An introduction to Solid State NMR and its Interactions

From tensor to NMR spectra

CECAM Tutorial – September 2009

Calculation of Solid-State NMR Parameters

Using the GIPAW Method

Thibault Charpentier - CEA Saclay

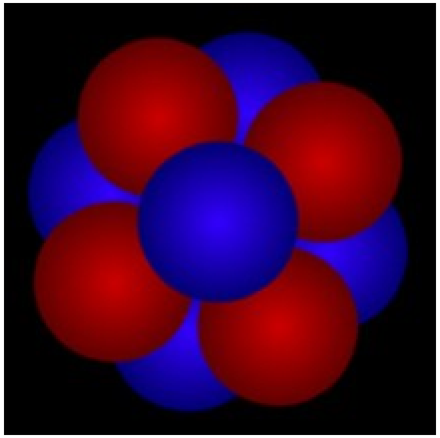
thibault.charpentier@cea.fr

Nuclear Magnetic Resonance

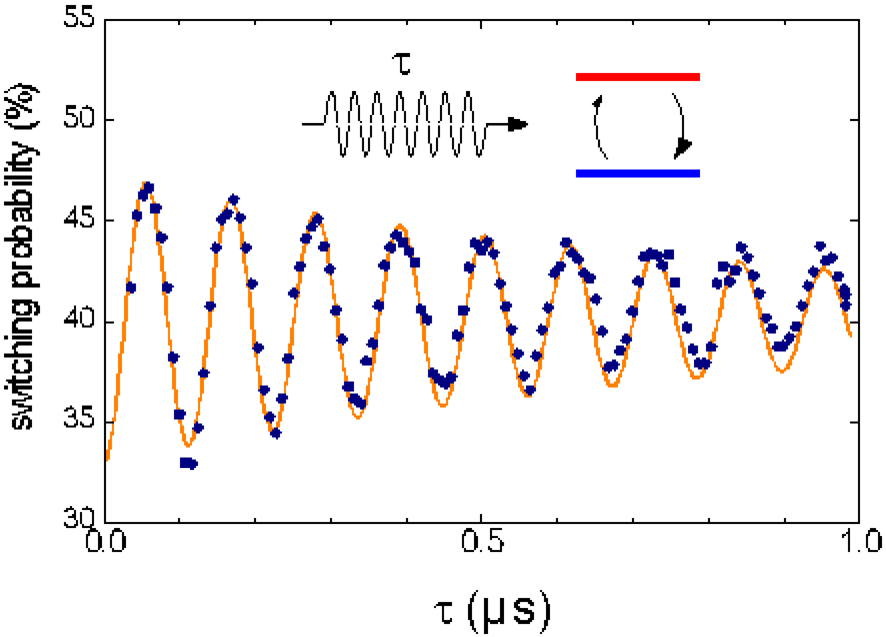
Spin

Magnetic Field

The Rabi oscillation



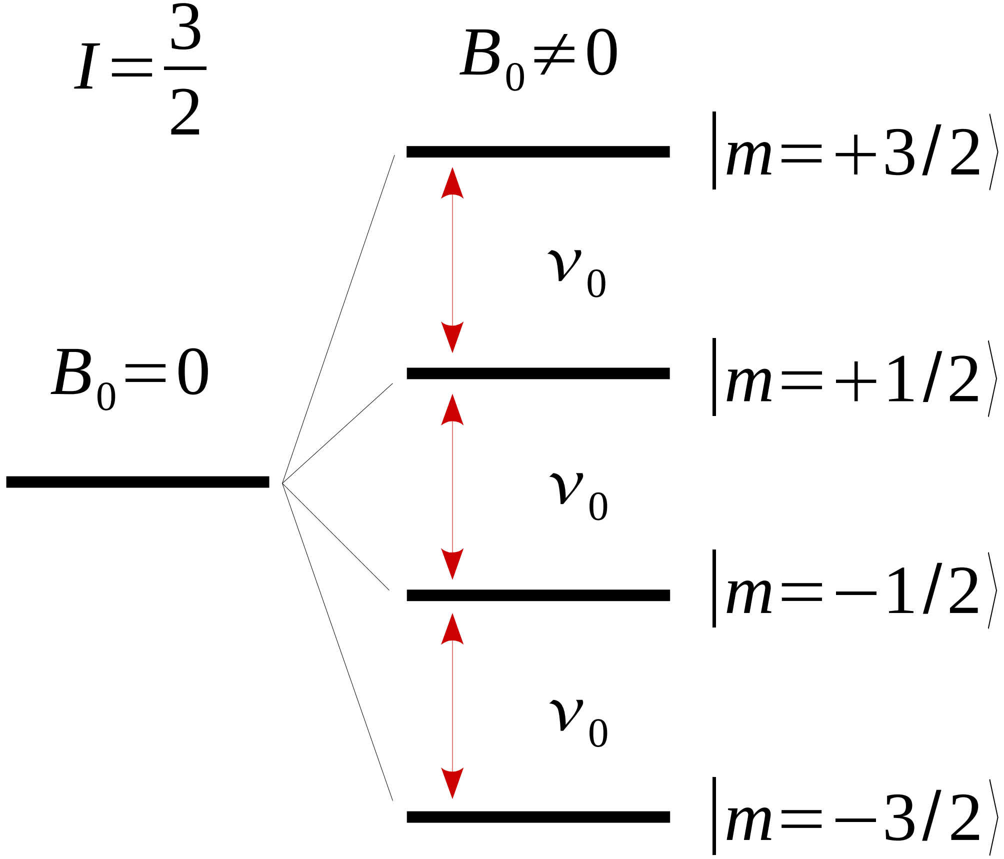
$$\vec{\mu}_N = \gamma_N \hbar \vec{I}$$



Rabi oscillations in quantum dots
Source: http://iramis.cea.fr/drecam/spec/Pres/Quantro/Qsite/projects/qip.htm

The Zeeman effect

$$I=\frac{3}{2}$$



$$E=-\vec{\mu}_N\,.\,\vec{B}_0$$

$$(\hbar)\,\hat{H}=-\gamma_N\hbar\,\vec{I}\,.\,\vec{B}_0=\hbar\,\omega_0 I_Z$$

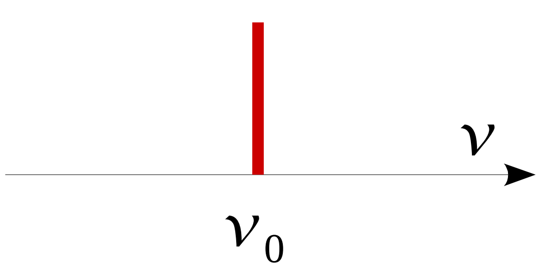
The Larmor frequency

$$\omega_0=-\gamma_N B_0$$

$$\nu_0=-\frac{\gamma_N}{2\pi}B_0$$

NMR spectrum of an *isolated nucleus*

$$\Delta m=\mp 1$$



The spin operators

$$I = \frac{3}{2}$$

$$\vec{I} = \begin{pmatrix} I_X \\ I_Y \\ I_Z \end{pmatrix}$$

$$I_Z |m\rangle = m|m\rangle$$

$$I_+ |m\rangle = \sqrt{I(I+1) - m(m+1)}\,|m+1\rangle$$

$$I_- |m\rangle = \sqrt{I(I+1) - m(m-1)}\,|m-1\rangle$$

$$I_Z = \begin{pmatrix} +3/2 & 0 & 0 & 0 \\ 0 & +1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{pmatrix}$$

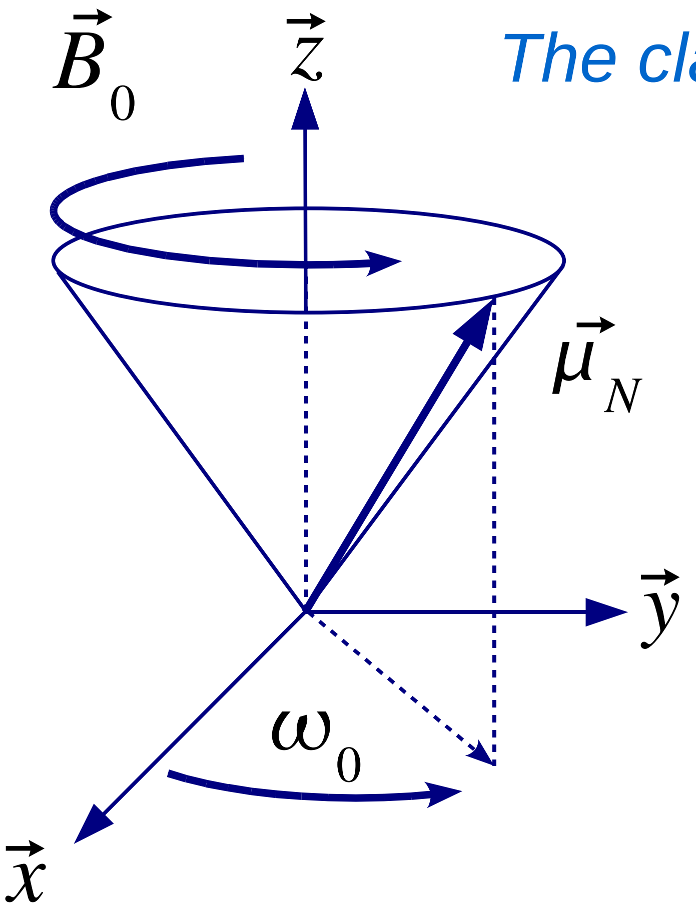
$$I_+ = \begin{pmatrix} 0 & \sqrt{3/2} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3/2} \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$I_X = \frac{1}{2}\left(I_+ + I_-\right)$$

$$I_Y = \frac{1}{2}\left(I_+ - i I_-\right)$$

$$I_- = \begin{pmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3/2} & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{3/2} & 0 \end{pmatrix}$$

The Larmor precession



The classical approach to Larmor precession

$$\frac{d\vec{\mu}_N}{dt} = \gamma_N \vec{\mu}_N(t) \wedge \vec{B}_0$$

The quantum approach to Larmor precession

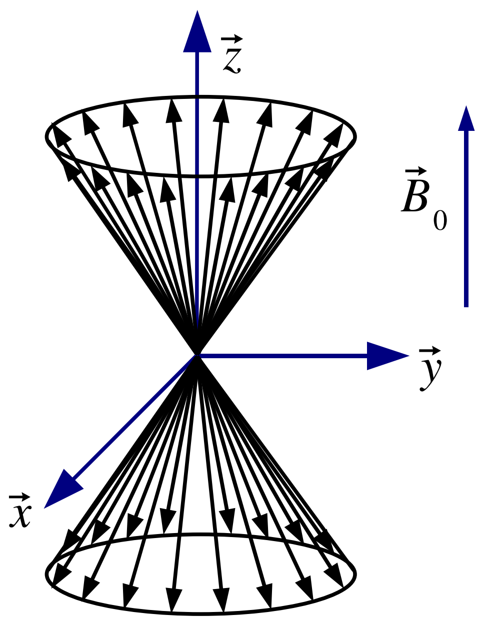
$$i\hbar \frac{d\langle \hat{\vec{I}} \rangle}{dt} = i\hbar \frac{d}{dt} \langle \psi(t) | \hat{\vec{I}} | \psi(t) \rangle = \langle \psi(t) | [\hat{H}, \hat{\vec{I}}] | \psi(t) \rangle = i\hbar \gamma_N \langle \hat{\vec{I}} \rangle \wedge \vec{B}_0$$

The nuclear magnetization

In NMR, the ***only direct observable*** is the ***macroscopic magnetization***

$$\vec{M} = \sum_i \vec{\mu}_i$$

But NMR spectroscopist know how to play with more complex objects...

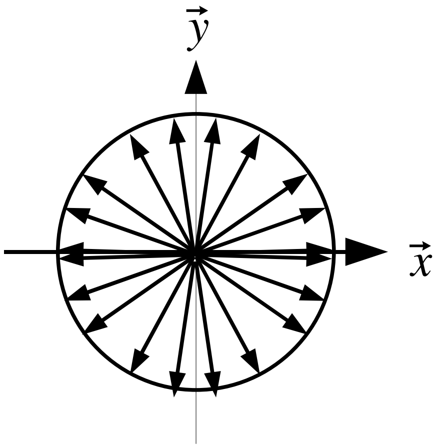


At equilibrium,

$$\frac{N_{up}}{N_{down}} \propto \exp\left(-\frac{\Delta E}{k_B T}\right)$$

the magnetization is along the magnetic field

$$M_z \neq 0$$



$$M_x = M_y = 0$$

Boltzman populations

Sensitivity of NMR

The Curie Law (high temperature limit)

$$M_0 = \chi_0 B_0 = N_I \frac{\gamma^2 \hbar^2 I(I+1)}{3kT} B_0$$

The quantum approach

$$\vec{M}_0 = N_I \langle \mu_N \rangle = N_I \gamma_N \hbar Tr\left[\vec{I}\rho_{eq}\right] \qquad \hat{H} = \hbar\omega_0 I_Z \qquad \rho_{eq} \propto \exp\left(-\frac{\hat{H}}{k_B T}\right)$$

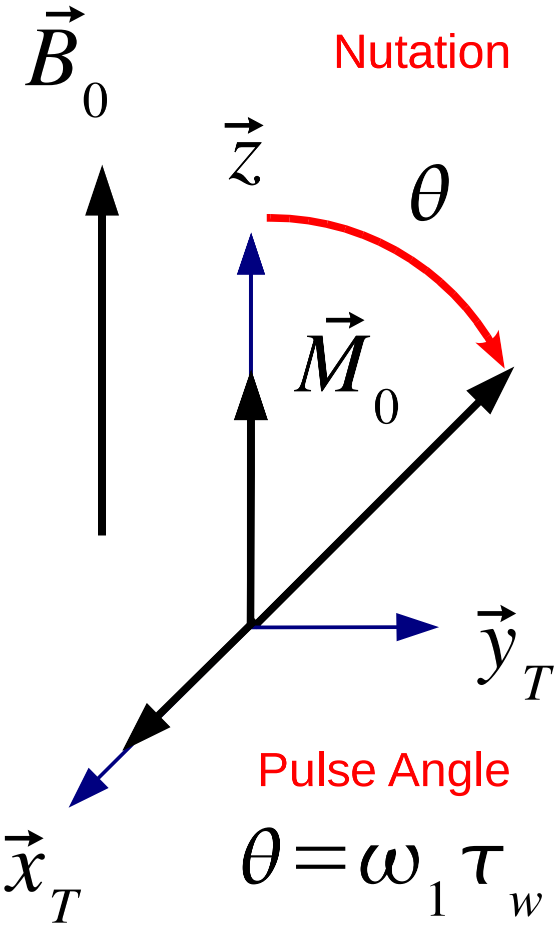
In the high temperature limit

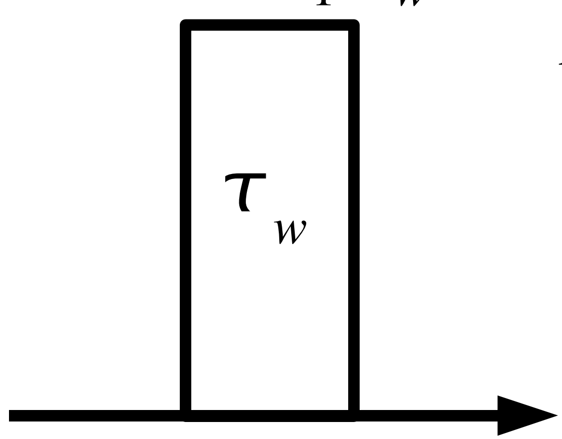
$$\rho_{eq} \propto -\frac{\omega_0}{k_B T} I_Z \qquad \vec{M}_{eq} = N_I \times \gamma_N \hbar \times \frac{\omega_0}{kT} \times Tr\left[I_Z^2\right]$$

Description of NMR experiments in term of I_α operators

The Resonance Phenomenum

Application of a tranverse RF magnetic field at the Larmor frequency produces the precession of the nuclear magnetization around the RF field (nutation) in the so-called rotating frame





$$\hat{H}(t) = \omega_0 \hat{I}_Z + \hat{H}_{RF}(t)$$

$$\hat{H}_{RF}(t) = -\gamma_N 2 B_1 \hat{I}_x \cos(\omega_{RF} t) = 2\omega_1 \hat{I}_x \cos(\omega_{RF} t)$$

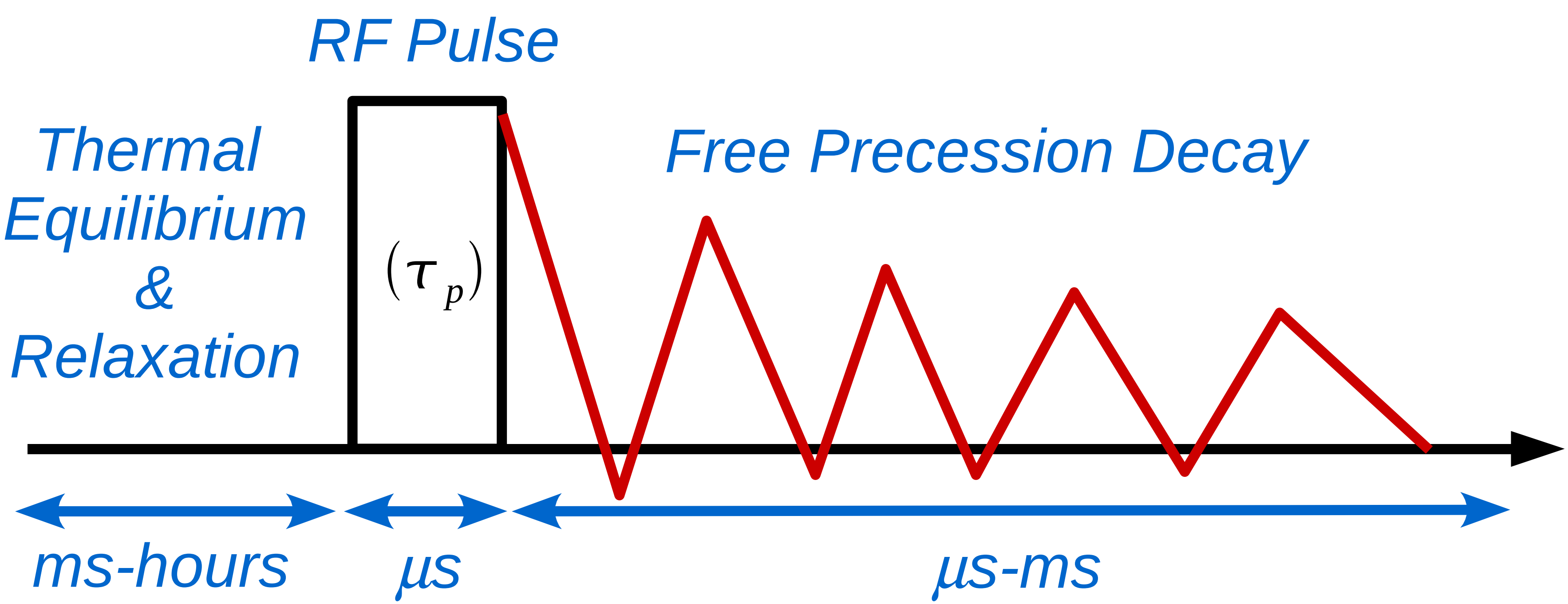
$$\left(\frac{d\langle\vec{\hat{I}}\rangle}{dt}\right)_{LAB} = \langle\vec{\hat{I}}\rangle \wedge \left(-\omega_0 \vec{z} + \underbrace{2\gamma_N B_1 \cos(\omega_{RF} t)\vec{x}}_{\text{Time Dependent}}\right)$$

$$\text{Rotating frame at } \omega_{RF} \text{ around } \vec{B}_0 : (\vec{x}, \vec{y}, \vec{z})_{LAB} \Rightarrow (\vec{x}, \vec{y}, \vec{z})_T$$

$$\left(\frac{d\langle\vec{\hat{I}}\rangle}{dt}\right)_{T} = \langle\vec{\hat{I}}\rangle \wedge \left(\underbrace{\{\omega_{RF} - \omega_0\}\vec{z} - \omega_1 \vec{x}_T}_{\text{Time Independent}}\right)$$

Pulsed Fourier Transform NMR

Typical Timing of a Solid State NMR experiment



Macroscopic Magnetization Motion

$$\vec{M}(\tau_p) = M_0 \vec{x}$$

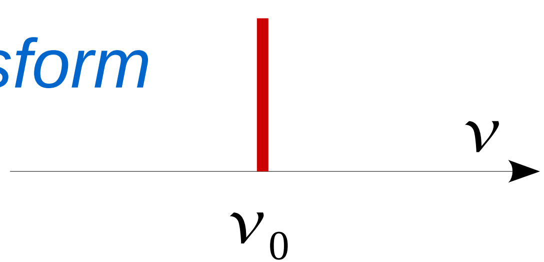
$$\vec{M}(0) = M_0 \vec{z}$$

$$\vec{M}(t+\tau_p) = M_0 \times \left(\vec{x} \cos(\nu_0 t) + \vec{y} \sin(\nu_0 t) \right)$$

The complex NMR signal

$$s(t) \propto M_0 \exp\left(-i \nu_0 t \right)$$

Fourier Transform



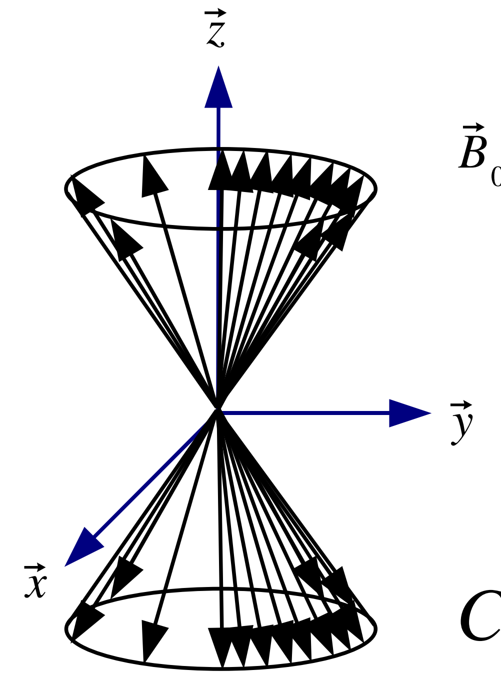
Pulsed Fourier Transform NMR

Bloch equations

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} + i\,\Delta M_y$$

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2} - i\,\Delta M_x$$

$$\frac{dM_z}{dt} = -\frac{M_z - M_{eq}}{T_1}$$



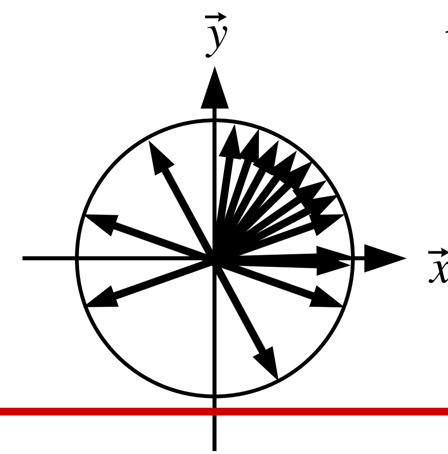
Coherent state

$M_x \neq 0 \; M_y \neq 0$

Density operator (quantum state)

$$\rho(t) = a_x(t) I_x + a_y(t) I_y + a_z(t) I_z$$

$$M_\alpha(t) \propto Tr\left[\!\left[I_\alpha . \rho(t) \right]\!\right]$$

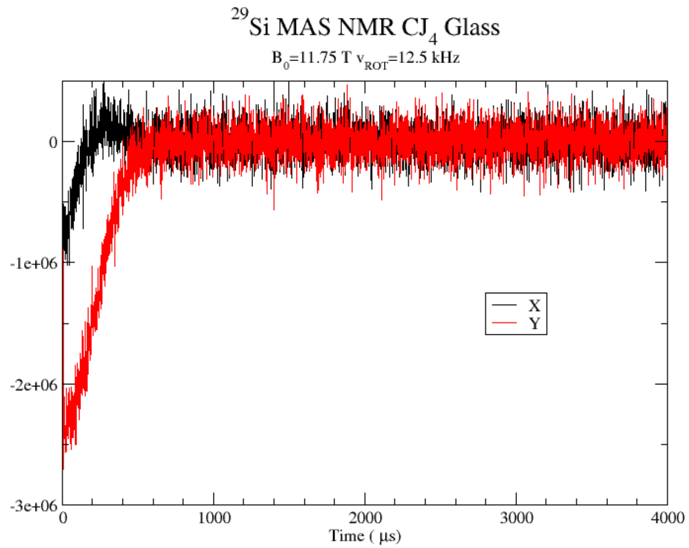


I_z *: magnetization ;* I_+ , I_- *single quantum coherence*

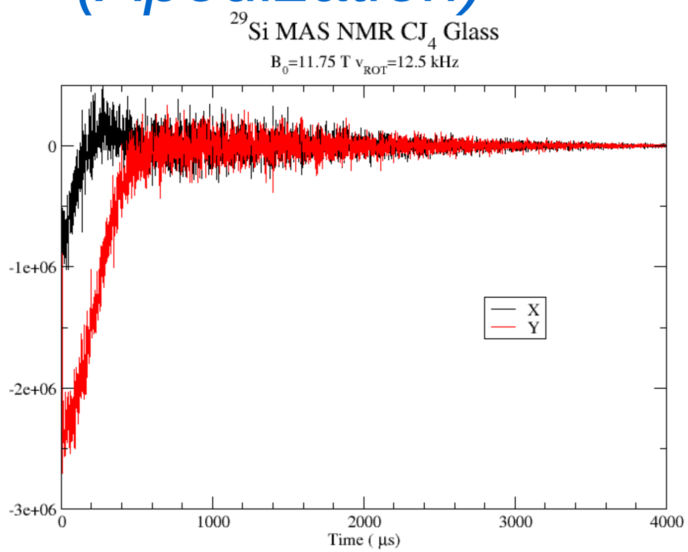
The only directly observable entity

Pulsed Fourier Transform NMR

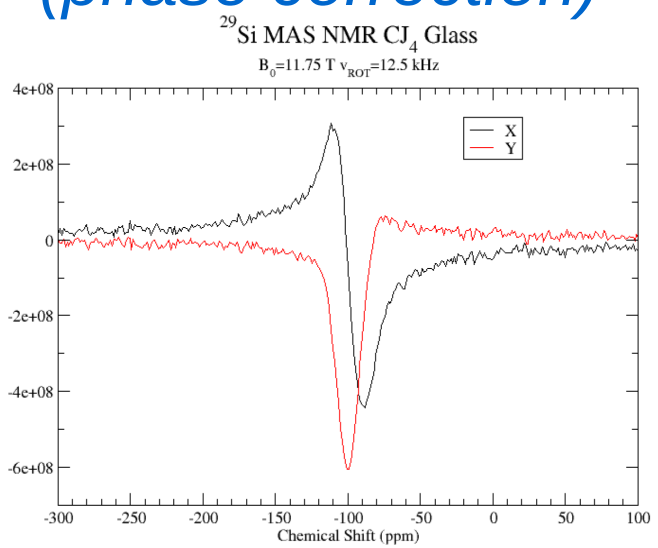
Free Precession Decay



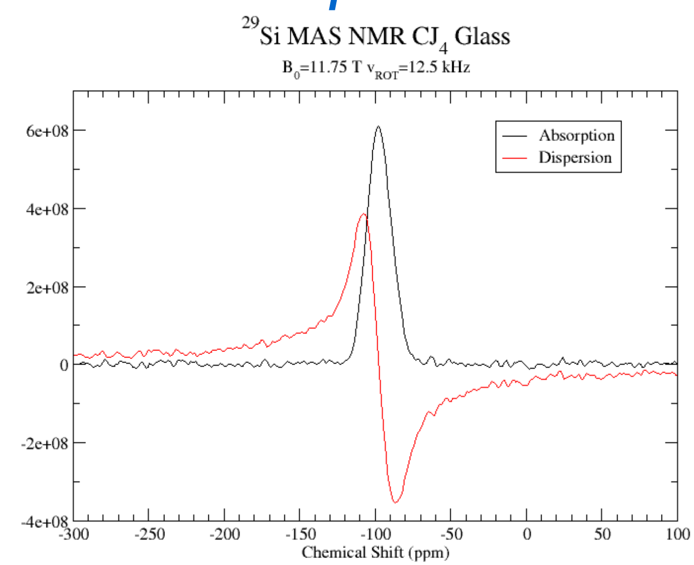
Signal Processing (Apodization)



Fourier Transform (phase correction)



NMR Spectrum



The NMR signal in theory

$$s(t) = Tr\left[I_+ \exp(-i\hat{H}t) I_x \exp(+i\hat{H}t) \right]$$

Initial state: I_x *System evolves under:* $\hat{H}$

One quantum transitions are observed: I_+

$$s(t) \propto \sum_m \left| \langle m+1 | I_+ | m \rangle \right|^2 \times \exp(-i\omega_{m,m+1} t)$$

The NMR frequencies

$$\omega_{m,m+1} = \langle m+1 | \hat{H} | m+1 \rangle - \langle m | \hat{H} | m \rangle$$

The contribution of each transition
to the signal amplitude is (isotropic !!)

$$\left| \langle m+1 | I_+ | m \rangle \right|^2$$

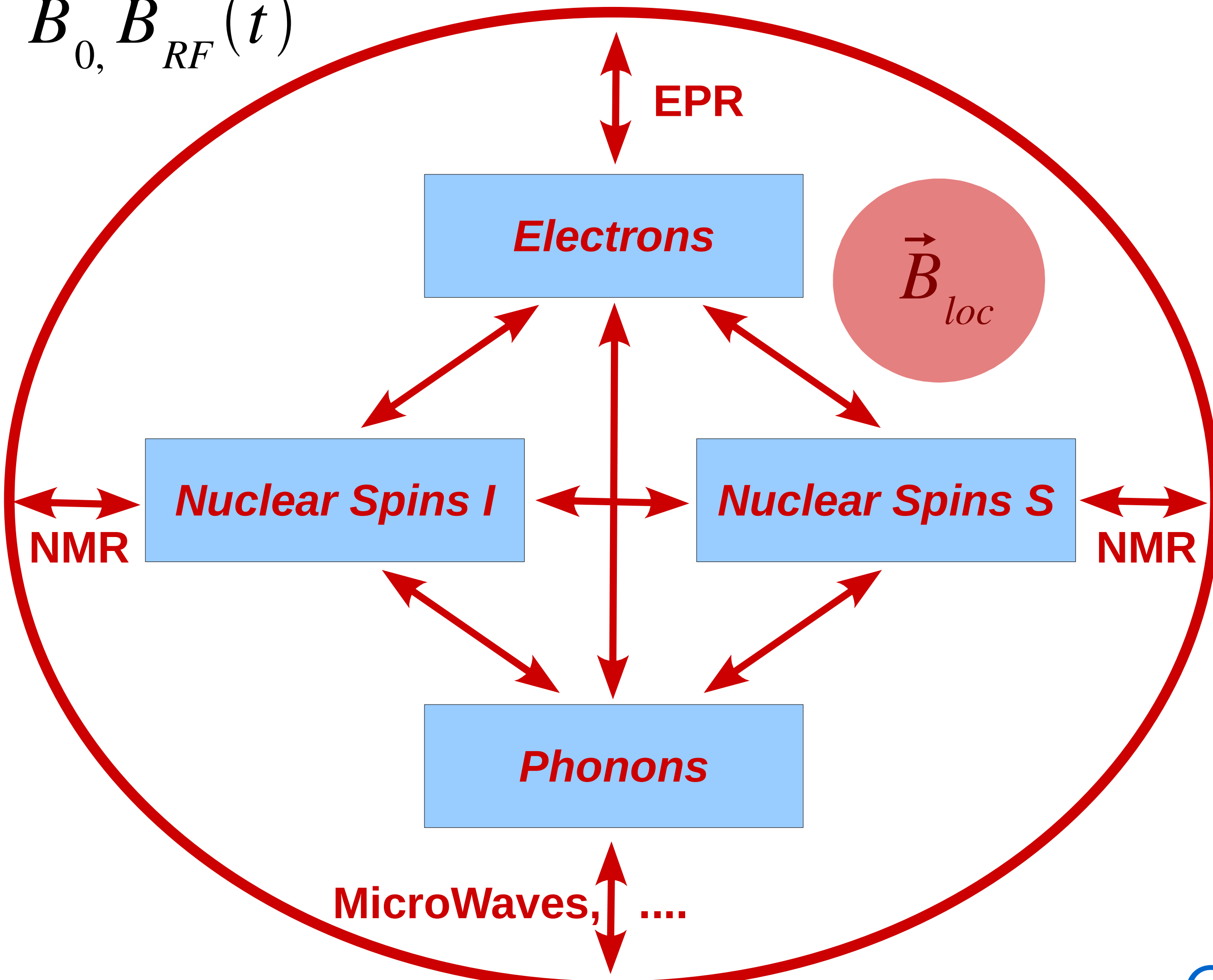
Hamiltonian of NMR interactions are needed $\hat{H}$

DFT calculations provide H !

NMR Interactions *A complex situation...*

$$\hat{H} = -\gamma_N \hbar \vec{\hat{I}} \cdot \left(\vec{B}_{ext} + \vec{B}_{local} \right) = \hat{H}_Z + \hat{H}_{inter.}$$

$\vec{B}_{0,} \vec{B}_{RF}(t)$



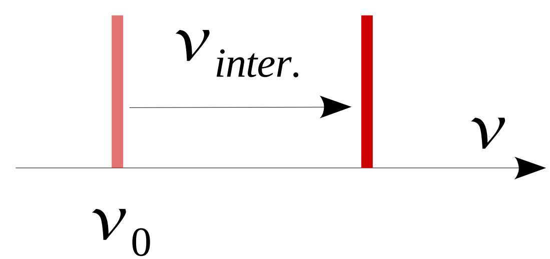
$$\hat{H} = \hat{H}_Z + \hat{H}_{CS} + \hat{H}_J + \hat{H}_D + \hat{H}_Q + \ldots$$

External fields to manipulate the system:

$\vec{B}_{0,} \vec{B}_{RF}(t)$

Internal fields:

$\vec{B}_{loc}$



Chemistry: $\nu_{inter.}$

NMR Interactions are tensors

$$\vec{B}_{loc} = A\vec{X} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \cdot \begin{pmatrix} X_x \\ X_y \\ X_z \end{pmatrix}$$

$$\hat{H} = -\gamma_N \hbar \times \vec{I} . \boldsymbol{A} . \vec{X}$$

Second-rank Tensor

$$\boldsymbol{A} = \boldsymbol{1}, \vec{X} = \vec{B}_{0,} \vec{B}_{RF}$$

Zeeman Interaction

$$\boldsymbol{A} = \boldsymbol{\sigma}, \vec{X} = \vec{B}_0$$

Magnetic shielding

$$\boldsymbol{A} = \boldsymbol{D}, \vec{X} = \vec{S}$$

Dipolar Magnetic couplings (through space)

$$\boldsymbol{A} = \boldsymbol{J}, \vec{X} = \vec{S}$$

Indirect Magnetic couplings (through bond)

$$\boldsymbol{A} = \boldsymbol{Q}, \vec{X} = \vec{I}$$

Quadrupolar Interaction (electric couplings)

NMR Interactions: PAS

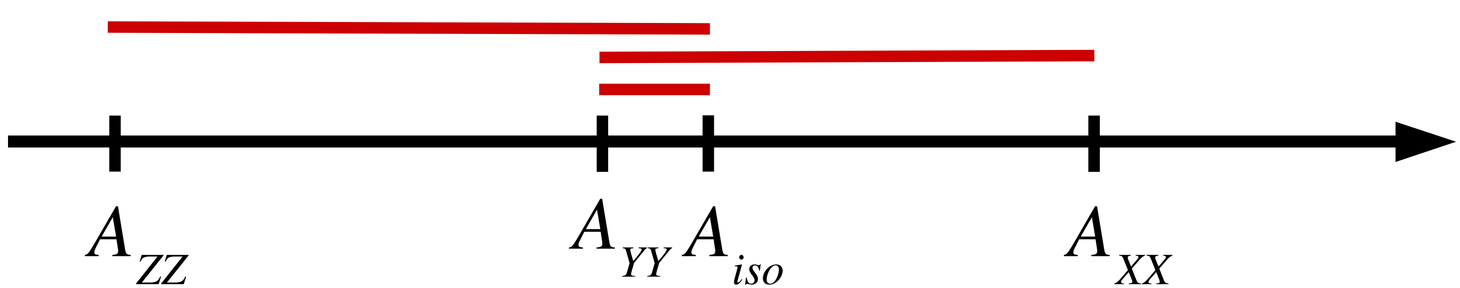
*Diagonalization of **A** yields the Principal Axis System (PAS)*

$$\boldsymbol{A} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} = \boldsymbol{X}_A^{-1} . \begin{pmatrix} A_{XX} & 0 & 0 \\ 0 & A_{YY} & 0 \\ 0 & 0 & A_{ZZ} \end{pmatrix} . \boldsymbol{X}_A = \boldsymbol{X}_A^{-1} . \boldsymbol{A}_{PAS} . \boldsymbol{X}_A$$

Principal Axes labeling:

$$A_{iso} = \frac{1}{3} Tr\left[\!\left[\boldsymbol{A} \right]\!\right]$$

$$\left| A_{ZZ} - A_{iso} \right| \geq \left| A_{XX} - A_{iso} \right| \geq \left| A_{YY} - A_{iso} \right|$$



NMR Interactions: PAS

Introducing a convenient representation for encoding this orientational dependence

$$\boldsymbol{A}_{PAS} = A_{iso}\mathbf{1} + \delta_A \begin{pmatrix} -1/2(1+\eta) & 0 & 0 \\ 0 & -1/2(1-\eta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Isotropic shift: $A_{iso} = 1/3\, Tr[\boldsymbol{A}]$

Strength of the anisotropy: $\delta_A = A_{ZZ} - A_{iso}$

Symmetry of the anisotropy (asymmetry parameter): $\eta_A = (A_{XX} - A_{YY})/\delta_A$

NMR Interactions: PAS

Relative orientation of the PAS with respect to a reference frame (crystallographic axes, laboratory frame, ...)

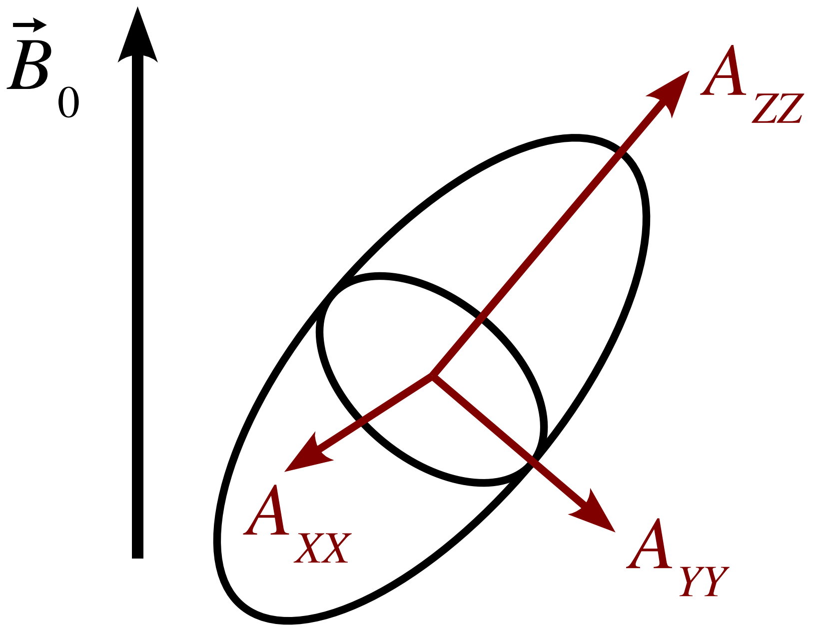
Factorization of $\mathbf{X}_A$ provides the *three Euler angles* $\alpha_A, \beta_A, \gamma_A$

$$\boldsymbol{X}_A = R(\alpha_A, \beta_A, \gamma_A) = \exp\left(-i\alpha_A I_z\right)\cdot\exp\left(-i\beta_A I_y\right)\cdot\exp\left(-i\gamma_A I_z\right)$$

(x,y,z) is the PAS of the reference frame

In NMR the position of a line (single crystal) is dependent upon the six parameters:

$$A_{iso}, \delta_A, \eta_A, \alpha_A, \beta_A, \gamma_A$$



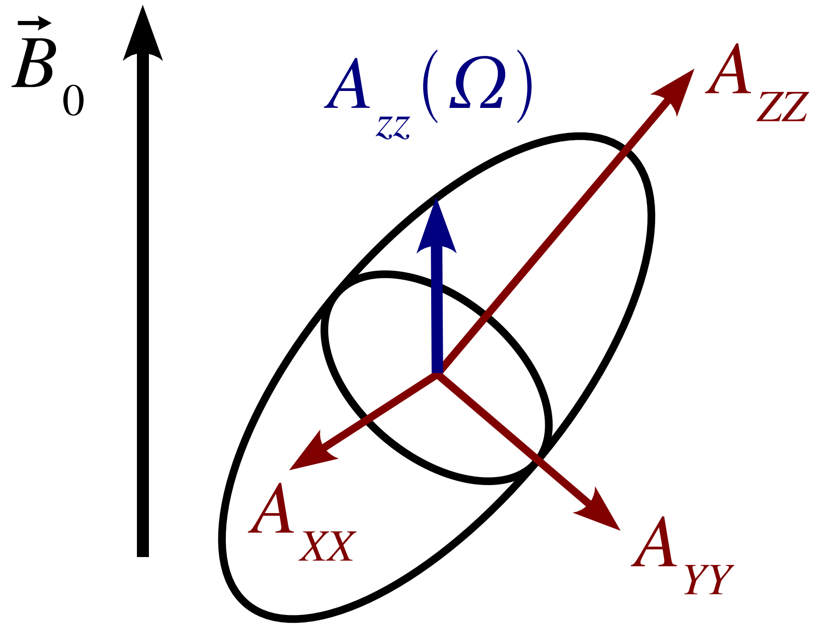
The secular approximation

High Field NMR: $\vec{B}_0 \gg \vec{B}_{loc}$

Perturbation Expansion of the NMR interactions

$$\hat{H}_Z \gg \hat{H}_{inter.} \rightarrow \hat{H}_{inter.} \approx \hat{H}_{CS}^{(1)} + \hat{H}_Q^{(1)} + \hat{H}_Q^{(2)} + \hat{H}_D^{(1)} + \hat{H}_J^{(1)} + \ldots$$

Keeping terms invariant under rotation around B_0



A general representation of the NMR interactions

Powerful Tensorial approach to derive all formula !

$$\hat{H}_{\lambda}(\Omega) = C_{\lambda} \sum_{m=-2}^{m+2} (-1)^{m} R_{2,-m}(\Omega) \times T_{2m}$$

Euler angles

$$\Omega = (\alpha, \beta, \gamma)$$

Spatial dependence $R_{2,m} = \sum_{n} \rho_{2,n}^{\lambda} D_{n,m}^{2}(\Omega)$

NMR parameters $\rho_{2,\pm 2}^{\lambda} = \frac{\eta_{\lambda}}{2}, \rho_{2,\pm 1}^{\lambda} = 0, \rho_{2,0}^{\lambda} = \sqrt{\frac{3}{2}} \delta_{\lambda}$

Spin Operator dependence $T_{2,m}$

$$[I_{z}, T_{2,m}] = m T_{2,m} \qquad T_{2,0}^{II} = \sqrt{\frac{1}{6}} \left(3 I_{Z}^{2} - I(I+1) \right)$$

(first order) secular approximation easy : m=0!

$$\hat{H}_{\lambda}^{(1)}(\Omega) = C_{\lambda} R_{2,0}(\Omega) \times T_{20}$$

The Chemical Shift Tensor

Absolute chemical shielding (GIPAW output) $\boldsymbol{\sigma}$

Isotropic chemical shift

$$\boldsymbol{\delta} = -\left(\boldsymbol{\sigma} - \sigma_{REF}\mathbf{1}\right)$$

$$\delta_{iso} = -\left(\sigma_{iso} - \sigma_{REF}\right)$$

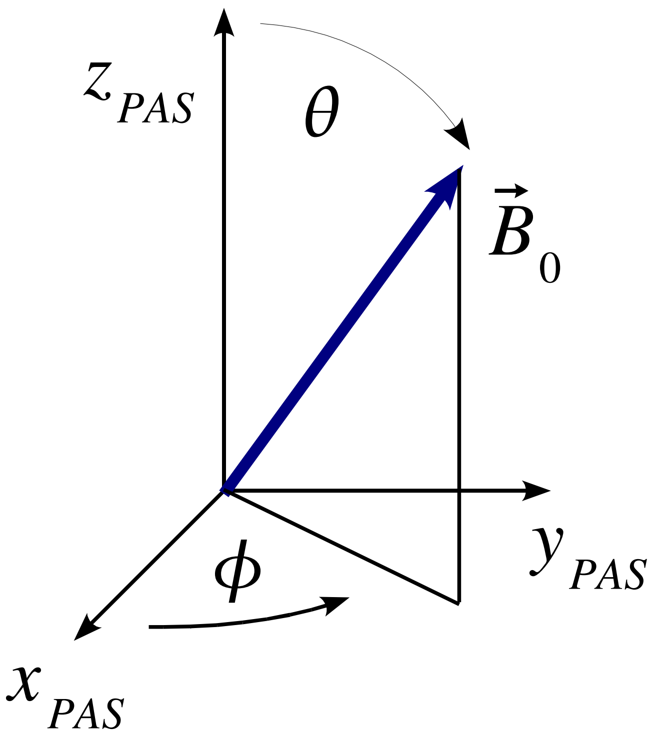
$$\delta_{iso}^{\exp}(ppm) = 10^6 \times \frac{\left(\delta_{iso}^{\exp} - \nu_{REF}\right)(Hz)}{\nu_{REF}(Hz)}$$

Chemical Shift Anisotropy (CSA) $\delta_\sigma, \eta_\sigma$

$$\hat{H}_{CSA} = \omega_{CS}(\theta, \phi) I_Z = \sqrt{\frac{2}{3}} R_{2,0}(\Omega) I_Z$$

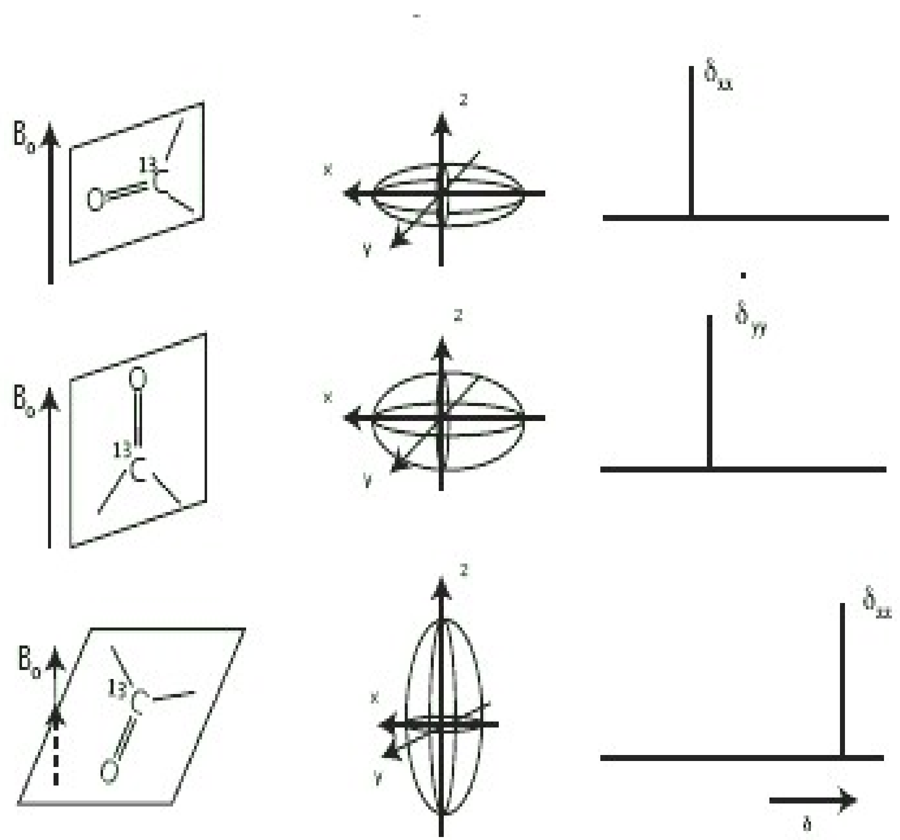
$$\omega_{CS}(\theta, \phi) = \omega_0\left(\delta_{XX}\sin^2\theta\cos^2\phi + \delta_{YY}\sin^2\theta\sin^2\phi + \delta_{ZZ}\cos^2\theta\right)$$

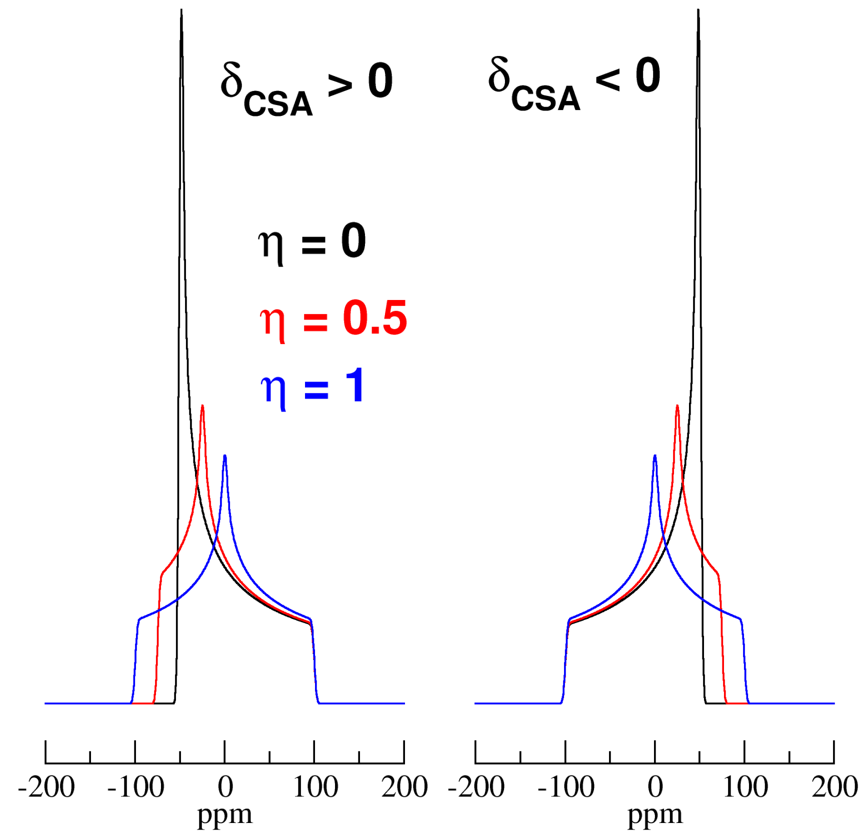
$$\omega_{CS}(\theta, \phi) = \omega_0\delta_{iso} + \frac{\omega_0\delta_\sigma}{2}\left\{3\cos^2(\theta) - 1 + \eta_\sigma\sin^2(\theta)\cos(2\phi)\right\}$$



NMR powder spectrum

$$S_{powder}(t)=\int \sin\theta\, d\theta\, d\phi \quad \exp(-i\,\omega(\theta,\phi)\,t) \Rightarrow TF \Rightarrow S_{powder}(\nu)$$





The quadrupole Interaction $I > 1/2$

*Electric coupling between the **nuclear quadrupole moment Q** and local electric field gradient V(**r**$_{nuc}$) at the nucleus*

Quadrupolar Coupling Constant (~ MHz) $C_Q = \frac{eQ}{h} V_{ZZ}$

Quadrupolar asymmetry parameter

$$\eta_Q = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \quad V_{iso} = 0$$

First order

$$H_Q^{(1)} = \frac{C_Q}{6I(2I-1)} \times R_{20}^Q(\Omega) \times T_{20}$$

$$T_{2,0} = \sqrt{\frac{1}{6}}\left(3 I_Z^2 - I(I+1)\right)$$

Second order (complex...)

$$H_Q^{(2)} = \frac{1}{\nu_0} \frac{C_Q}{6I(2I-1)} \times \sum_{l=0,2,4} A^l \sum_{k=-l,l} B_k^l(\eta) D_{l,0}^k\left(\Omega\right)$$

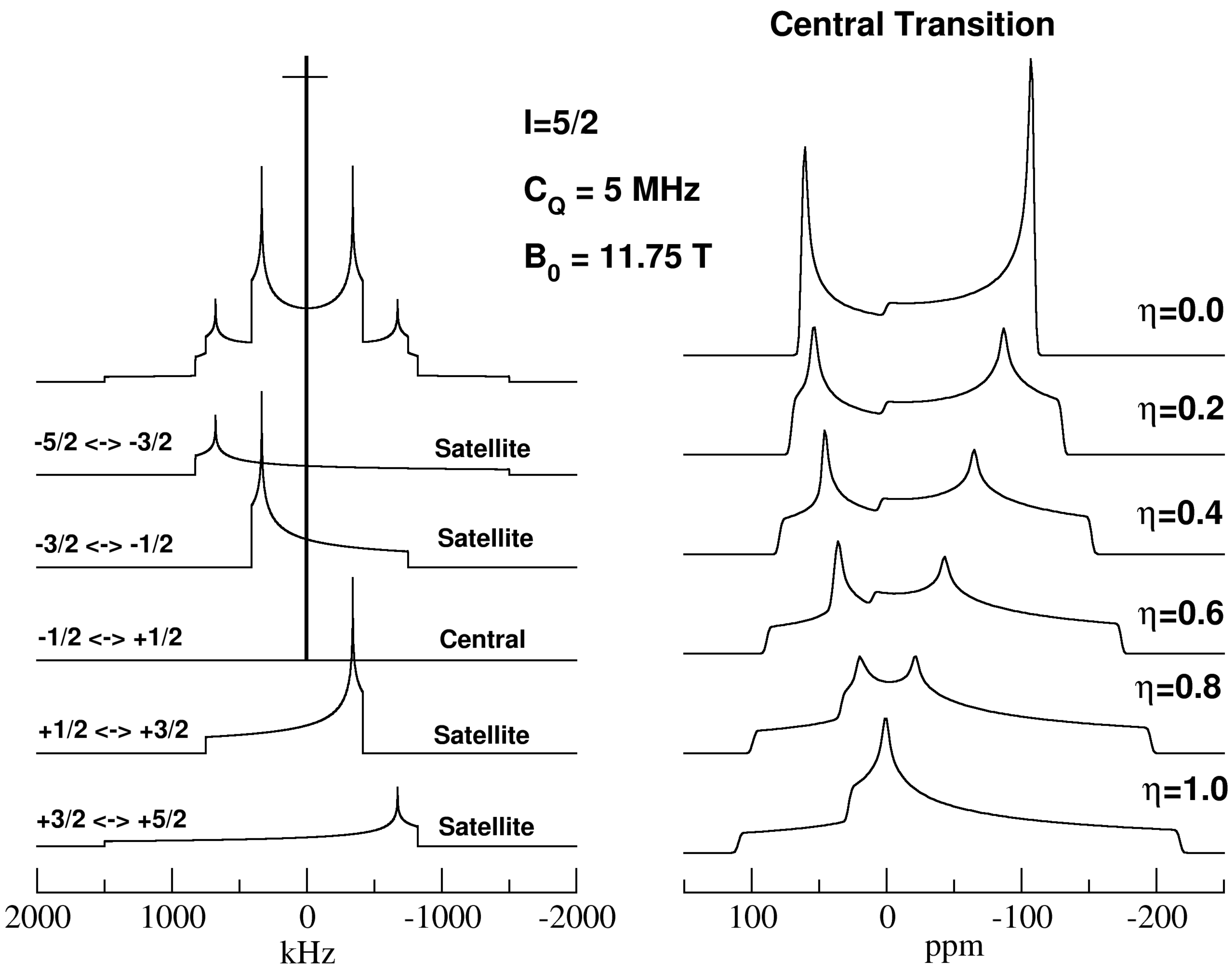
$$A^l = f(I_Z^3, I_Z)$$

Second Order Quadrupolar Induced Shift !

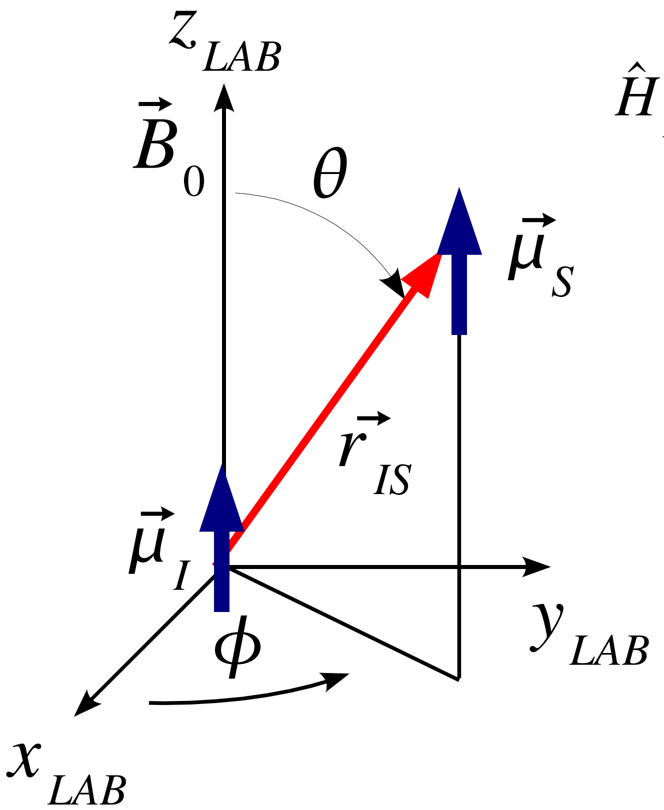
$$\delta_Q^{(2)} = A^0 B_0^0(\eta)$$ *Isotropic shift*

Quadrupolar nuclei

Powder Quadrupolar Static spectra



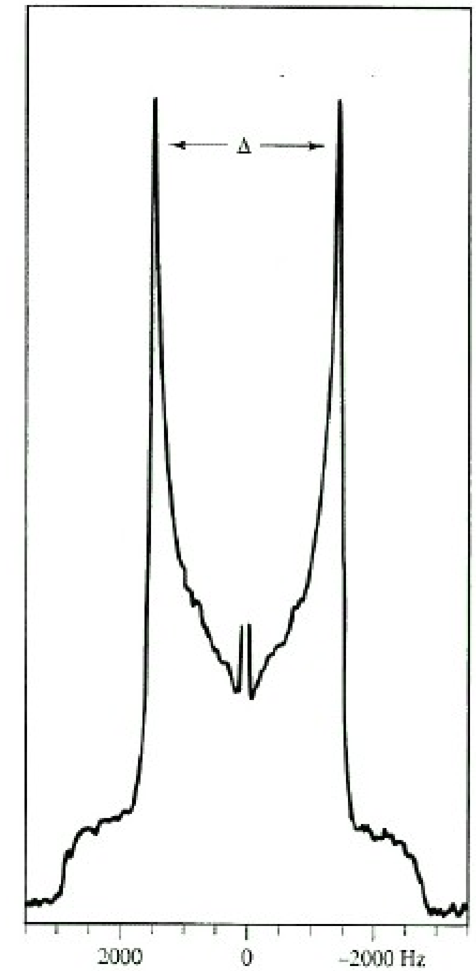
The Dipolar Interaction



$$\hat{H}_D = \frac{\hbar\gamma_I\gamma_S}{r_{IS}^3}\left\{\vec{I}.\vec{S} - \frac{3}{r_{IS}^2}\left(\vec{I}\cdot\vec{r}_{IS}\right)\left(\vec{S}\cdot\vec{r}_{IS}\right)\right\} = \vec{I}\cdot\boldsymbol{D}\cdot\vec{S}$$

$$\eta = 0$$

$$\boldsymbol{D}^{PAS} = \frac{-2\hbar\gamma_I\gamma_S}{r_{IS}^3}\begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



^{13}C-^{13}C acetic acid at T=80K

Engelsberg et al., J. Magn. Reson., 1990, 88, 393.

Homonuclear $$H_D^{(1)} = \frac{\hbar\gamma_I\gamma_S}{r_{IS}^3} \times R_{20}^D(\Omega) \times T_{20}^{IS}$$

Heteronuclear $$H_D^{(1)} = \frac{\hbar\gamma_I\gamma_S}{r_{IS}^3} \times R_{20}^D(\Omega) \times \sqrt{\frac{3}{2}}\, I_Z S_Z$$

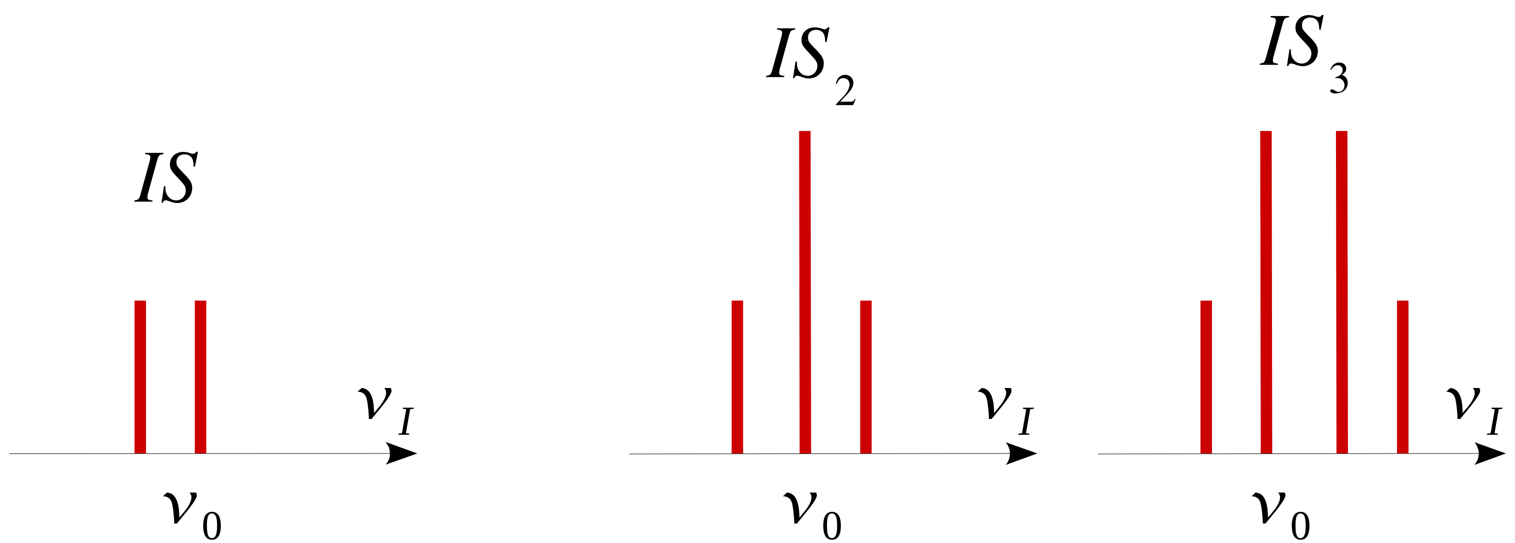
Indirect J coupling

Small interaction (~Hz), anisotropic effects (so far) neglected

$$H_J = \vec{I}\left(J_{iso}\mathbf{1} + \boldsymbol{J}_{ani}\right)\vec{S} \approx J_{iso}\vec{I}\cdot\vec{S}$$

Like spins $\quad J_{iso} \geq \left|\delta^I_{iso} - \delta^S_{iso}\right| \qquad H_J = J_{iso}\vec{I}\cdot\vec{S}$

Unlike spins $\quad J_{iso} \leq \left|\delta^I_{iso} - \delta^S_{iso}\right| \qquad H_J = J_{iso} I_Z S_Z$



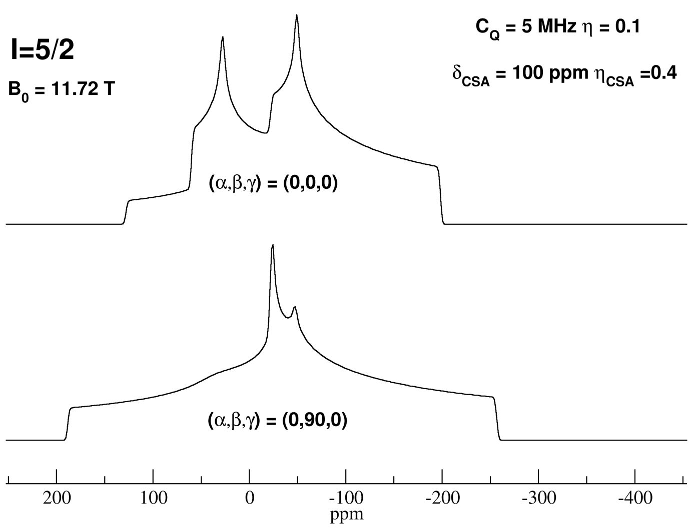
Multiple interactions

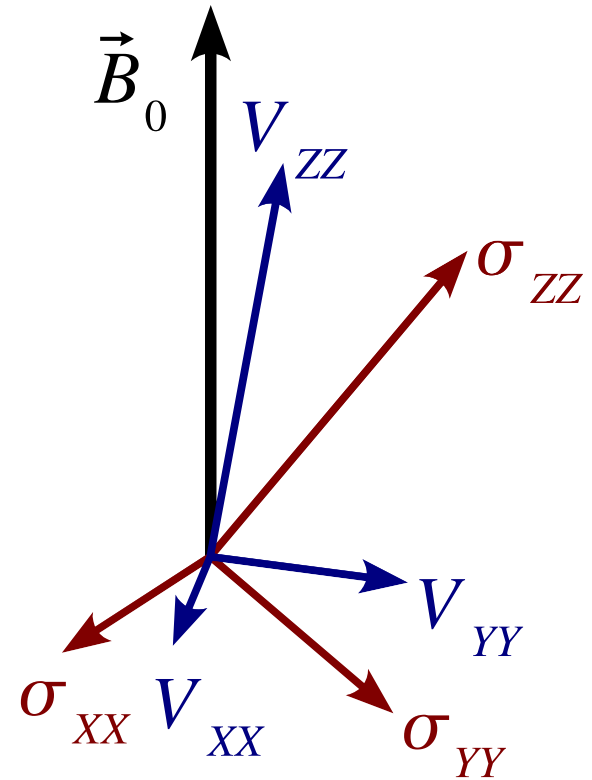
*Lineshape is also dependant upon the relative orientation of CSA **PAS** with respect to quadrupolar **PAS** (or vice-versa)*

In the crystallographic axes frame (GIPAW calculation)

$$X_{\sigma,c} = R(\alpha_{\sigma,c}, \beta_{\sigma,c}, \gamma_{\sigma,c}) \quad X_{Q,c} = R(\alpha_{Q,c}, \beta_{Q,c}, \gamma_{Q,c})$$

$$X_{\sigma,c} X_{Q,c}^{-1} = R(\alpha_{\sigma,Q}, \beta_{\sigma,Q}, \gamma_{\sigma,Q})$$





High Resolution NMR

Brownian Motion in Liquids

$$\hat{H}\left(\Omega(t)\right)=\hat{H}_{iso}+\hat{H}_{ani}\left(\Omega(t)\right)$$

$$\overline{\hat{H}_{ani}\left(\Omega(t)\right)}=0$$

Only isotropic contributions !

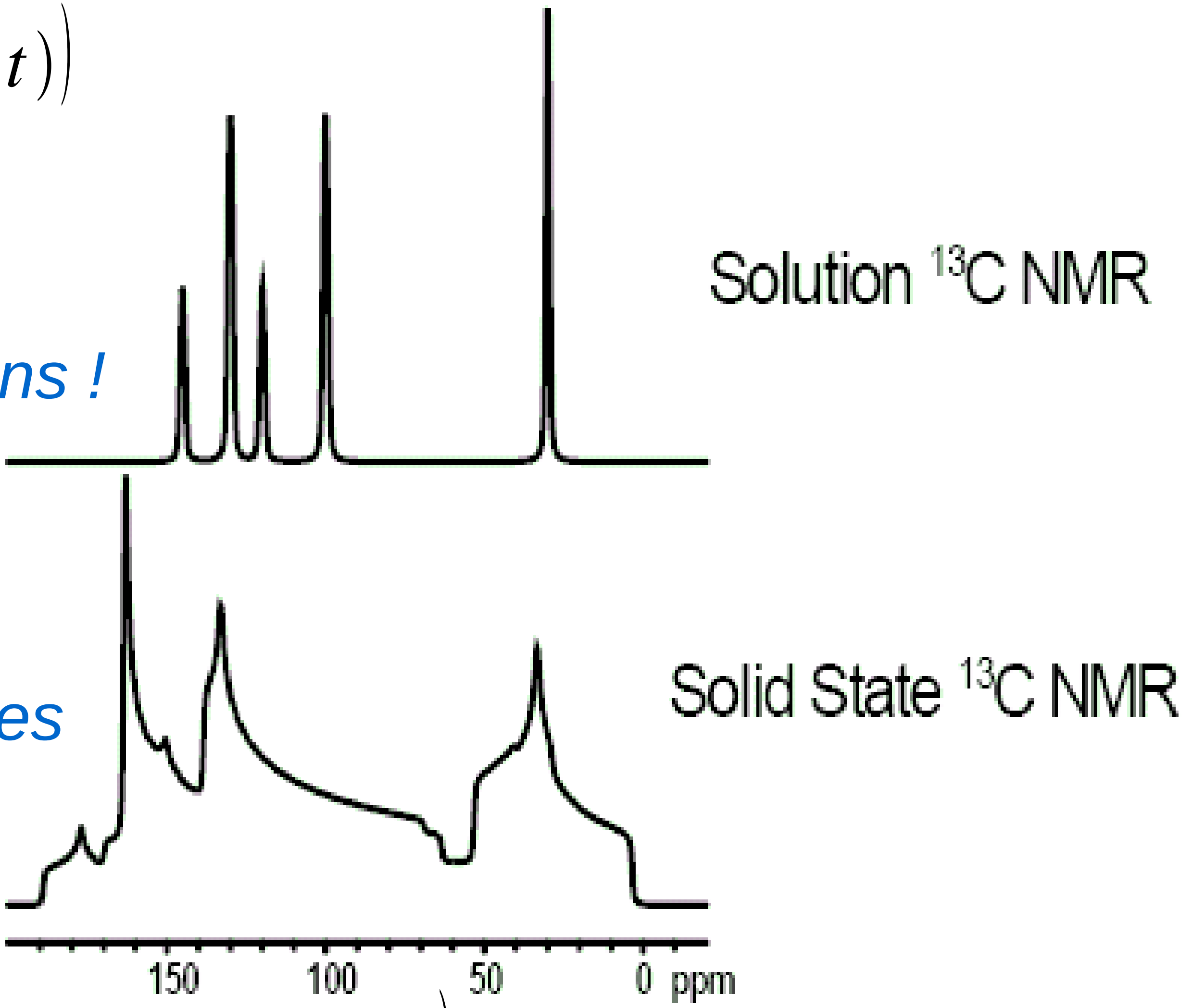
$$\delta_{iso}, J_{iso}$$

In rigid lattices, broad lines

$$\delta_{iso}, J_{iso}$$

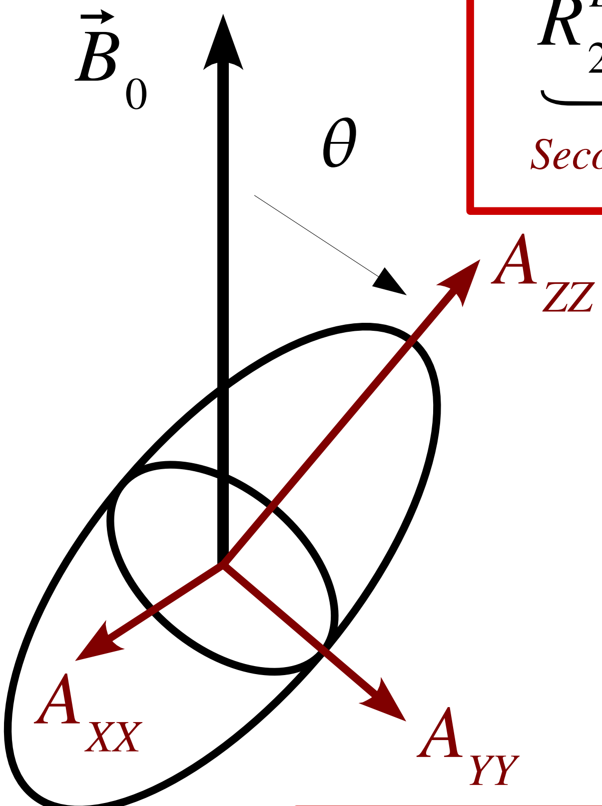
+

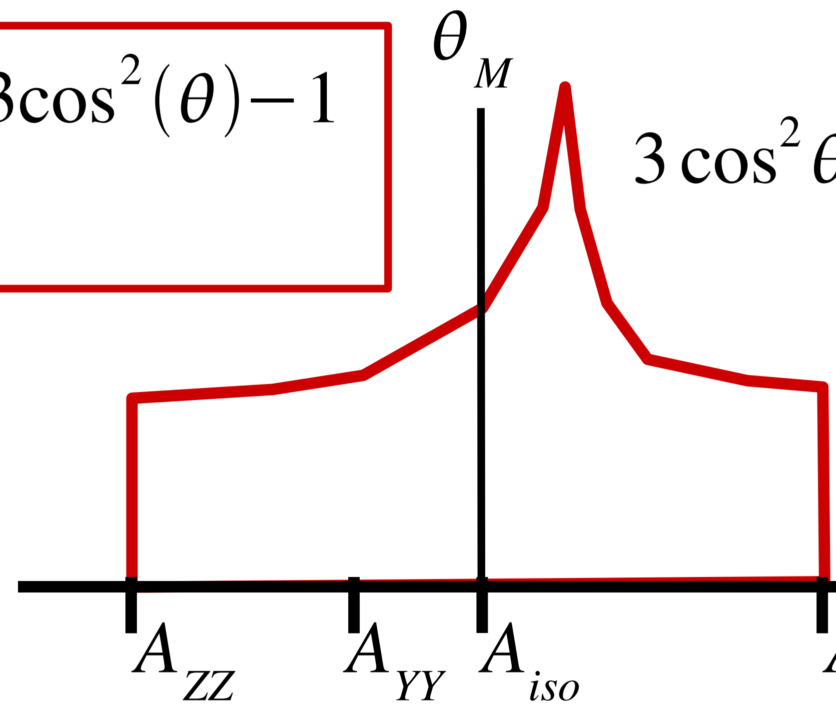
$$\delta_{CSA}, \eta_{CSA}, C_Q, \eta_Q, \left(\alpha_{CSA,Q}, \beta_{CSA,Q}, \gamma_{CSA,Q}\right)$$



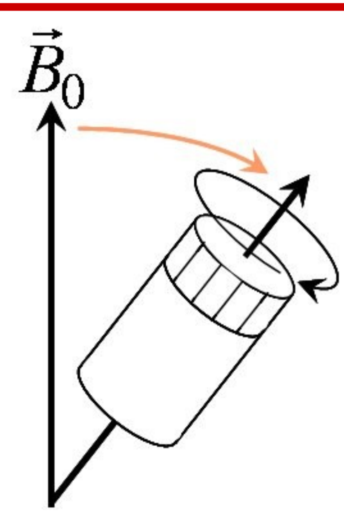
Magic Angle Spinning Sample

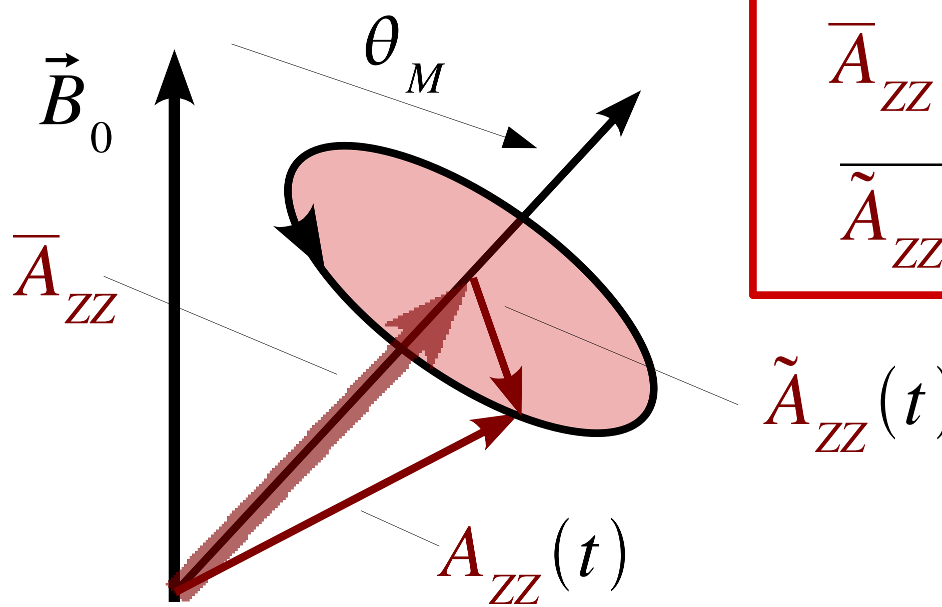
$$\underbrace{R^{D}_{20}(\Omega)}_{\textit{Second Rank}} \propto 3\cos^2(\theta)-1$$





$$3\cos^2\theta_M - 1 = 0$$





$$\overline{A}_{ZZ}(\theta_M)=0$$

$$\overline{\tilde{A}_{ZZ}(t)}=0$$

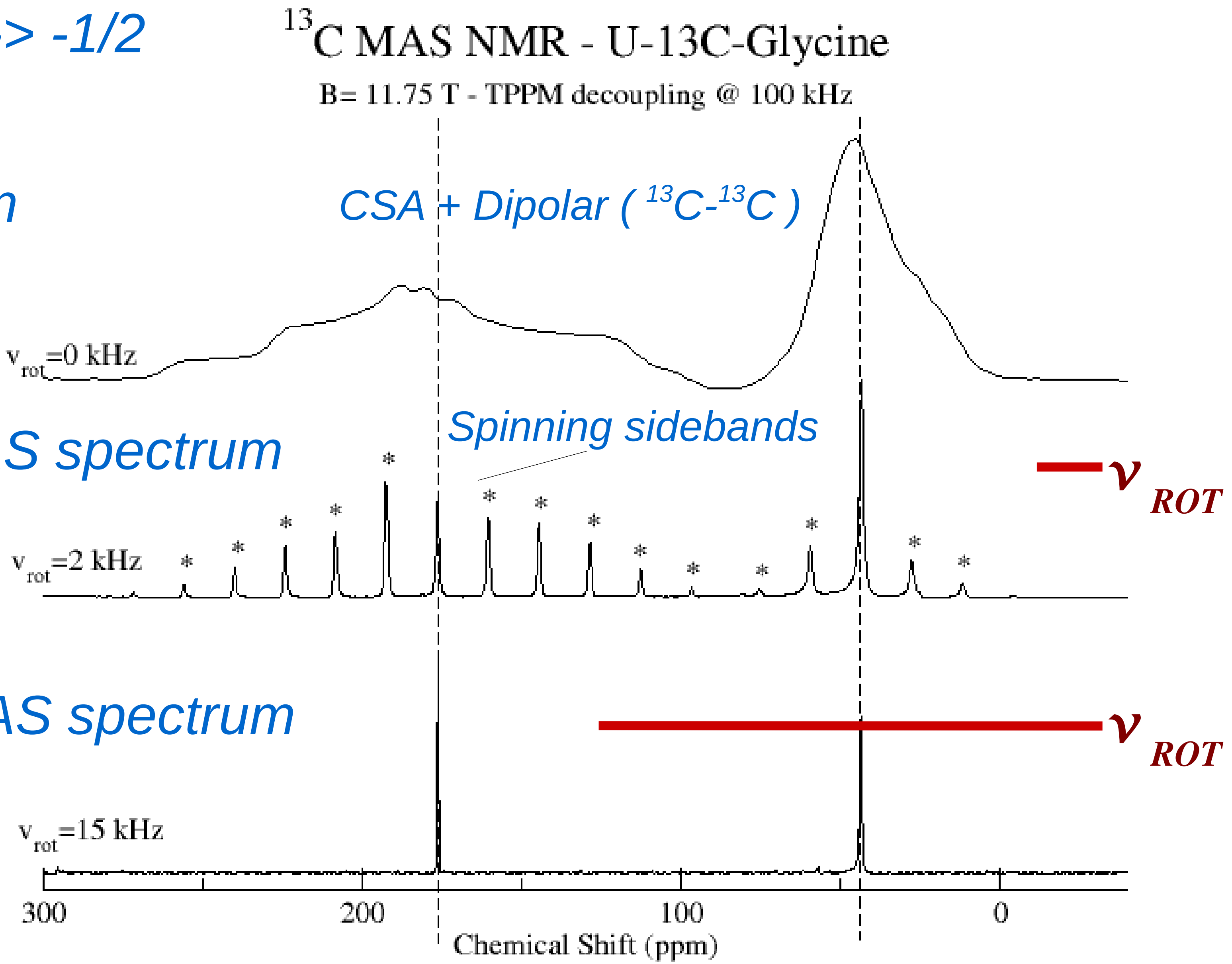
MAS at work $I = 1/2$

+1/2 <-> -1/2

Static spectrum

Low speed MAS spectrum

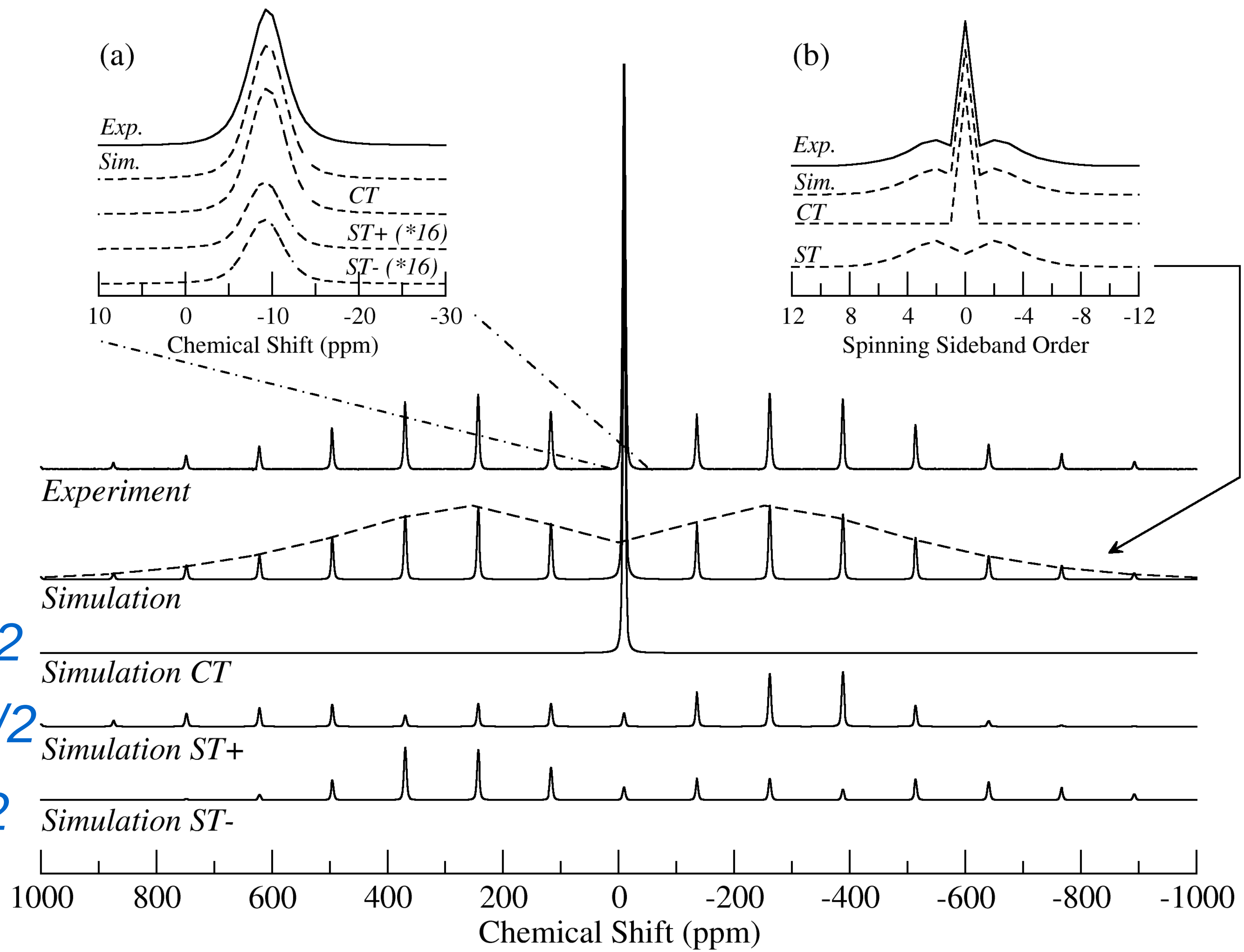
High speed MAS spectrum



Proton decoupling is necessary (sample rotation + spin rotation !)

MAS at work ^{23}Na $I = 3/2$

$NaAlH_4$



+1/2 <-> -1/2

+3/2 <-> +1/2

-3/2 <-> -1/2

$B_0 = 7.05$ T $\nu_{ROT} = 10$ kHz

MAS at work

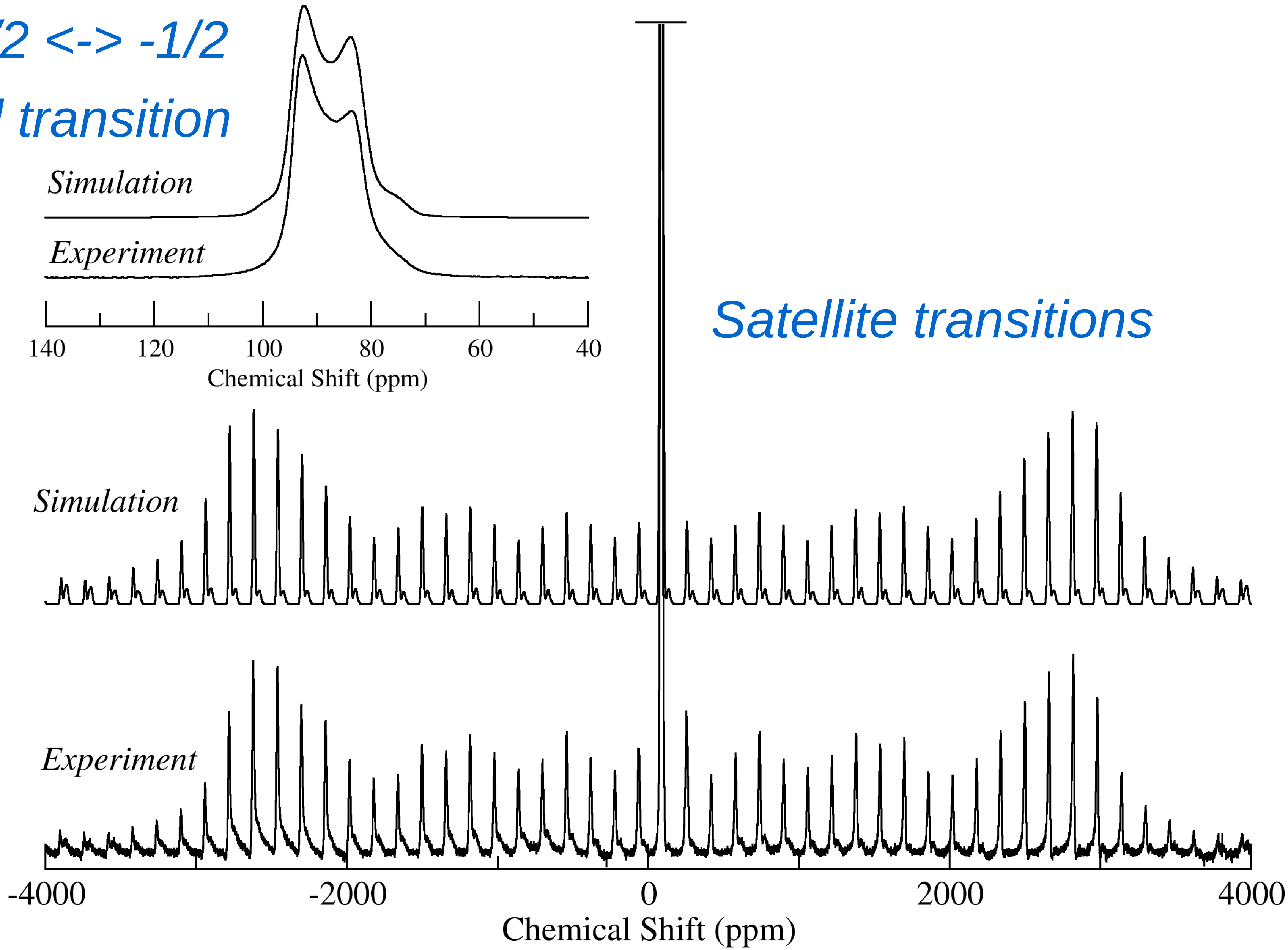
$NaAlH_4$

^{27}Al $I=5/2$

+1/2 <-> -1/2

Central transition

Satellite transitions



$B_0 = 7.05\ T$ $\nu_{ROT}=10\ kHz$

The MAS NMR signal in theory

$$s(t) \propto \sum_m \left| \langle m+1 | I_+ | m \rangle \right|^2 \times \exp\left(-i \int_0^t \omega_{m,m+1}(u)\, du \right)$$

Time-dependent transitions frequencies:

$$\omega_{m,m+1} = \langle m+1 | \hat{H}(t) | m+1 \rangle - \langle m | \hat{H}(t) | m \rangle$$

Euler angles of the PAS in the rotor fixed frame

$$\omega_{m,m+1}(\alpha,\beta,\gamma) = \omega_0(\alpha,\beta) + \sum_{m\neq 0} \omega_m(\alpha,\beta) \exp\{-i m (\omega_{ROT} t + \gamma)\}$$

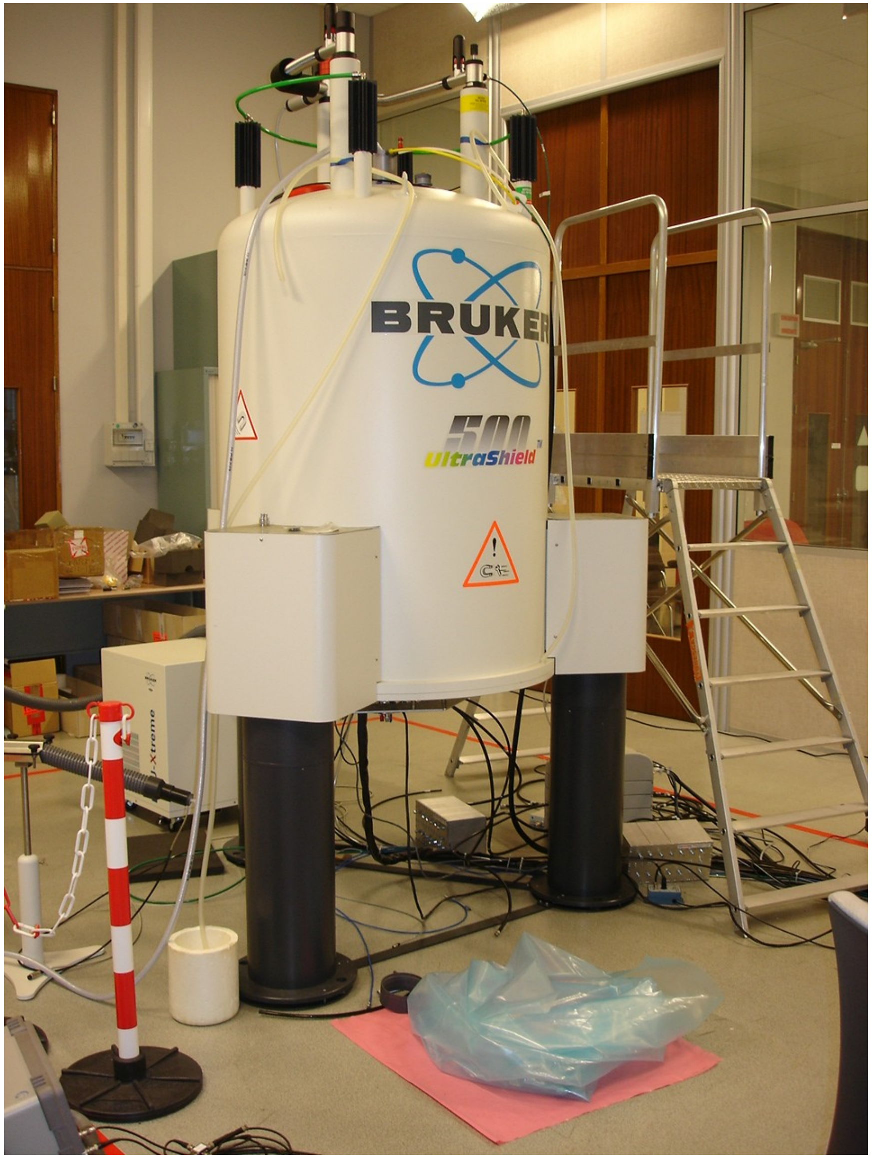
$$\int d\gamma \exp\left\{ -i \int_0^t \omega_{m,m+1}(u)\, du \right\} = e^{-i\omega_0 t(\alpha,\beta)} \times \sum_k \left| I_k(\alpha,\beta) \right|^2 e^{-ik\omega_{ROT} t}$$

$\omega_0(\alpha,\beta)$: *MAS lineshape*

$I_k(\alpha,\beta)$: *spinning sidebands pattern*

The NMR Laboratory

torturing probe...



MAS probe

MAS Rotor

Superconducting magnet

NMR parameters: DFT vs Experiment

Quadrupolar parameters (I>1/2) (MHz) C_Q, η_Q

Isotropic Chemical shift (ppm) δ_{iso}

Chemical shift anisotropy (ppm) δ_{CSA}, η_{CSA}

Relative orientation of CSA PAS in Quad. PAS (Three Euler angles) $\left(\alpha_{CSA,Q}, \beta_{CSA,Q}, \gamma_{CSA,Q}\right)$

Isotropic J couplings (1-3 bonds) $^{(1)}J_{Si-O}$ $^{(2)}J_{Si-O-Si}$

NMR provides methods for measurements of Dipolar interactions (only the structure is needed)