor for site j

Assignment of the Principal Axes

We use the following convention to assign the principal axes:



- The Z-axis is the one for which the principal value is the furthest from the isotropic shift
- The Y-axis is the one for which the principal value is the closest to the isotropic shift
- The X-axis is the other one

Ordering of the principal values:

$$|\delta^j_{ZZ} - \delta^j_{iso}| \geq |\delta^j_{XX} - \delta^j_{iso}| \geq |\delta^j_{YY} - \delta^j_{iso}|$$

Herzfeld and Berger, J. Chem. Phys. 73, 6021, 1980

Chemical-Shift Anisotropy Tensor

$$\delta = \delta_{iso}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} + \begin{pmatrix}0 & \alpha_{xy} & \alpha_{xz}\\ \alpha_{yx} & 0 & \alpha_{yz}\\ \alpha_{zx} & \alpha_{zy} & 0\end{pmatrix} + \begin{pmatrix}\beta_{xx} & \beta_{xy} & \beta_{xz}\\ \beta_{yx} & \beta_{yy} & \beta_{yz}\\ \beta_{zx} & \beta_{zy} & \beta_{zz}\end{pmatrix}$$

$$\delta^j_{iso} = \frac{1}{3}(\delta_{XX} + \delta_{YY} + \delta_{ZZ})$$ Isotropic chemical shift

$$\delta^j_{aniso} = \delta^j_{ZZ} - \delta^j_{iso}$$

CSA value

$$\eta^j = \frac{\delta^j_{YY} - \delta^j_{XX}}{\delta^j_{aniso}}$$

CSA asymmetry (shape)

$$\Delta\delta^j = \delta^j_{ZZ} - \delta^j_{XX}$$

CSA span

$$\delta^j_{PAS} = \delta^j_{iso}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} \qquad + \delta^j_{ZZ}\begin{pmatrix}-\frac{1}{2}(1+\eta^j) & 0 & 0\\ 0 & -\frac{1}{2}(1+\eta^j) & 0\\ 0 & 0 & 1\end{pmatrix}$$

Anet, O'Leary, Conc. Magn. Reson. 3, 193, 1991

Chemical-Shift Anisotropy Tensor

$$H_{CSA} = -\gamma\hbar I.\delta.B_0$$

$$\delta^j_{iso}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} \qquad \delta^j_{ZZ}\begin{pmatrix}-\frac{1}{2}(1+\eta^j) & 0 & 0\\ 0 & -\frac{1}{2}(1+\eta^j) & 0\\ 0 & 0 & 1\end{pmatrix}$$

Only term in solution-state, trace of the CSA tensor and invariant quantity

The orientation-dependent anisotropic term leading to spectral broadening

$$\delta^j_{iso} = \frac{1}{3}(\delta_{XX} + \delta_{YY} + \delta_{ZZ})$$ Isotropic chemical shift

$$\delta^j_{aniso} = \delta^j_{ZZ} - \delta^j_{iso}$$

CSA value

$$\eta^j = \frac{\delta^j_{YY} - \delta^j_{XX}}{\delta^j_{aniso}}$$

CSA asymmetry (shape)

$$\Delta\delta^j = \delta^j_{ZZ} - \delta^j_{XX}$$

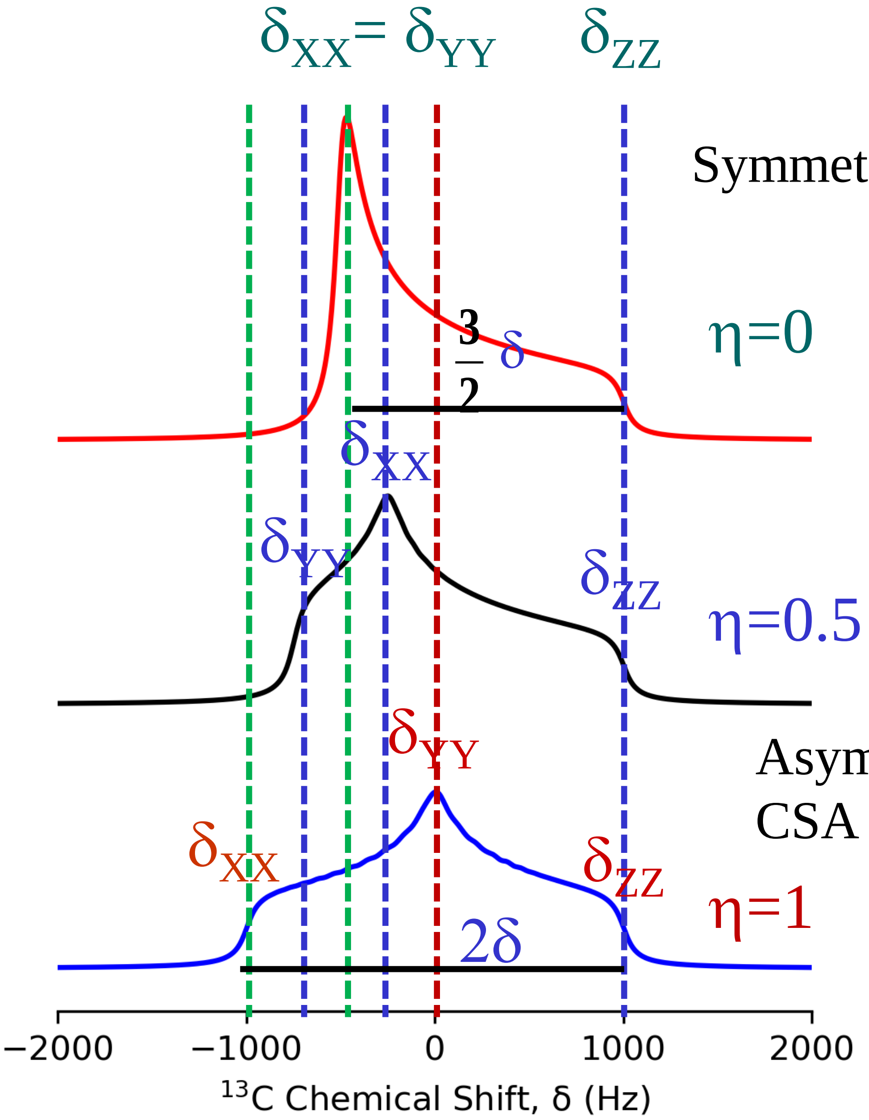
CSA span

Anet, O'Leary, Conc. Magn. Reson. 3, 193, 1991

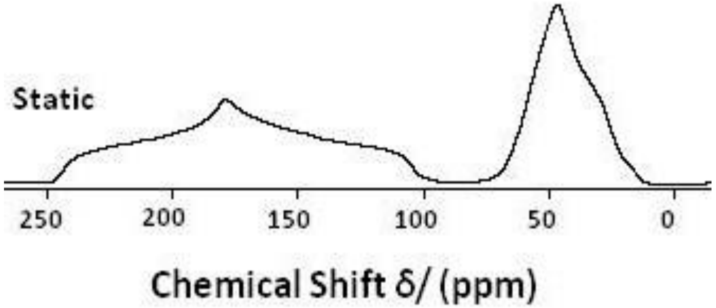
CSA Powder Line Shapes

δ=1 kHz

Symmetric CSA tensor



Asymmetric CSA tensor



Static ^{13}C spectrum of glycine

Chemical-Shift Anisotropy Hamiltonian

CSA Hamiltonian upon secular averaging:

$$H_{CS}^{j} = -\gamma_j \delta_{zz}^{j}(\Theta) B_0 I_{jz}$$

Total Hamiltonian for a site *j*:

$$H_0^j = H_{static}^j + H_{CS}^j = \omega_0^j I_{jz}$$

The chemically-shifted Larmor frequency:

$$\omega_0^j = -\gamma^j B_0 \, (1 + \delta_{zz}^j(\Theta))$$

In isotropic liquids
the chemically-shifted Larmor frequency:

$$\omega_0^j = -\gamma^j B_0 \, (1 + \delta_{iso}^j)$$

In liquids crystals, the resonance position depends upon the orientation (or phase transition which can shift the peak):

$$\overline{\delta_{zz}^j(\Theta)} \neq \delta_j^{iso}$$

Tensors and PAS

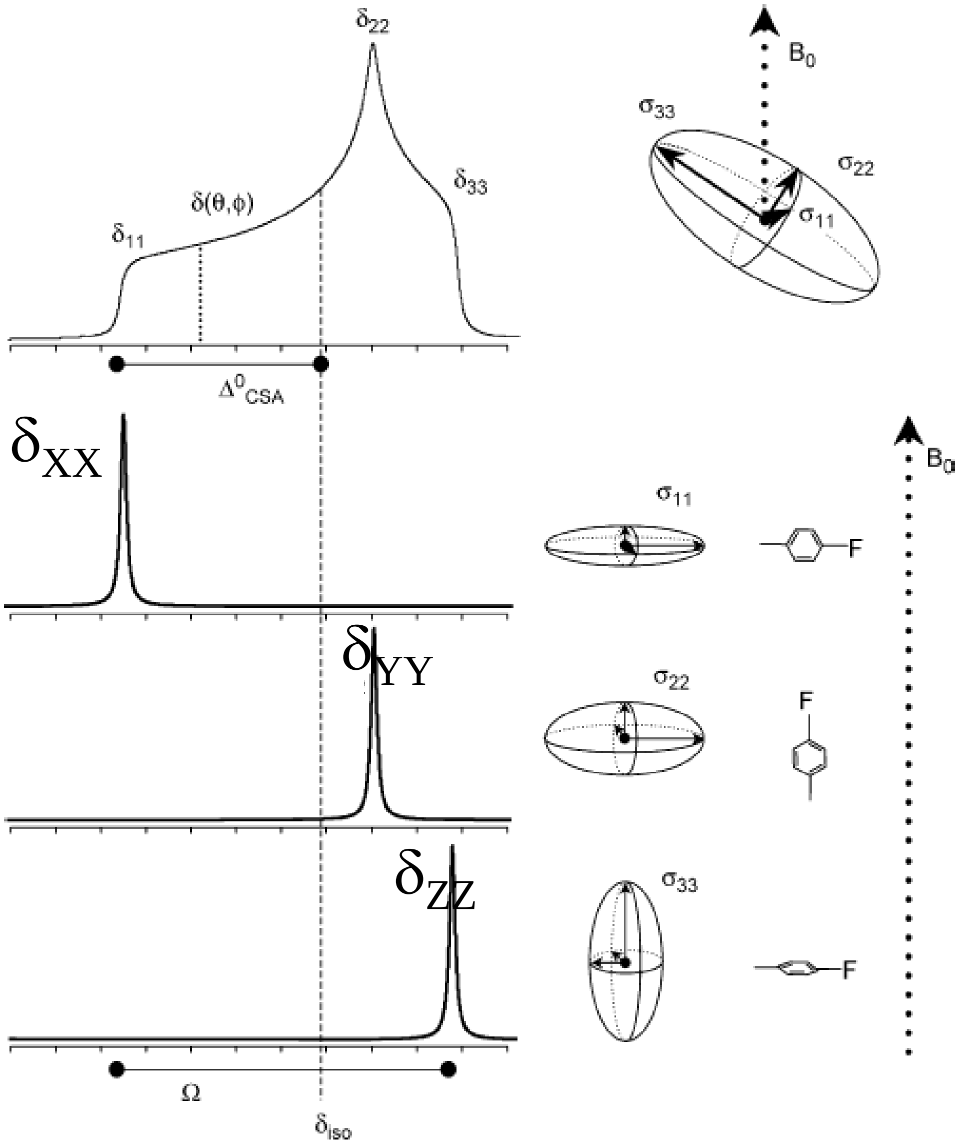
All these tensors, CSA (later DD tensor), are best treated in their principal axis system, PAS, where the tensor is *Diagonal*.

The interaction tensor of each nuclear spin is treated in its PAS.

The PAS *Z*-axis of the CSA tensor corresponds to the long axis of the elliposid representing the CSA tensor.

The PAS *Z*-axis of the DD tensor between the nuclear spins *i* and *j* is along the vector joining the nuclear spins *i* and *j* (here *X* and *Y* are arbitrary).

Chemical-Shift Anisotropy: Response



A. S. Ulrich, Progress in Nuclear Magnetic Resonance Spectroscopy 6 46 (2005) 1–21

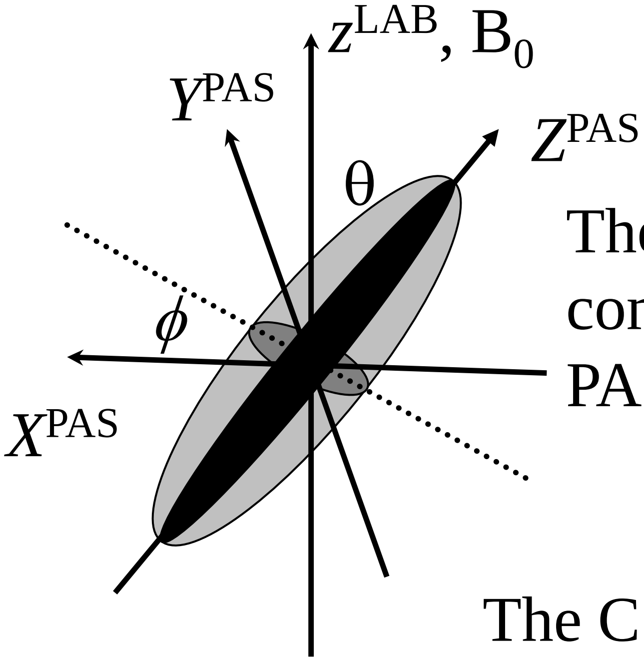
CSA Shielding Convention

- We will use the deshielding convention for the chemical shift, δ (as opposed to another convention, shielding convention, σ):

$$\sigma^{j}_{aniso} = -\delta^{j}_{aniso}$$

Chemical-Shift Anisotropy Tensor

$$H_{CSA} = -\gamma\hbar\delta_{zz}^{lab} B_0 I_z$$ In the lab frame



The orientation dependence of the CSA tensor comes on account of a transformation from PAS to LAB frame, through θ and ϕ

The CS frequency then becomes

$$\omega_{CSA}(\theta,\phi) = -\omega_0\delta_{iso} - \frac{1}{2}\omega_0\delta(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi)$$

$\eta=0$, axially symmetric tensor, $\delta_{xx}=\delta_{yy}$

Chemical-Shift Anisotropy Tensor

In the lab frame, Hamiltonian

$$\boldsymbol{H}_{CSA} = -\gamma\hbar\delta_{zz}^{lab}\boldsymbol{B}_0\boldsymbol{I}_z$$

In the lab frame, energy from CS

$$\boldsymbol{E}_{CSA} = -\gamma\hbar\delta_{zz}^{lab}\boldsymbol{B}_0 < \boldsymbol{I},\boldsymbol{m} \,|\, \boldsymbol{I}_z \,|\, \boldsymbol{I},\boldsymbol{m} >$$

Spectral frequency for ½ to –½

$$\omega_{CSA} = -\gamma\delta_{zz}^{lab}\boldsymbol{B}_0 = -\omega_0\delta_{zz}^{lab}$$

Remember

$$\delta_{zz}^{lab} = (0 \quad 0 \quad 1)\delta^{lab}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Tensor from a frame *f* to lab

$$\delta_{zz}^{lab} = \boldsymbol{P}^{f}\delta^{f}\boldsymbol{P}^{f^{T}}$$

$$\boxed{\omega_{CSA}(\theta,\phi) = -\omega_0\delta_{iso} - \frac{1}{2}\omega_0\delta(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi)}$$

Chemical-Shift Frequency: From PAS to Lab

CS contribution to the spectral frequency:

$$\omega_{CSA} = -\omega_0 \mathbf{P}^f \boldsymbol{\delta}^f \mathbf{P}^f$$

Euler angles transformation:

$$\mathbf{P}^{PAS} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\phi)$$

Chemical-shift frequency:

$$\omega_{CSA}(\theta,\phi) = -\omega_0(\delta_{XX}\sin^2\theta\cos^2\phi + \delta_{YY}\sin^2\theta\sin^2\phi + \delta_{ZZ}\cos^2\phi)$$

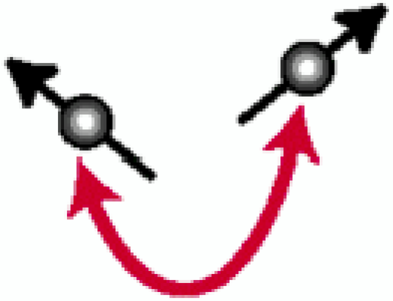
Using definitions:

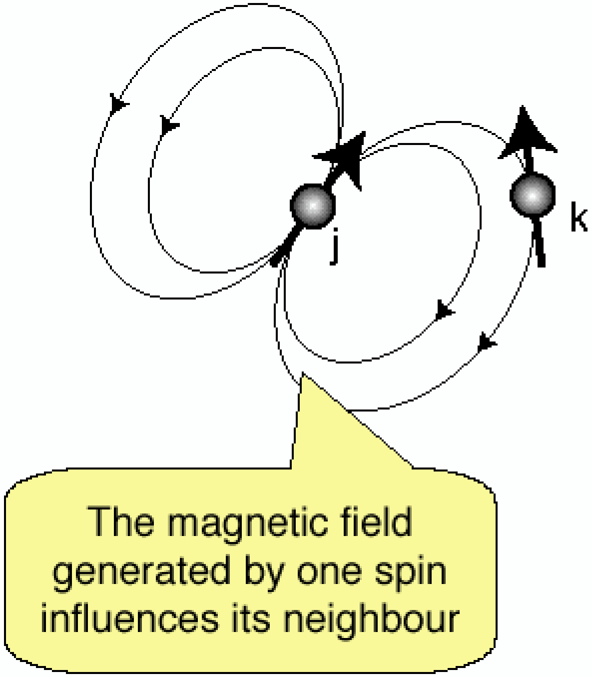
$$\omega_{CSA}(\theta,\varphi) = -\omega_0\delta_{iso} - \frac{1}{2}\omega_0\delta(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\varphi)$$

$$\downarrow$$

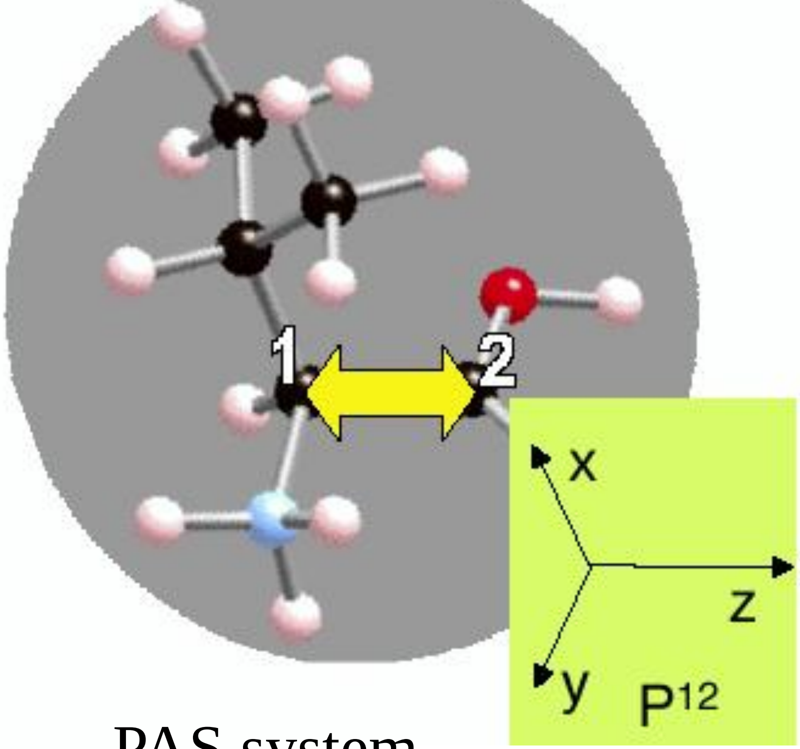
$-\omega_0\delta_{iso} = \omega_{iso}$ Isotropic chemical-shift frequency

Dipole-Dipole Interaction





The magnetic field generated by one spin influences its neighbour



PAS system
of a DD tensor

DD coupling is the direct magnetic interaction between two nuclear spins, orientation dependent, both distance and angles

Dipole-Dipole Hamiltonian

DD Hamiltonian: $$H_{DD}^{jk} = -\frac{\mu_0}{4\pi}\gamma_j\gamma_k\hbar[\frac{I_j.I_k}{r_{ij}^3} - 3\frac{(I_j.e_{jk})(I_k.e_{jk})}{r_{jk}^5}]$$

In dyadic form: $$H_{DD}^{jk} = -\frac{\mu_0}{4\pi}\frac{\gamma_j\gamma_k\hbar}{r_{jk}^3}I_j.D_{jk}.I_k$$

Dipole-dipole coupling constant : $$b_{jk} = -\frac{\mu_0}{4\pi}\frac{\gamma_j\gamma_k\hbar}{r_{jk}^3}$$ (In rad/s)

The DD coupling in Hz: $$\frac{b_{jk}}{2\pi}$$

- Two protons at 3A separation, DD coupling = -4.5 kHz
- Two ^{13}C at 1.5A separation, DD coupling = -2.2 kHz
- Two ^{13}C at 5A separation, DD coupling = -61 Hz
- Two ^{13}C at 8 A separation, DD coupling = -15 Hz :

Dipole-Dipole Hamiltonian

DD Hamiltonian:

$$H_{DD}^{jk} = b_{jk}[I_j.I_k - 3(I_j.e_{jk})(I_k.e_{jk})]$$

$$H_{DD}^{jk} = b_{jk}[I_j.1.I_k - 3I_j.e_{jk}.I_k]$$

$$H_{DD}^{jk} = b_{jk} I_j.D_{jk}.I_k$$

D is a 3X3 matrix given by:

$$< u | D | v >= \delta_{uv} - 3e_{uv}$$

$u,v \equiv x, y,$ for example

In general, D_{jk} is given by:

$$D_{jk} = \begin{pmatrix} 1-3e_{xx} & -3e_{xy} & -3e_{xz} \\ -3e_{yx} & 1-3e_{yy} & -3e_{yz} \\ -3e_{zx} & -3e_{zy} & 1-3e_{zz} \end{pmatrix}$$

Dipole-Dipole Hamiltonian

$$D_{jk} = \begin{pmatrix} 1-3e_{xx} & -3e_{xy} & -3e_{xz} \\ -3e_{yx} & 1-3e_{yy} & -3e_{yz} \\ -3e_{zx} & -3e_{zy} & 1-3e_{zz} \end{pmatrix} \longrightarrow D_{jk}^{PAS} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}$$

Trace = 0, no isotropic part, only the rank 2 anisotropic part present

Since, only the Z-axis needs to be defined for DD tensor
in the PAS, *X* and Y are arbitrary

Dipolar Alphabet

$$H_{DD}^{jk} = -b_{jk}(A+B+C+D+E+F)$$

$$A = I_{jz}S_{jz}(3\cos^2\theta_{jk} - 1)$$

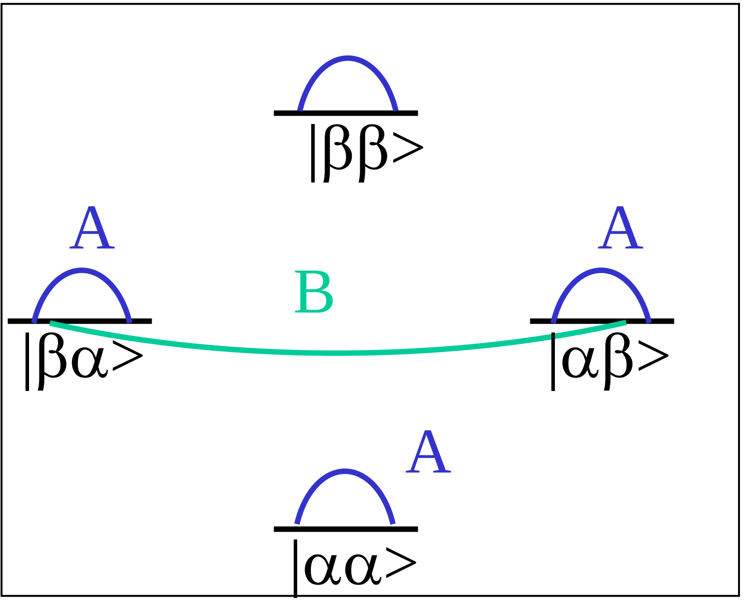
$$B = -\frac{1}{4}(I_{j+}S_{k-} + I_{j-}S_{k+})(3\cos^2\theta_{jk} - 1)$$

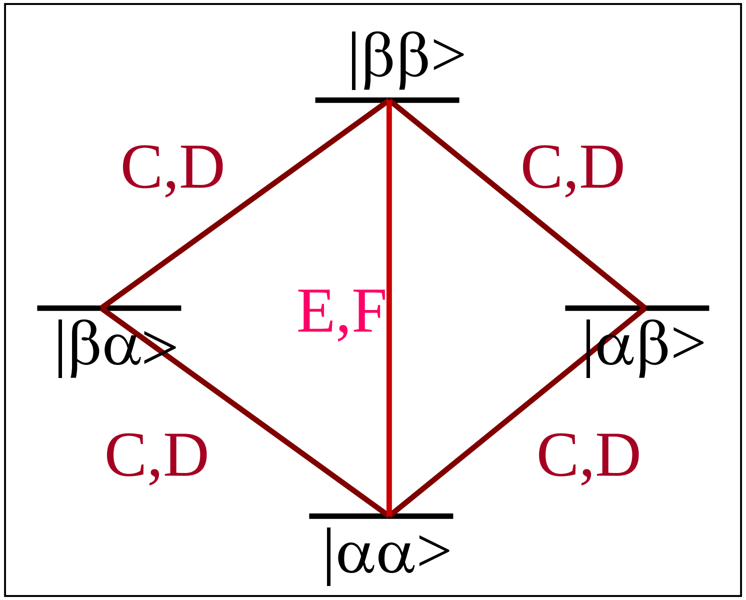
$$C = -\frac{3}{2}(I_{jz}S_{k+} + I_{j+}S_{kz})\sin\theta_{jk}\cos\theta_{jk}e^{-i\varphi}$$

$$D = -\frac{3}{2}(I_{jz}S_{k-} + I_{j-}S_{kz})\sin\theta_{jk}\cos\theta_{jk}e^{i\varphi}$$

$$E = -\frac{3}{4}(I_{j+}S_{k+})\sin^2\theta_{jk}e^{-2i\varphi}$$

$$F = -\frac{3}{4}(I_{j-}S_{k-})\sin^2\theta_{jk}e^{2i\varphi}$$



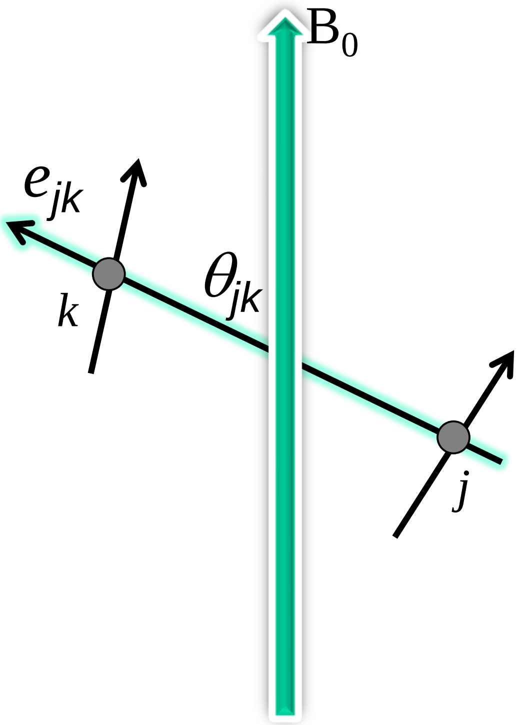


Heteronuclear Dipole-Dipole Hamiltonian

High-field, secular approximation:

$$H = H_Z + H_{DD}^{jk}$$

$$= -(\omega_{0I} I_{jz} + \omega_{0S} S_{jz}) + b_{jk} A$$



$$d_{jk} = b_{jk} \frac{1}{2}(3\cos^2\theta_{jk} - 1)$$

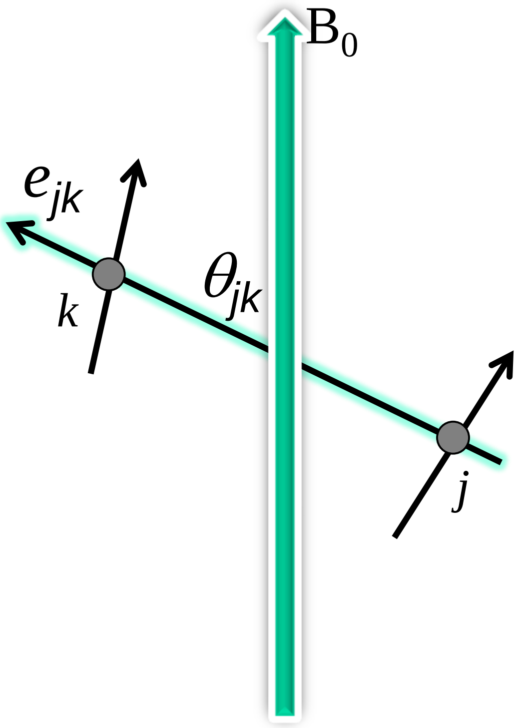
$$A = d_{jk} 2 I_{jz} S_{jz}$$

$$H_{DD}^{jk}(\theta_{jk}) = d_{jk} 2 I_{jz} S_{jz}$$

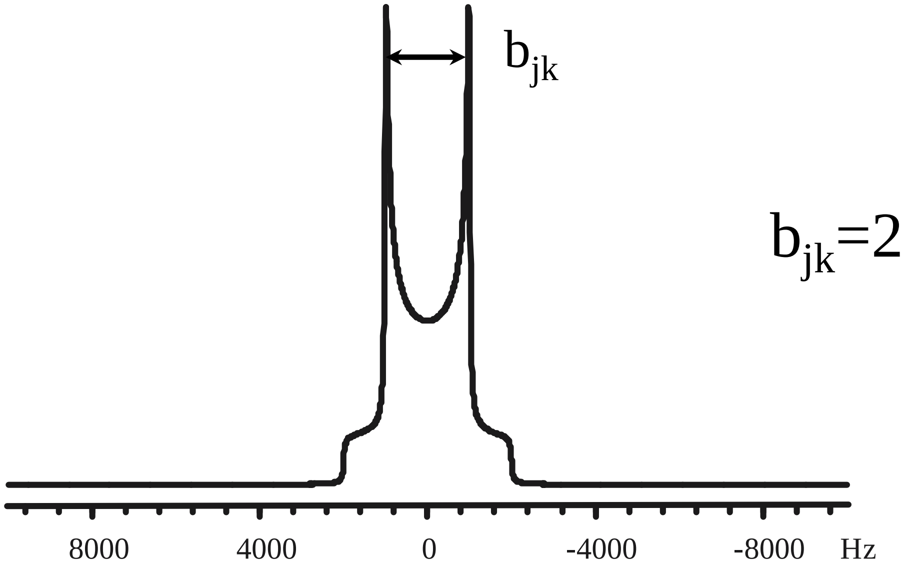
The S spectrum coupled to I then will have two transitions, one having $(1-3\cos^2\theta)$ dependence, and the other - $(1-3\cos^2\theta)$ dependence, hence, mirror images. Both of them have the same isotropic frequency ω_{0S}.

Heteronuclear Dipole-Dipole Powder Line Shapes: Pake Doublet

$$H_{DD}^{jk}(\theta_{jk}) = d_{jk}\,2I_{jz}S_{jz}$$



The S spectrum coupled to I then will have two transitions, one having $(1\text{-}3\cos^2\theta)$ dependence, and the other $-(1\text{-}3\cos^2\theta)$ dependence, hence, mirror images. Both of them have the same isotropic frequency ω_{0S}.



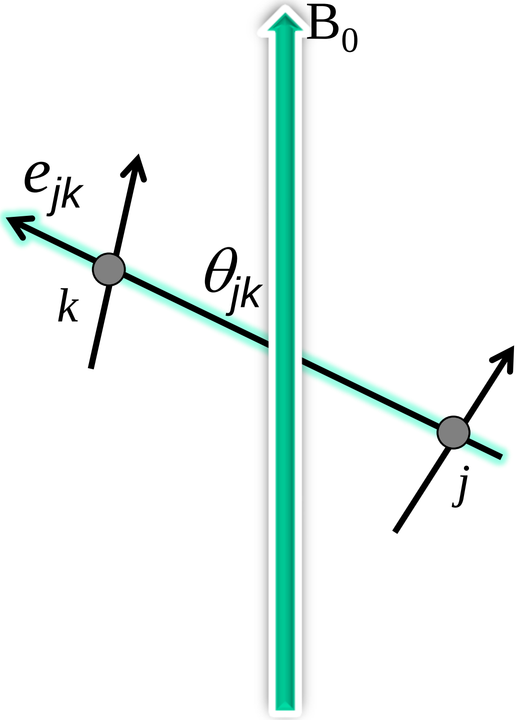
b_{jk}=2000 Hz

Homonuclear Dipole-Dipole Hamiltonian

High-field, secular approximation:

$$H = H_Z + H_{DD}^{jk}$$

$$= -(\omega_{0I} I_{jz} + \omega_{0S} S_{jz}) + b_{jk}(A + B)$$



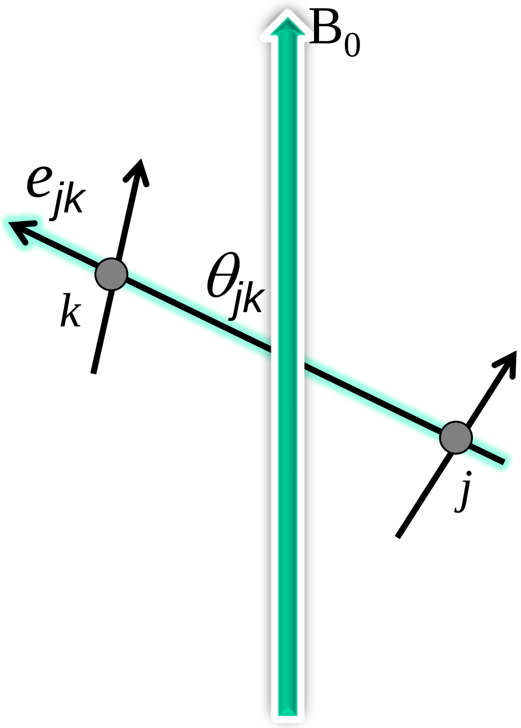
$$d_{jk} = b_{jk}\frac{1}{2}(3\cos^2\theta_{jk} - 1)$$

$$H_{DD}^{jk}(\theta_{jk}) = d_{jk}(3I_{jz}S_{kz} - I_j . S_j)$$

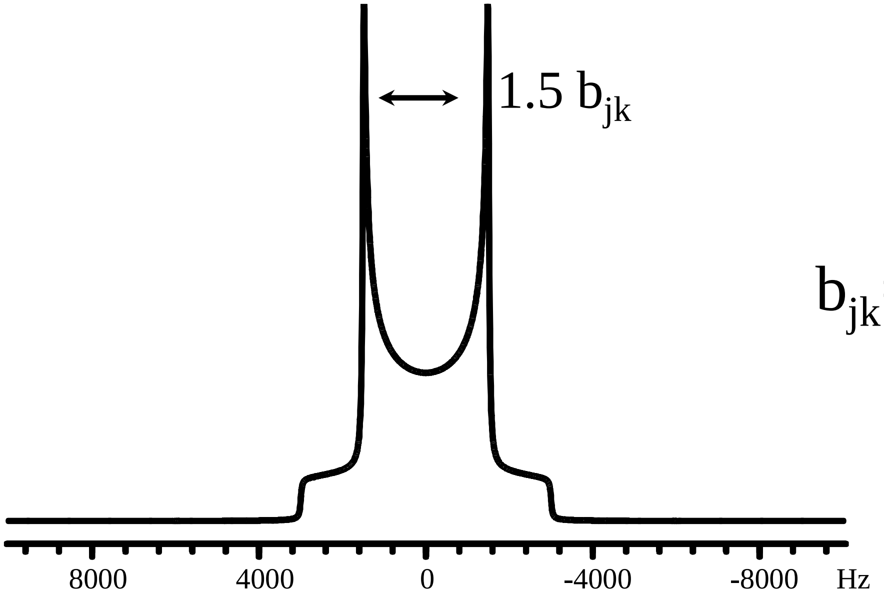
The S spectrum coupled to I then will have two transitions, one having (1-3cos$^2\theta$) dependence, and the other - (1-3cos$^2\theta$) dependence, hence, mirror images. Both of them have the same isotropic frequency ω_{0S}.

Homonuclear Dipole-Dipole Powder Line Shapes: Pake Doublet

$$H_{DD}^{jk}(\theta_{jk}) = d_{jk}\, 2I_{jz}S_{jz}$$

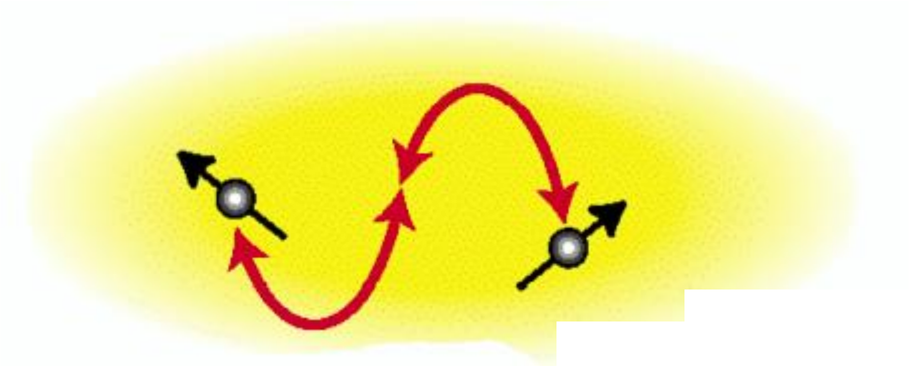


The S spectrum coupled to I then will have two transitions, one having $(1\text{-}3\cos^2\theta)$ dependence, and the other - $(1\text{-}3\cos^2\theta)$ dependence, hence, mirror images. Both of them have the same isotropic frequency ω_{0S}.



b_{jk}=2000 Hz

Scalar Coupling Hamiltonian



$$H_{jk}^{J} = 2\pi J_{jk} I_j . I_k$$

Scalar coupling is a magnetic interaction between the nuclear spins mediated via an electron cloud, through-bond Interaction.

Too weak in solid-state NMR, still observable with the advent of high-resolution schemes.

J-Coupling Hamiltonian: Homonuclear

$$H^{J}_{jk} = 2\pi J_{jk} \mathbf{I}_j . \mathbf{I}_k$$

$$\Big\downarrow \text{ High field}$$

First-order secular term:

$$H_J = 2\pi J_{jk} \mathbf{I}_j . \mathbf{I}_k$$

J-Coupling Hamiltonian: Heteronuclear

$$H_{jk}^{J} = 2\pi J_{jk} I_{j} . I_{k}$$

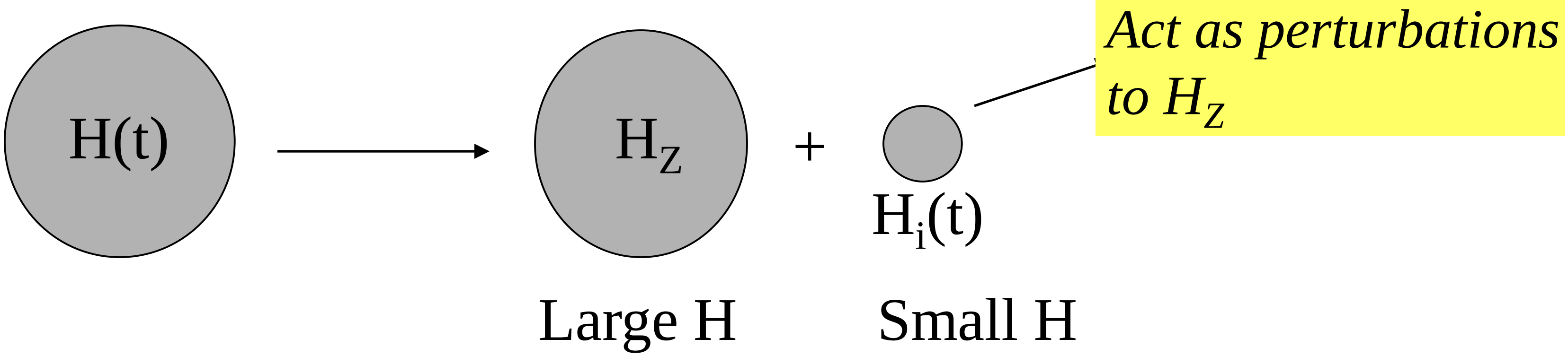
$$\Big\downarrow$$

High field

First-order secular term:

$$H_{jk}^{J} = 2\pi J_{jk} I_{jz} I_{kz}$$

Secular Approximation



$H(t) \longrightarrow H_Z + H_i(t)$

Act as perturbations to H_Z

Large H

Small H

- Only those parts of $H_i(t)$ that have the same eigenfunction as H_Z (having matrix elements in the eigen basis of H_Z) will contribute to energy level shifts in the first-order

- This means, to first-order energy correction, we need consider only those parts of $H_i(t)$ such that $[H_Z,H_i]=0$; Secular Approximation

- In solution-state, this is often disguised as weak-coupling (AX), but not valid in strong-coupling cases (AB)

Secular approximation simplifies our internal Hamiltonians

Secular Approximation

Strictly speaking, secular approximation is more than commutativity. If A is the large Hamiltonian and B is the small Hamiltonian, a matrix element of B may be dropped if its magnitude is small compared to the corresponding difference in the eigenvalues of A

Consider $A = \omega_0 I_z ; B = \omega_x I_x + \omega_z I_z$

Eigenvalues= $\frac{1}{2}\omega_0, -\frac{1}{2}\omega_0$

B representation in the basis of A

$$B = \frac{1}{2}\begin{pmatrix} \omega_z & \omega_x \\ \omega_x & -\omega_z \end{pmatrix}$$

$$\downarrow$$

Secular approximation:

$$B = \frac{1}{2}\begin{pmatrix} \omega_z & 0 \\ 0 & -\omega_z \end{pmatrix}$$

Provided, the following condition holds good (besides commutativity)

$$\omega_x << \omega_0$$

Scalar Coupling Hamiltonian

The J-coupling tensor on account of the rapid molecular tumbling has only the isotropic part

The secular part of the J-coupling Hamiltonian depends on whether the two coupled spins are homonuclear or heteronuclear

Homonuclear case:

$$H_{jk}^{J} = 2\pi J_{jk} I_j . I_k$$

$$= 2\pi J_{jk}(I_{jx} I_{kx} + I_{jy} I_{ky} + I_{jz} I_{kz})$$

Heteronuclear case:

$$H_{jk}^{J} = 2\pi J_{jk} I_{jz} I_{kz}$$

Unlike chemical shifts, J-coupling is independent of the applied magnetic field

Scalar Coupling Hamiltonian: Secular Approximationa

$$A=\omega_{01}I_{1z}+\omega_{02}I_{2z};B=2\pi J_{12}I_{1}.I_{2}$$

Basis sets of A=|+1/2,+1/2>, =|+1/2,-1/2>, =|-1/2,+1/2>, =|-1/2,1/2>

$$A=\frac{1}{2}\begin{pmatrix}\omega_{01}+\omega_{02} & 0 & 0 & 0\\ 0 & \omega_{01}-\omega_{02} & 0 & 0\\ 0 & 0 & -\omega_{01}+\omega_{02} & 0\\ 0 & 0 & 0 & -\omega_{01}-\omega_{02}\end{pmatrix}$$

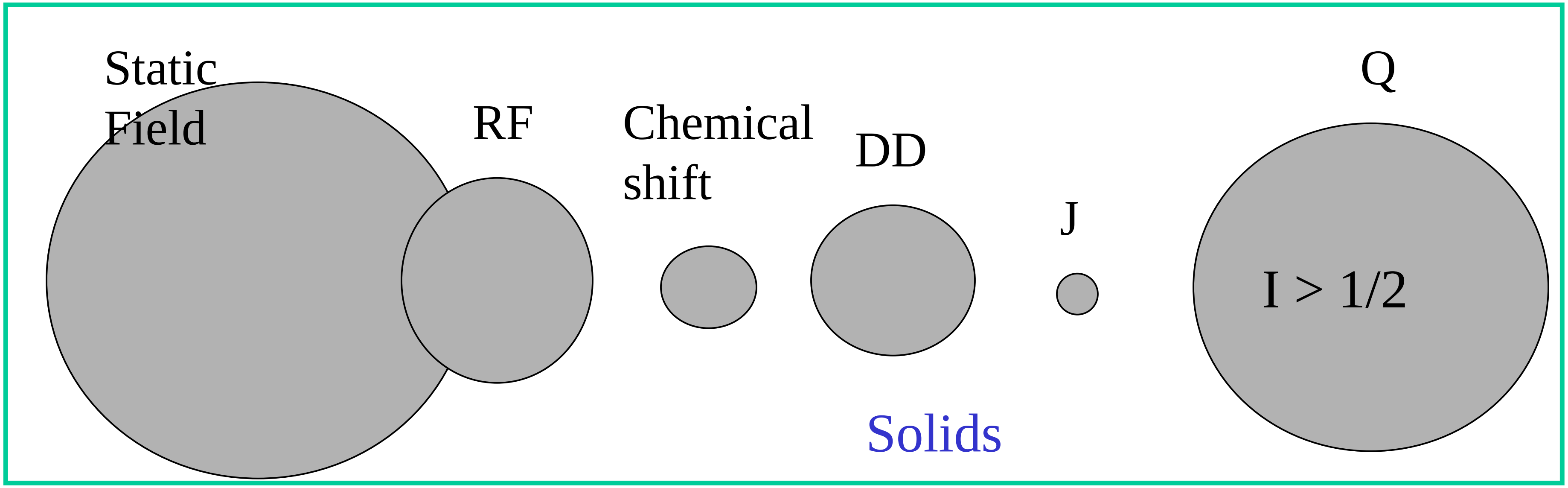
$$B=\begin{pmatrix}\frac{1}{2}\pi J_{12} & 0 & 0 & 0\\ 0 & -\frac{1}{2}\pi J_{12} & \pi J_{12} & 0\\ 0 & \pi J_{12} & -\frac{1}{2}\pi J_{12} & 0\\ 0 & 0 & 0 & \frac{1}{2}\pi J_{12}\end{pmatrix}$$

Secular approximation is valid (and then B will be diagonal) when

$$|\,\omega_{01}-\omega_{02}\,|<<|\,\pi J_{12}\,|$$

This condition is satisfied for heteronuclear case (γ_1 and γ_2 different, of when the chemical-shift difference is sufficiently large for homonuclear case (weak coupling)

Relative Magnitude of Interactions: After Motional Averaging



Static Field

RF

Chemical shift

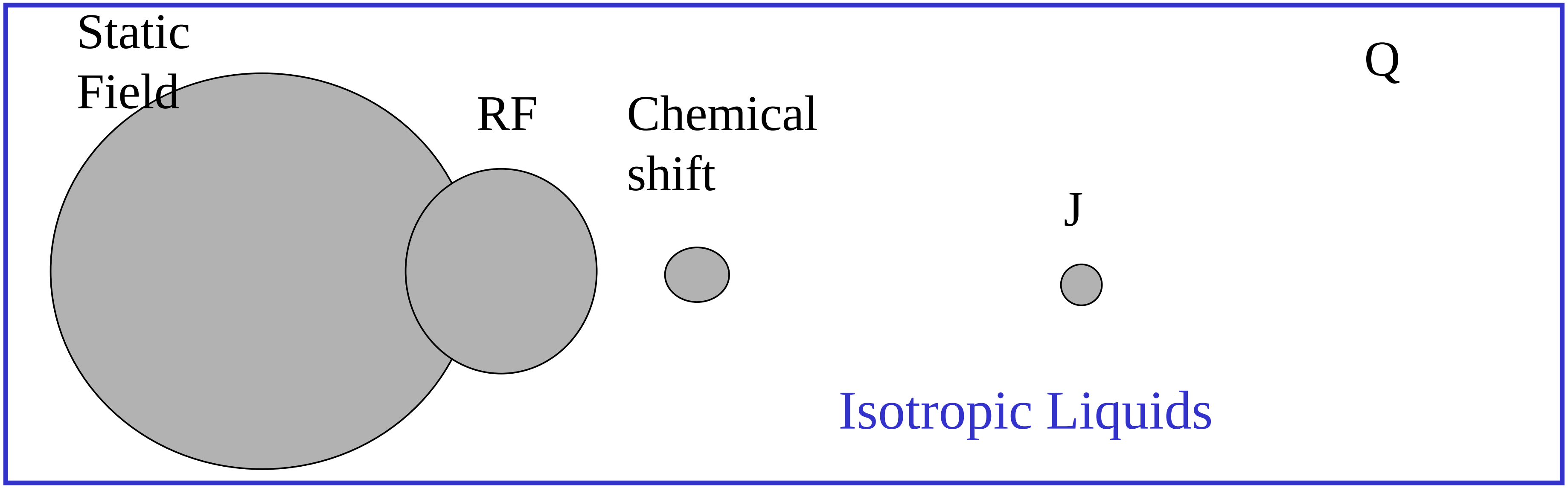
DD

J

Q

I > 1/2

Solids



Static Field

RF

Chemical shift

J

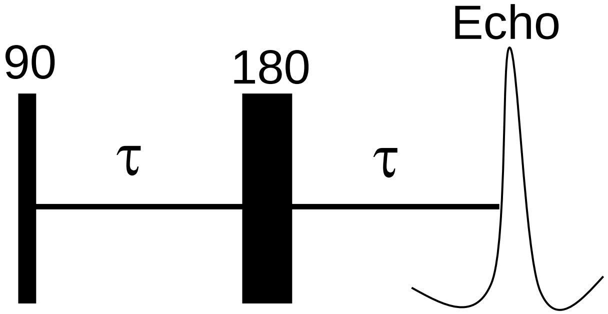
Q

Isotropic Liquids

M. H. Levitt, Spin Dynamics

Experiments under Static Conditions

Spin Echoes: Spin-1/2

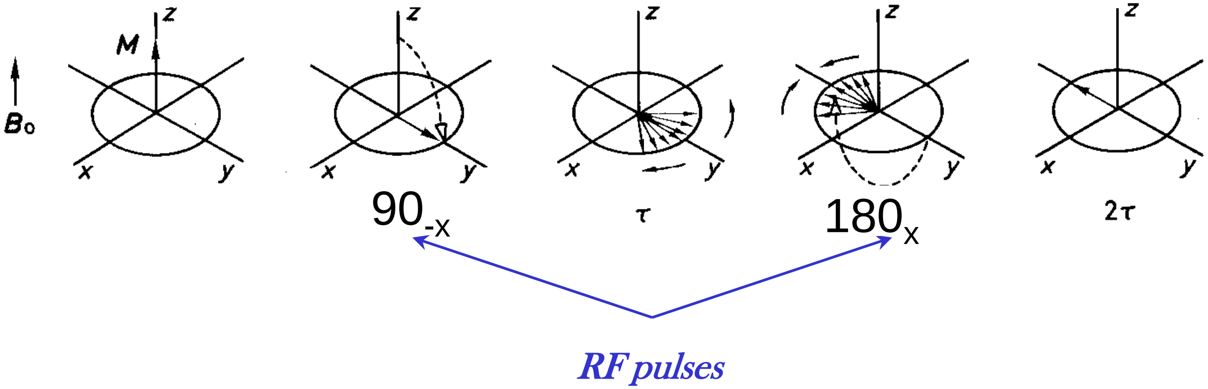


Spin-echo experiment
Refocuses chemical-shift interaction
and heteronuclear dipole-dipole interaction

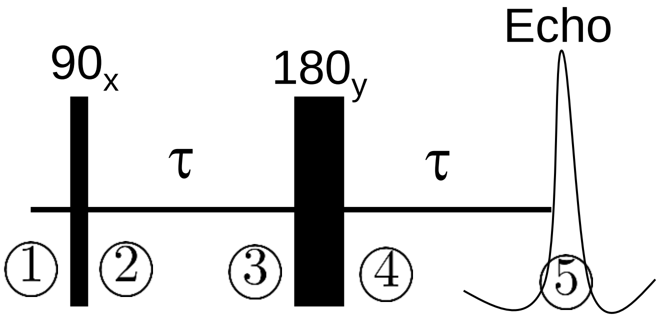
$$\mathcal{H}_{CS} \propto I_z$$

$$\mathcal{H}_{DD}^{hetero} \propto I_z S_z$$

Spin Echo (Hahn Echo) Sequence:



Spin Echoes: Spin-1/2-Density Matrix Analysisx



Spin-echo experiment
Refocuses chemical-shift interaction
and heteronuclear dipole-dipole interaction

$$\mathcal{H} = \omega_0 I_z$$

$$\rho_{\textcircled{1}} = \rho^{eq} = \tfrac{1}{2}1 + \tfrac{1}{2}BI_z \qquad \rho_{\textcircled{2}} = -\tfrac{1}{2}BI_y$$

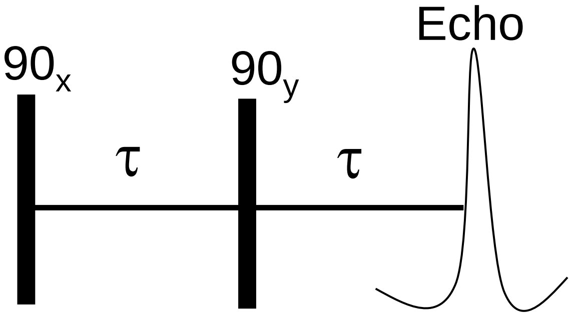
$$\rho_{\textcircled{3}} = \tfrac{1}{2}B[-I_y\cos\omega_0\tau + I_x\sin\omega_0\tau]\exp(-\lambda\tau)$$

$$\rho_{\textcircled{4}} = \tfrac{1}{2}B[-I_y\cos\omega_0\tau - I_x\sin\omega_0\tau]\exp(-\lambda\tau)$$

$$\begin{aligned}\rho_{\textcircled{5}} &= \frac{1}{2}B[-I_y\cos^2\omega_0\tau + I_x\cos\omega_0\tau\sin\omega_0\tau - I_x\cos\omega_0\tau\sin\omega_0\tau \\ &\quad - I_y[\sin^2\omega_0\tau]\exp(-\lambda\tau) \\ &= -\frac{1}{2}BI_y\exp(-\lambda\tau)\end{aligned}$$

$\rho_{\textcircled{5}}$ is independent of the resonance offset, ω_0
$\Longrightarrow$ the signal at ⑤ is independent of B_0
$\Longrightarrow$ echo/refocussing

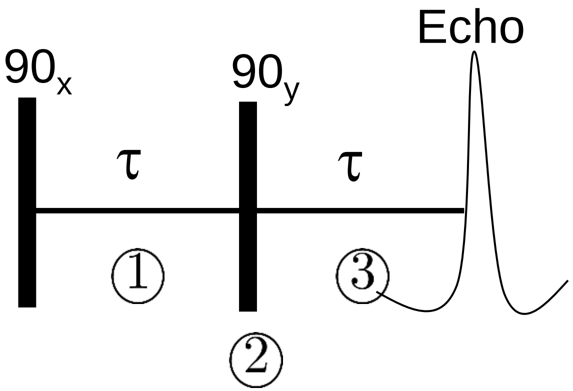
Spin Echoes: Spin-1/2 but Homonuclear



Echo experiment to refocus homonuclear dipole-dipole coupling

$$\mathcal{H}_{DD}^{homo} =\propto 3I_{1z}I_{2z} - I_1 \cdot I_2$$

Homonuclear Spin Echo: Analysis



Echo experiment to refocus homonuclear dipole-dipole coupling

$$\mathcal{H}_{DD}^{homo} = \propto 3I_{1z}I_{2z} - I_1 \cdot I_2$$

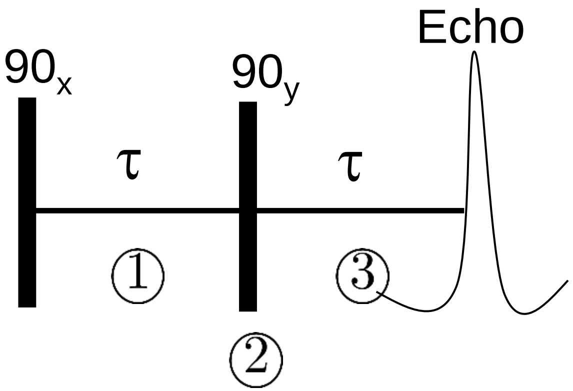
$$\rho(2\tau) = U_{③}(2\tau,\tau)U_{②}(\tau,\tau)U_{①}((\tau,0)\rho(0)[U_{①}(\tau,0)]^{-1}[U_{②}(\tau,\tau)]^{-1}[U_{③}]^{-1}((2\tau,\tau)$$

$$\rho(0) = I_{1y} + I_{2y}$$

$$U_{①}(\tau,0) = e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}}, U_{②}(\tau,\tau) = e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}}, U_{③}(2\tau,\tau) = e^{\frac{-i\mathcal{H}_{DD}^{homo}\tau}{\hbar}}$$

$$\mathcal{H}_{DD}^{homo} = A(3I_{1z}I_{2z} - I_1 \cdot I_2)$$

Homonuclear Spin Echo: Analysis



Echo experiment to refocus homonuclear dipole-dipole coupling

$$\mathcal{H}^{homo}_{DD} = \propto 3I_{1z}I_{2z} - I_1 \cdot I_2$$

$$U_{\textcircled{1}}(\tau,0) = e^{\frac{-i\mathcal{H}^{homo}_{DD}\tau}{\hbar}}$$

$$U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}(\tau,0) = e^{-i\frac{\pi}{2}I_y}e^{\frac{-i\mathcal{H}^{homo}_{DD}\tau}{\hbar}} = e^{-i\frac{\pi}{2}I_y}e^{\frac{-i\mathcal{H}^{homo}_{DD}\tau}{\hbar}}e^{i\frac{\pi}{2}I_y}e^{-i\frac{\pi}{2}I_y}$$

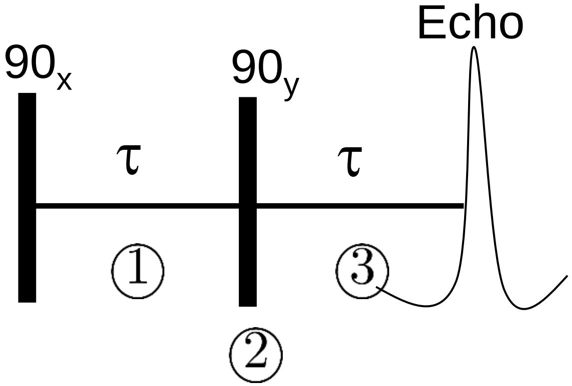
$$= e^{-iA(3I_{1x}I_{2x}-I_1\cdot I_2)\tau}e^{-i\frac{\pi}{2}I_y}$$

$$U_{\textcircled{3}}(2\tau,\tau)U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}(\tau,0) = e^{-iA(3I_{1z}I_{2z}-I_1\cdot I_2)\tau}$$

$$e^{-iA(3I_{1x}I_{2x}-I_1\cdot I_2)\tau}e^{-i\frac{\pi}{2}I_y}$$

$$= e^{-iA(I_1\cdot I_2-3I_{1y}I_{2y})\tau}e^{-i\frac{\pi}{2}I_y}$$

Homonuclear Spin Echo: Analysis



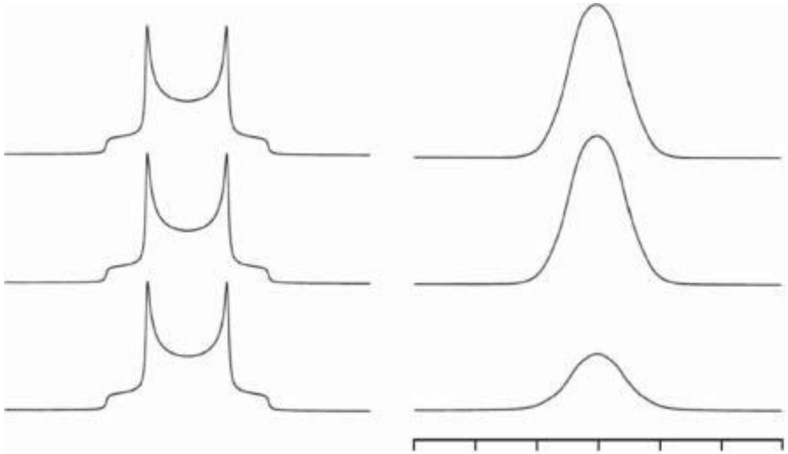
Echo experiment to refocus homonuclear dipole-dipole coupling

$$\mathcal{H}_{DD}^{homo} = \propto 3I_{1z}I_{2z} - I_1 \cdot I_2$$

$$\rho(2\tau) = U_{\textcircled{3}}(2\tau,\tau)U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}((\tau,0)\rho(0)[U_{\textcircled{1}}(\tau,0)]^{-1}[U_{\textcircled{2}}(\tau,\tau)]^{-1}[U_{\textcircled{3}}]^{-1}((2\tau,\tau)$$

$$U_{\textcircled{3}}(2\tau,\tau)U_{\textcircled{2}}(\tau,\tau)U_{\textcircled{1}}(\tau,0) = e^{-iA(I_1 \cdot I_2 - 3I_{1y}I_{2y})\tau}e^{-i\frac{\pi}{2}I_y}$$

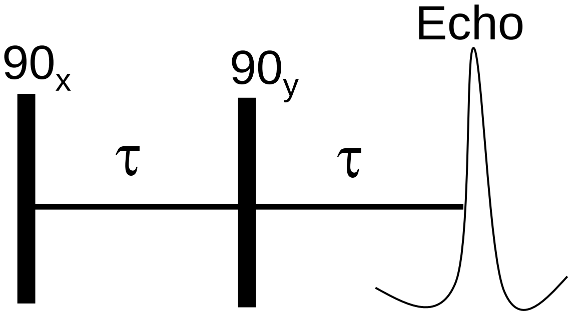
$$\rho(2\tau) = I_{1y} + I_{2y} = \rho(0)$$



That is the echo!

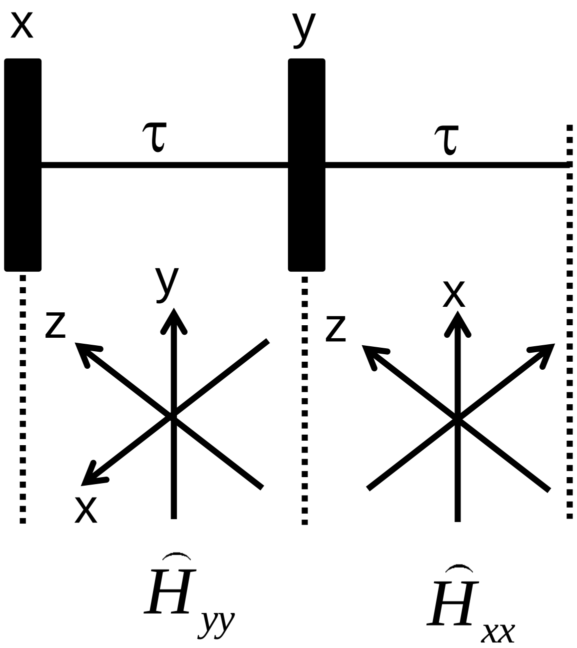
Mueller and Geppi, Solid State NMR, Principles, Methods and Applications

Spin Echoes: Spin-1/2 but Homonuclear



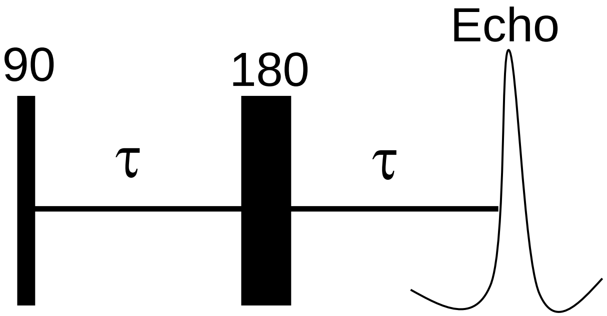
Echo experiment to refocus homonuclear dipole-dipole coupling

$$H = H_{zz} \approx [3I_{1z}I_{2z} - I_1.I_2]$$



$$H(2\tau) = H_{yy} + H_{xx} = [3I_{1z}I_{2z} - I_1.I_2] = -H_{zz}$$

Heteronuclear Recoupling



Spin-echo experiment
Refocuses chemical shift interaction
and heteronuclear dipole-dipole interaction

$$H_{CS} \propto I_z$$

$$H_{DD}^{hetero} \propto I_z S_z$$

Heteronuclear recoupling experiments may be considered as some sort of echo experiments.

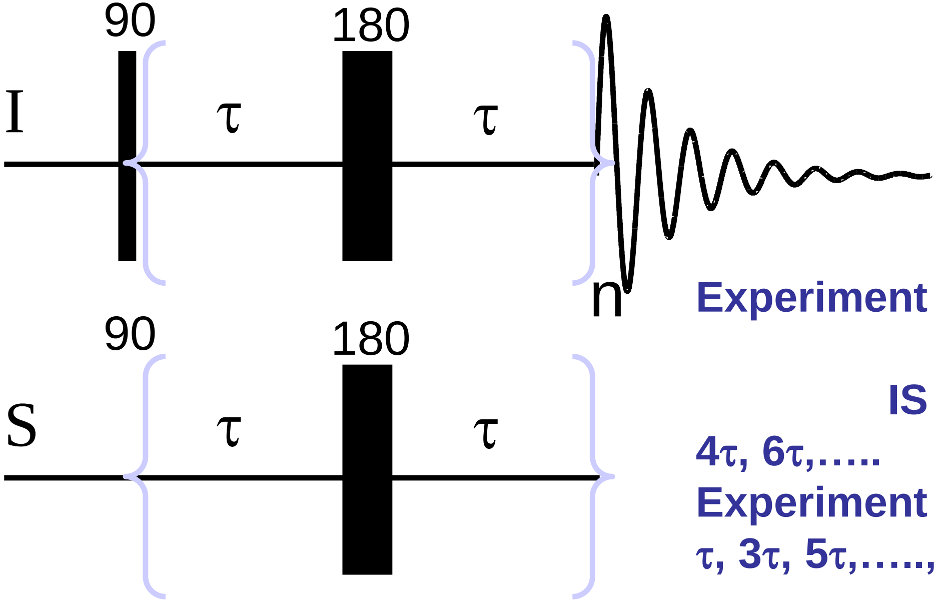
Echo experiments refocus the heteronuclear dipole-dipole interactions, hence, how to measure them?

Apply RF pulses on one of the coupled spins, this prevents the complete refocusing.

The principle is to monitor to what extent the RF pulses perturb the refocusing and this gives a measure of the IS heteronuclear dipole-dipole coupling.

Spin-Echo Double Resonance: SEDOR

Measurement of heteronuclear dipole-dipole couplings in static samples



Experiment 1: Pulses applied only to the I spins

IS dipolar interaction refocused at 2τ, 4τ, 6τ,…..

Experiment 2: Pulses applied to both the spins at τ, 3τ, 5τ,….., prevents refocusing at 2τ, 4τ, 6τ,….

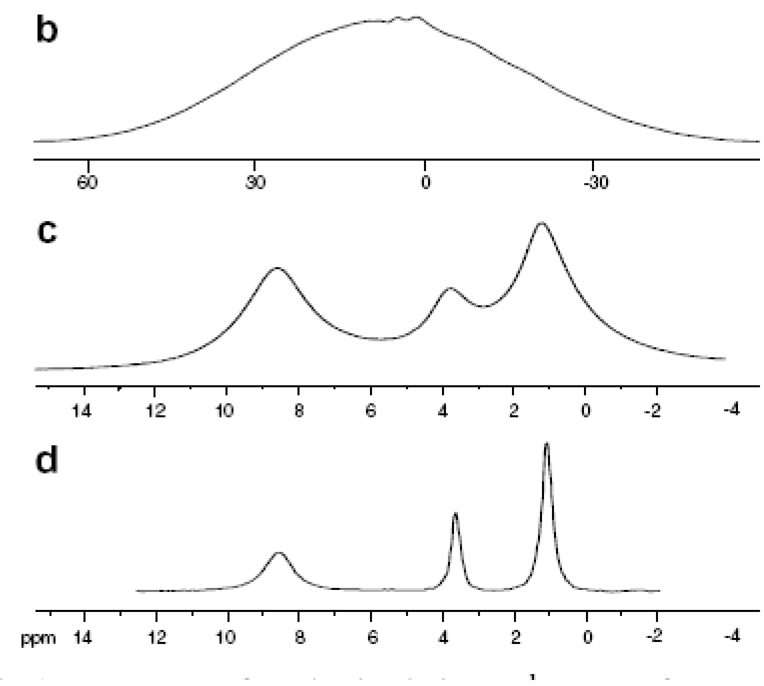
The difference in the echo maxima intensity between the two experiments reflects the IS dipolar coupling, and hence, the distance between I and S spins

Kaplan, Hahn, Bull. Am. Phys. Soc. 2, 384, 1957
Emshwiller, Hahn, Kaplan, Phys. Rev. 118, 414, 1960

Slicther, Principles of NMR, 1980
Wang, Slichter, Sinfelt, PRL, 53, 82, 1984
Shore et al., Phy. Rev. Lett. 58, 953, 1987

^{1}H Spectra: Necessity of RF+MAS

Alanine



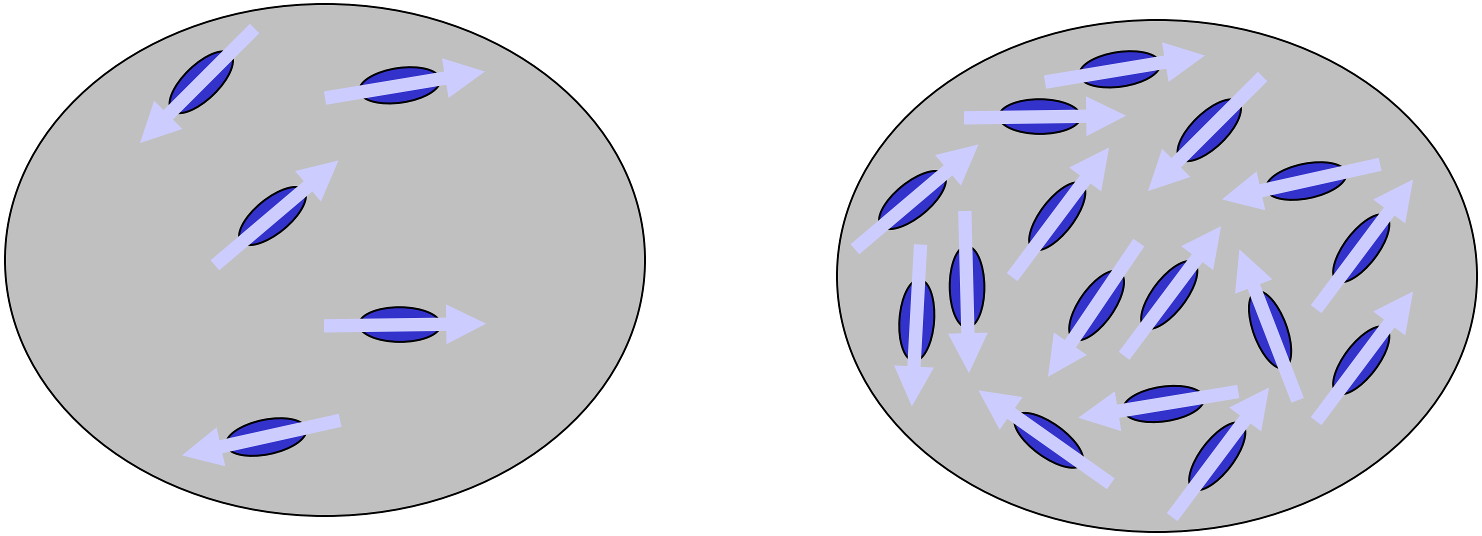
ν_R = 5 kHz

ν_R = 30 kHz

PMLG (ν_R = 12 kHz)

500 MHz

Rare and Abundant Spins

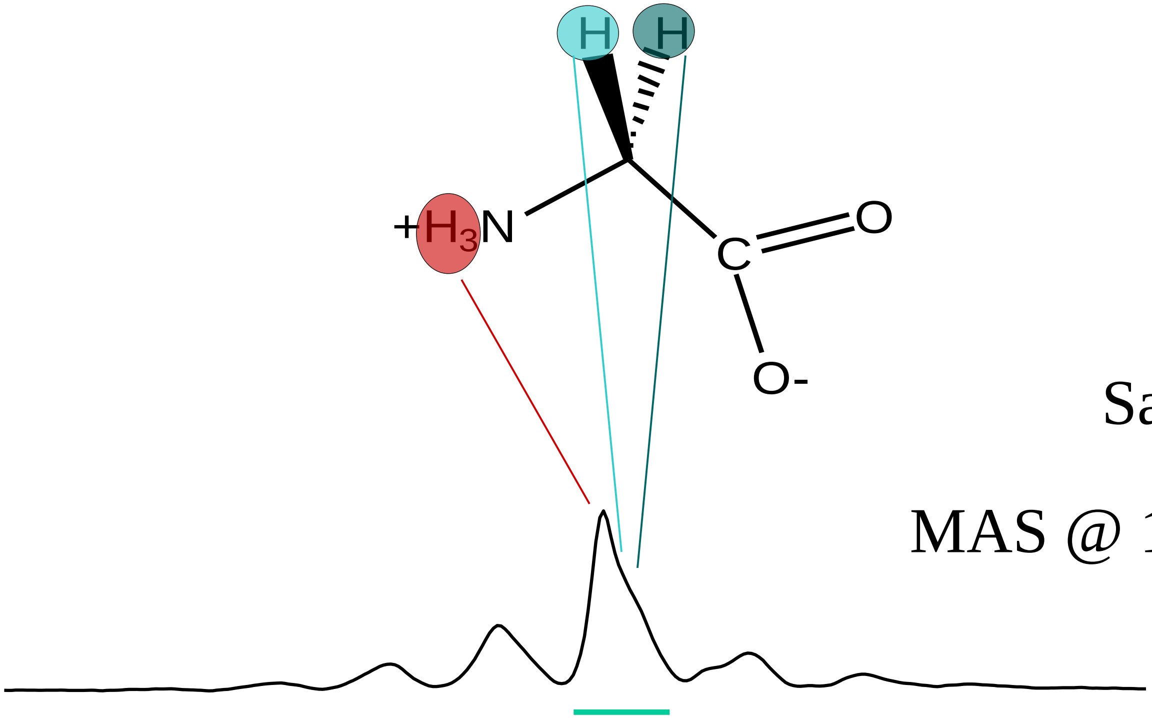


Homonuclear dipolar interactions among protons lead to severe line broadening, 0 to tens of kHz

The interaction is homogeneous, the Hamiltonian does not commute with itself at any time

To average out homogeneously broadened spectral line, the external perturbation (MAS) has to exceed the interaction strength, this is often impossible

Typical Proton Spectra



Sample of glycine

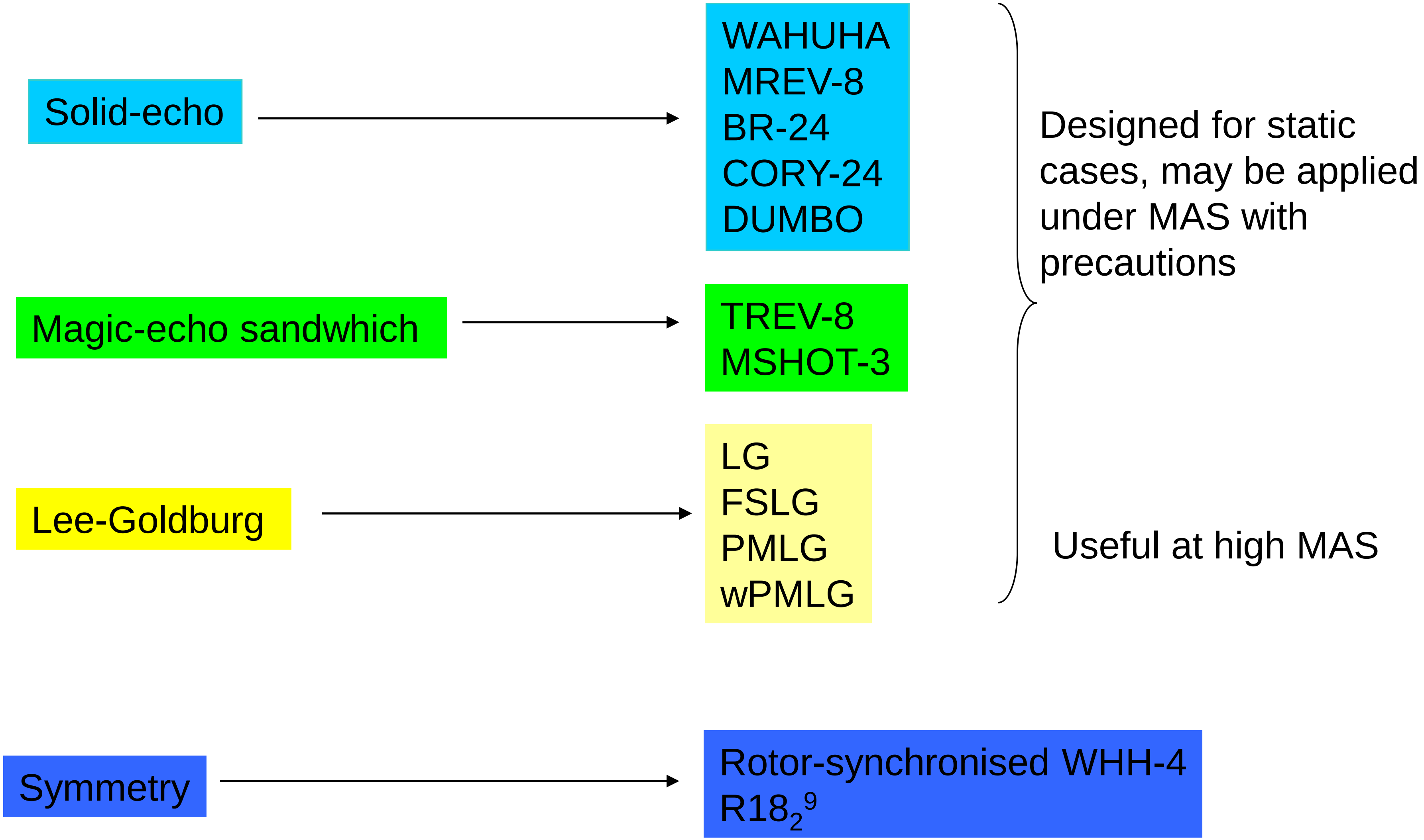
MAS @ 15 kHz

12 ppm=6000 Hz @ 500 MHz spectrometer

- Not possible to spin the interaction out-MAS fails

- Think of spinning out the spins-RF possibilities

Homonuclear Dipolar Decoupling Schemes



Solid-echo → WAHUHA, MREV-8, BR-24, CORY-24, DUMBO

Magic-echo sandwhich → TREV-8, MSHOT-3

Lee-Goldburg → LG, FSLG, PMLG, wPMLG

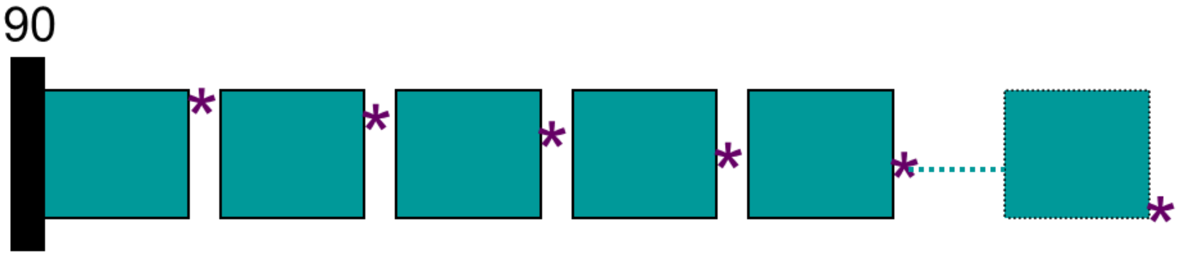
Designed for static cases, may be applied under MAS with precautions

Useful at high MAS

Symmetry → Rotor-synchronised WHH-4, $R18_2^9$

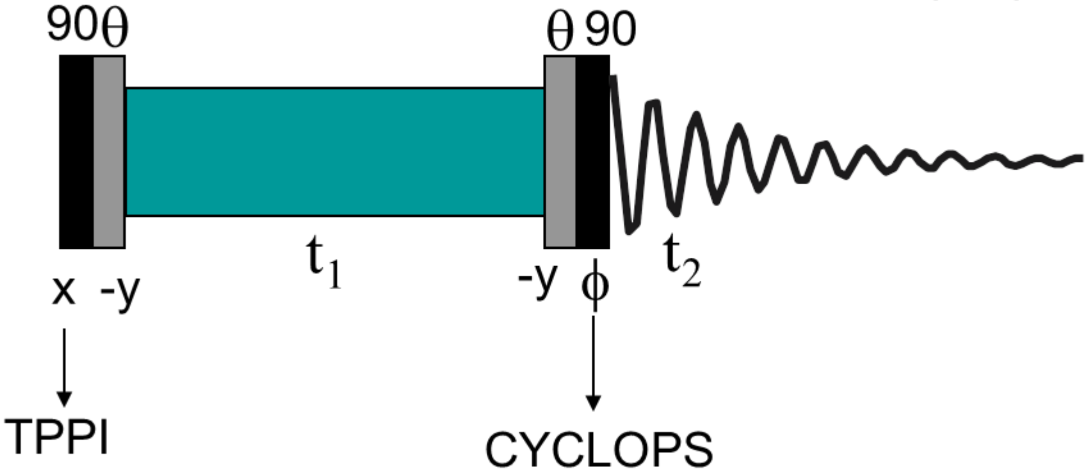
Schematic of Pulse Sequences for 1H Spectroscopy

One-dimensional schemes with windowed multiple-pulse irradiation



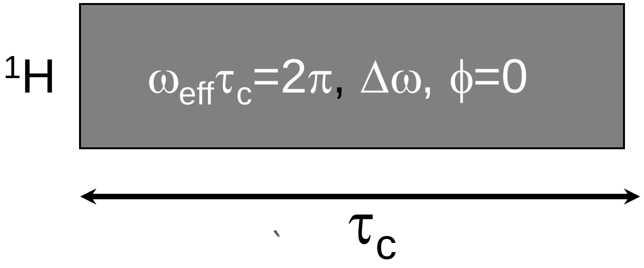
$\phi = 0, 90, 180, 270$

Two-dimensional schemes with multiple-pulse irradiation

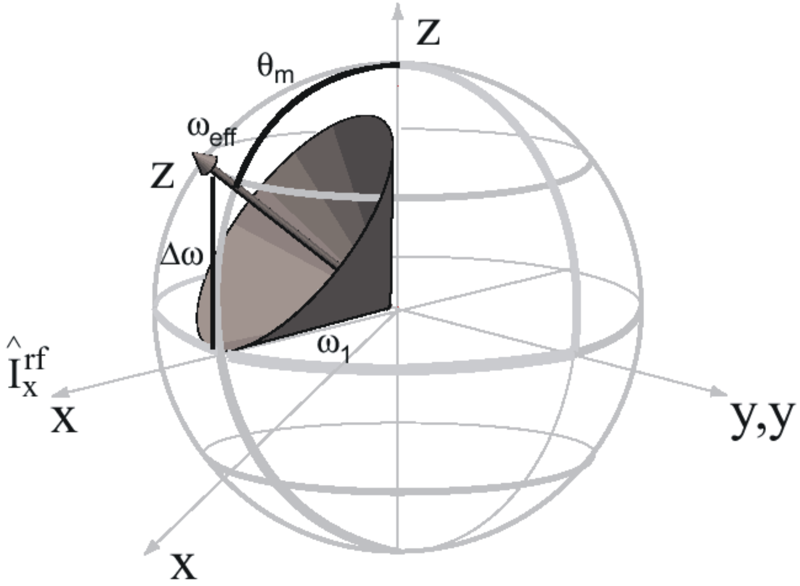


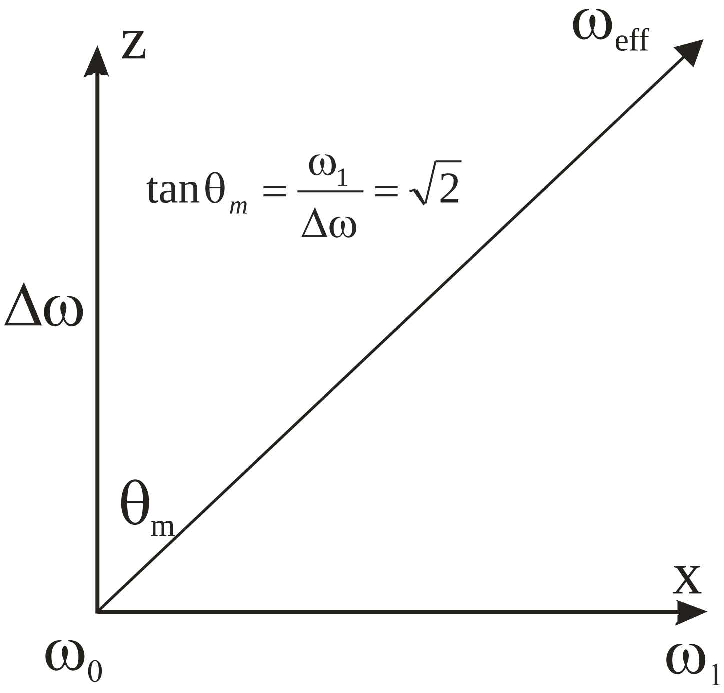
Homonuclear dipolar decoupling scheme

Lee-Goldburg, LG



RF irradiation at $\Delta\omega$ and phase +x



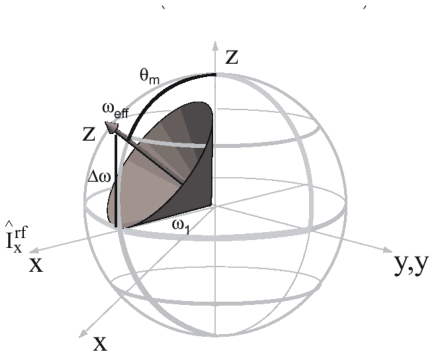


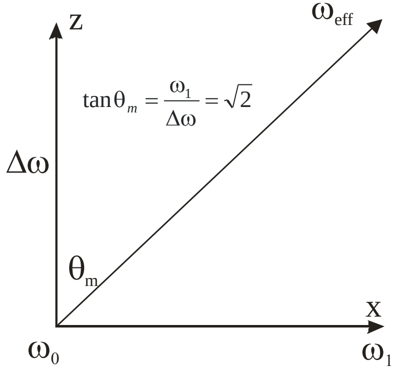
$$\tan\theta_m = \frac{\omega_1}{\Delta\omega} = \sqrt{2}$$

The first and, probably, the most popular homonuclear dipolar decoupling scheme

Lee-Goldburg, LG

LG condition:





$$\frac{\omega_1}{\Delta\omega} = \sqrt{2} = \tan 54.7$$

$$\tau_{LG} = \frac{2\pi}{\omega_{eff}}$$

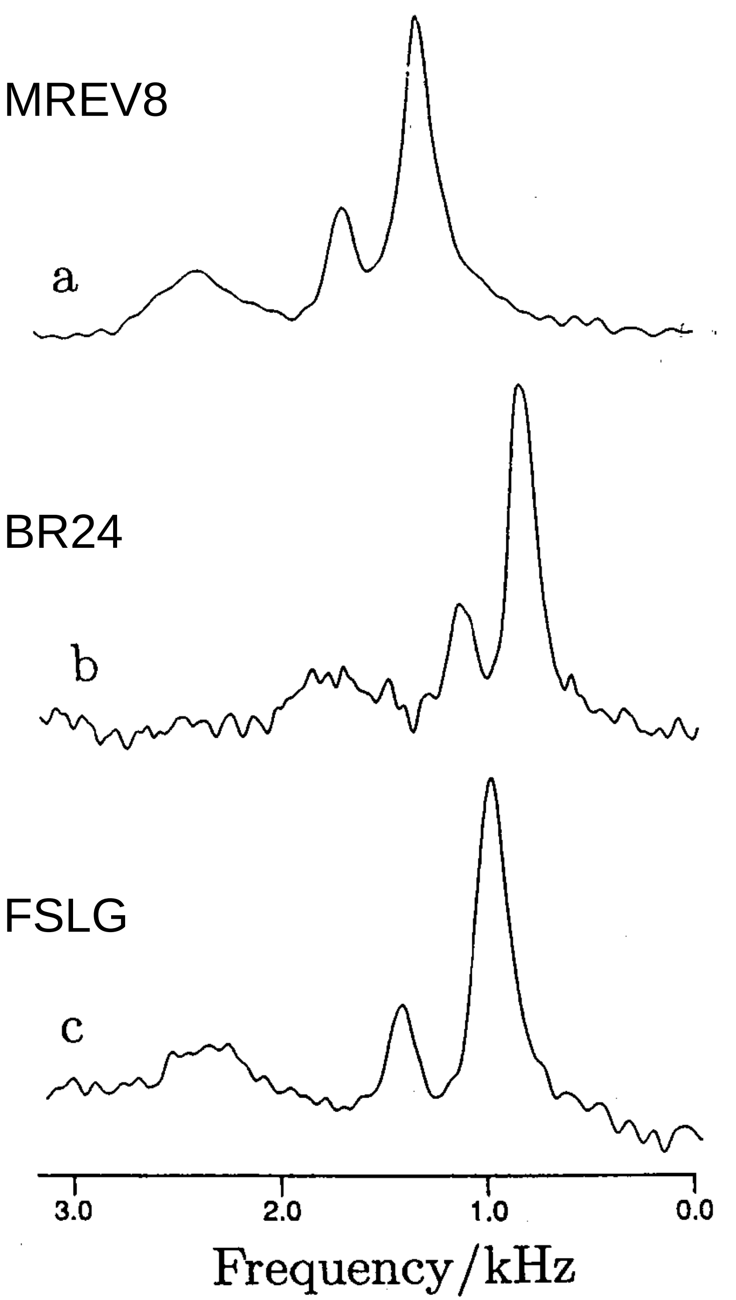
$$\omega_{eff} = \sqrt{\omega_1^2 + \Delta\omega^2}$$

Homonuclear dipole-dipole couplings are scaled to zero to the first order

FSLG Spectra

Spectra

Alanine



MREV8

BR24

FSLG

MAS about 3000 Hz
RF about 80 kHz

SSNMR, 2, 151, 1993

Summary of NMR Interactions

Interaction	Liquids	Solids	Field (B_0) dependence	Notes
Zeeman (chemical shift)	Line position	Line position and structure	Linear	For liquids this is just the position of each peak, but for solids each peak can have a range of chemical shifts depending on the orientation of its electronic environment with the magnetic field. This is known as the chemical shift anisotropy and can have a larger range for nuclei in more asymmetric electronic environments.
Radiofrequency pulses	Amplitude	Amplitude	None	Same for liquids and solids
J coupling	Line structure	Not normally observed (?!)	None*	Basically the same for solids and liquids but not normally observed in solids due to much wider lines
Dipolar coupling	Relaxation	Line structure	None*	Averages to zero in liquids due to isotropic motions (but does still result in relaxation effects). In solids can completely dominate the spectra especially for large γ nuclei like protons
Quadrupolar interaction (spin > ½)	Relaxation	Line structure	None*	Averages to zero in liquids due to isotropic motions, but in solids can completely dominate the spectra especially for nuclei with large quadrupole moments (^{14}N, ^{2}H) in asymmetric electronic environments.

***To first order**

Magic-Angle Spinning, MAS

Reality

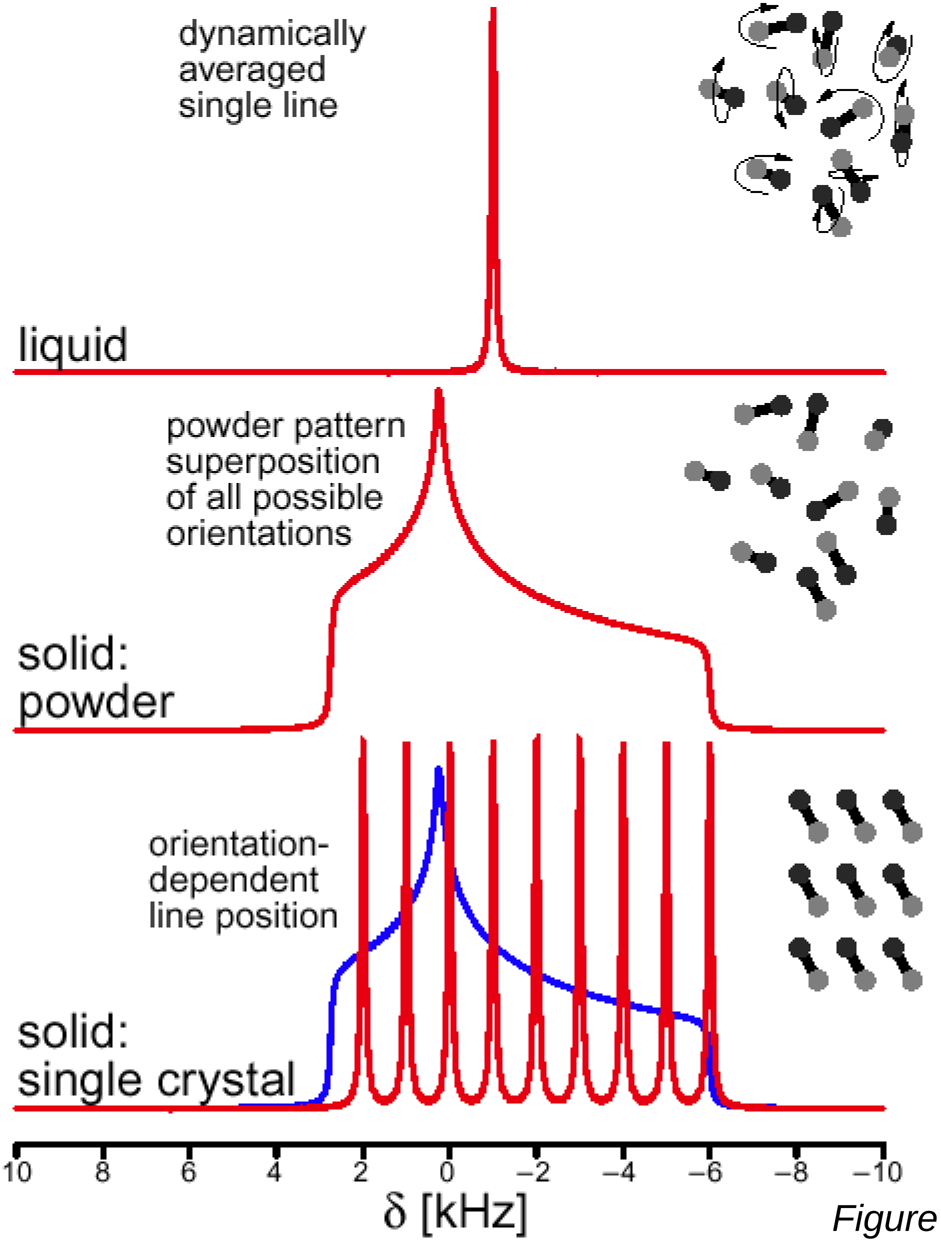
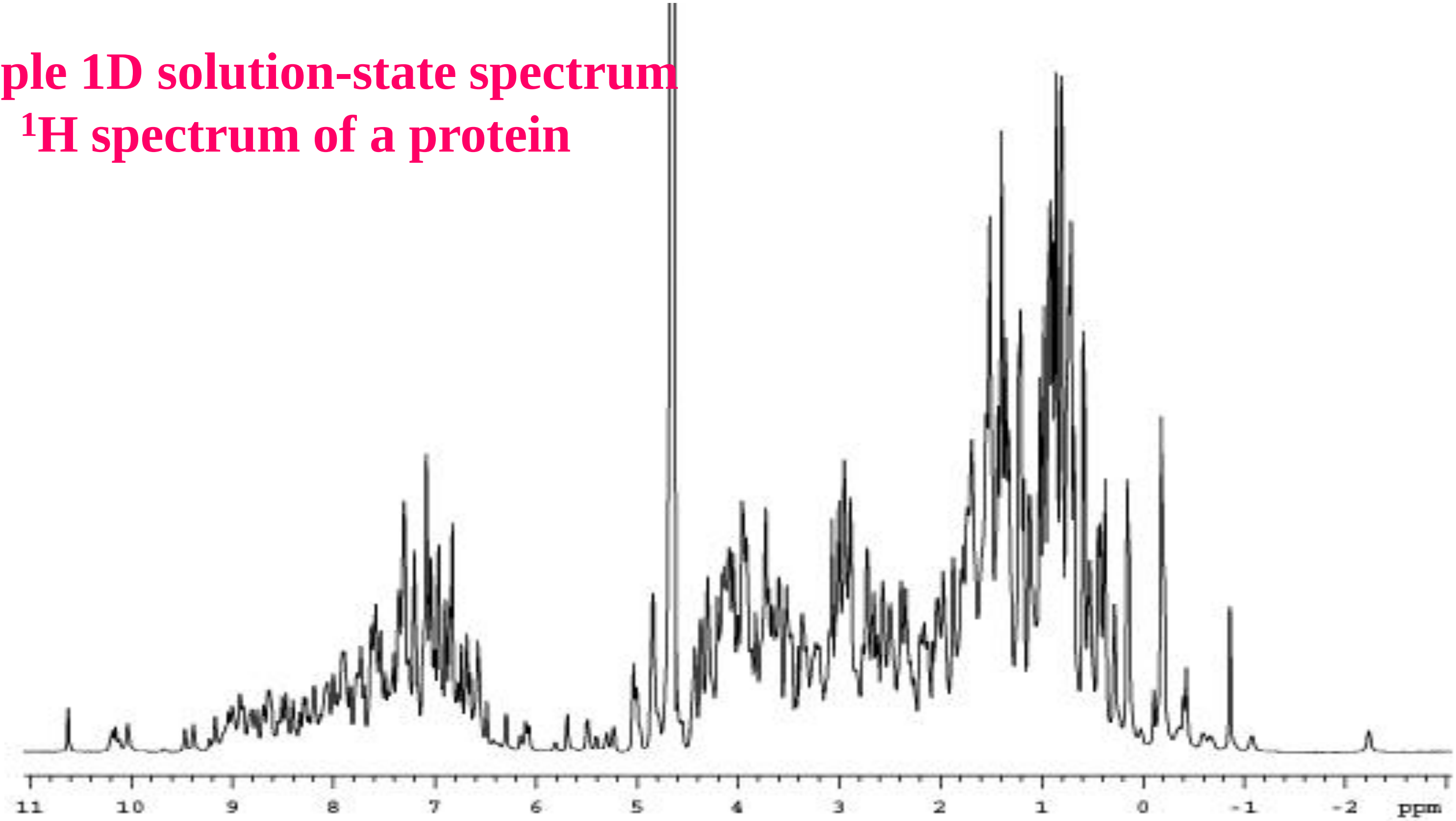


Figure courtesy: Matthias Ernst

Reality

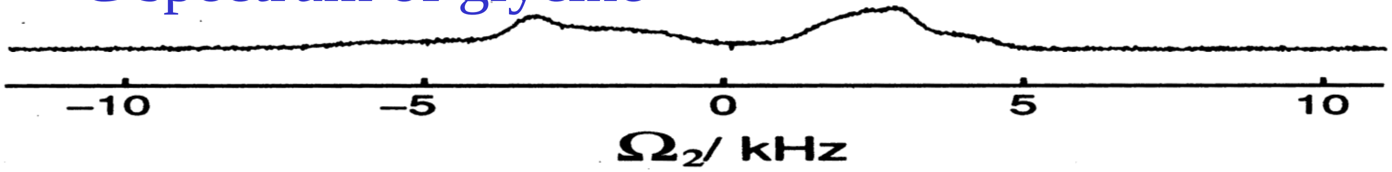
Simple 1D solution-state spectrum

^{1}H spectrum of a protein



Simple 1D solid-state spectrum

^{13}C spectrum of glycine



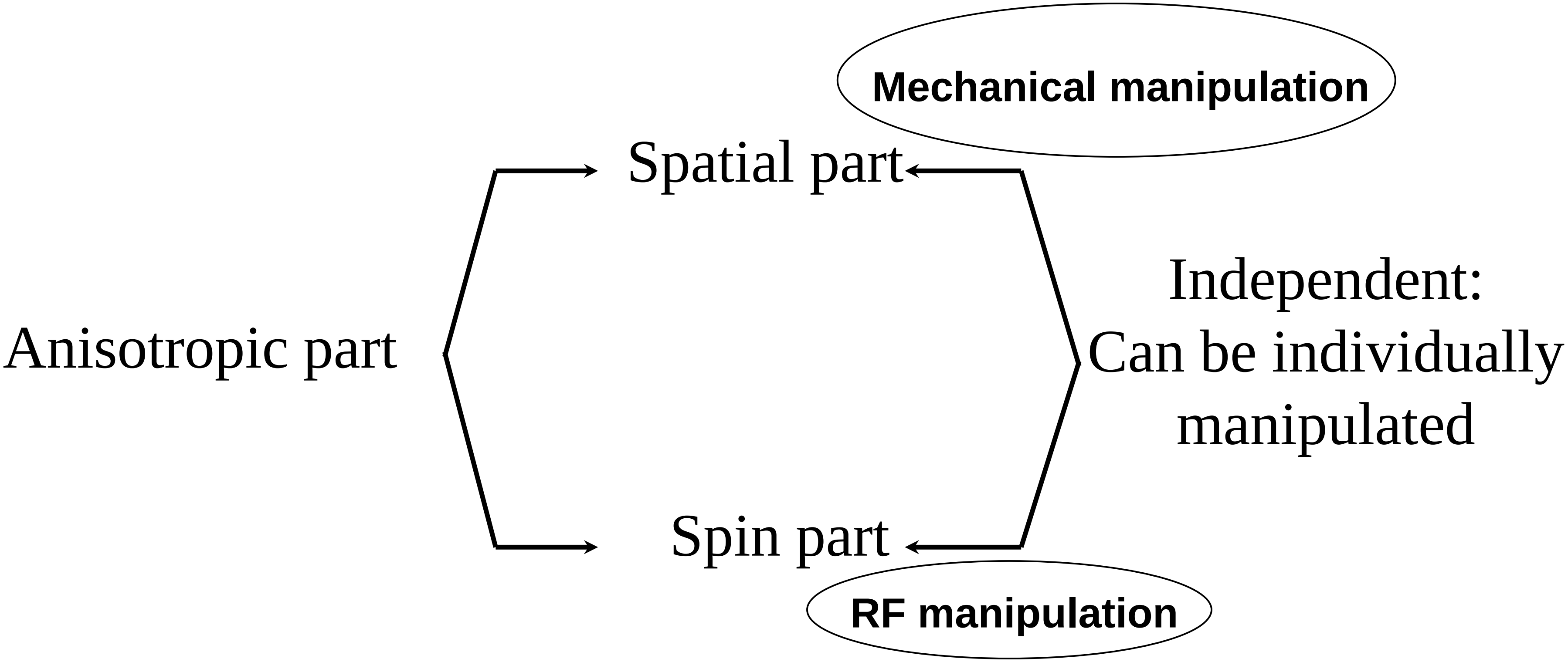
Remedies

- Mimick the inherent averaging processes in solution-state to obtain high-resolution, isotropic information

- Goal #1:(Resolution and Sensitivity): Remove anisotropic parts and retain only isotropic parts: Decoupling

- Goal #2:(Let us have the cake and eat it as well) Get back the anisotropic parts for elucidation of geometry parameters: Recoupling

Remedies



Anisotropic part

Spatial part

Spin part

Mechanical manipulation

RF manipulation

Independent:
Can be individually
manipulated

Hamiltonians and their Manipulation

$$H_{TOTAL} = \left[H_{SPACE} \otimes H_{SPIN} \right]^{anisotropic} + H^{isotropic}$$

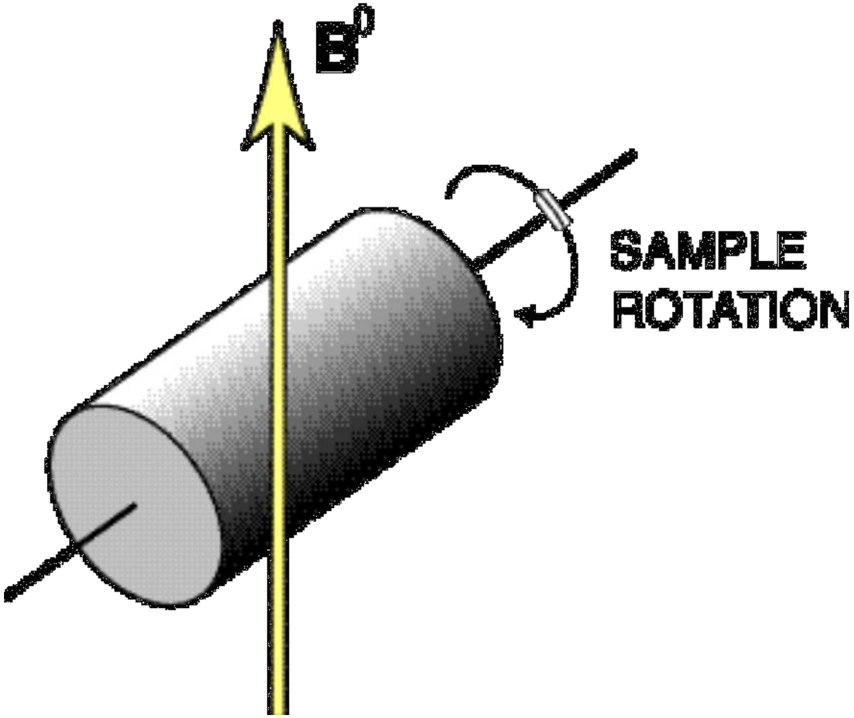
Spatial Part: Manipulation

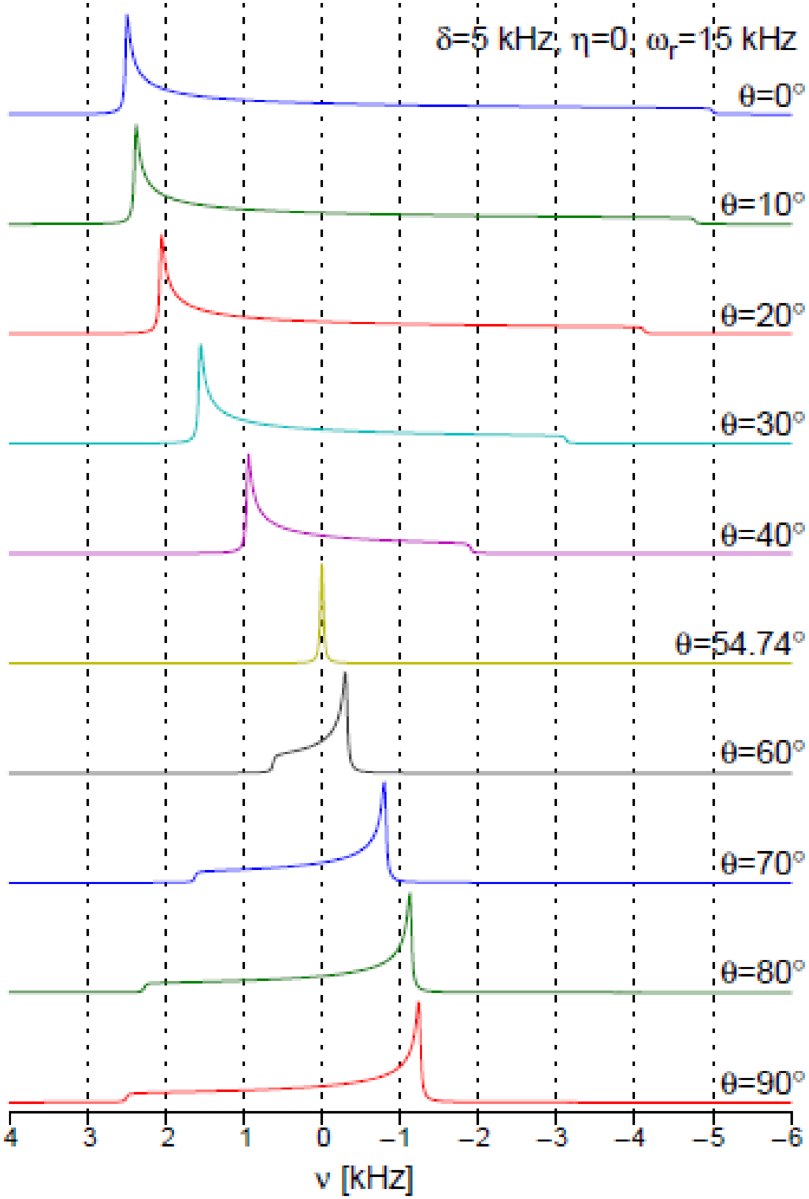
- Rotating the crystallites in a given powder
- Sample spinning: Mechanical manipulation
- Easier to visualise
- Difficult to implement

Spin Part: Manipulation

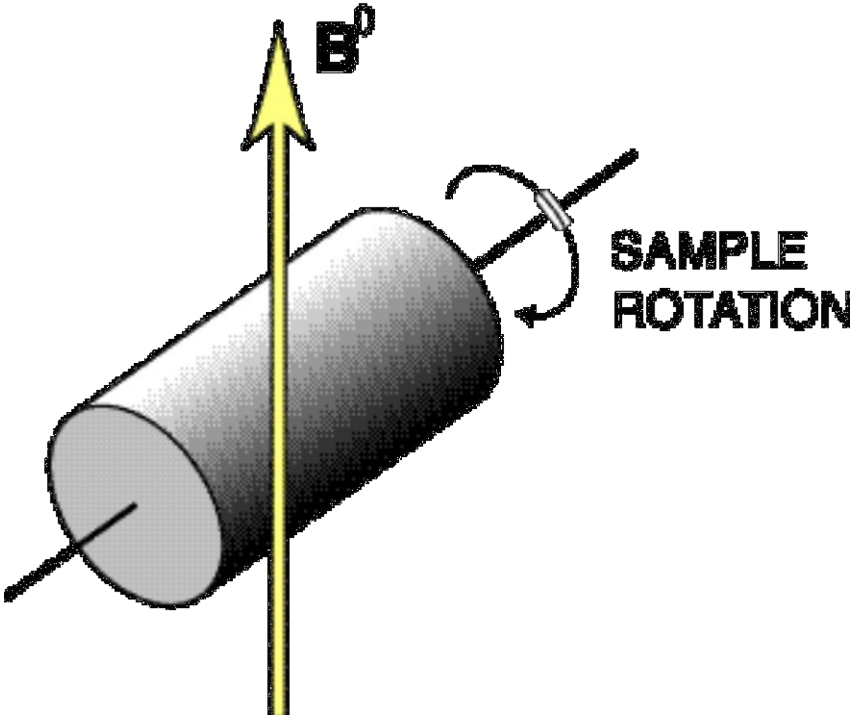
- Rotating the spins in a given powder
- Spins rotation: Manipulation by RF pulses
- Easier to implement
- Difficult to visualise

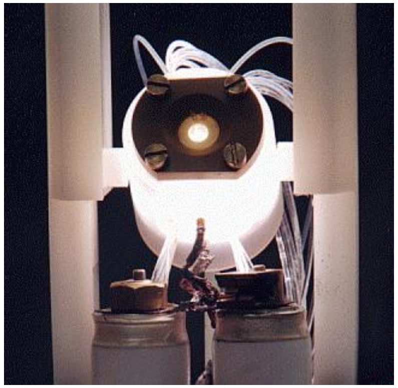
Powder at Various Rotor Angles: Spinning





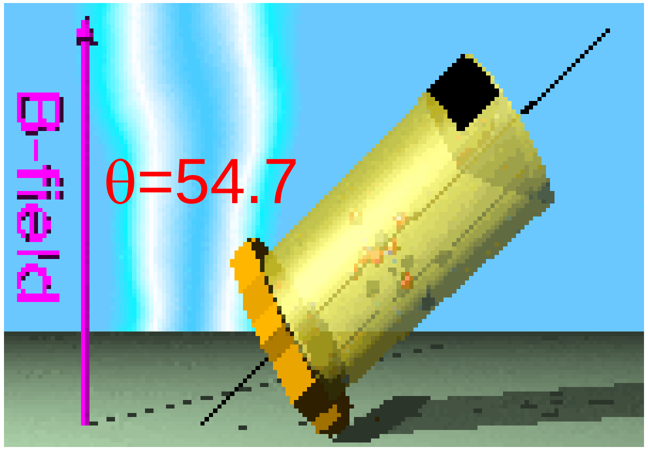
Magic-Angle Spinning (MAS)

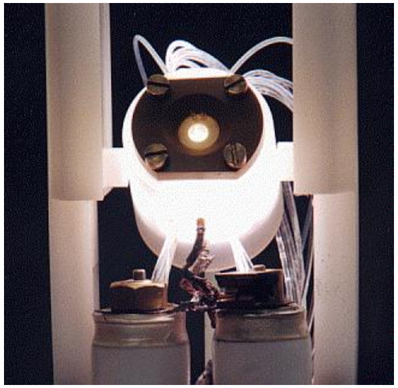




Average out the chemical shift anisotropy, to achieve good sensitivity and resolution

Magic-Angle Spinning (MAS)

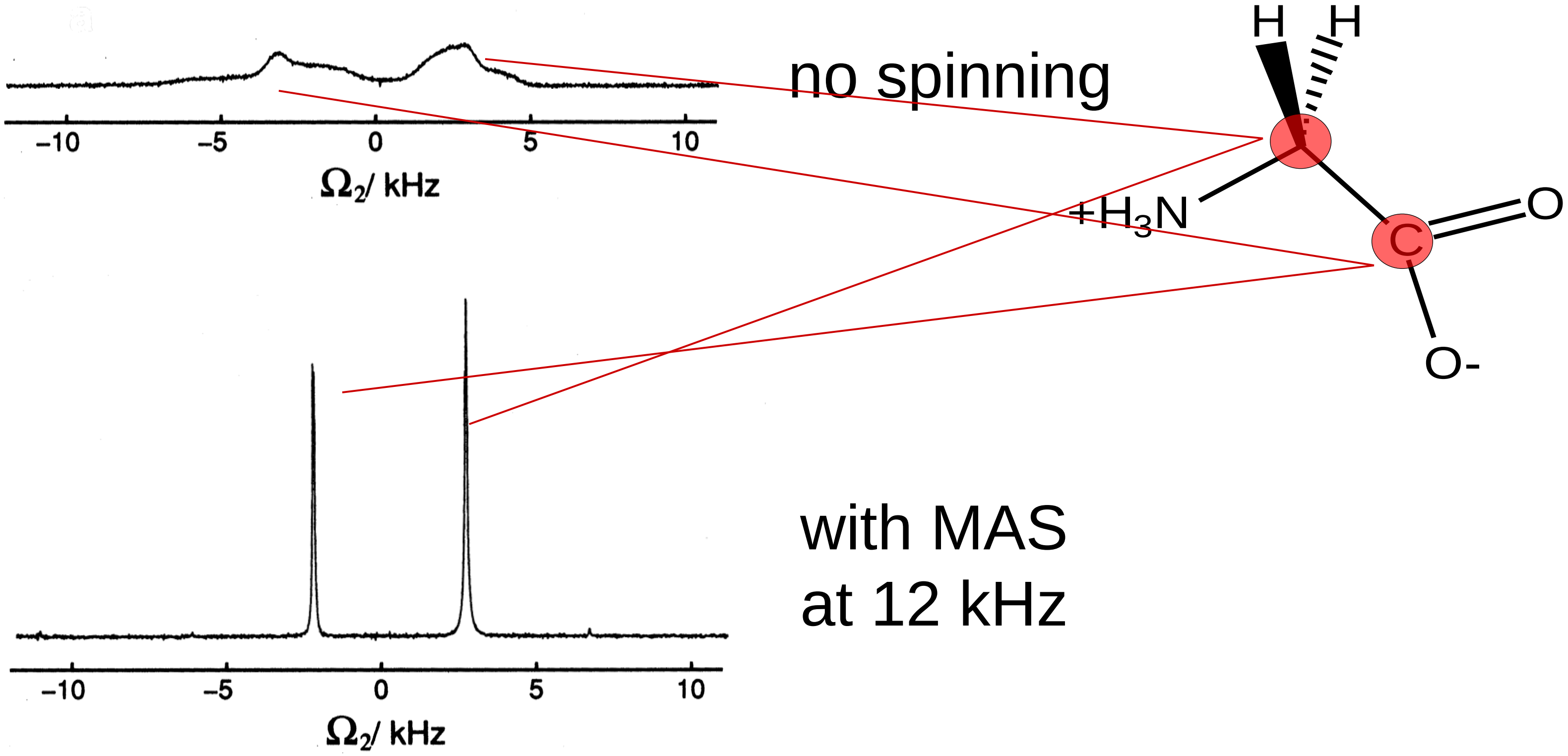




Averages out the chemical shift anisotropy, to achieve good sensitivity and resolution

Resolution and Sensitivity Enhancement by MAS

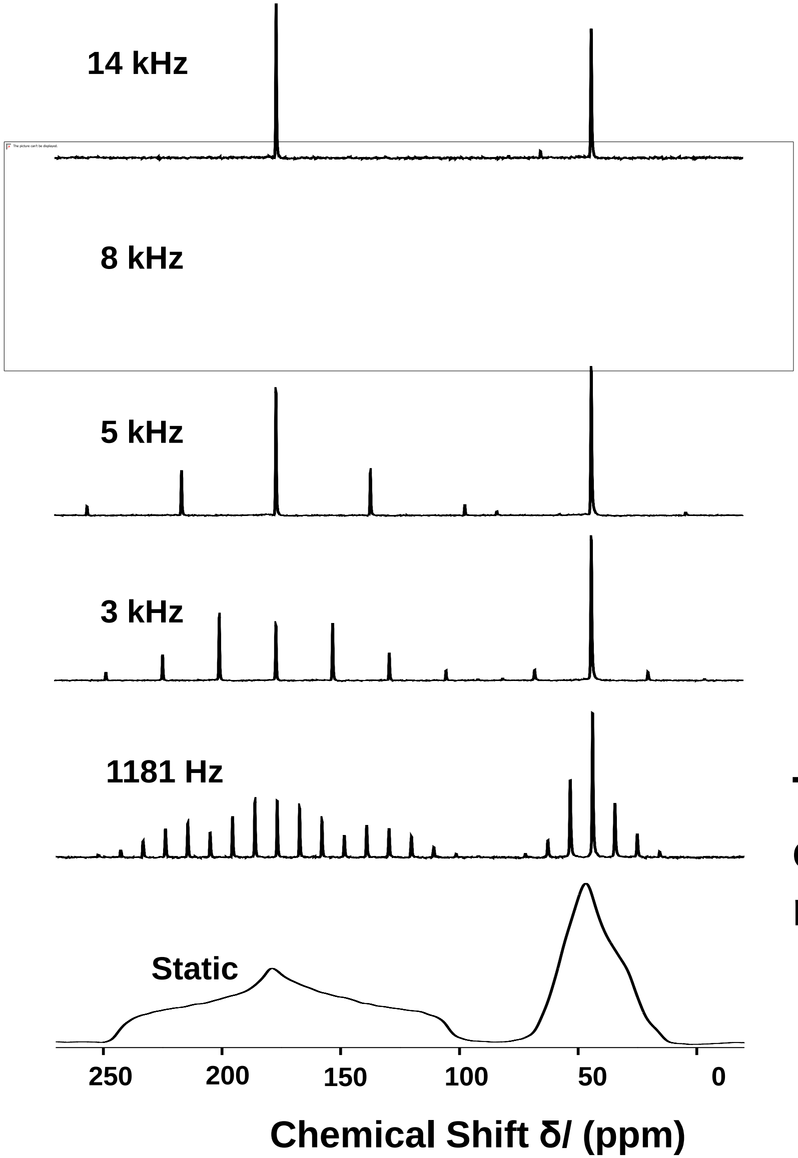
^{13}C spectra of [$^{13}C_2$]-glycine



no spinning

with MAS
at 12 kHz

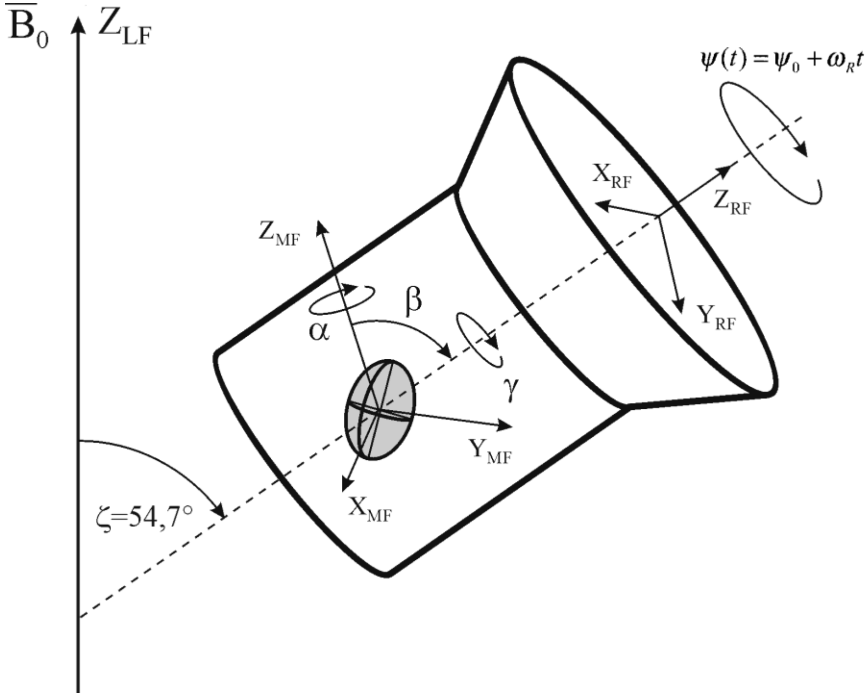
Magic-Angle-Spinning Spectra: Resolution Enhancement

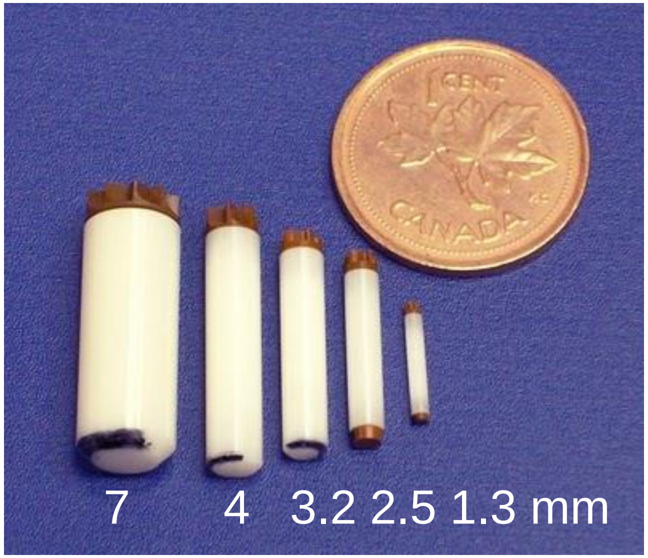


Glycine

The powder pattern breaks up into a centreband and sidebands spaced at integer multiples of the rotor frequency

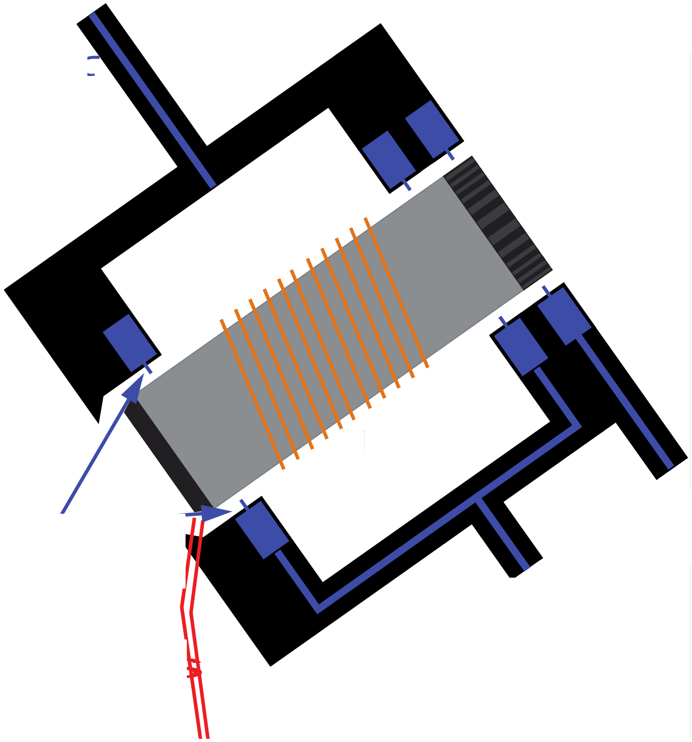
MAS Rotor Types





Angular Frequency to Linear Velocity

Magic Angle Spinning (MAS)



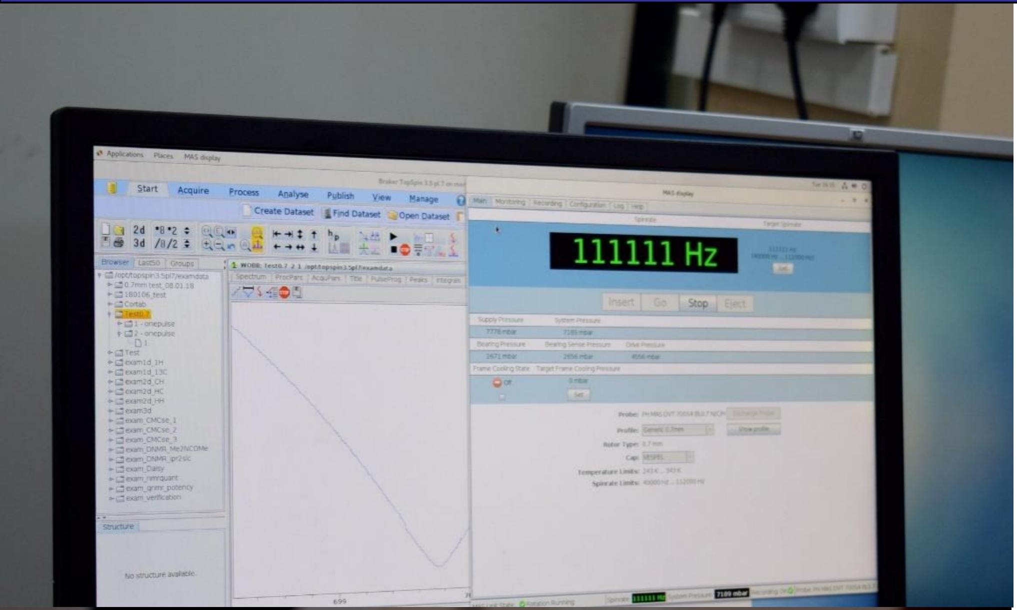
A 0.8 mm rotor spinning at 100 kHz …

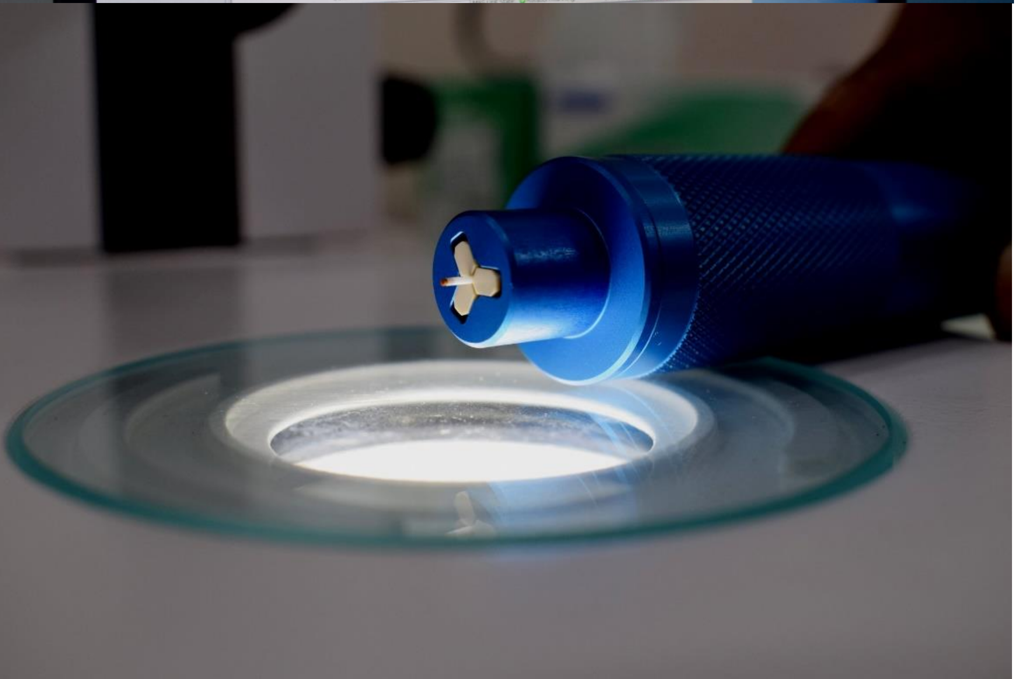
… has a speed of 250m/s when rolling along the ground…

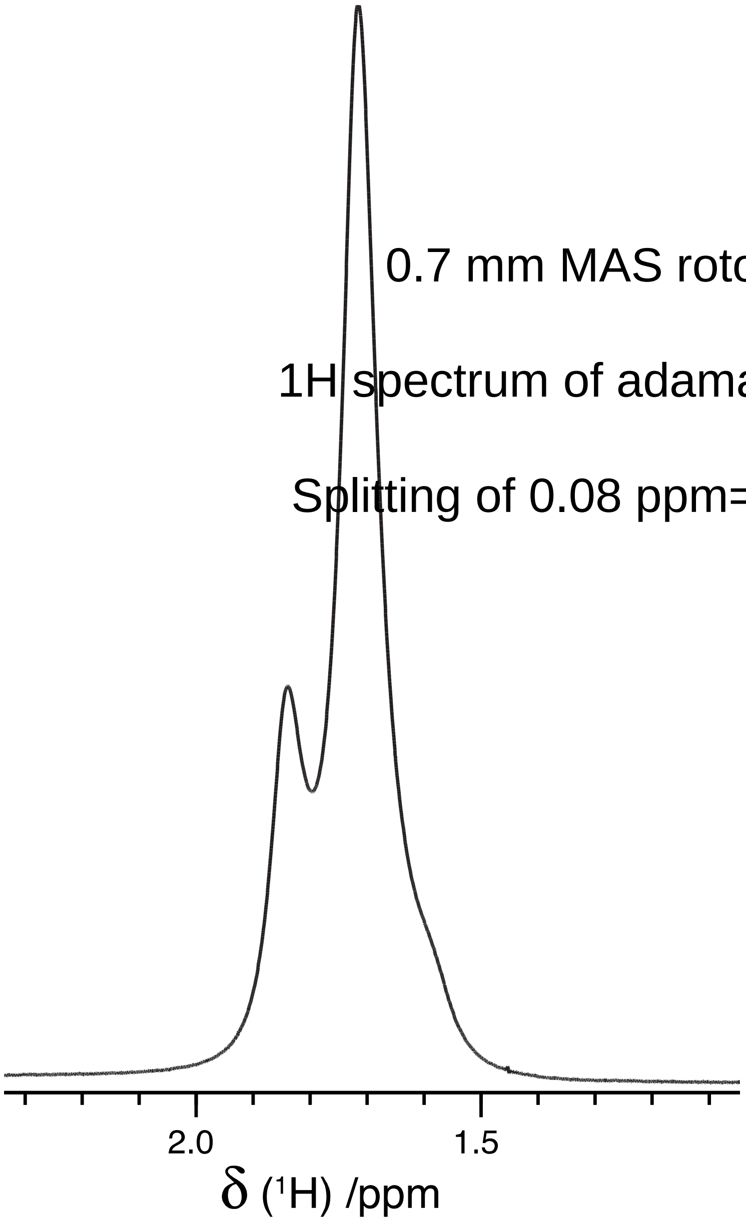
……. needs only 44 hours to roll around the earth….

Angular frequency ~ 120-130 kHz

Ultra Fast MAS in TIFR Hyderabad





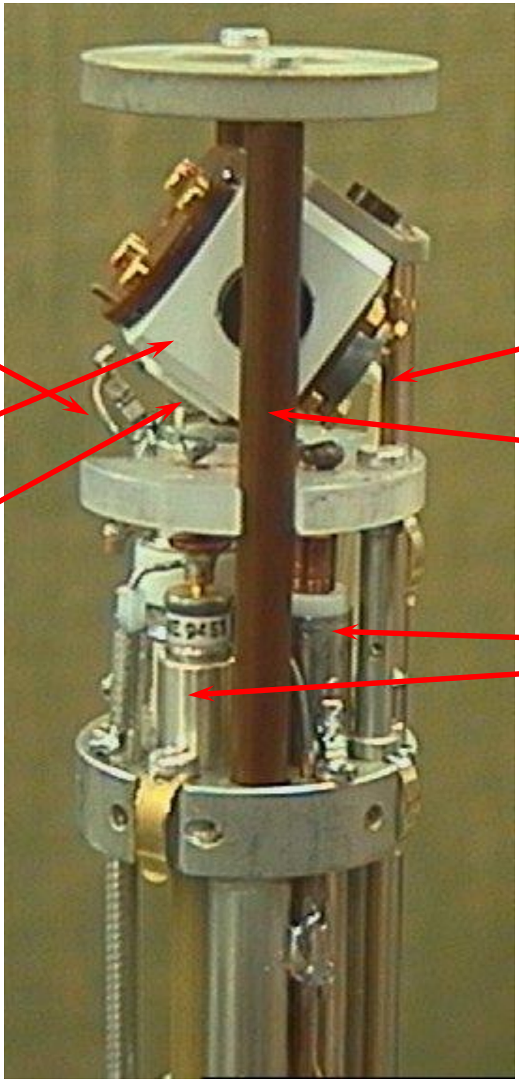


0.7 mm MAS rotor

1H spectrum of adamantane

Splitting of 0.08 ppm= 7 Hz

Standard Bore MAS Probe



proton trap

stator flip mechanism

bearing gas inlet

BN stator

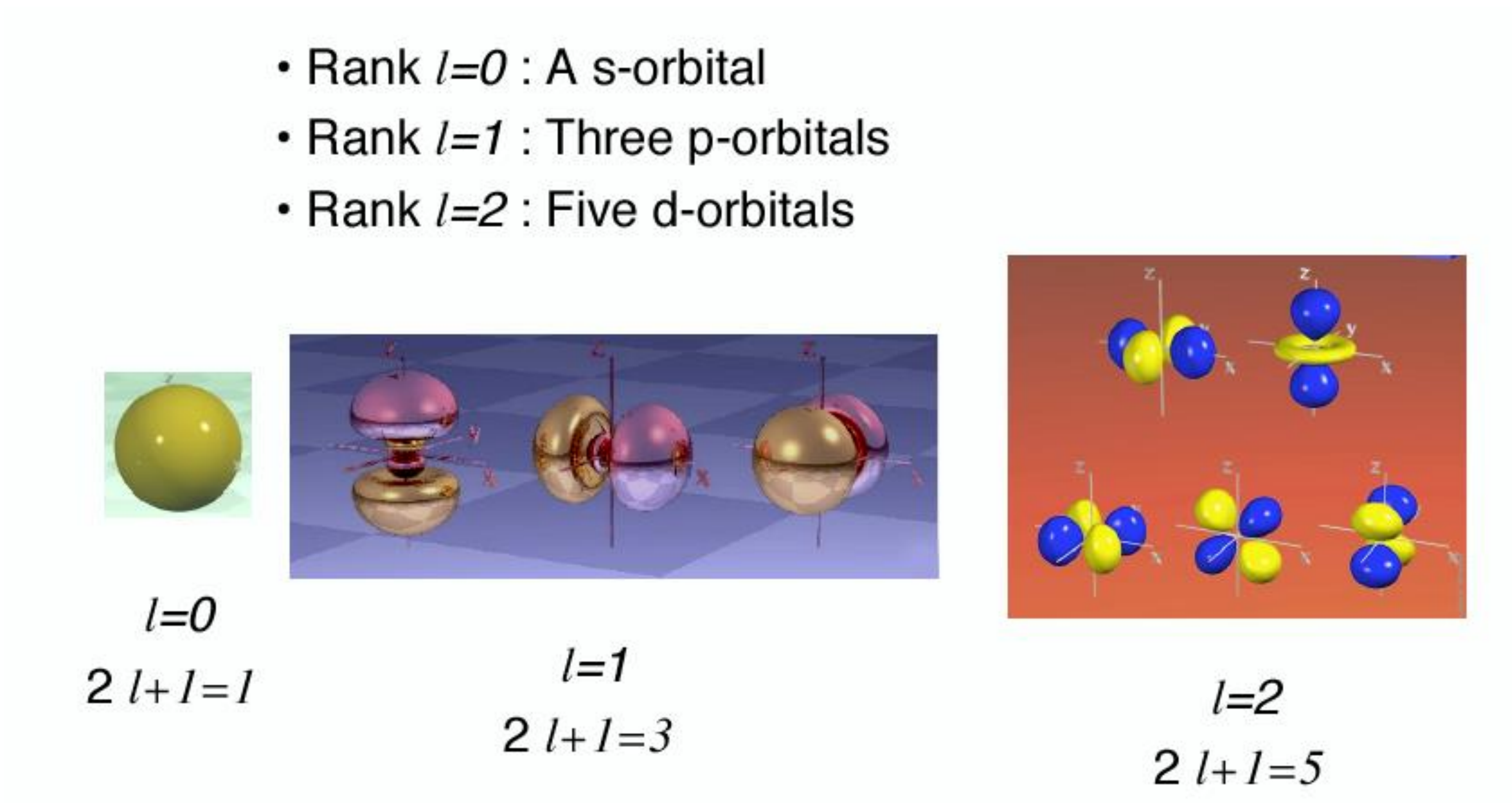
RF coil

RF electronics

Rotational Signatures of the Internal Spin Interactions

Interaction	Space Rank l	Spin Rank λ
Iso-CS	0	1
CSA	2	1
J	0	0
Hetero-DD	2	1
Homo-DD	2	2

Spherical Tensors: Examples



- Rank *l=0* : A s-orbital
- Rank *l=1* : Three p-orbitals
- Rank *l=2* : Five d-orbitals

$l=0$

$2l+1=1$

$l=1$

$2l+1=3$

$l=2$

$2l+1=5$

Spherical Tensors

A spherical tensor of rank ℓ is a set of 2ℓ+1 objects such that

when any of them is rotated in three dimensions, the result is a superposition of the same set of objects

Rotation of spherical tensors

$$R(\Omega)T_{lm}R(\Omega)^{\dagger} = \sum_{m'=-l}^{l} T_{lm'}D^{l}_{mm'}(\Omega)$$

Complex numbers

Rotation operator

Spherical tensor element of rank ℓ

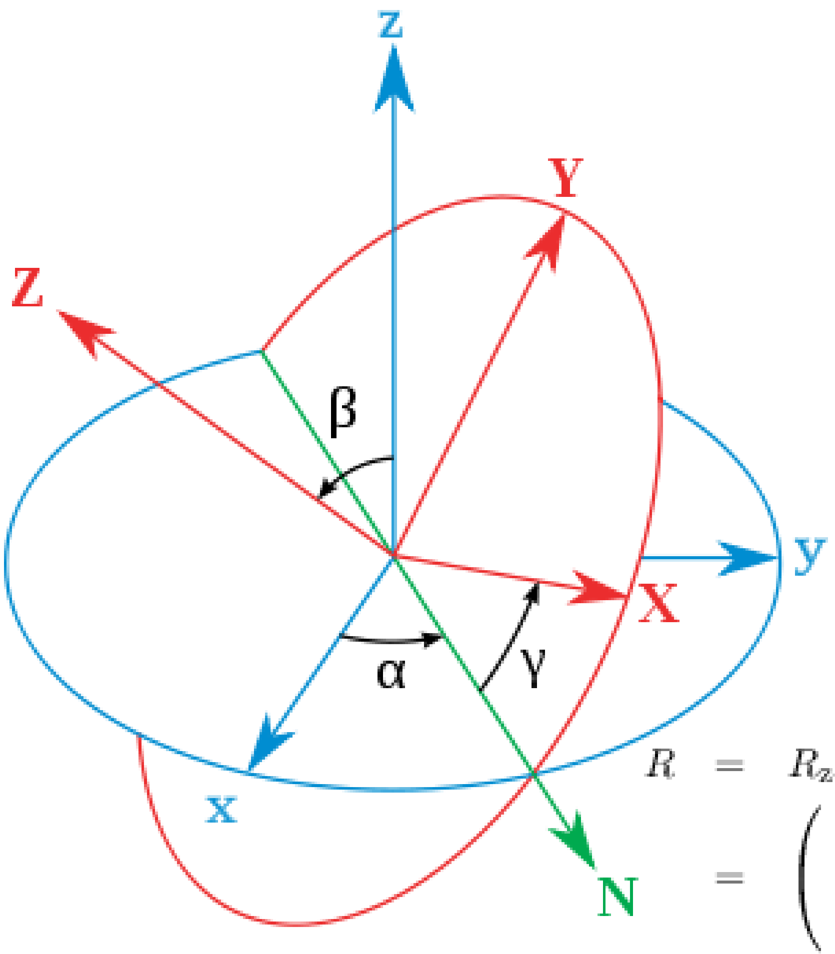
Rotational Signatures of the Internal Spin Interactions

Interaction	Space Rank l	Spin Rank λ
Iso-CS	0	1
CSA	2	1
J	0	0
Hetero-DD	2	1
Homo-DD	2	2

Rotation of molecules

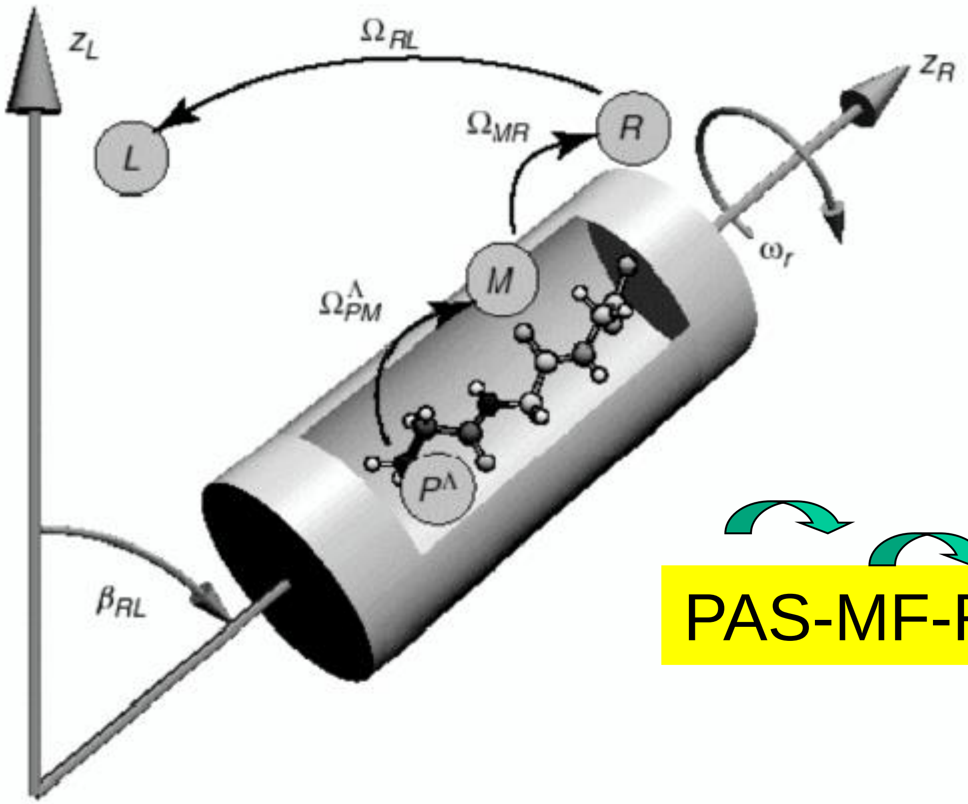
Rotation of spins

Euler Angles



$$
\begin{aligned}
R &= R_{z''}(\gamma)\cdot R_{y'}(\beta)\cdot R_{z}(\alpha)\\
&= \begin{pmatrix} c\gamma & s\gamma & 0\\ -s\gamma & c\gamma & 0\\ 0 & 0 & 1 \end{pmatrix}\cdot\begin{pmatrix} c\beta & 0 & -s\beta\\ 0 & 1 & 0\\ s\beta & 0 & c\beta \end{pmatrix}\cdot\begin{pmatrix} c\alpha & s\alpha & 0\\ -s\alpha & c\alpha & 0\\ 0 & 0 & 1 \end{pmatrix}\\
&= \begin{pmatrix} c\gamma c\beta c\alpha - s\gamma s\alpha & c\gamma c\beta s\alpha + s\gamma c\alpha & -c\gamma s\beta\\ -s\gamma c\beta c\alpha - c\gamma s\alpha & -s\gamma c\beta s\alpha + c\gamma c\alpha & s\gamma s\beta\\ s\beta c\alpha & s\beta s\alpha & c\beta \end{pmatrix}
\end{aligned}
$$

Reference Frames in Solid-State NMR



PAS-MF-RF-LF

Transformation via the relevant Euler angles necessary for visualisation and simulations

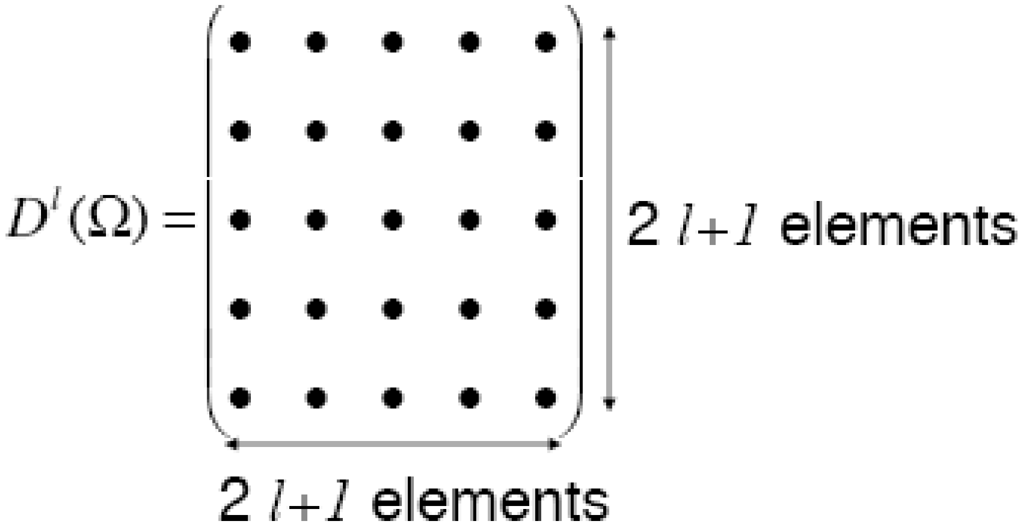
Rotation of Spherical Tensors

$$R(\Omega)T_{lm}R(\Omega)^{\dagger} = \sum_{m'=-l}^{l} T_{lm'}D^{l}_{mm'}(\Omega)$$

Rotation operator
for Euler angles Ω

Elements of Wigner matirx
for Euler angles Ω

Wigner Matrices



$$D^l_{m'm}(\Omega) = \exp(-im'\alpha)\, d^l_{m'm}(\beta)\exp(-im\gamma)$$

Wigner matrix element

Reduced Wigner matrix element

Reduced Wigner Matrix Elements (Rank 0 and 1)

$$d^0(\beta) = 1$$

$$d^1_{00}(\beta)$$

$$d^1_{mm'}(\beta) = \begin{array}{cccc} \frac{1}{2}(1+\cos\beta) & -\sin\beta/\sqrt{2} & \frac{1}{2}(1-\cos\beta) & m=-1 \\ \sin\beta/\sqrt{2} & \cos\beta & -\sin\beta/\sqrt{2} & m=0 \\ \frac{1}{2}(1-\cos\beta) & \sin\beta/\sqrt{2} & \frac{1}{2}(1+\cos\beta) & m=1 \\ m'=-1 & m'=0 & m'=1 & \end{array}$$

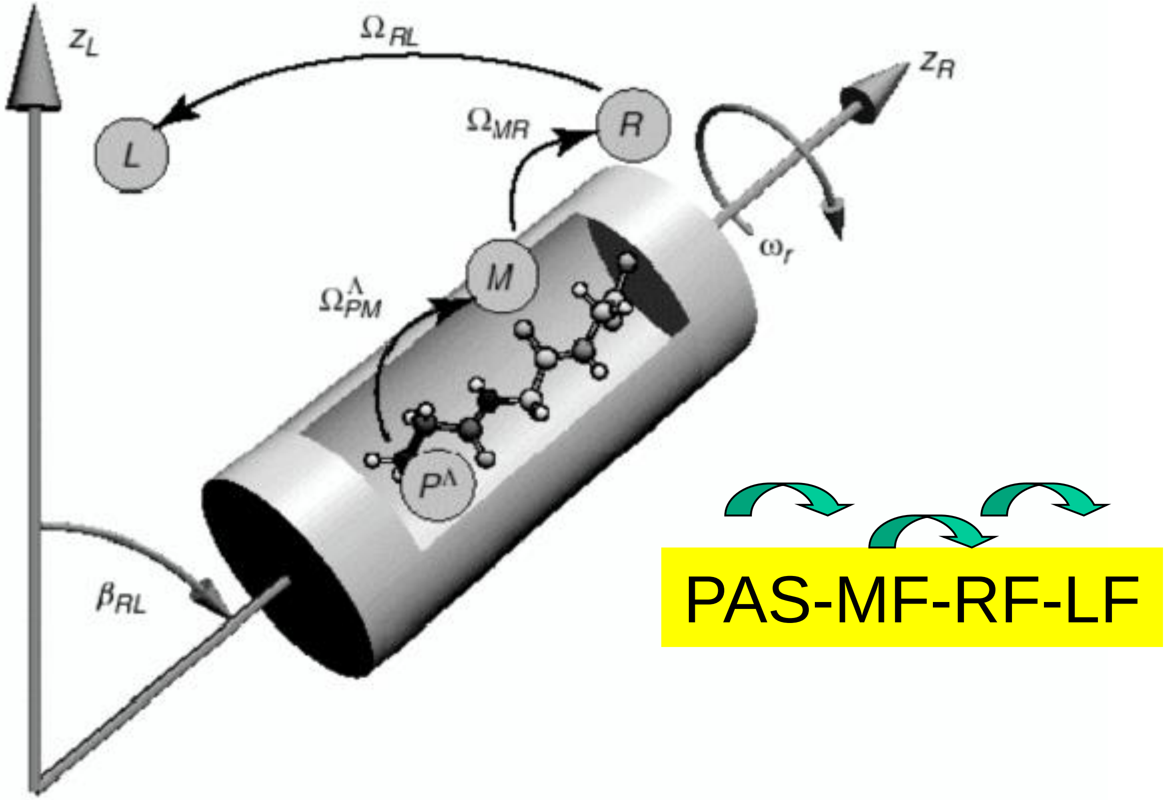
Reduced Wigner Matrix Elements (Rank 2)

$$d^{2}_{00}(\beta)$$

$$d^{2}_{mm'}(\beta)=$$

$$\begin{array}{cc}
\begin{pmatrix}
\frac{1}{4}(1+cos\beta)^2 & -\frac{1}{2}sin\beta(1+cos\beta) & \sqrt{\frac{3}{8}}sin^2\beta & -\frac{1}{2}sin\beta(1-cos\beta) & \frac{1}{4}(1-cos\beta)^2 \\
\frac{1}{2}sin\beta(1+cos\beta) & \frac{1}{2}(2cos^2\beta+cos\beta-1) & -\sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(2cos^2\beta-cos\beta-1) & -\frac{1}{2}sin\beta(1-cos\beta) \\
\sqrt{\frac{3}{8}}sin^2\beta & \sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(3cos^2\beta-1) & -\sqrt{\frac{3}{8}}sin2\beta & \sqrt{\frac{3}{8}}sin^2\beta \\
\frac{1}{2}sin\beta(1-cos\beta) & -\frac{1}{2}(2cos^2\beta-cos\beta-1) & \sqrt{\frac{3}{8}}sin2\beta & \frac{1}{2}(2cos^2\beta+cos\beta-1 & -\frac{1}{2}sin\beta(1+cos\beta) \\
\frac{1}{4}(1-cos\beta)^2 & \frac{1}{2}sin\beta(1-cos\beta) & \sqrt{\frac{3}{8}}sin^2\beta & \frac{1}{2}sin\beta(1+cos\beta) & \frac{1}{4}(1+cos\beta)^2
\end{pmatrix} &
\begin{array}{c} m=-2 \\ \\ \\ \\ \\ \\ \\ \\ m=2 \end{array} \\
\begin{array}{ccccc} m'=-2 & m'=-1 & m'=0 & m'=1 & m'=2 \end{array} &
\end{array}$$

Reference Frames in Solid-State NMR



PAS-MF-RF-LF

Transformation via the relevant Euler angles necessary for visualsation and simulations

Wigner Matrix Chains

$$D^{l}(\Omega_{AC}) = D^{l}(\Omega_{AB}) D^{l}(\Omega_{BC})$$

$$D^{l}_{m'm}(\Omega_{AC}) = \sum_{m''=-l}^{l} D^{l}_{m'm''}(\Omega_{AB}) D^{l}_{m''m}(\Omega_{BC})$$

$$D^{l}(\Omega_{AD}) = D^{l}(\Omega_{AB}) D^{l}(\Omega_{BC}) D^{l}(\Omega_{CD})$$

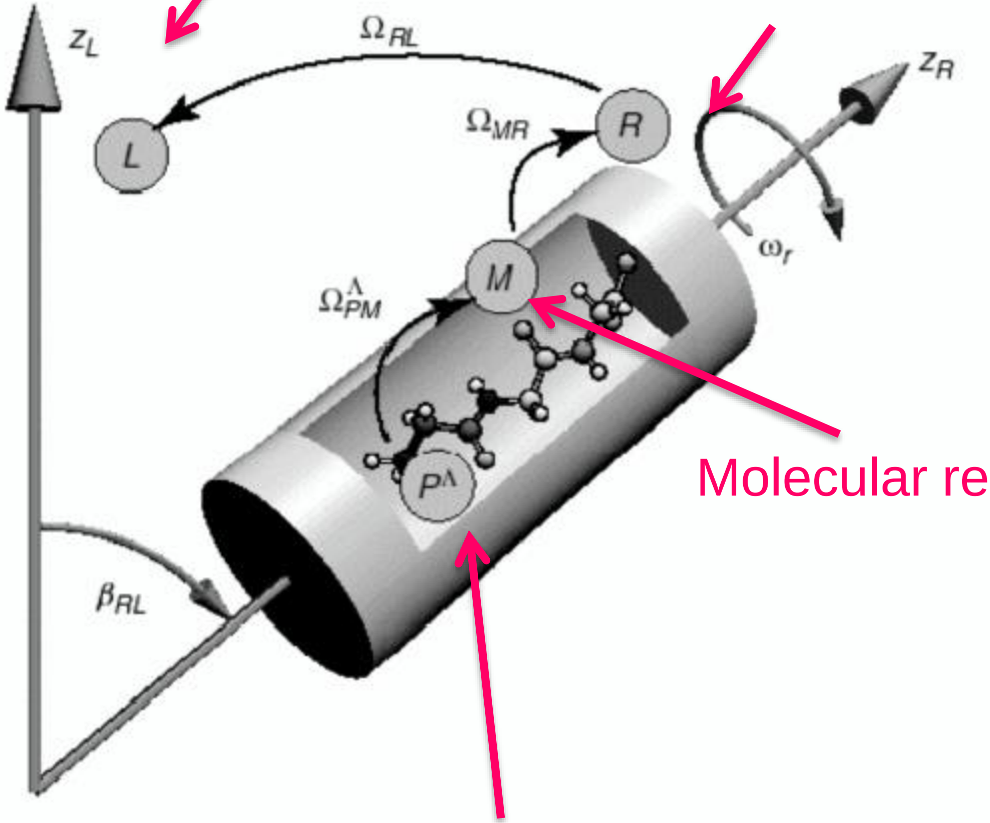
$$D^{l}_{m'm}(\Omega_{AD}) = \sum_{m''=-l}^{l} \sum_{m'''=-l}^{l} D^{l}_{m'm''}(\Omega_{AB}) D^{l}_{m''m'''}(\Omega_{BC}) D^{l}_{m'''m}(\Omega_{CD})$$

Frame Transformations of Spherical Tensors

$$\begin{pmatrix} [T_{2,-2}]^A \\ [T_{2,-1}]^A \\ [T_{2,0}]^A \\ [T_{2,1}]^A \\ [T_{2,2}]^A \end{pmatrix} = \begin{pmatrix} \ddots & \vdots & \iddots \\ \cdots & D^2(\Omega_{AB}) & \cdots \\ \iddots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} [T_{2,-2}]^B \\ [T_{2,-1}]^B \\ [T_{2,0}]^B \\ [T_{2,1}]^B \\ [T_{2,2}]^B \end{pmatrix}$$

$$\begin{pmatrix} [T_{2,-2}]^A \\ [T_{2,-1}]^A \\ [T_{2,0}]^A \\ [T_{2,1}]^A \\ [T_{2,2}]^A \end{pmatrix} = \begin{pmatrix} \ddots & \vdots & \iddots \\ \cdots & D^2(\Omega_{AB}) & \cdots \\ \iddots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \ddots & \vdots & \iddots \\ \cdots & D^2(\Omega_{BC}) & \cdots \\ \iddots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} [T_{2,-2}]^C \\ [T_{2,-1}]^C \\ [T_{2,0}]^C \\ [T_{2,1}]^C \\ [T_{2,2}]^C \end{pmatrix}$$

Chain of Reference Frames in Solid-State NMR



Laboratory reference frame

Rotor reference frame

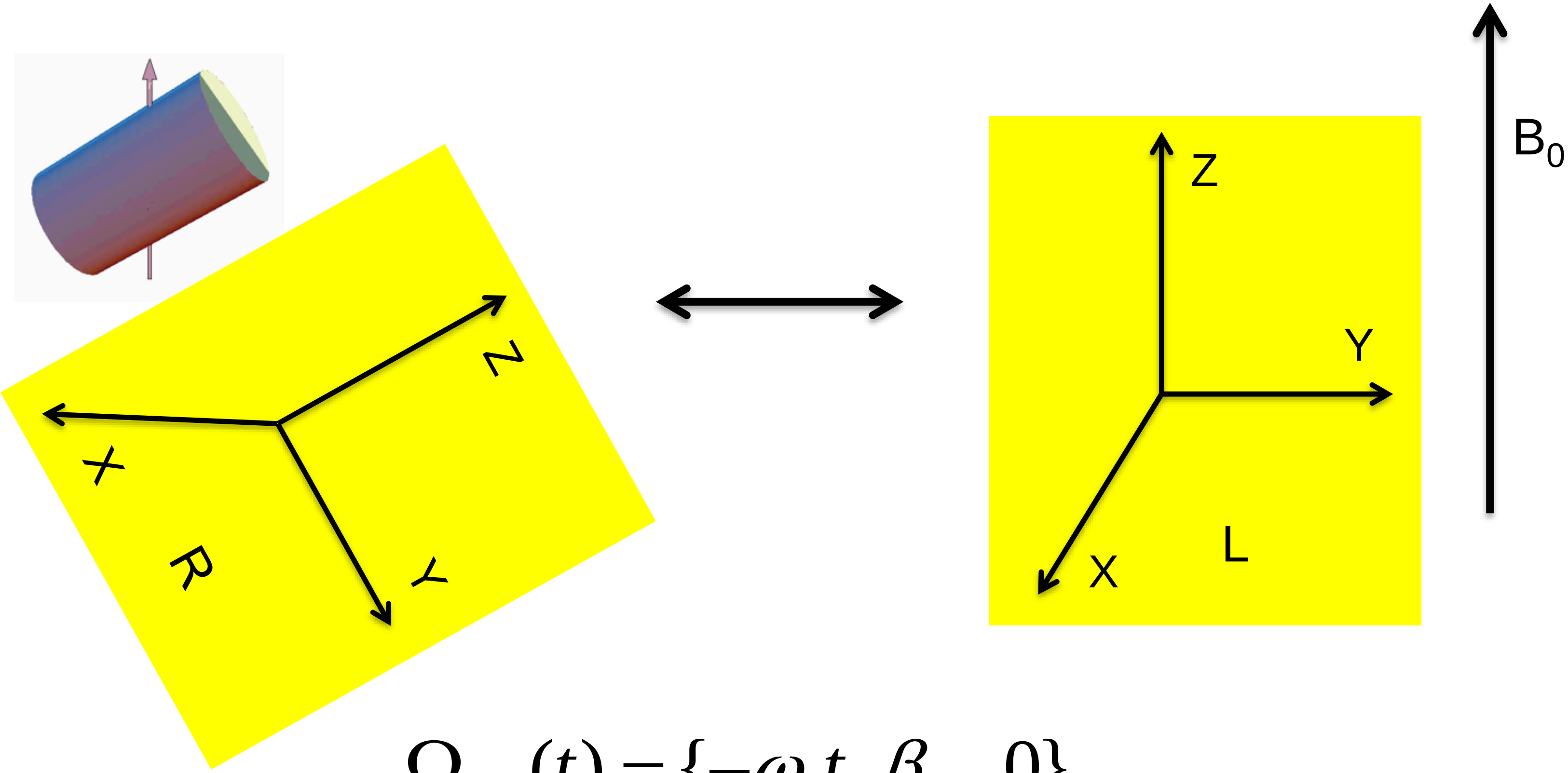
Molecular reference frame

Principal axis frame of a spin interaction

Rotor to Lab Frame Transformation

Rotor reference frame

Lab reference frame

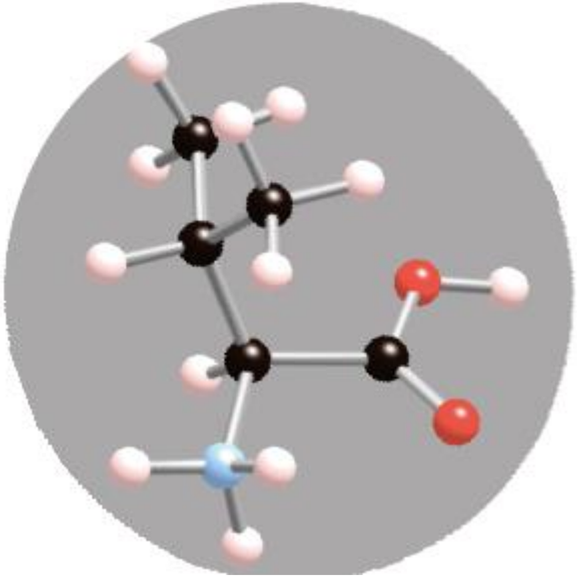


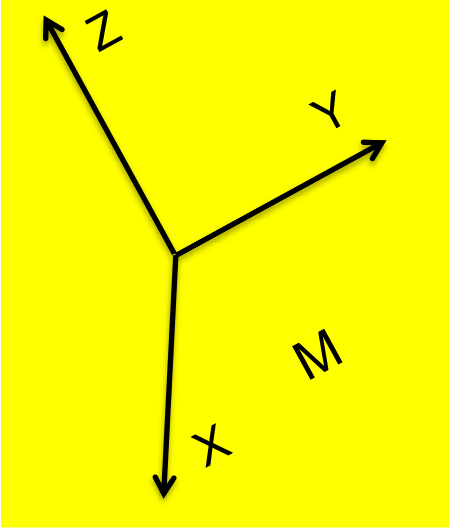
$$\Omega_{RL}(t)=\{-\omega_r t,\beta_{RL},0\}$$

Spinning frequency

Rotor (magic) angle

Molecular Frame





Molecular frame is more arbitrary, although in certain cases, calculations are simpler with a good choice

Ω_{MR} Different Euler angles for different molecules

Chain of Transformations in Solid-State NMR

$$D^{l}(\Omega^{\Lambda}_{PL}) = D^{l}(\Omega^{\Lambda}_{PM})D^{l}(\Omega^{\Lambda}_{MR})D^{l}(\Omega^{\Lambda}_{RL}(t))$$

Orientation of an interaction, Λ, with respect to the molecular frame. Depends only on the interaction, not on time or crystallite

Orientation of the rotor wrt
To the static field, time dependent

Orientation of molecular frame wrt to rotor frame, depends only on crystallite, not on interaction or time

Irreducible Tensor Representation of the Hamiltonians

$$H = \sum_{m=-l}^{l} [A_{lm}]^L [T_{l-m}]^L$$

Space part Spin part

$$H = \sum_{m=-2}^{2} [A_{2m}]^L [T_{2-m}]^L$$

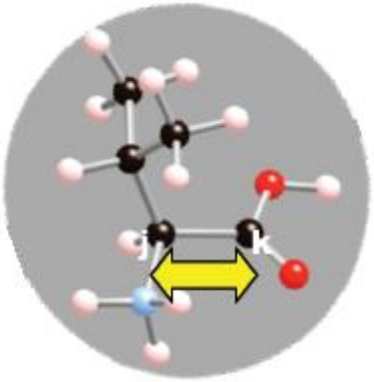
NMR case

$$H = [A_{20}]^L [T_{20}]^L$$

High field,
secular approximation

DD Coupling Hamiltonian

$$H_{DD}^{jk} = [A_{20}^{jk}]^{L}[T_{20}^{jk}]^{L}$$



$$T_{2}^{jk} = \begin{pmatrix} T_{2-2}^{jk} \\ T_{2-1}^{jk} \\ T_{20}^{jk} \\ T_{21}^{jk} \\ T_{22}^{jk} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} I_j^- I_k^- \\ \frac{1}{2}\left(I_j^- I_{kz} + I_{jz} I_k^-\right) \\ 6^{-1/2}\left\{2 I_{jz} I_{kz} - \frac{1}{2}\left(I_j^+ I_k^- - I_j^- I_k^+\right)\right\} \\ -\frac{1}{2}\left(I_j^+ I_{kz} + I_{jz} I_k^+\right) \\ \frac{1}{2} I_j^+ I_k^+ \end{pmatrix}$$

Spin tensor

$$[A_{2}^{jk}]^{P} = \begin{pmatrix} 0 \\ 0 \\ 6^{1/2} b_{jk} \\ 0 \\ 0 \end{pmatrix} \qquad b_{jk} = -\left(\frac{\mu_0}{4\pi}\right)\frac{\hbar \gamma_j \gamma_k}{r_{jk}^{3}}$$

Space tensor in the PAS

DD Coupling Hamiltonian

$$H_{DD}^{jk} = [A_{20}^{jk}]^L [T_{20}^{jk}]^L$$

$$= \sum_{m=-2}^{2} [A_{20}^{jk}]^P D_{m0}^{2}(\Omega_{PL}^{jk}) [T_{20}^{jk}]^L$$

$$= [A_{20}^{jk}]^P D_{00}^{2}(\Omega_{PL}^{jk}) [T_{20}^{jk}]^L$$

$$= [A_{20}^{jk}]^P d_{00}^{2}(\beta_{PL}^{jk}) [T_{20}^{jk}]^L$$

Zero at the magic angle

$$= b_{jk} \frac{1}{2}(3\cos^2\theta_{PL}^{jk} - 1)\{2I_{jx}I_{ky} - \frac{1}{2}(I_j^+ I_k^- - I_j^- I_k^+)\}$$

Isotropic Chemical-Shift Hamiltonian

$$H_{iso}^{j} = \omega_{iso}^{j} I_{jz}$$

Spin rank 1

$$\omega_{iso}^{j} = \delta_{iso}^{j} \omega_{0}^{j}$$

Space rank 0

$$\omega_{0}^{j} = -\gamma^{j} B_{0}$$

CSA Hamiltonian

Spin rank 1

$$H_{CSA}^{j} = [A_{20}^{j}]^{L}[T_{20}^{j}]^{L}B_{0} = [A_{20}^{j}]^{L}I_{jz}B_{0}$$

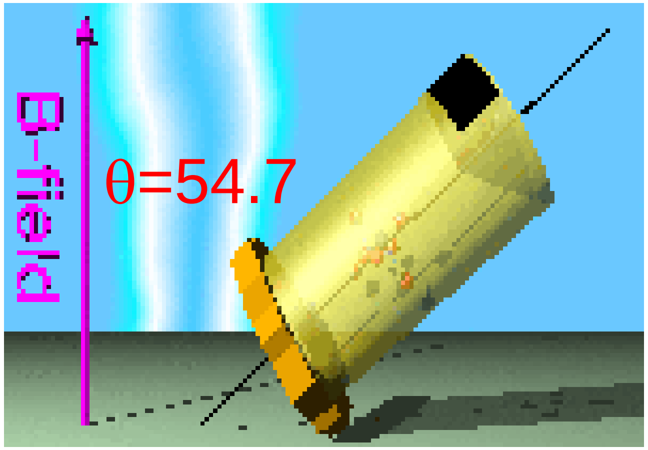
Space rank 2

Space tensor in the PAS

$$[A_{2}^{j}]^{P} = \omega_{aniso}^{j}\begin{pmatrix} -6^{-1/2}\eta^{j} \\ 0 \\ 1 \\ 0 \\ -6^{-1/2}\eta^{j} \end{pmatrix}$$

$$\omega_{aniso}^{j} = \delta_{aniso}^{j}\,\omega_{0}^{j}$$

Average Hamiltonian Theory and MAS



$$\alpha_{RL} = -\omega_r t$$

$$\beta_{RL} = 54.7$$

$$\gamma_{RL} = \text{arbitrary}$$

Isolated spin-1/2 experiencing CSA:

$$H^j(t) = \omega^j_{iso} I_{jz} + H^j_{CSA}(\Omega_{MR}, t)$$

CSA Hamiltonian under MAS

$$H^j_{CSA} = [A^j_{20}]^L I_{jz} B_0$$

$$= \sum_{m=-2}^{2} [A^j_{2m}]^R D^2_{m0}(\Omega_{RL}) I_{jz} B_0$$

$$= \sum_{m'=-2}^{2} \sum_{m=-2}^{2} [A^j_{2m'}]^M D^2_{m'm}(\Omega_{MR}) D^2_{m0}(\Omega_{RL}) I_{jz} B_0$$

$$= \sum_{m'=-2}^{2} \sum_{m=-2}^{2} [A^j_{2m'}]^M D^2_{m'm}(\Omega_{MR}) e^{im\omega_r t} d^2_{m0}(\beta_{RL}) I_{jz} B_0$$

Concept of Average Hamiltonian

If the Hamiltonian is such that:

- It is periodic, H(t),=H(t+NT)
- It varies sufficiently fast with respect to time

Then the spin system behaves as if it is subjected to a time average of H(t) over the period T (then the Hamiltonian also becomes time independent):

$$H(t) \Rightarrow \overline{H}^{(1)} = \frac{1}{T}\int H(t)dt$$

Average Hamiltonian

Average CSA Hamiltonian Under MAS

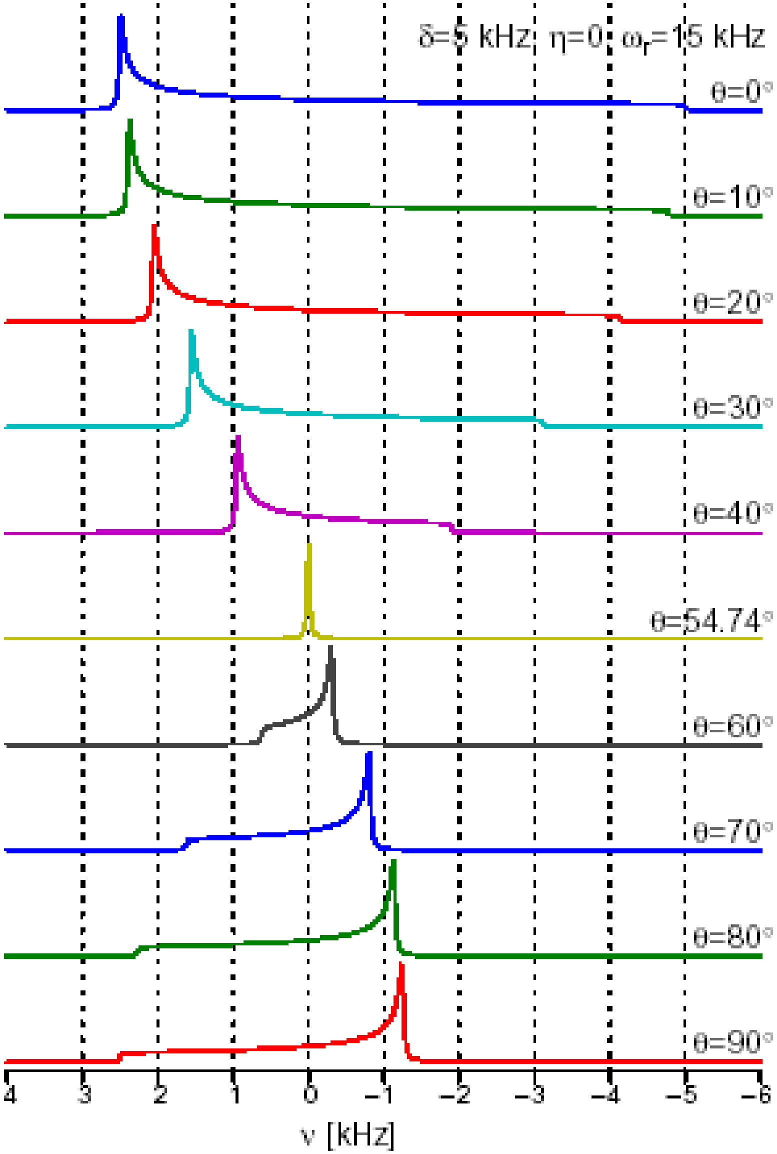
$$H^{j}_{CSA}(\Omega_{MR}) = \sum_{m'=-2}^{2} \sum_{m=-2}^{2} [A^{j}_{2m'}]^{M} D^{2}_{m'm}(\Omega_{MR}) \overline{e^{im\omega_{r}t}} d^{2}_{m0}(\beta_{RL}) I_{jz} B_{0}$$

$$= \sum_{m'=-2}^{2} [A^{j}_{2m'}]^{M} D^{2}_{m'0}(\Omega_{MR}) d^{2}_{00}(\beta_{RL}) I_{jz} B_{0}$$

Zero for β_{RL}=54.7

Exact MAS, hence, averages CSA to zero, provided the rotation is sufficiently fast.

CSA Powder Pattern and Rotation Angle



For angles other than 54.7, scaled versions of static powder pattern appear, with scale factor ranging from 1 to –0.5

Isotropic spectrum results at the magic angle, 54.7

DD Hamiltonian Under MAS

$$H_{DD}^{jk}(\Omega_{MR},t)=[A_{20}^{jk}]^{L}[T_{20}^{jk}]^{L}$$

$$=\sum_{m=-2}^{2}[A_{2m}^{jk}]^{R}D_{m0}^{2}(\Omega_{RL})[T_{20}^{jk}]^{L}$$

$$=\sum_{m'=-2}^{2}\sum_{m=-2}^{2}[A_{2m'}^{jk}]^{M}D_{m'm}^{2}(\Omega_{MR})D_{m0}^{2}(\Omega_{RL})[T_{20}^{jk}]^{L}$$

$$=\sum_{m'=-2}^{2}\sum_{m=-2}^{2}[A_{2m'}^{jk}]^{M}D_{m'm}^{2}(\Omega_{MR})e^{im\omega_{r}t}d_{m0}^{2}(\beta_{RL})[T_{20}^{jk}]^{L}$$

Average DD Hamiltonian Under MAS

$$H^{jk}_{DD}(\Omega_{MR},t) = \sum_{m'=-2}^{2}\sum_{m=-2}^{2}[A^{jk}_{2m'}]^{M} D^{2}_{m'm}(\Omega_{MR})\overline{e^{im\omega_r t}}\, d^{2}_{m0}(\beta_{RL})[T^{jk}_{2m'}]^{L}$$

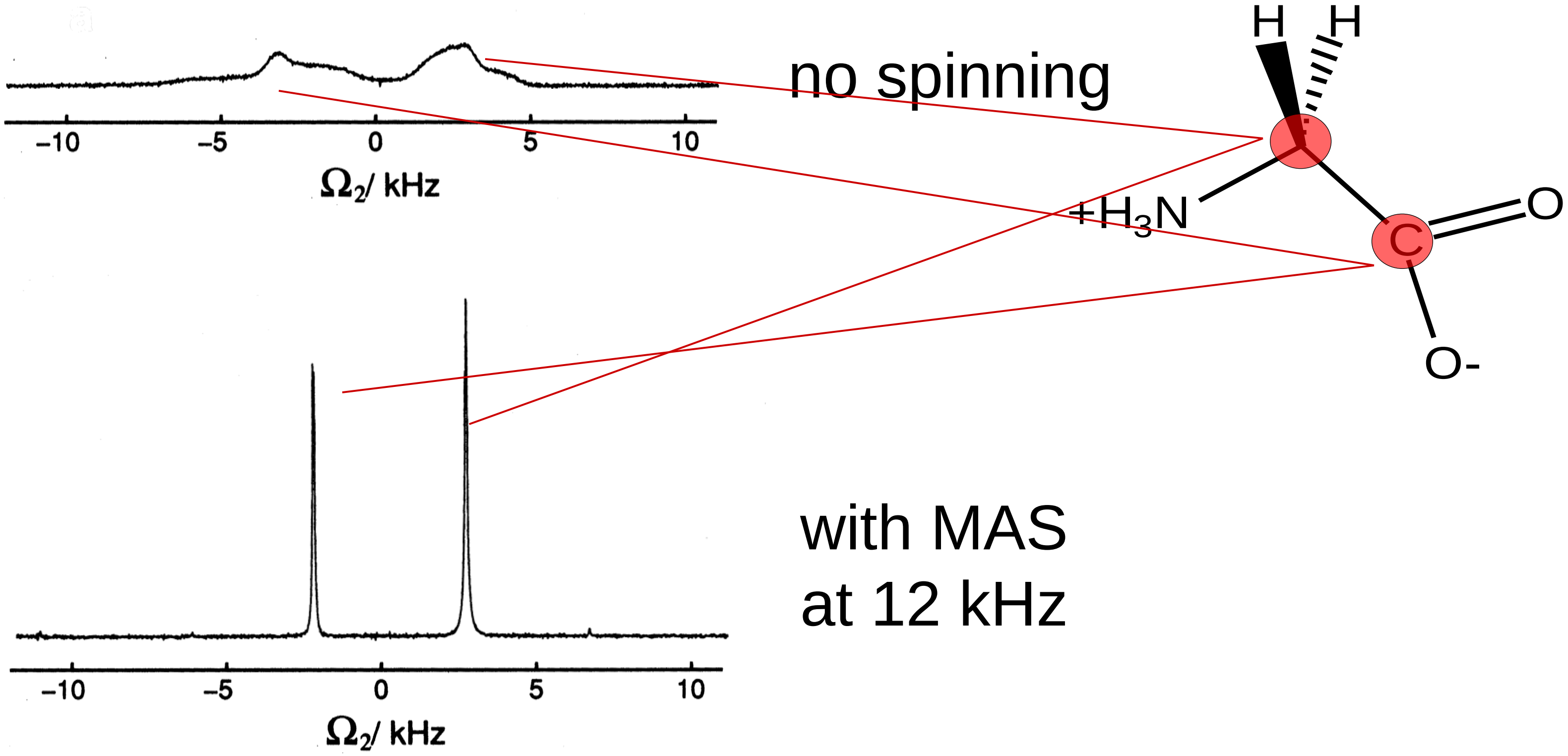
$$= \sum_{m'=-2}^{2}[A^{jk}_{2m'}]^{M} D^{2}_{m'0}(\Omega_{MR}) d^{2}_{00}(\beta_{RL})[T^{jk}_{20}]^{L}$$

Zero for β_{RL}=54.7

Exact MAS, hence, averages DD to zero, provided the rotation is sufficiently fast.

Resolution and Sensitivity Enhancement by MAS

^{13}C spectra of $[^{13}C_2]$-glycine



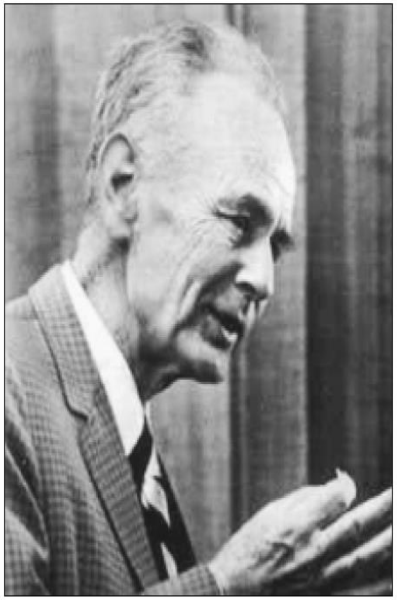
no spinning

with MAS
at 12 kHz

Tracking Spins in NMR

Floquet

Floquet theory



Wilhelm Magnus

Magnus expansion
Average Hamiltonian theory

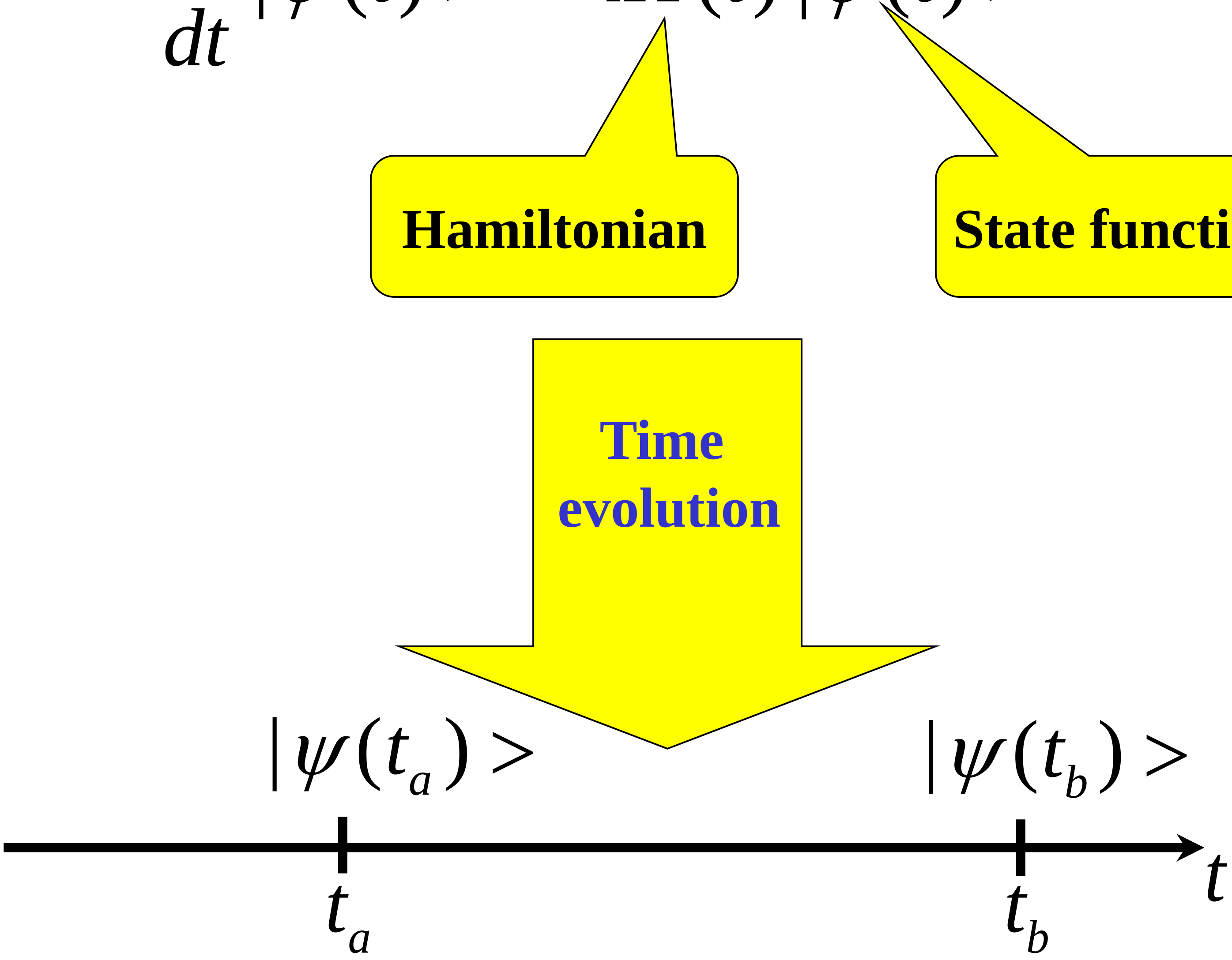
F. Fer

Fer expansion

Many more: Wilcox, Salzman, Pechukas, Burum

Time Development of the Spin System

$$\frac{d}{dt}|\psi(t)>=-iH(t)|\psi(t)>$$



Hamiltonian

State function

Time evolution

$|\psi(t_a)>$

$|\psi(t_b)>$

t_a

t_b

t

Heteronuclear Spin Decoupling

Spin Decoupling

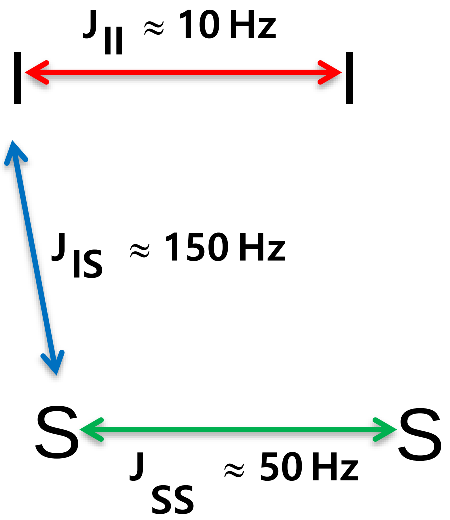
Spin manipulation

Heteronuclear dipolar decoupling
^{13}C observation

Homonuclear dipolar decoupling
^{1}H observation

Heteronuclear Couplings in NMR

Liquids


I

I

S

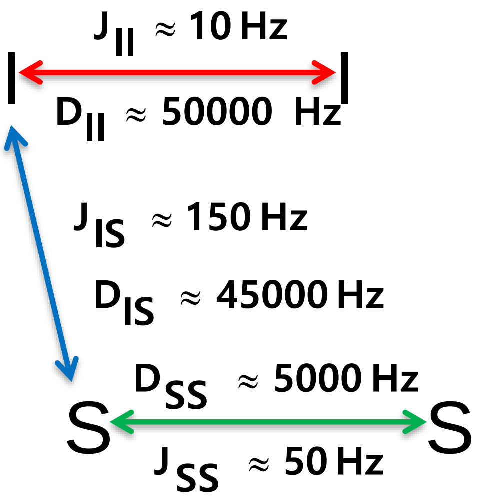
S

$J_{II} \approx 10$ Hz

$J_{IS} \approx 150$ Hz

$J_{SS} \approx 50$ Hz

Static solids


I

I

S

S

$J_{II} \approx 10$ Hz

$D_{II} \approx 50000$ Hz

$J_{IS} \approx 150$ Hz

$D_{IS} \approx 45000$ Hz

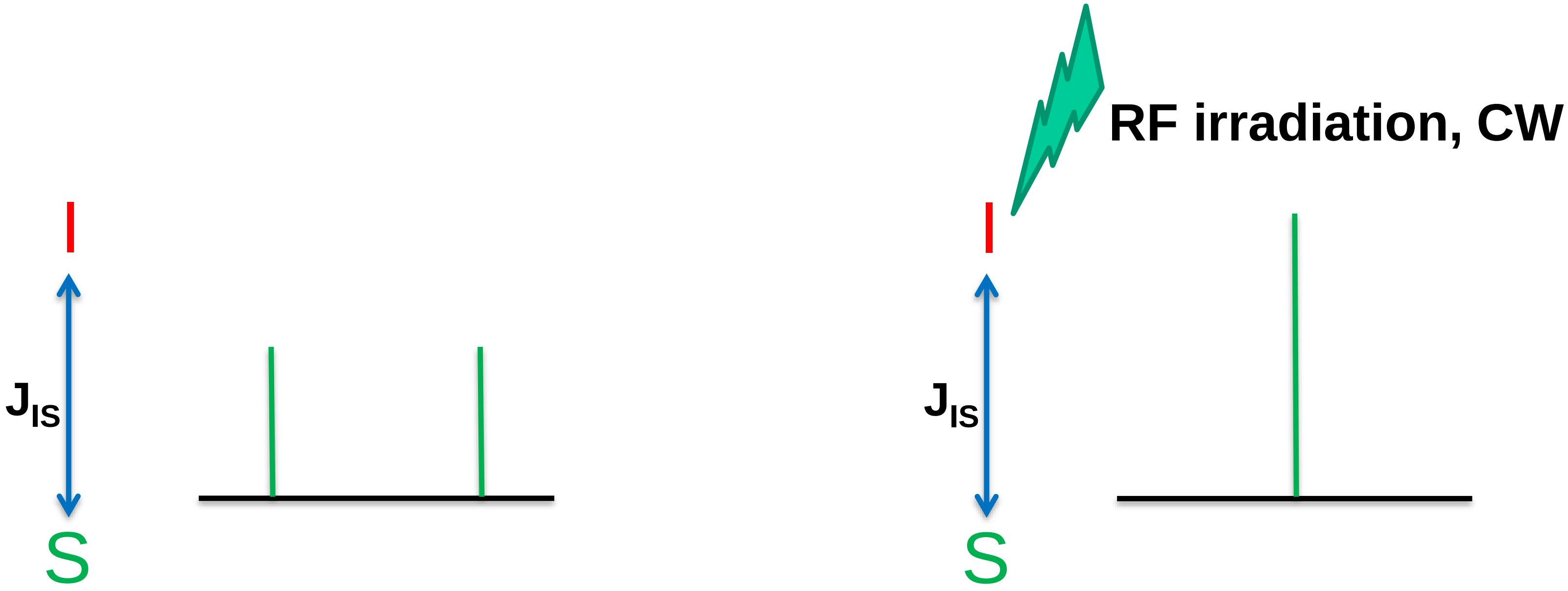
$D_{SS} \approx 5000$ Hz

$J_{SS} \approx 50$ Hz

- **Spin-spin couplings in soilds are much larger than those in liquids, dipolar vs. scalar**

- **Dipolar couplings are anisotropic and, hence, orientation dependent**

Heteronuclear Decoupling in Solution-State NMR

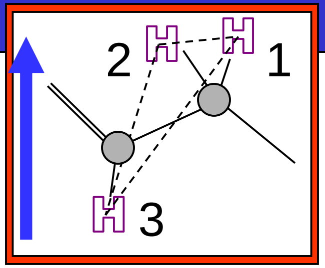


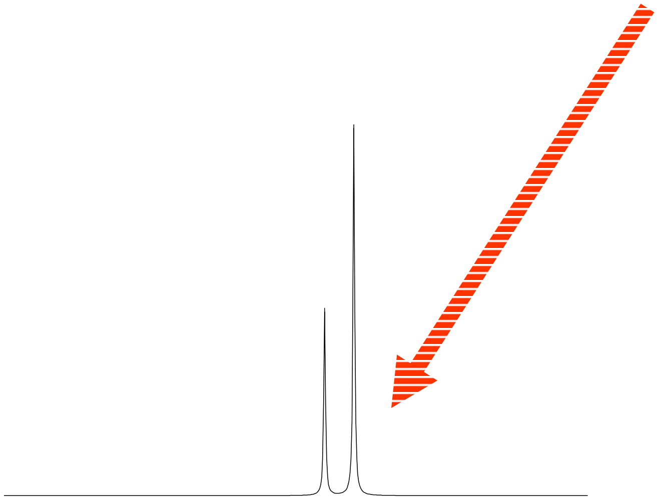
- CW RF irradiation collapses the J-multiplet on the S spins
- Pulse sequences for decoupling:
  - CW irradiation
  - Multiple-pulse schemes (MLEV, WALTZ, FLOPSY,…..)
  - Adiabatic inversion (WURST,…)

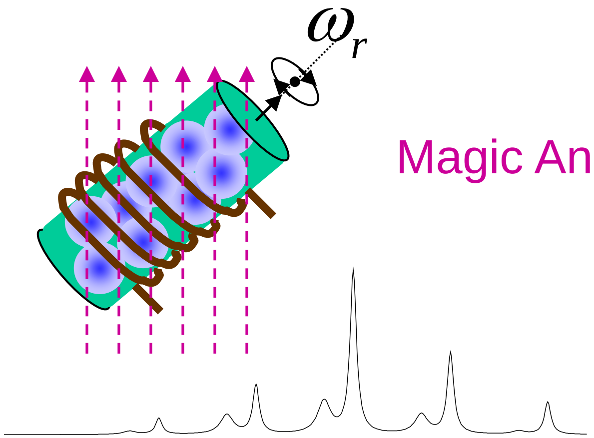
^{13}C Spectra in Solid-State NMR-The Problem

carbon-13 spectrum

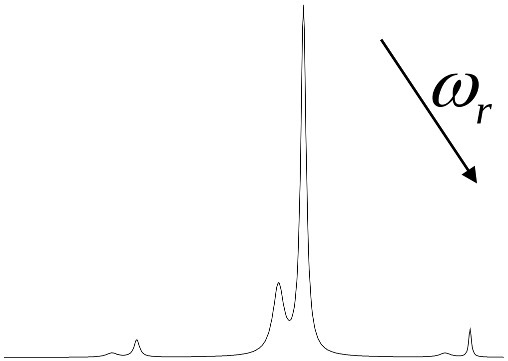
(CS+CSA+DD) proton
(CS+CSA+DD) carbon

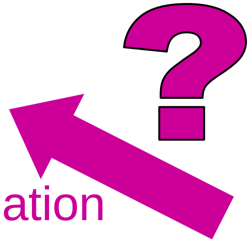




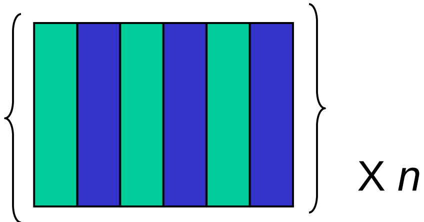


Magic Angle Spinning



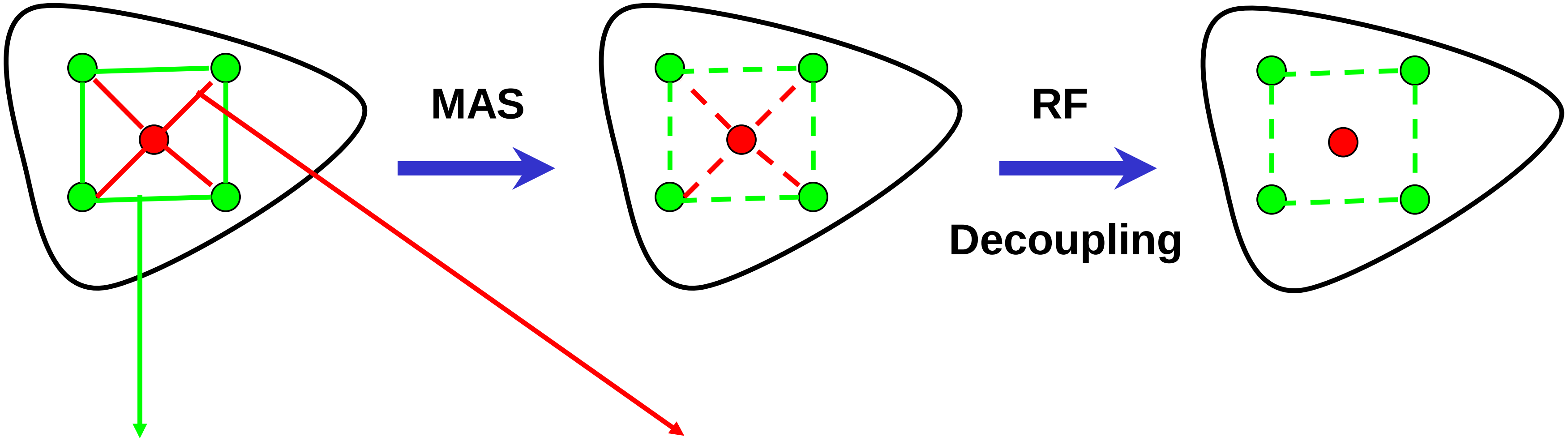


Two pulse phase modulation
Bennett 1995



And other techniques: **CM**; **SPINAL**, A-,FMPM, $C12_2^{-1}$
'04, '00 , '01-, '97 , '99

Heteronuclear Dipolar Decoupling



MAS

RF

Decoupling

Homonuclear dipolar coupling

Heteronuclear dipolar coupling

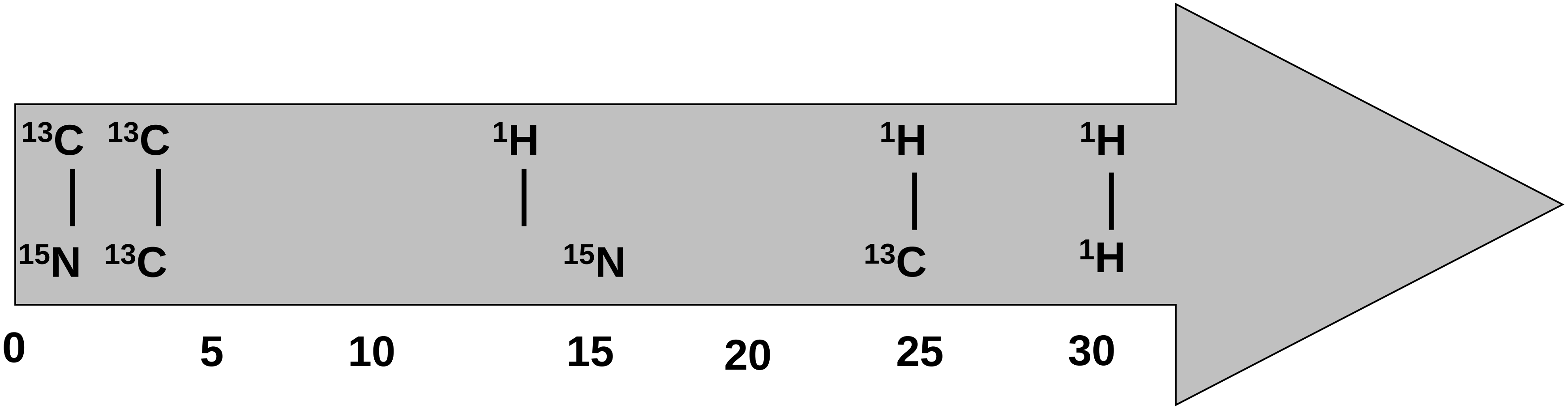
🟢 **Abundant spins ^{1}H**

🔴 **Rare spins ^{13}C, ^{15}N**

Typical ^{1}H-^{13}C coupling= 25 kHz

Dipolar Couplings: Homo and Hetero

Order of magnitude



^{13}C–^{15}N

^{13}C–^{13}C

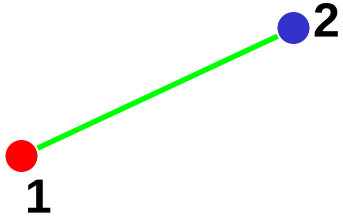
^{1}H–^{15}N

^{1}H–^{13}C

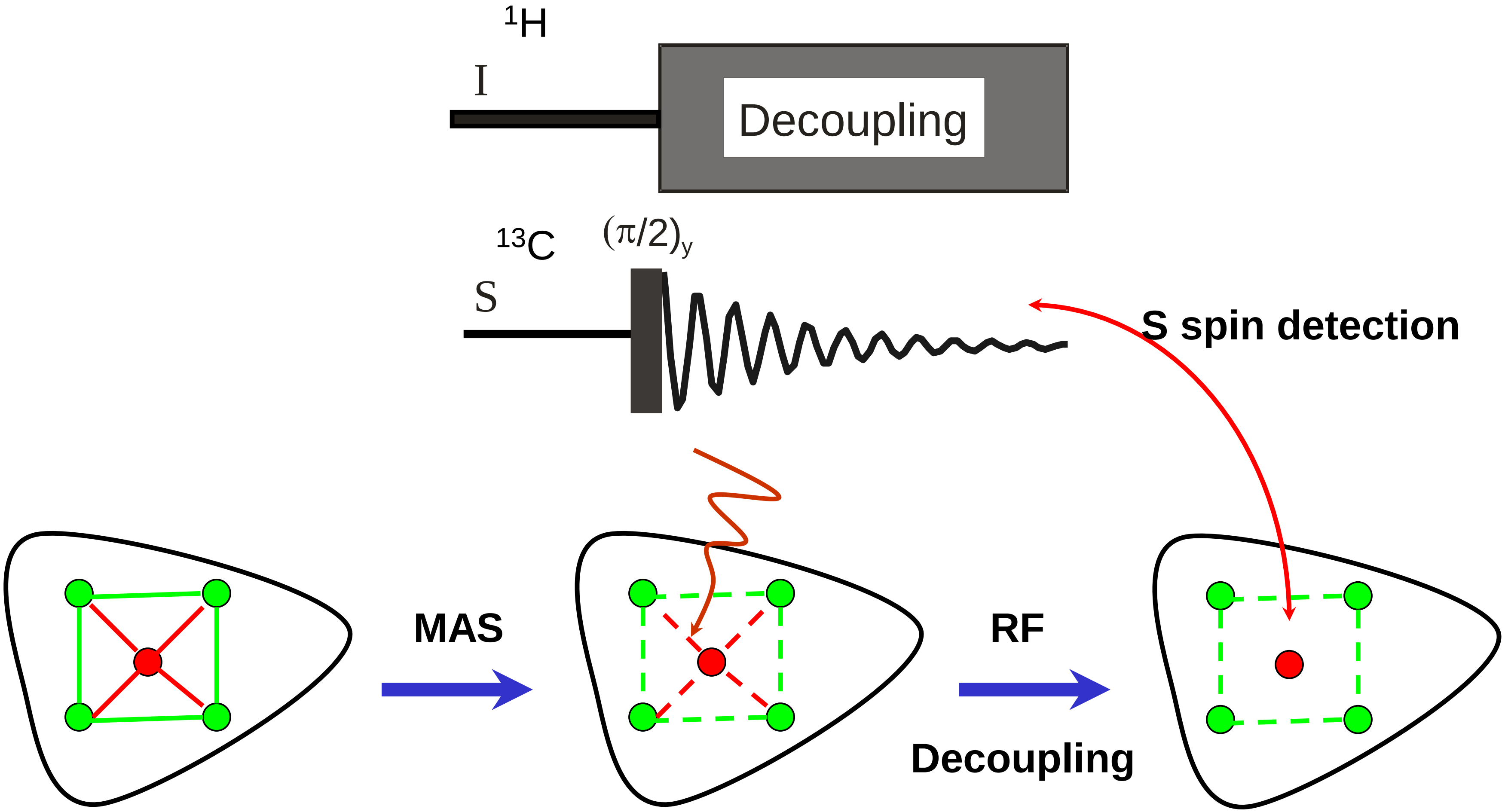
^{1}H–^{1}H

0 5 10 15 20 25 30

$|b_{12}|/2\pi$ [kHz]



Heteronuclear Dipolar Decoupling

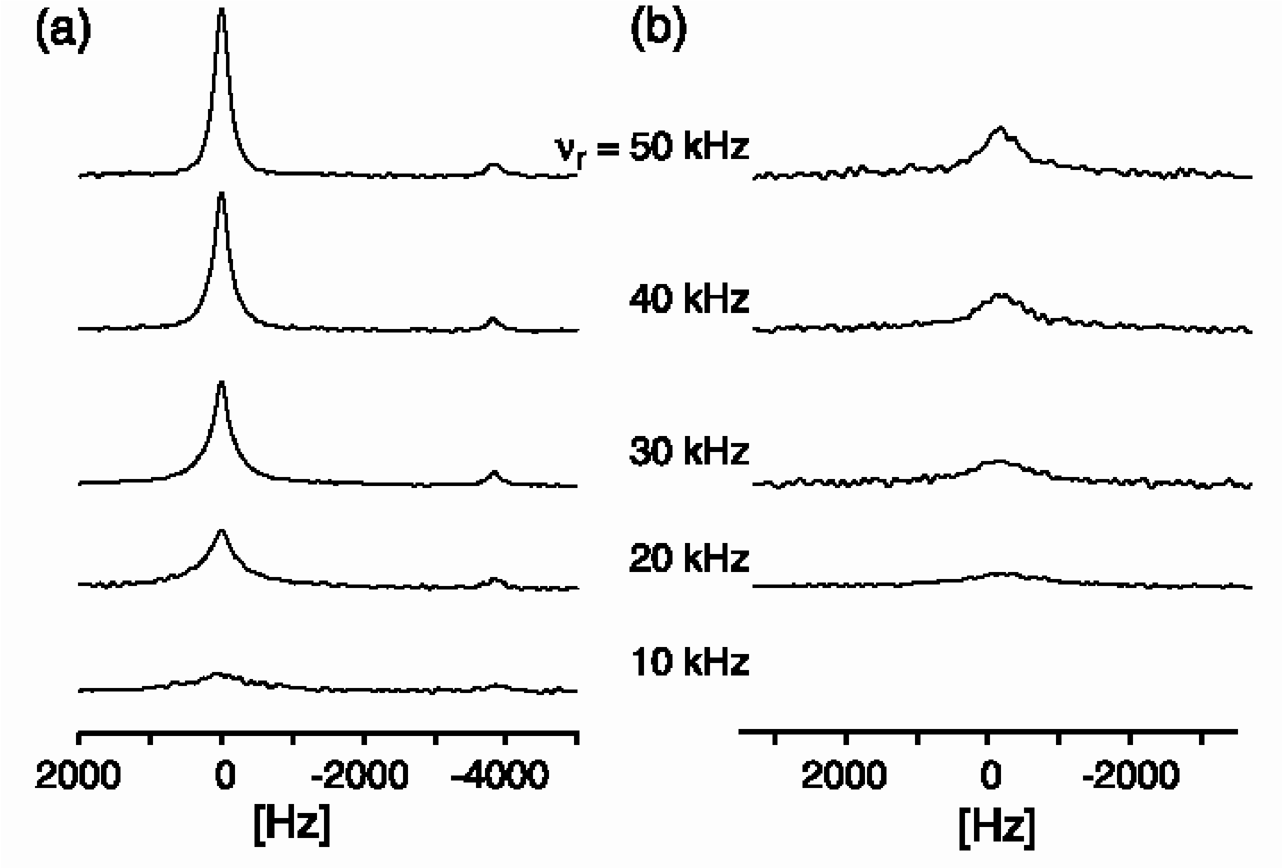


Why Decoupling? Why Not Just MAS?

2-^{13}C-Alanine

2-^{13}C-Glycine

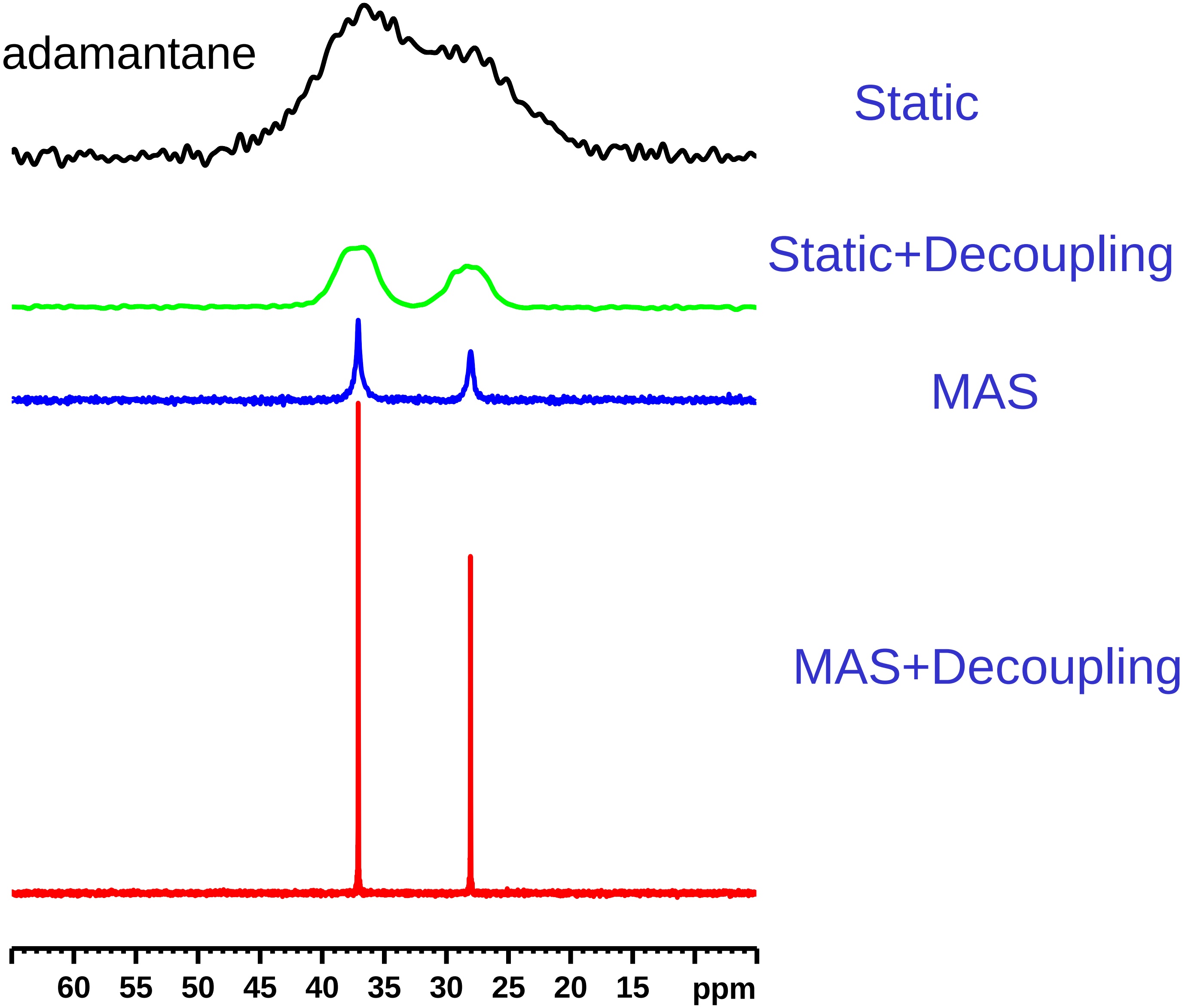
No decoupling



The best line widths with MAS only still about 10-15 times higher than with RF decoupling and MAS

MAS + Heteronuclear Dipolar Decoupling

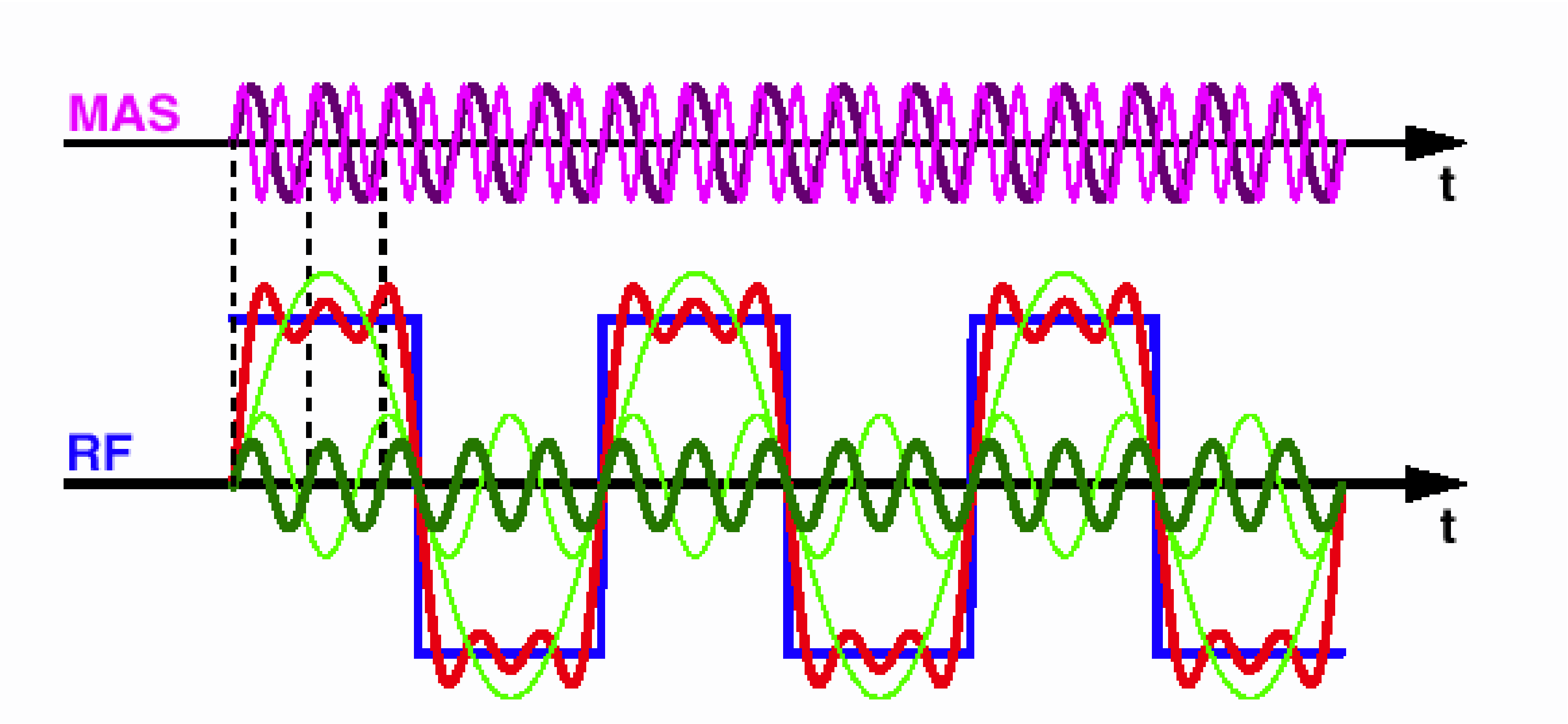
^{13}C spectra of adamantane



Magic-Angle Spinning and Radiofrequency Irradiation: Caveats

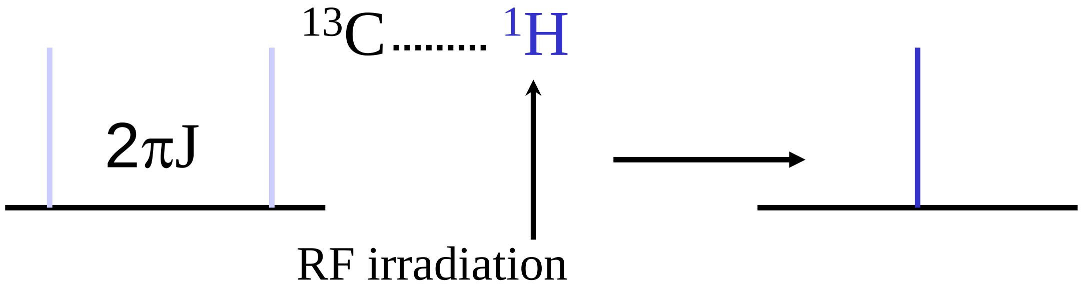
- Interference effects between MAS and RF as both are time-dependent processes
- Conditions such as $n\omega_r=\omega_1$ should be avoided
  - These are the conditions that recouple heteronuclear dipolar coupling
  - Rotary-resonance, RR, conditions, mainly at n=1,2
- Conditions such as ½ $\omega_r=\omega_1$ also should be avoided
  - These are the conditions that recouple homonulcear dipolar interactions
  - HORROR condition

Interference between MAS and RF



Some of the RF Fourier components match with the RF profile, and may lead to interference, sometimes constructive, sometime destructive

Decoupling Schemes: Simplification of Spectra



^{13}C......... ^{1}H

2πJ

RF irradiation

$$H = \Omega_S^0 S_z + \Omega_I^0 I_z + 2\pi J I_z S_z + \omega_{nut}^I I_x$$

RF irradiation

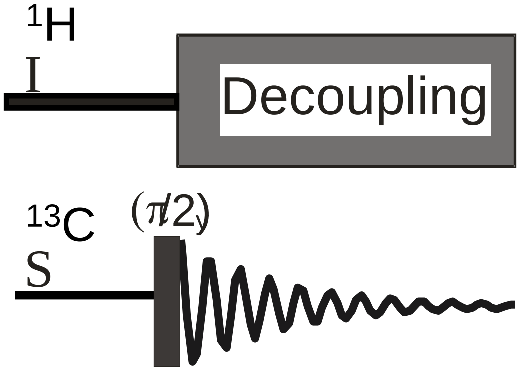
$$\overline{H} \cong \Omega_S^0 S_z$$

Average Hamiltonian!

RF irradiation on one spin simplifies the spectrum of a J coupled heteronuclear spin

Similar approach is possible in solid-state, to remove heteronuclear dipolar couplings between rare and abundant spins to get a simpler and resolved spectrum of the rare spins

Continuous-Wave (CW) Decoupling



$$H_{DD}^{hetero} = 2I_z S_z$$

Consider the rotation of the I_z operator due to the application of the RF irradiation on I along the +x axis. The I_z operator will experience a continuous precession as the long CW irradiation for decoupling can be thought of as being composed of a series of 2π pulses.

$$\left(H_{DD}^{hetero}\right)_{toggling} \approx S_z \int_0^{n2\pi} \frac{d(\omega t)}{n2\pi} (I_z \cos\omega t + I_y \sin\omega t)$$

The average vanishes over integer precession periods and tends to zero for Long irradiation times

CW decoupling is perhaps robust and efficient, but not the ideal one

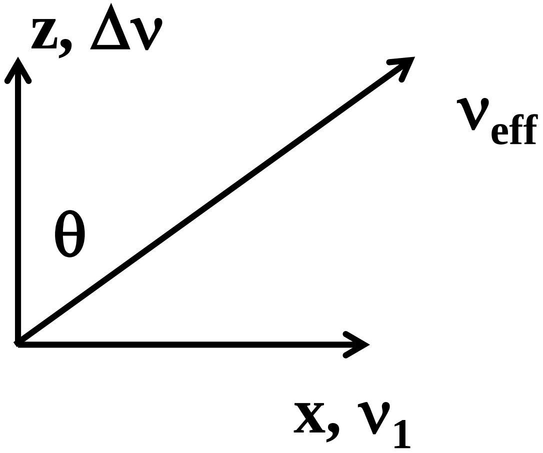
Predict CW Decoupling with AHT?

Non-modulated RF irradiation: $H_{RF} = \nu_1 (I_x \cos\Phi + I_y \sin\Phi); \Phi = \nu_{RF} t + \phi$

Rotating frame total H: $H = \Delta\nu I_z + \nu_1 (I_x \cos\phi + I_y \sin\phi); \Delta\nu = \nu^0 - \nu_{RF}$

Effective z-rotation: $H = R_z(\phi)\{\Delta\nu I_z + \nu_1 I_x\} R_z(-\phi)$

$$H = R_z(\phi) R_y(\theta)\{\nu_{eff} I_z\} R_y(-\theta) R_z(-\phi)$$



$$\nu_{eff} = \sqrt{\Delta\nu^2 + \nu_1^2}$$

$$\tan\theta = \frac{\nu_1}{\Delta\nu}$$

Predict CW Decoupling with AHT?

$$H = R_z(\phi)R_y(\theta)\{\nu_{eff} I_z\}R_y(-\theta)R_z(-\phi)$$

Associate : $\alpha = \nu_{eff} t; \beta = -\theta; \gamma = -\phi$ (arbitrary,can be zero)

Transformation of heteronuclear dipole-dipole Hamiltonian:

H in lab frame: $H_{DD}^{jk}(t) = [A_{20}^{jk}]^L [T_{20}^{jk}]^L$

H in interaction frame:

$$\tilde{H}_{DD}^{jk} = [A_{20}^{jk}]^L R_z(\phi)R_y(\theta)\{\sum_{m=-1}^{1} [T_{10}^{jk}]^L D_{m0}^1(\alpha,\beta,0)\}R_z(-\phi)R_y(-\theta)$$

$$D_{m0}^1(\alpha,\beta,0) = e^{-im\alpha} d_{m0}^1(\beta)$$

Predict CW Decoupling with AHT?

$$\tilde{H}^{jk}_{DD} = [A^{jk}_{20}]^L R_z(\phi) R_y(\theta) \{ \sum_{m=-1}^{1} [T^{jk}_{10}]^L D^1_{m0}(\alpha,\beta,0) \} R_z(-\phi) R_y(-\theta)$$

$$D^1_{m0}(\alpha,\beta,0) = e^{-im\alpha} d^1_{m0}(\beta)$$

Use AHT, only m=0 survives, hence, the first-order term of the int. frame H:

$$\overline{\tilde{H}^{jk}_{DD}}^{(1)} = [A^{jk}_{20}]^L R_z(\phi) R_y(\theta) \{ [T^{jk}_{10}]^L d^1_{00}(\alpha,\beta,0) \} R_z(-\phi) R_y(-\theta)$$

Zero for β=90

$$\nu_{eff} = \sqrt{\Delta\nu^2 + \nu_1^2}$$

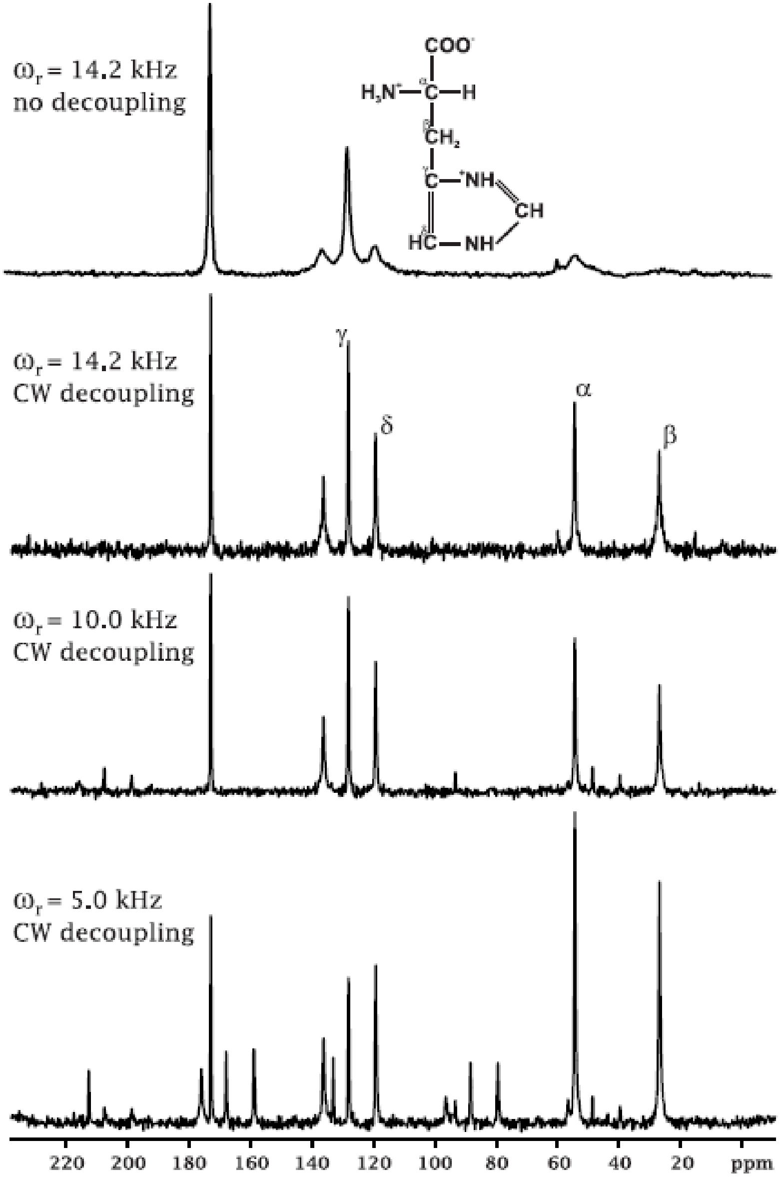
$$\tan\theta = \frac{\nu_1}{\Delta\nu}$$

CW irradiation, perpendicular to the magnetic field, under on resonance removes heteronuclear dipole-dipole couplings to the first order, if applied strong enough.

Continuous-Wave Decoupling

- The most sensitive test for checking the efficiency of CW (or for that matter any decoupling scheme) is monitoring the CH_2 spectral line intensity and line shape
- CH_2 group normally has the strongest homonuclear dipolar couplings among protons and heteronuclear dipolar couplings among protons and carbons
- As a thumb rule, higher the RF power, better is the efficiency of CW decoupling
- Thumb rule may fail for certain spin systems, at high MAS rates and is often a brute-force approach
- Remember the longstanding thumb rule: spin system (as any thing else in the universe) always prefer modulations (amplitude/phase) at the appropriate rate

Continuous Wave Heteronuclear Dipolar Decoupling



Histidine

500 MHz for ^{1}H

**Homonuclear dipolar couplings:
A culprit**

M. Ernst, J. Magn. Reson. 1-34, 162, 2003

Continuous-Wave Decoupling: When does it Work?

- **Efficient heteronuclear spin decoupling requires presence of some homonuclear dipolar coupling**
  - **Spin-diffusion and self-decoupling, helps in modulating DD^{hetero} and removing them more efficiently**

- **For a given RF amplitude, higher MAS leads to poor decoupling, as DD^{homo} interaction gets reduced, hence, increasing line widths**

- **For a given MAS, higher RF amplitudes normally improve decoupling**

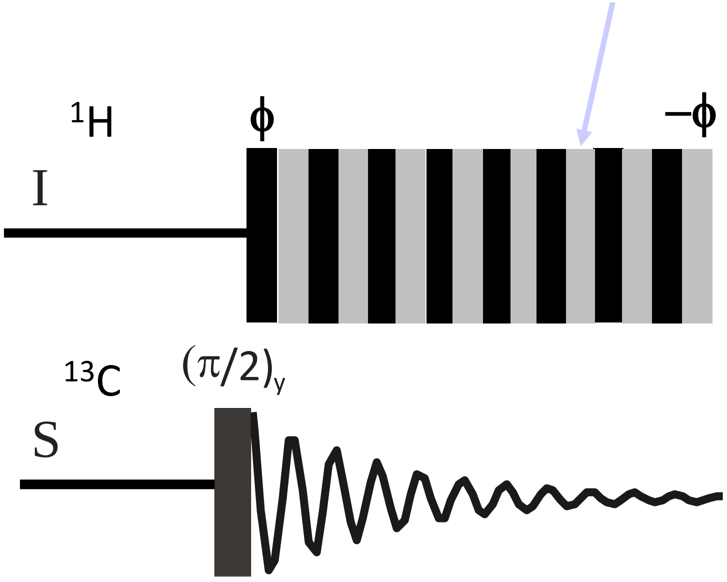
- **Higher RF followed by a lower MAS (in systems of weak DD^{homo}) leads to truncation effects and introduction of cross-terms between CSA and DD which also become more drastic in high-fields**

- **Higher MAS followed by a lower RF can work more or less well everywhere unless the interactions are very strong**

- **Hence, the general recipe for normal solids, is high MAS and low RF or high RF and low MAS**

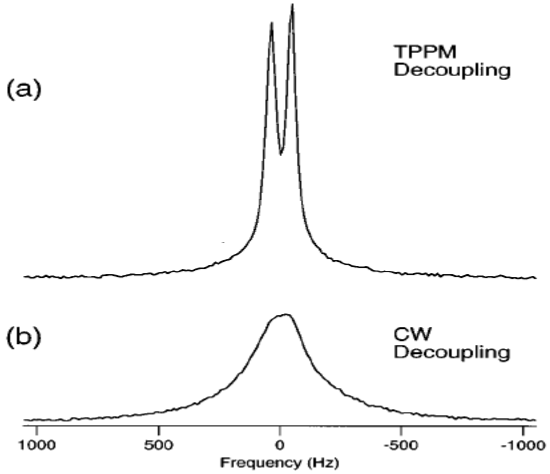
Two-Pulse Phase Modulation (TPPM)

τ_{TPPM} close to 180 degrees

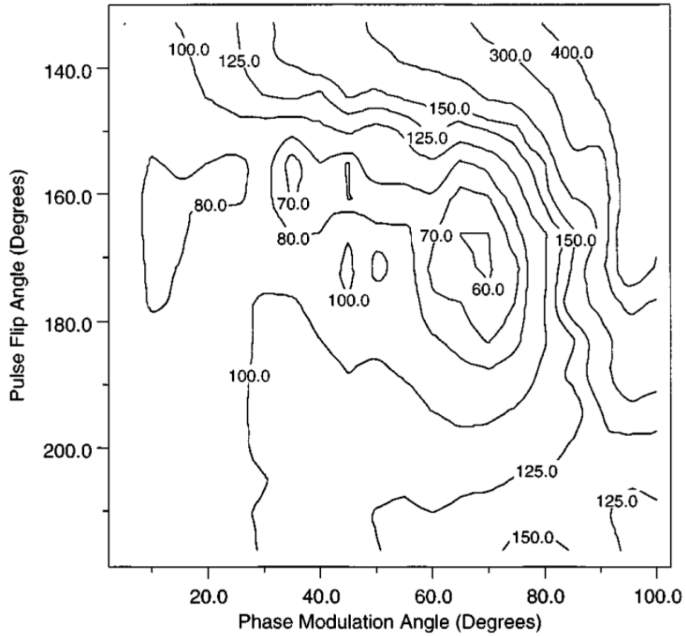


2ϕ ranges from 10-70

^{13}C spectrum of Ca(Formate)$_2$



Shortcomings of TPPM



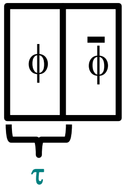
A phase alternated strong RF pulse irradiation is applied on the proton spins to effect heteronuclear dipolar decoupling

Both τ_{TPPM} and ϕ need to be optimised

Bennett…Griffin, J. Chem. Phys. 103, 6951, 1995

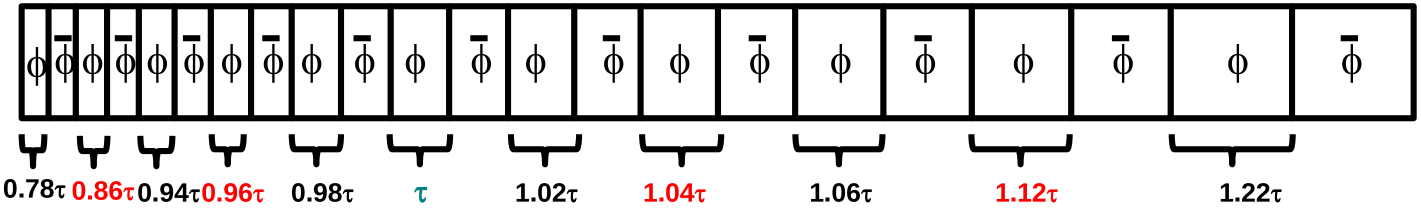
Some (Better) Decoupling Schemes

TPPM



$\bar{\phi} = -\phi$

SW$_f$-TPPM



SW$_f$-TPPM$_{SC}$

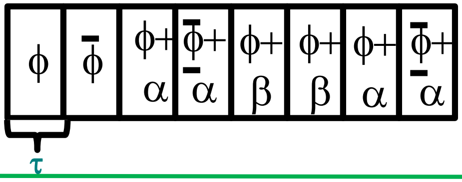
$R\bar{R}\bar{R}R$

R=SW$_f$-TPPM

SPINAL64

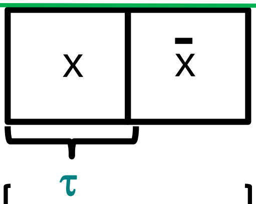
$R\bar{R}\bar{R}R\bar{R}RR\bar{R}$

R=



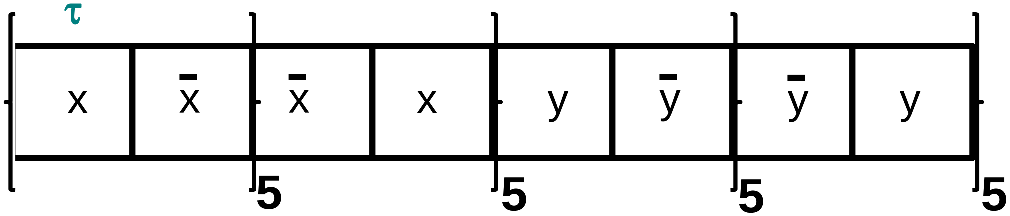
Normally $\beta=2\alpha$

XiX



$\tau=n\tau_r$

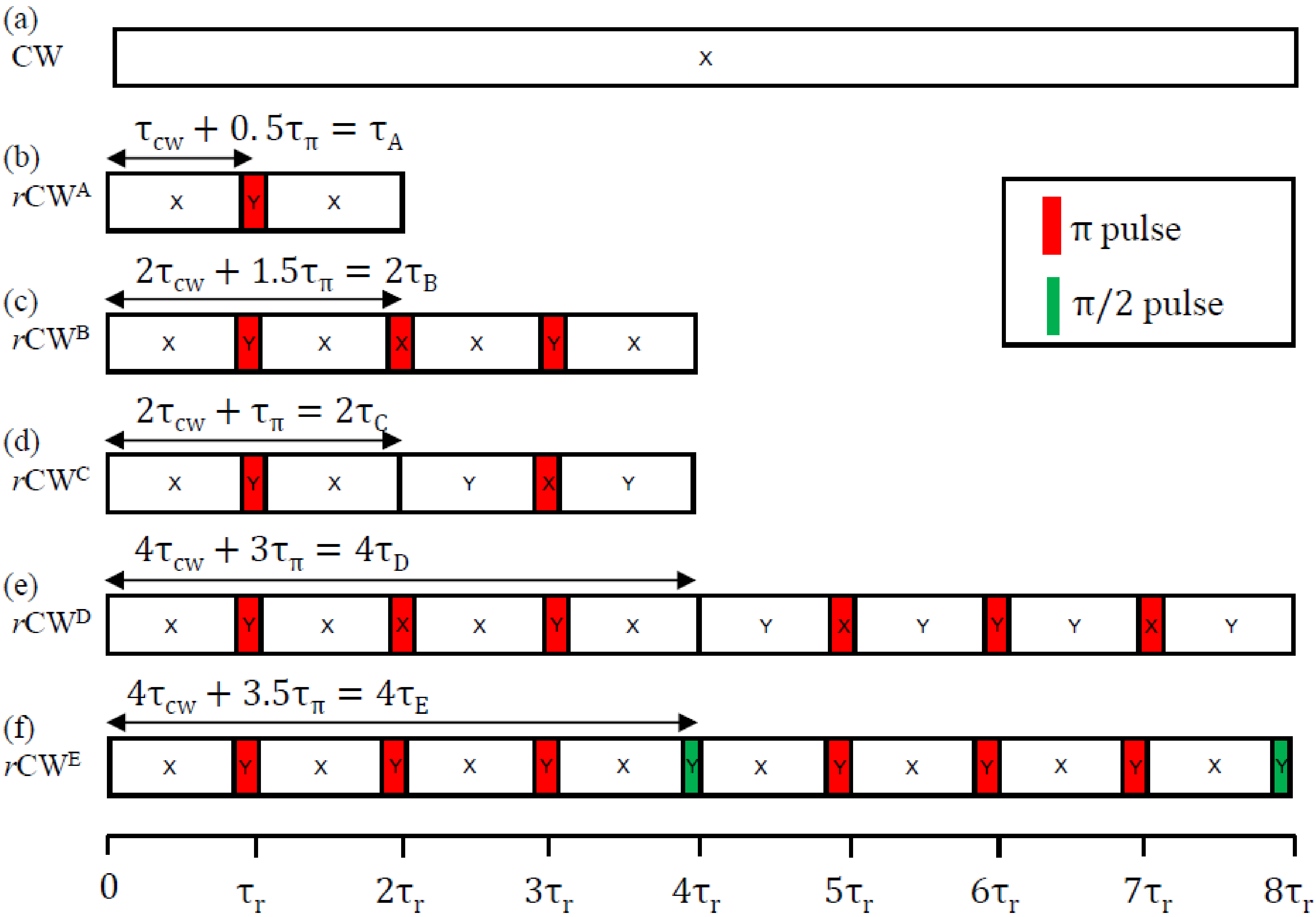
PISSARRO



$\tau=n\tau_r$

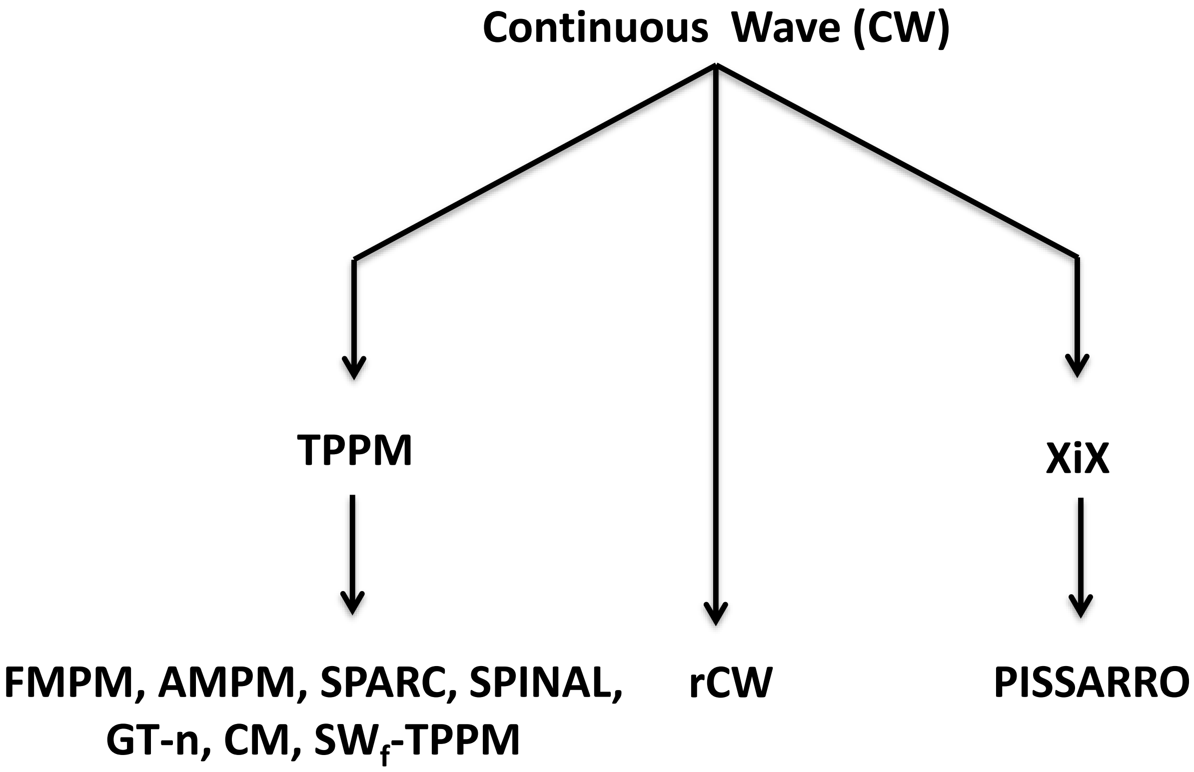
1. Bennett et al. J. Chem . Phys. 103, 6951, 1995
2. Thakur *et al*., Chem. Phys. Letts., 426 (2006) 459
3. Augustine *et al*., Magn. Reson. Chem., 48 (2010) 798
4. Fung et al., J. Magn. Reson. 142, 97, 2000
5. Detken *et al*., Chem. Phys. Lett. 356 (2002) 298 247
6. Weingarth *et al*., Chem. Phys. Lett. 466 (2008)

Some More Decoupling Schemes



Vinther…..Nielsen, JCP, 137, 214202, 2013

Hierarchy of Decoupling Schemes



Continuous Wave (CW)

TPPM

XiX

FMPM, AMPM, SPARC, SPINAL, GT-n, CM, SW_f-TPPM

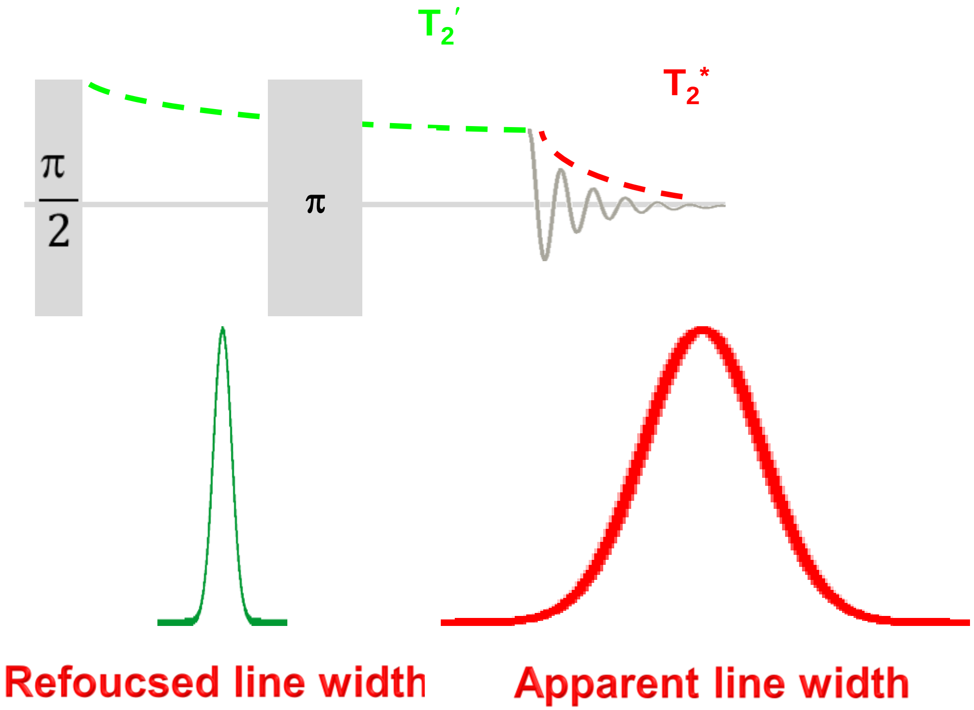
rCW

PISSARRO

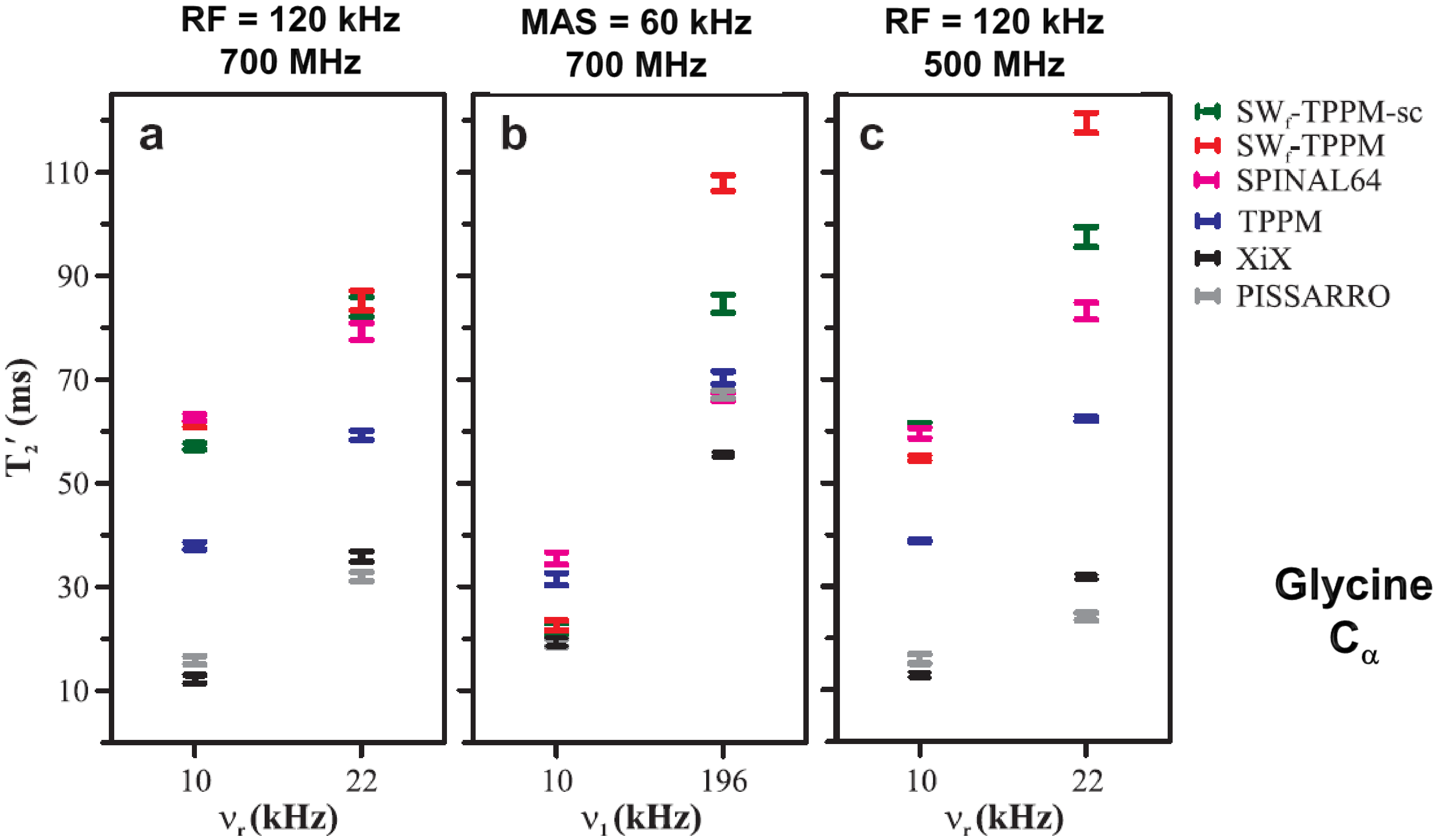
Decoupling Schemes: Effective Transverse Relaxation Time

- **Although, at high MAS frequencies, limiting line width seems to have been reached for existing decoupling schemes, it is quite possible that the decoupling schemes have an influence on the effective transverse relaxation times**

- **Effective Transverse relaxation times are governed by *Homogeneous interactions***



Decoupling Schemes: Effective Transverse Relaxation Time



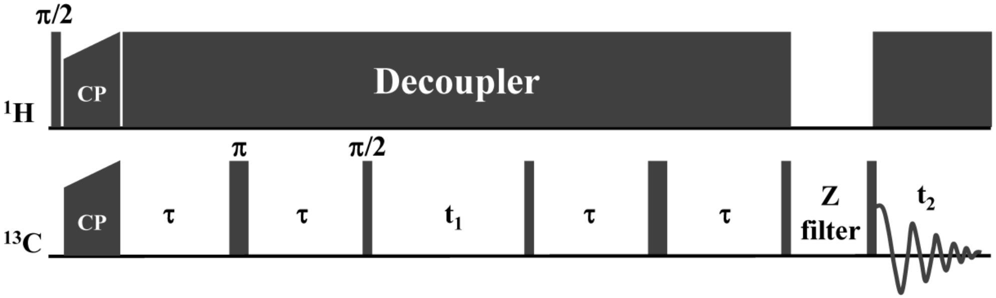
Glycine C_α

Mithu *et al.*, J. Magn. Reson. 220 (2012)

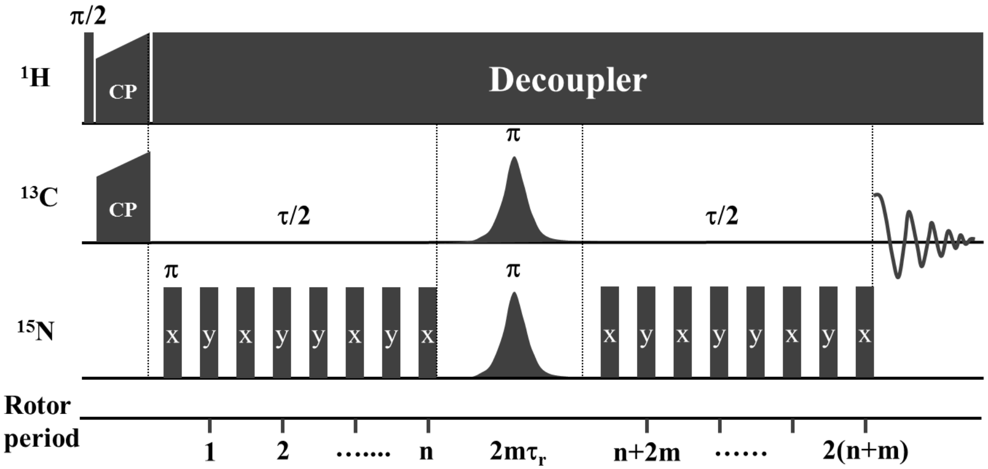
Decoupling Schemes: Effective Transverse Relaxation Time

- **Longer T_2' values play a crucial role in experiments involving long spin-echo periods in their pulse sequences.**

z-filtered refocused Incredible Natural Abundance Double Quantum Experiment (zfr-INADEQUATE)

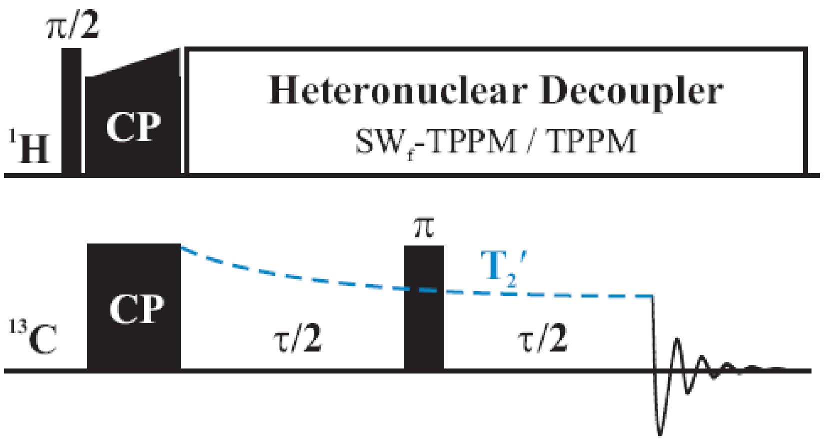


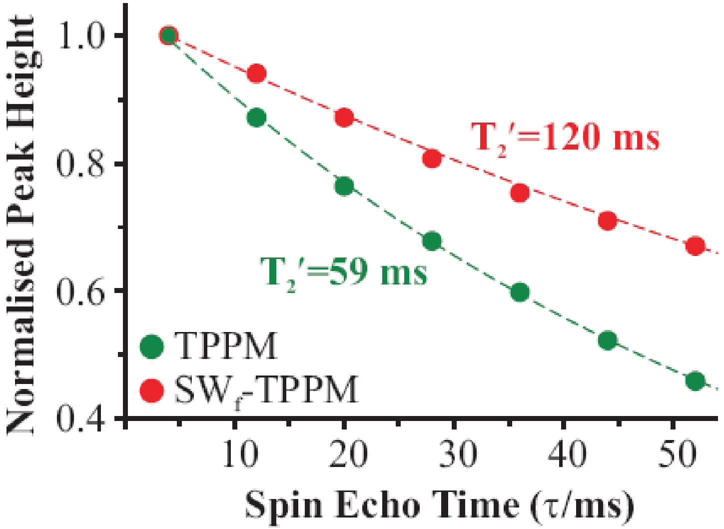
frequency-selective Rotational Echo Double Resonance (fs-REDOR)

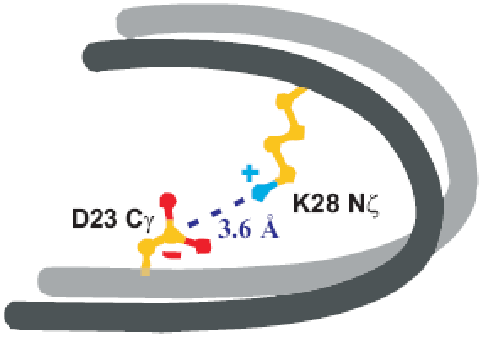


1. Cadars *et al*., J. Magn. Reson., 188 (2007) 24. 2. Jaroneic *et al*., J. Am. Chem. Soc., 123 (2001) 3507.

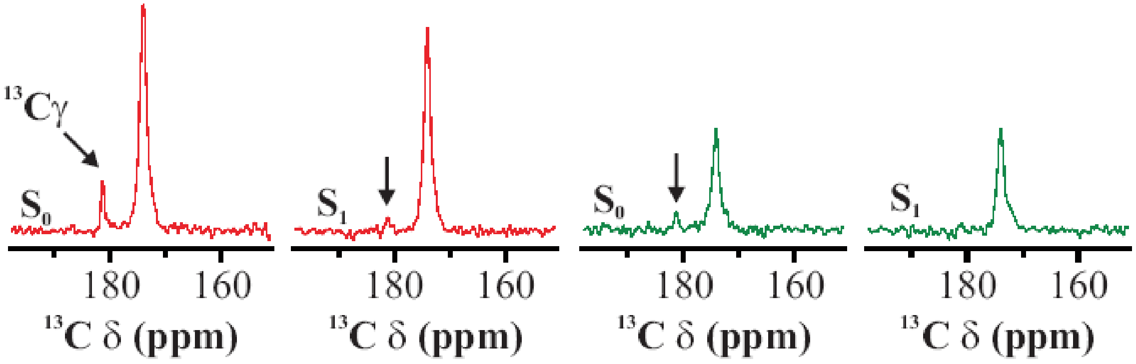
Effective Transverse Relaxation Time: fsREDOR







Aβ$_{42}$ Amyloid Fibrils



^{13}Cγ-^{15}Nζ fs-REDOR

Effective Transverse Relaxation Time: INADEQUATE

- **Longer T_2' values play a crucial role in experiments involving long spin-echo periods in their pulse sequences.**

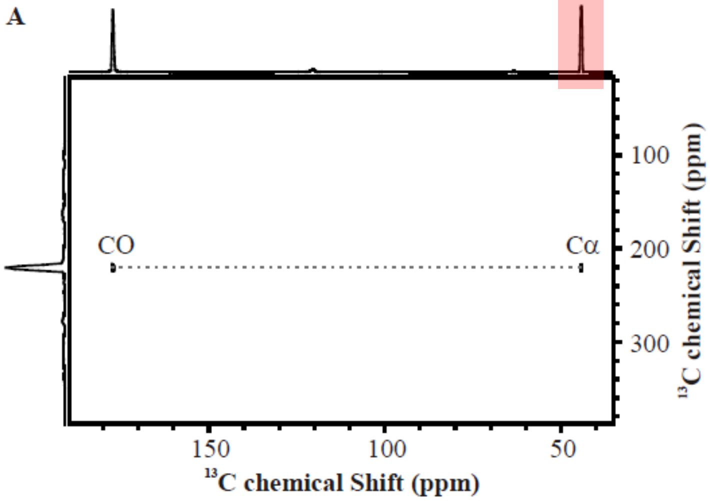
SW_fTPPM

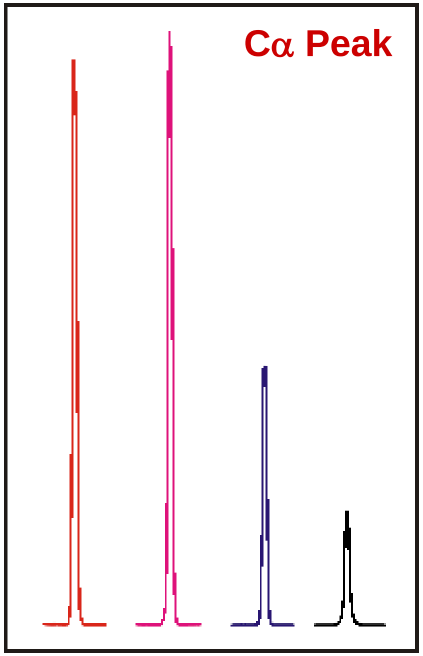
MAS = 10 kHz

RF = 115 kHz

B_0=500 MHz

zfr-INADEQUATE Spectrum of $^{13}C_2,^{15}N$ Glycine

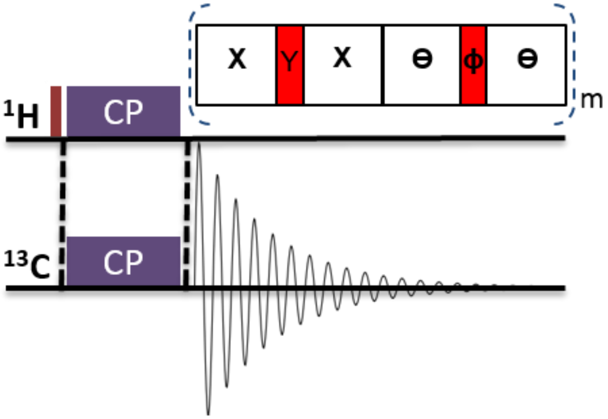




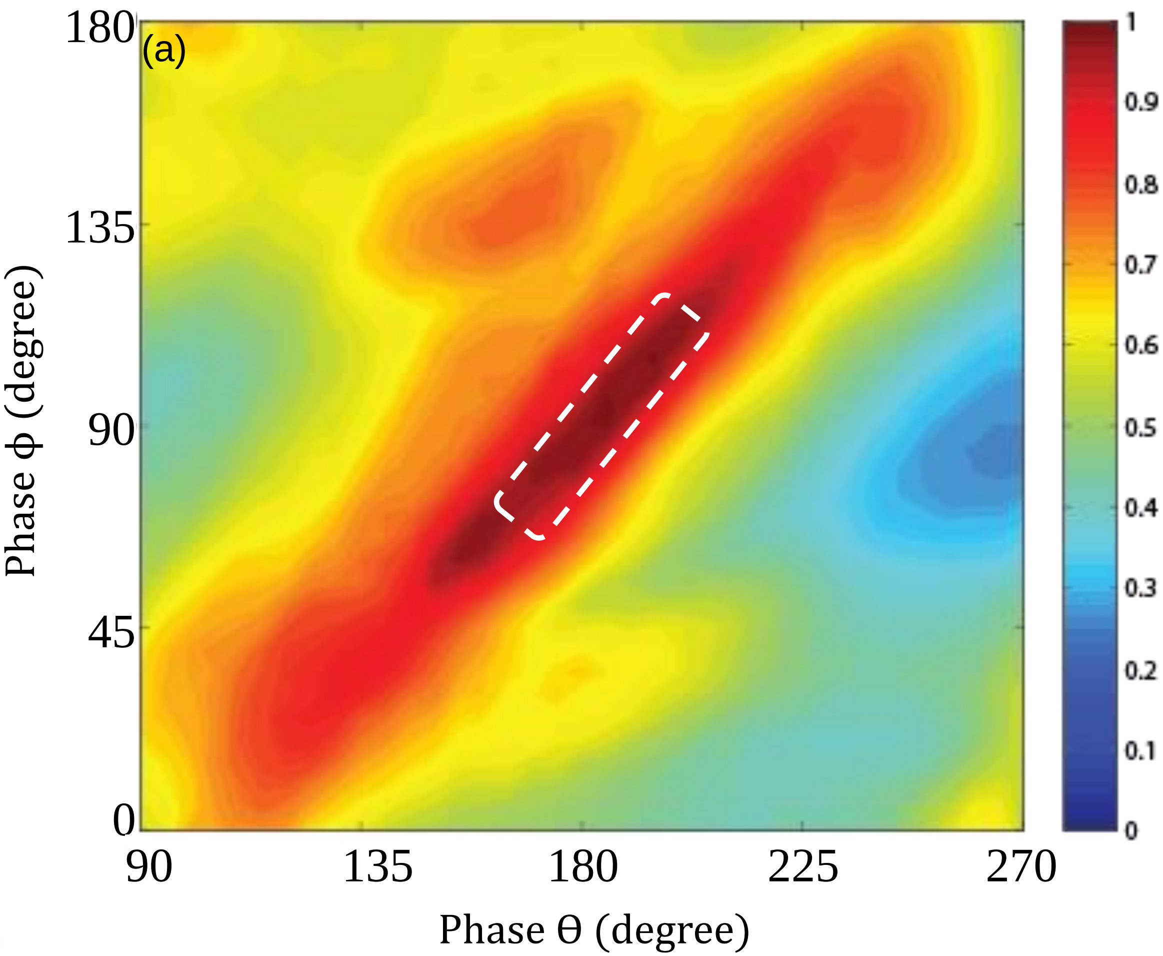
Decoupling Scheme {ϕ}	T_2'	CH_2 (Gly)
SW_fTPPM {10}	1.00	1.00
SPINAL64 {6}	1.02	1.05
TPPM {10}	0.62	0.46
XiX	0.20	0.20

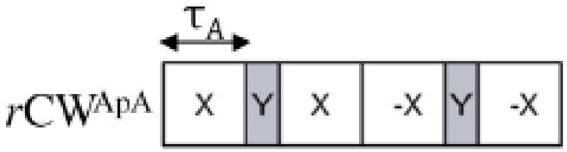
🟥 SW_fTPPM
🟥 SPINAL64
🟦 TPPM
⬛ XiX

Supercycling *r*CW?



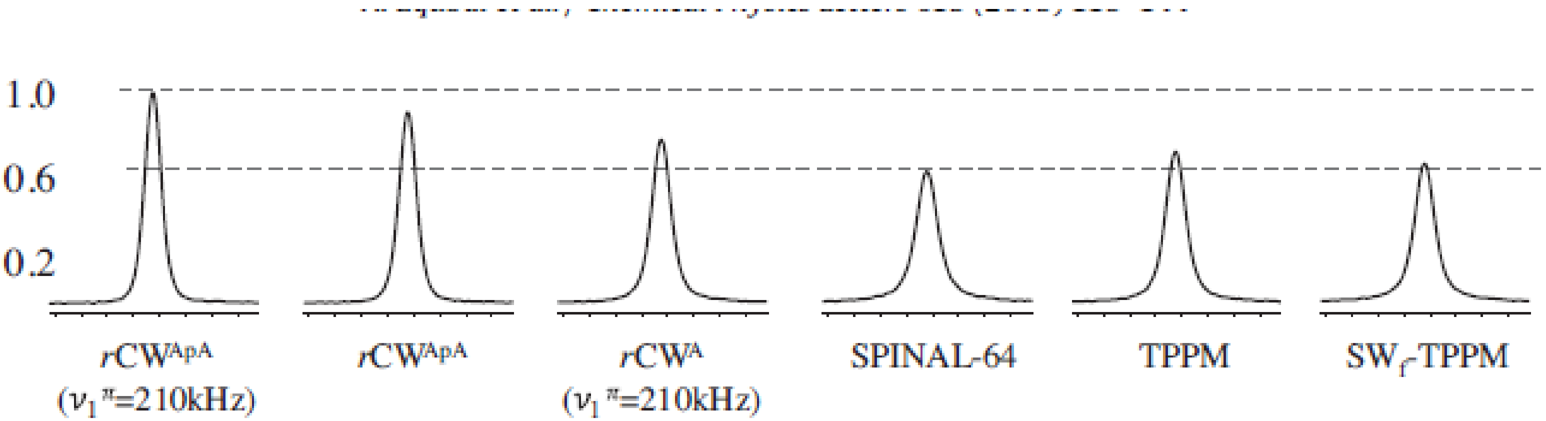
Best Condition:
When **Θ = 180º**
φ= 90º





Equbal et al. Chem. Phys. Lett. 635 (2015) 339

rCW^{ApA} Performance

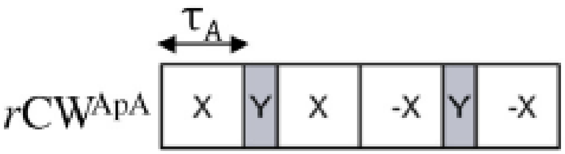


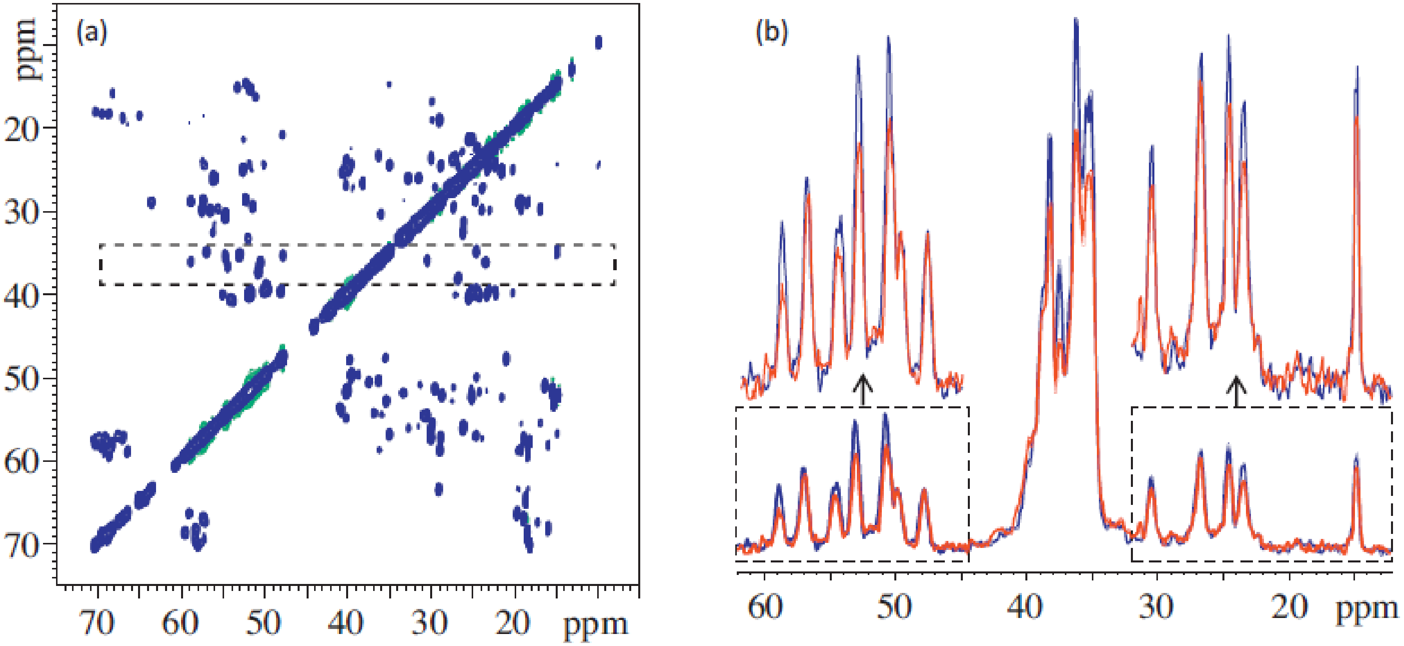
700 MHz
RF 90 kHz
MAS 25 kHz

Equbal et al. Chem. Phys. Lett. 635 (2015) 339

Efficient decoupling

*r*CW^{ApA} Performance



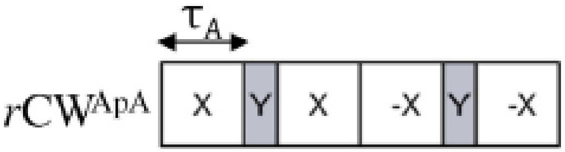


700 MHz RF 90 kHz MAS 15 kHz
GB1 protein sample

Equbal et al. Chem. Phys. Lett. 635 (2015) 339

rCW^{ApA} Conditions: Take Home Message

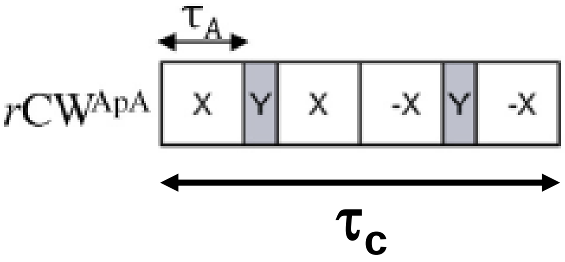
Low MAS, High RF: Set $\tau_A/\tau_r = 0.98$



τ_Y corresponds to 180 degree flip angle

High MAS, Low RF:

$$\frac{\tau_c}{\tau_r} = 4\frac{\nu_r}{\nu_1} \qquad \frac{2\tau_Y}{\tau_c} = 0.15$$



Cross Polarisation

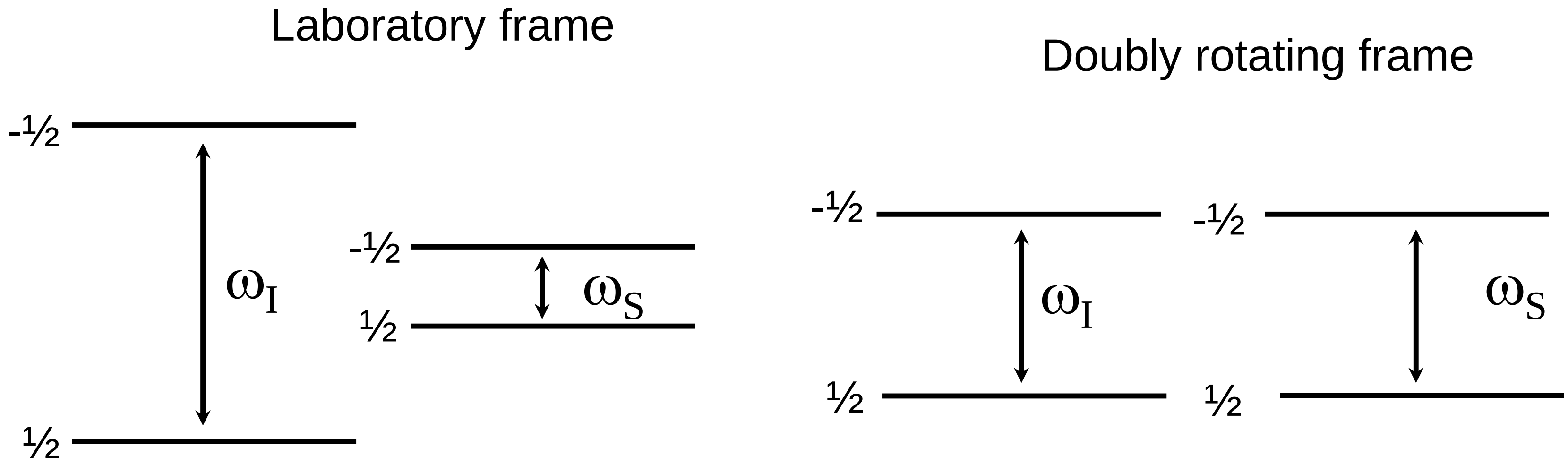
Sensitivity Issues in Solid-State NMR

- Resolution for rare spins provided by MAS and heteronuclear dipolar decoupling
- Rare spins have low gyromagnetic ratios, and low natural abundance and hence very poor signal sensitivity
- Coupled with poor signal sensitivity rare spins also have long T_1 making experiment times longer

Sensitivity of Various Nuclei

Nucleus	Spin	Natural Abund. %	S/N	Measuring Time
^{1}H	½	100	1	1
^{19}F	½	100	0.858	1.36
^{19}P	½	100	0.104	92
^{39}K	3/2	93.08	2.2e-5	2.1e5
^{13}C	½	1.108	3.5e-14	8.1e6
^{109}Ag	½	48.65	2.27e-4	2e7
^{43}Ca	7/2	0.13	3.2e-5	9.7e8
^{15}N	½	0.365	1.2e-5	7e9
^{2}H	1	0.0156	5.8e-6	3e10

Cross Polarisation, CP



Laboratory frame

Doubly rotating frame

Energy levels of both nuclei are matched in the doubly rotating frame.
A spin-lock RF field is equivalent to producing a rotating-frame transformation.
Hence, we need a continuous spin-lock RF field on both the nuclei for CP.

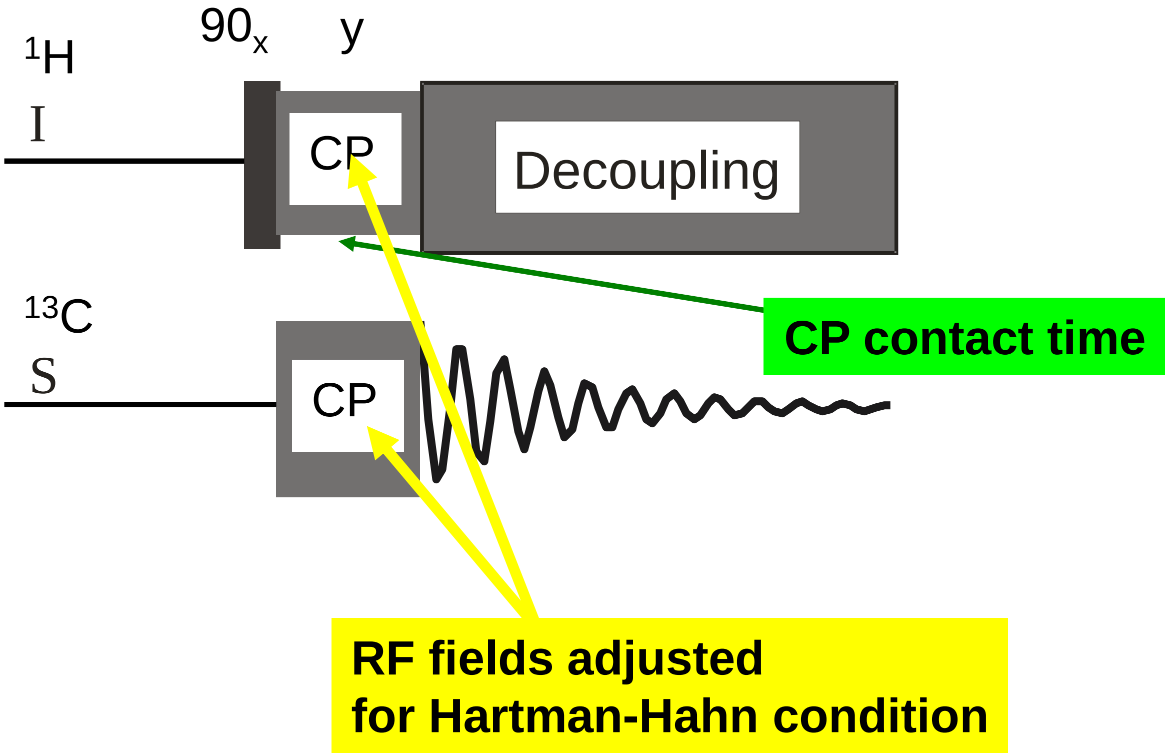
A match of the energy levels is produced when the nutation frequencies of both the spins along the effective RF field direction are the same: $B_{1I}=B_{1S}$ or in other words $\gamma_I \omega_{1I}=\gamma_S \omega_{1S}$

Hartman-Hahn condition

CP Pulse Sequence+Decoupling

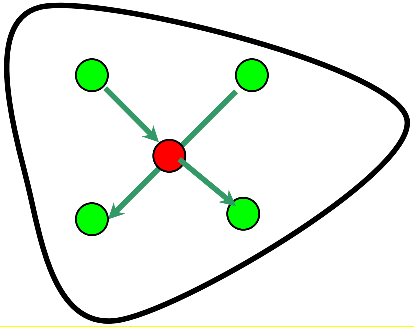
MAS and heteronuclear decoupling lead to resolution

CP leads to sensitivity



CP contact time

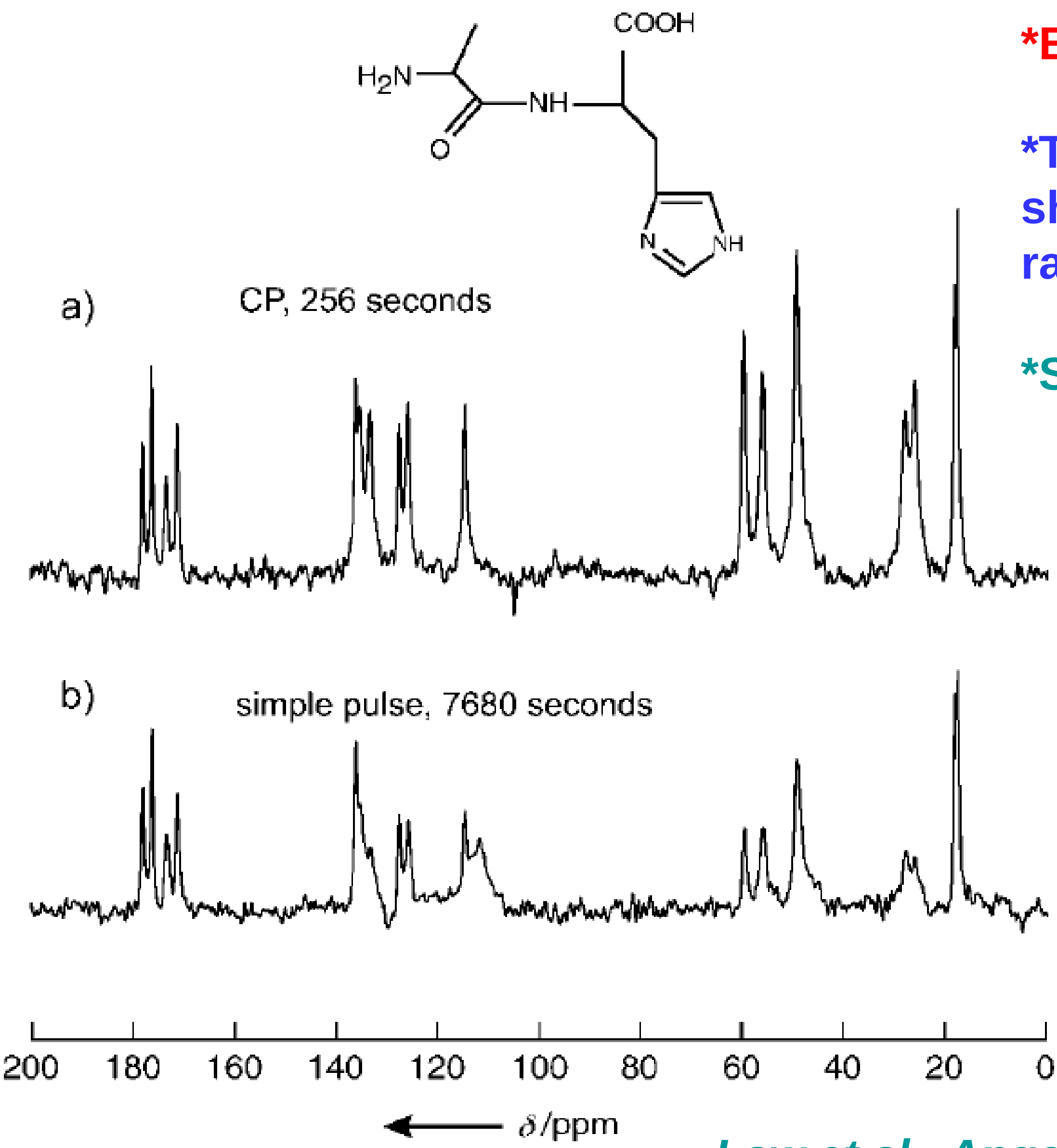
RF fields adjusted for Hartman-Hahn condition



Magnetisation transfer

CPMAS, basic pulse block in solid-state NMR for both sensitivity and resolution

CPMAS Spectrum



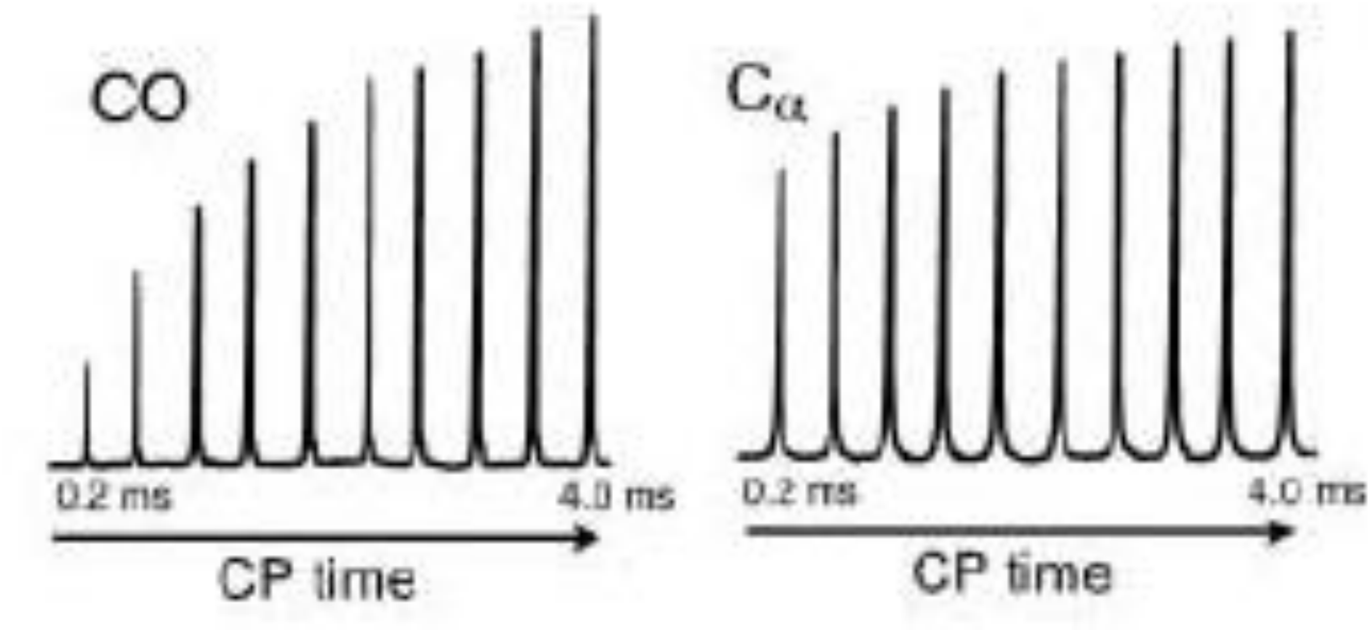
*Enhanced signal, ~γ_I/γ_S

*T_1 of abundant high-γ nuclei shorter than that of the rare low-γ nuclei

*Spatial proximity

Law et al., Angen.Chem. Int.Ed., 41, 3096, 2002

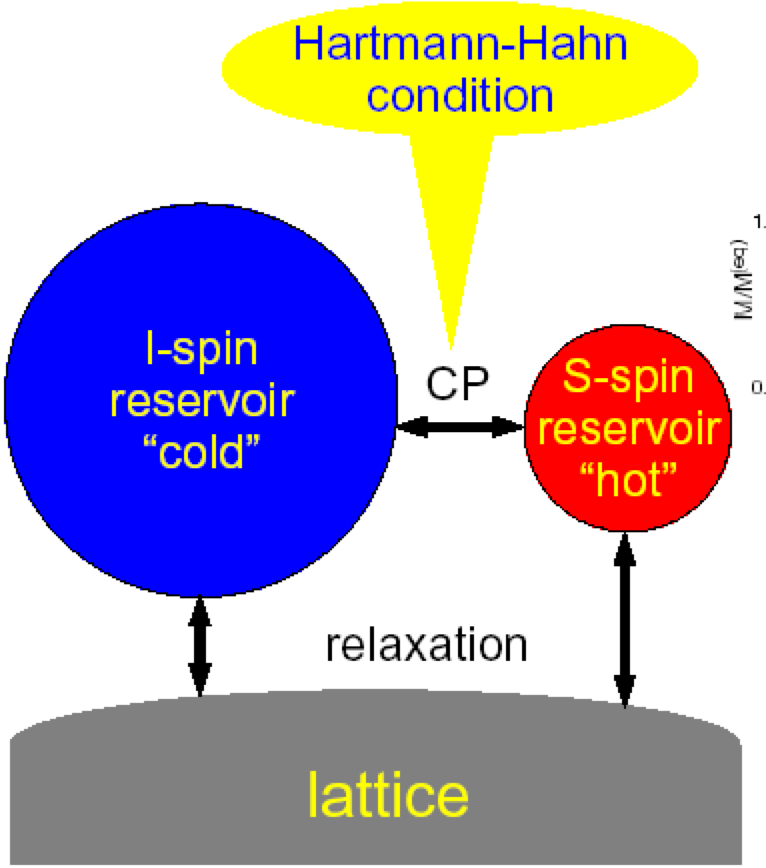
Cross-Polarisation Profile



$^{13}C_\alpha$ is polarised faster as it is directly bonded to H, unlike the carbonyl ^{13}C
Typical contact times on the order of 100 μs to 10 ms

Law et al., Angen.Chem. Int.Ed., 41, 3096, 2002

Cross-Polarisation: Spin Baths



Hartmann-Hahn condition

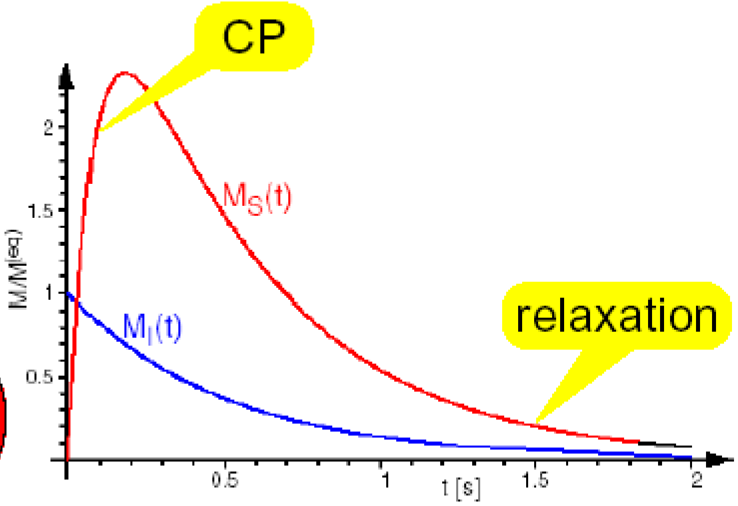
I-spin reservoir "cold"

CP

S-spin reservoir "hot"

relaxation

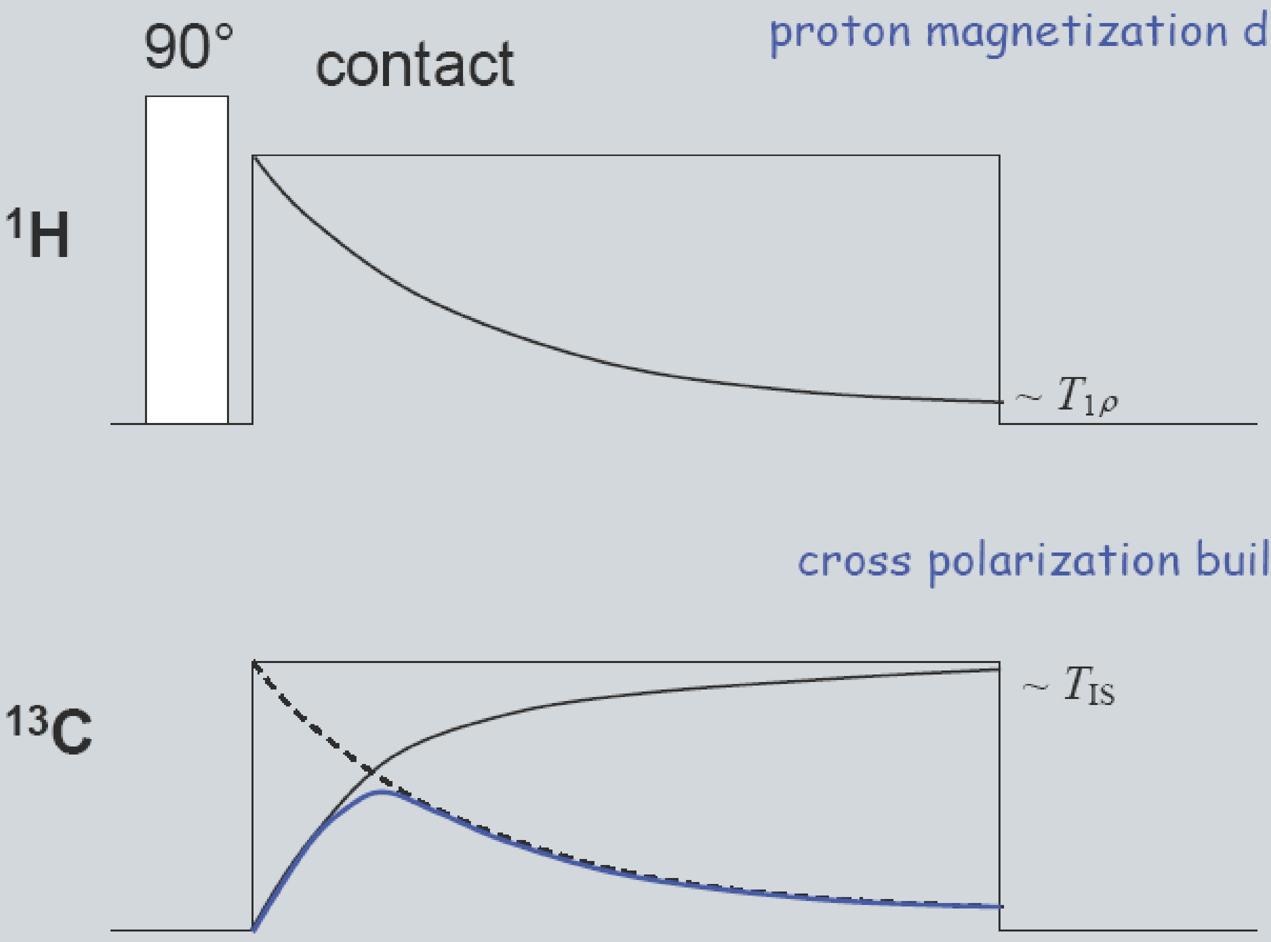
lattice



$\gamma_I / \gamma_S = 4$

M.Mehring, Basic Principles of High-Resolution NMR in Solids

Cross-Polarisation Dynamics



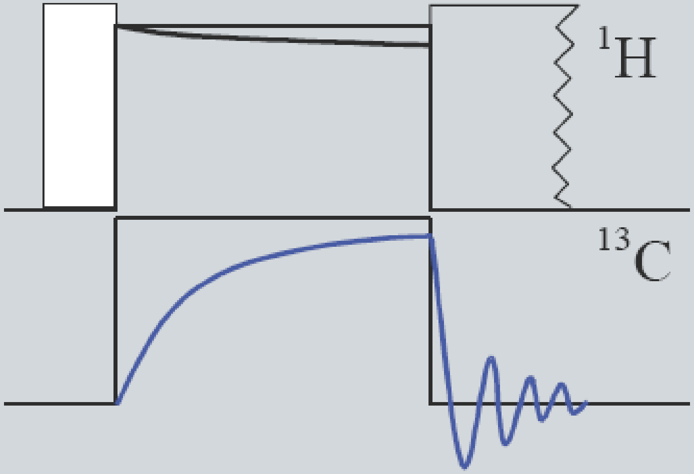
proton magnetization decays with $T_{1\rho}$

cross polarization builds up with T_{IS}

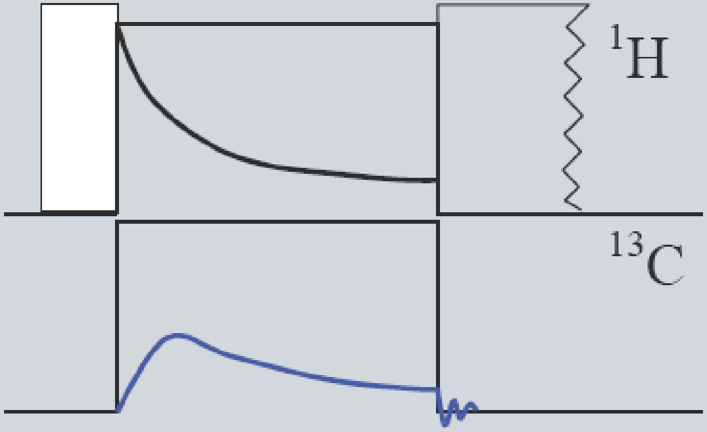
signal follows combined effect of buildup and decay

Cross-Polarisation Dynamics

best case: $T_{1\rho} \gg T_{IS}$



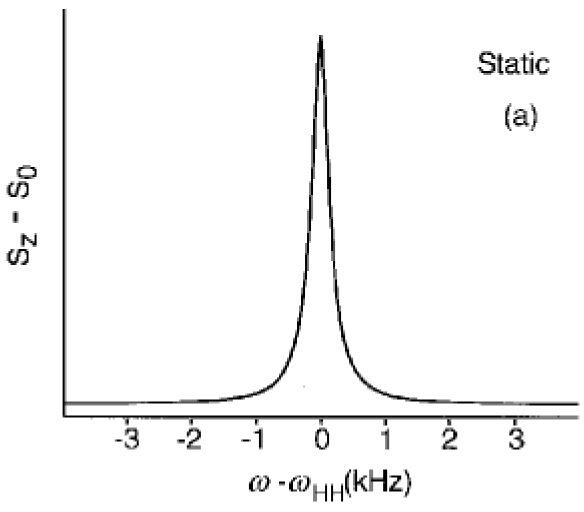
worst case: $T_{1\rho} \ll T_{IS}$



Cross-Polarisation Dynamics

- **Contact time, practical considerations for ^{13}C**
  - **Short T_{IS} (~500 us): directly attached protons (-CH_3, -CH_2-, >CH-)**
  - **Long T_{IS} (>1-2 ms): quaternary carbons (>C<, -COO-, substituted aromatic sysmtes,…), high mobility**
  - **Short $T_{1\rho}$: paramagnetic systems/impurities (e.g. in coal), high mobility**

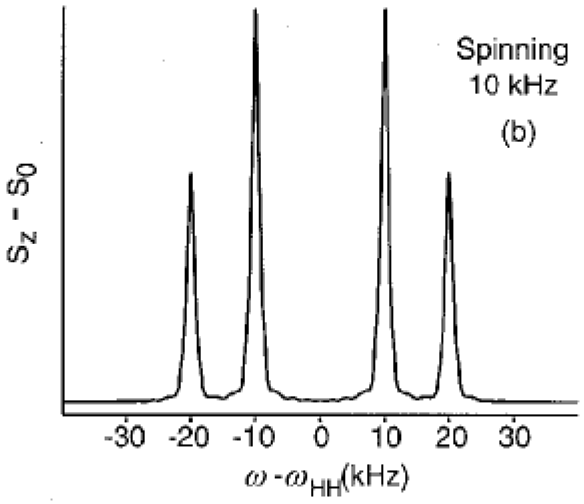
Cross-Polarisation: Matching Profiles



Hartman-Hahn condition

$$\omega_{nut}^{I} = \omega_{nut}^{S}$$

Width of the matching curve is proportional to the heteronuclear diolar coupling



Hartman-Hahn condition

$$\omega_{nut}^{I} = \omega_{nut}^{S} \pm n\omega_{r}$$

Sidebands observable when the MAS rate is on the order of H_{DD}^{hetero} and the I-spin resonance line width

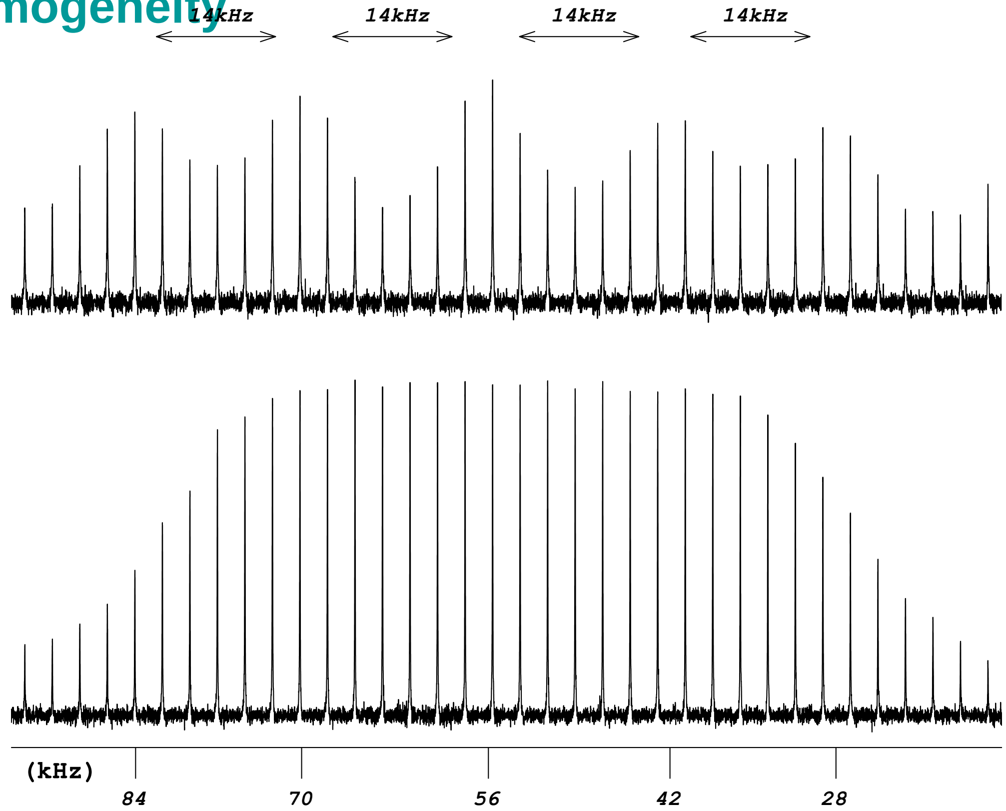
Cross-Polarisation Matching Profiles: Problems

CP is very inefficient at:

High MAS rates

In the presence of RF fluctuations

In the presence of RF inhomogeneity



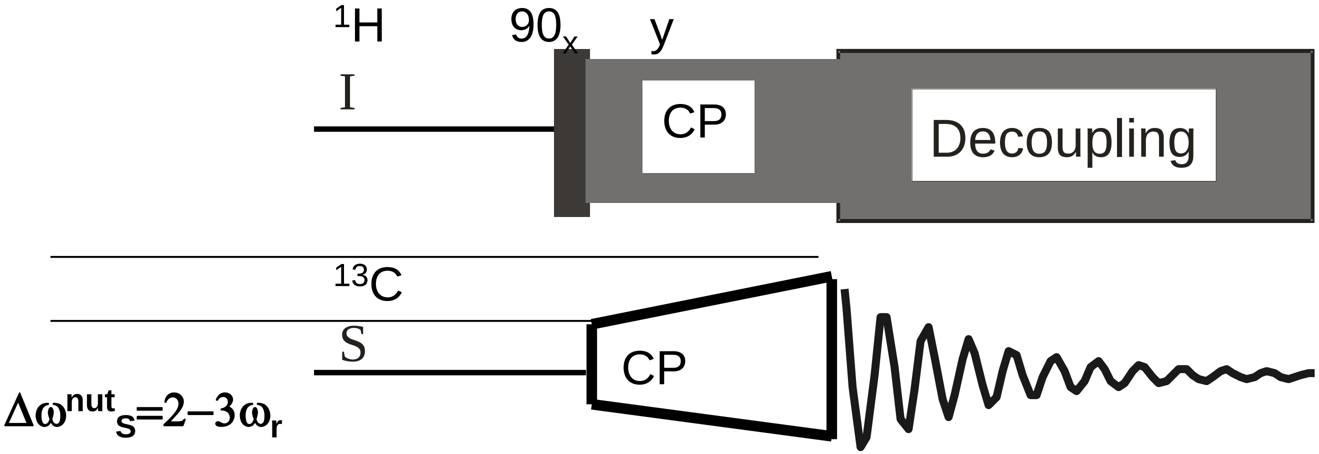
MAS 14 kHz

Glycine

MAS 4 kHz

RAMP-CP

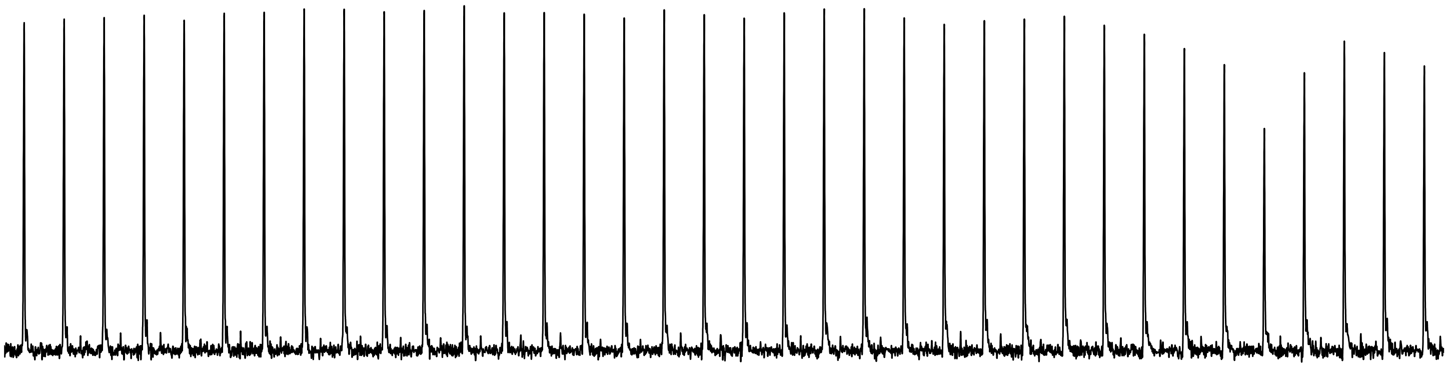
Remedy: Vary the RF amplitude on one of the spins to cover a sufficient range of frequencies: RAMP-CP



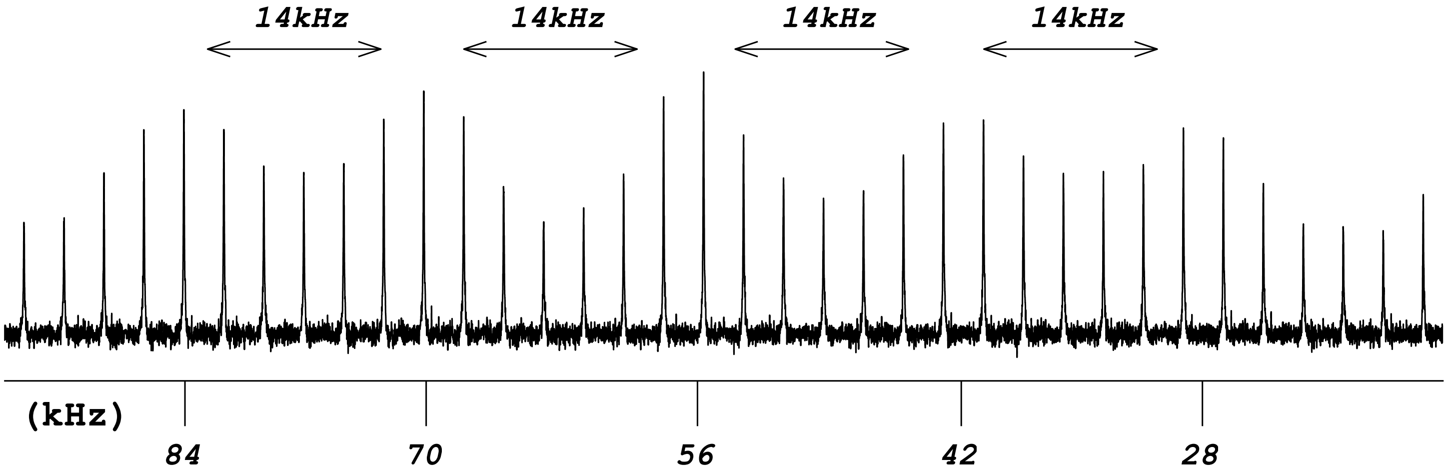
RAMP-CP gives stable performance at high-MAS rates

Peersen, Wu, Kustanovich, Smith, JMR, A104, 334, 1993

RAMP-CP

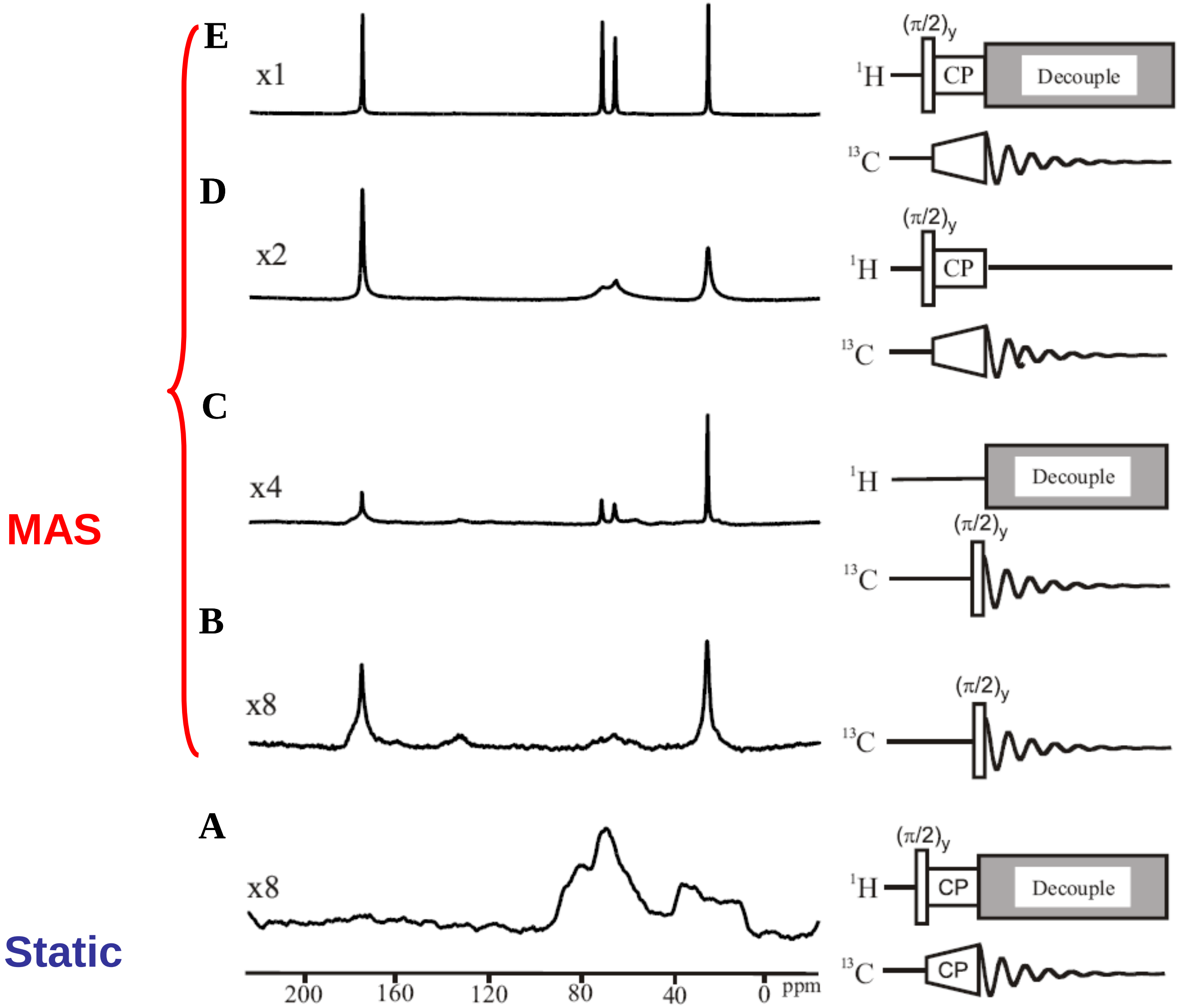


Glycine, MAS at 14 kHz

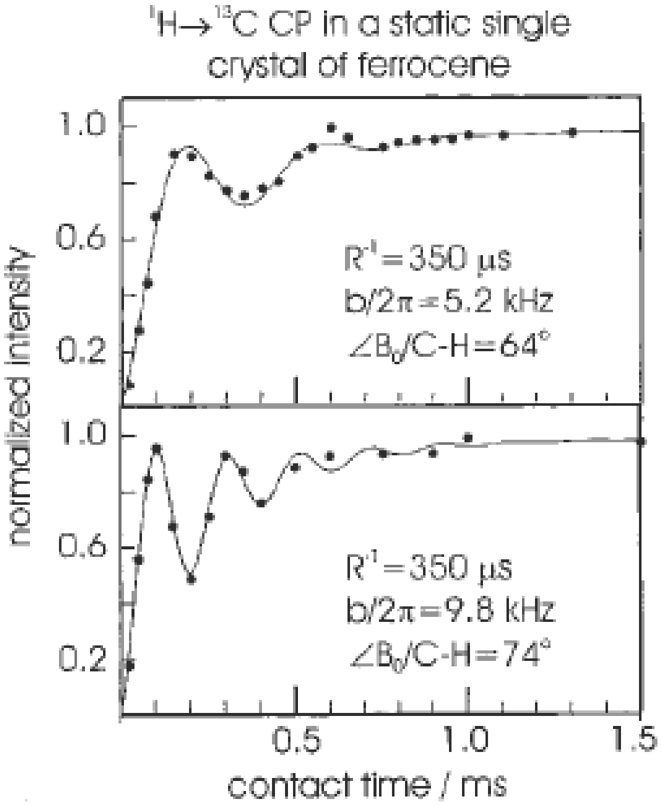


Peersen, Wu, Kustanovich, Smith, JMR, A104, 334, 1993

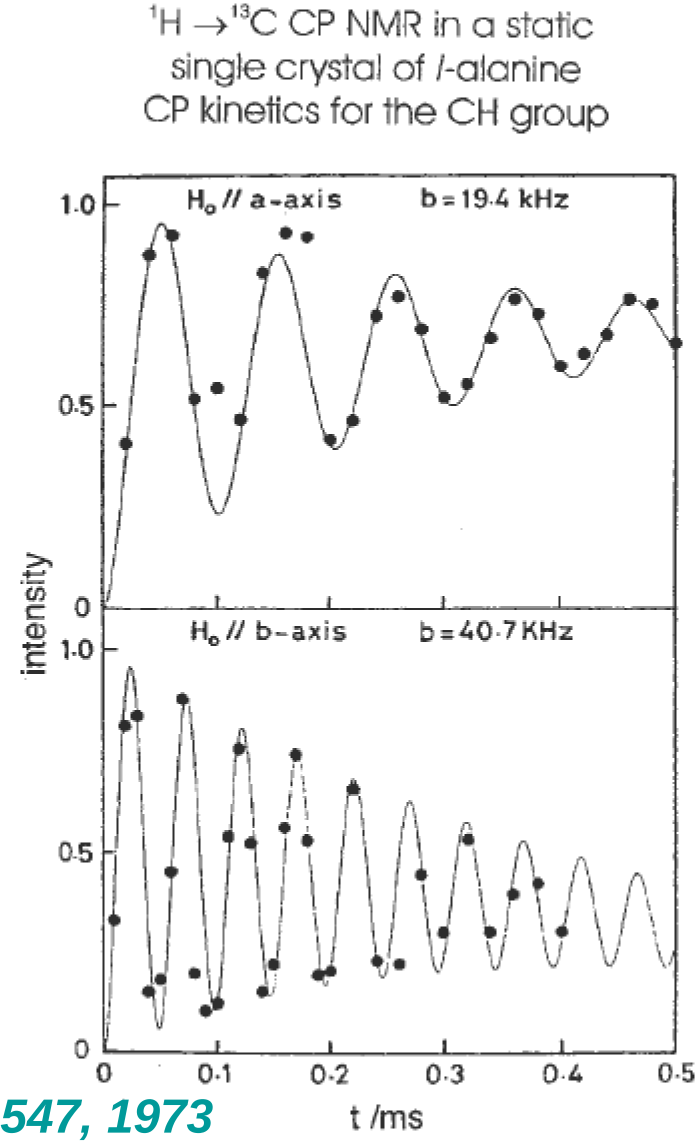
CPMAS and Decoupling



Cross-Polarisation: Transient Oscillations



$^1H \rightarrow {}^{13}C$ CP in a static single crystal of ferrocene



$^1H \rightarrow {}^{13}C$ CP NMR in a static single crystal of *l*-alanine CP kinetics for the CH group

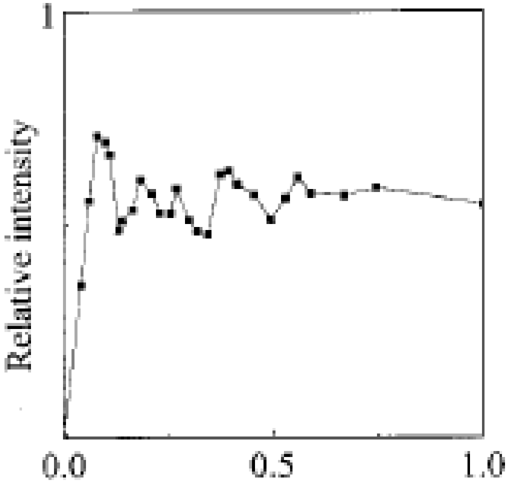
Transient oscillations in single crystal

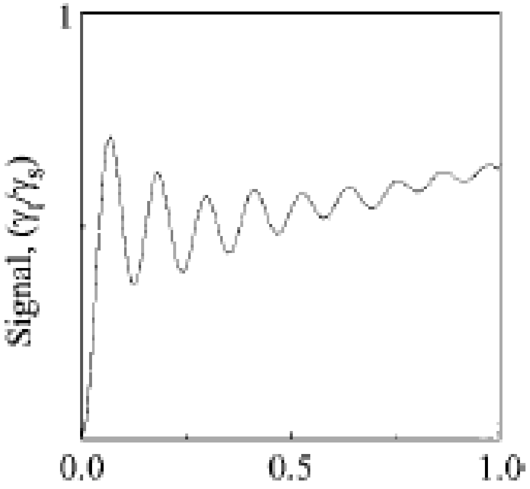
Mueller, Anilkumar, Baumann, Ernst, PRL, 58, 2547, 1973

Kolodziejski and Klinowski, Chem. Rev. 102, 613, 2002

Cross-Polarisation: Transient Oscillations

^{13}CH of Alanine



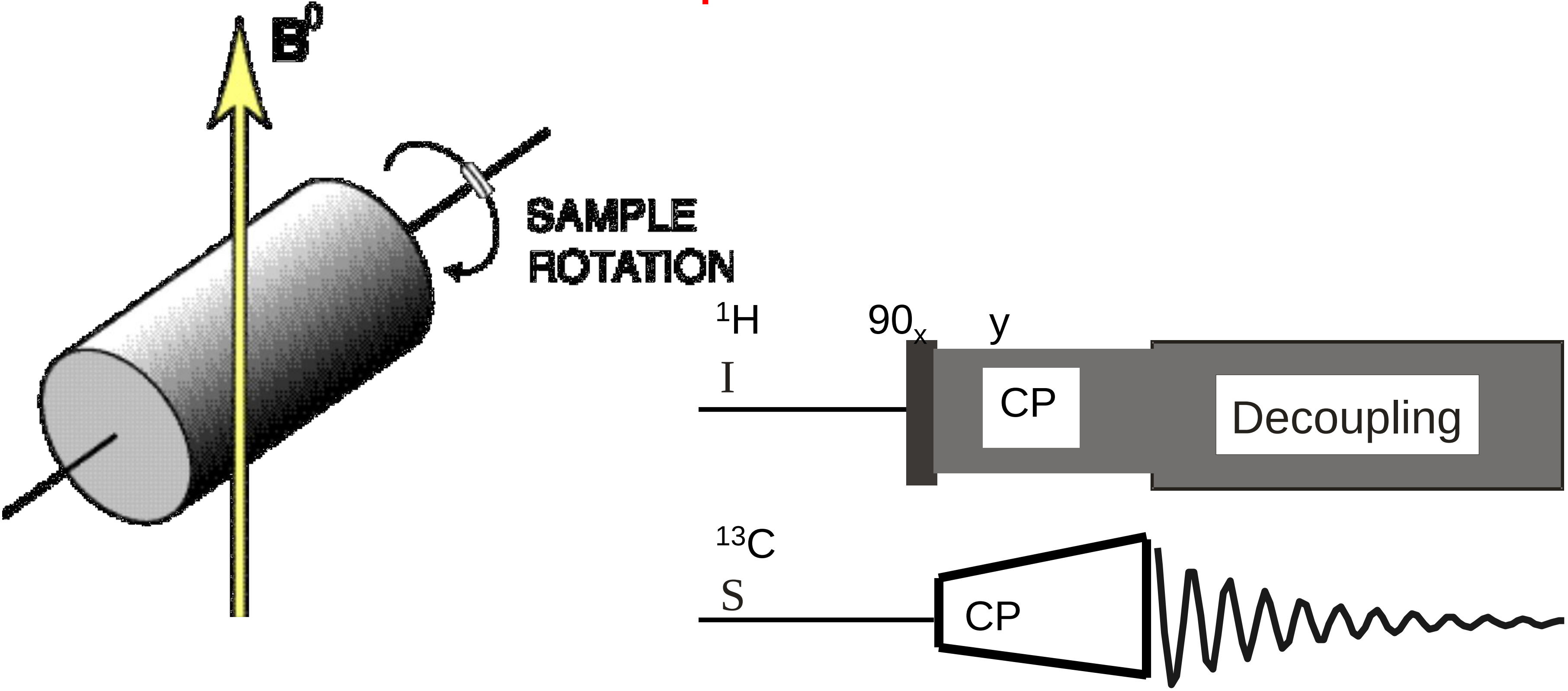


Transient oscillations may lead to quanitative estimates of heteronuclear dipolar coupling and distances

Ladizhansky and Vega, JCP, 112, 7158, 2000

CPMAS

The routine way towards high-resolution and sensitivity in solid-state NMR experiments



$\theta=54.7$

Stejskal, Schaefer, Waugh, JMR, 18,560,1975
Stejskal, Schaefer, Waugh, JMR, 28,105,1977