An introduction to Solid State NMR and its Interactions

High Resolution NMR

CECAM Tutorial – September 2009

Calculation of Solid-State NMR Parameters

Using the GIPAW Method

Thibault Charpentier - CEA Saclay

thibault.charpentier@cea.fr

High Resolution NMR

Brownian Motion in Liquids

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

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

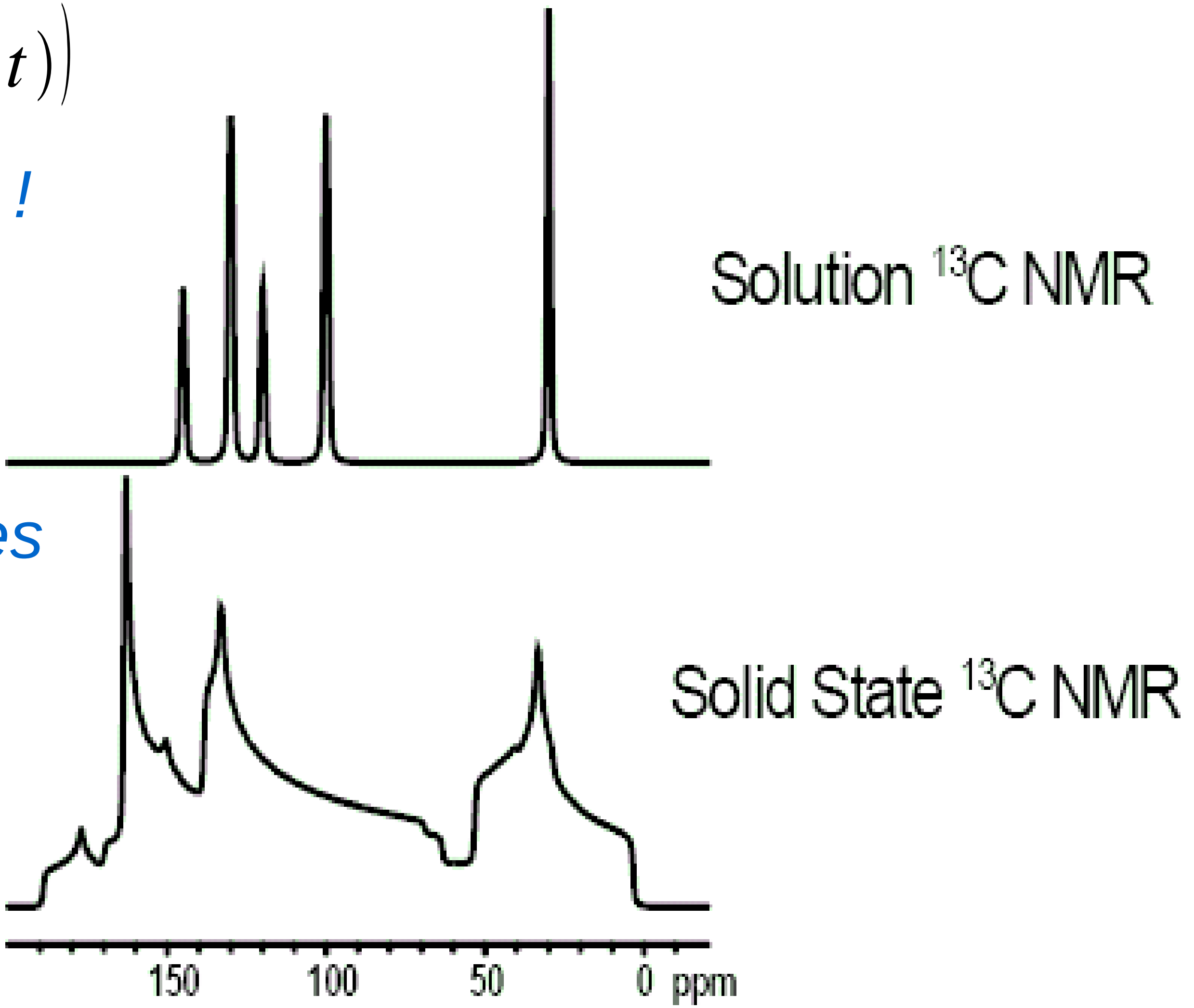
Only isotropic interactions !

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

In a rigid lattice, broad lines

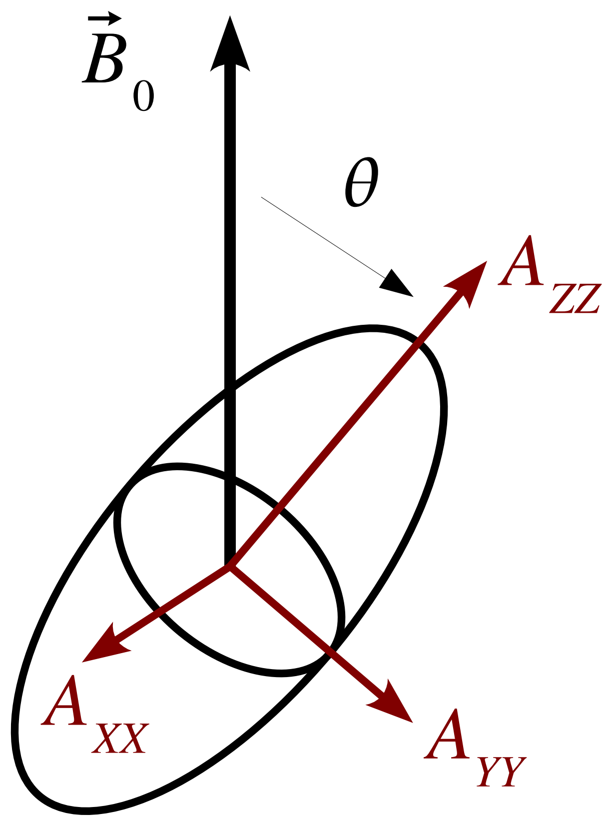
+

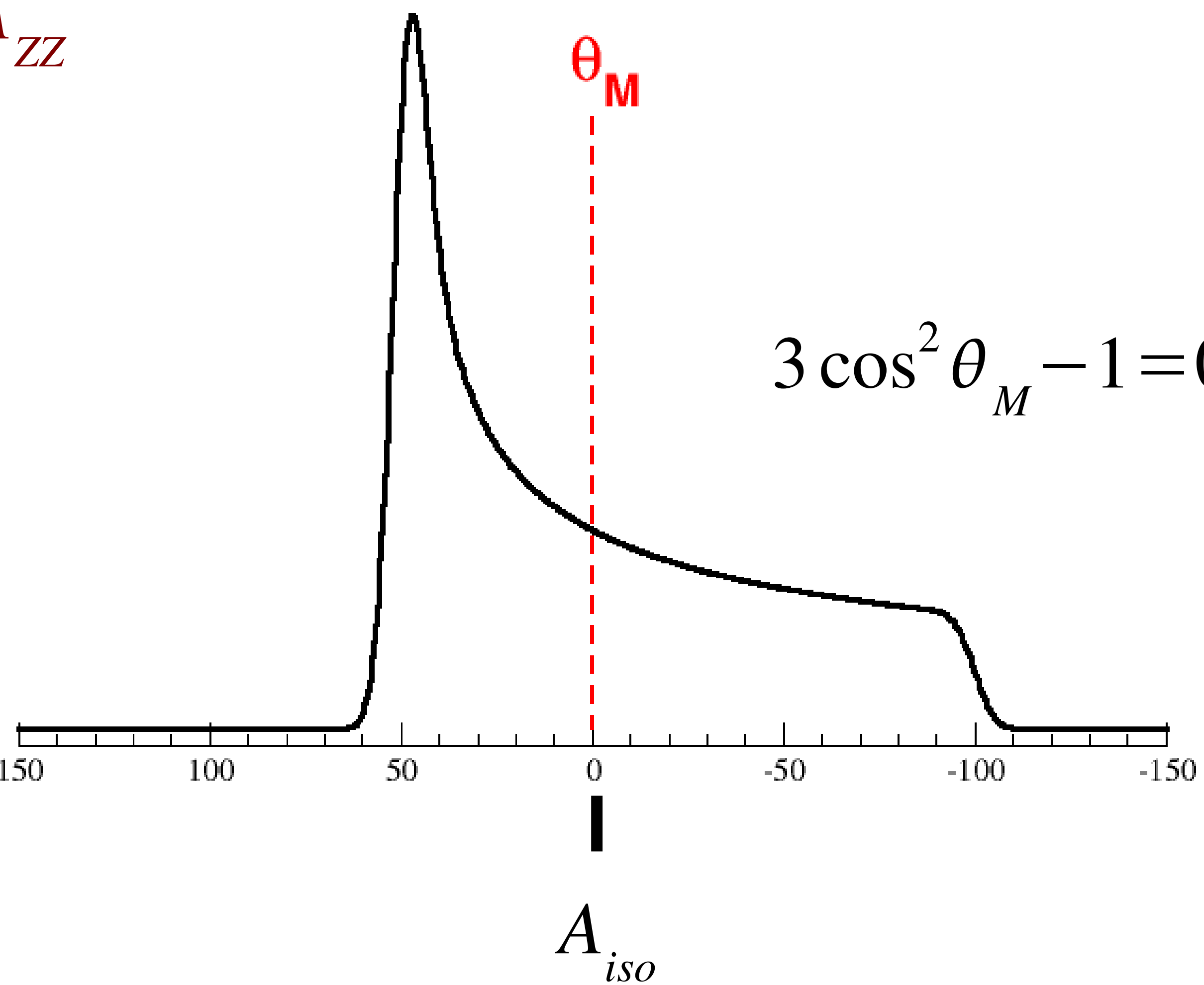
$$\delta_{CSA}, \eta_{CSA}, C_Q, \eta_Q,$$
$$\left(\alpha_{CSA,Q}, \beta_{CSA,Q}, \gamma_{CSA,Q}\right),$$
$$dipolar\ interactions\ldots$$



Magic Angle Sample Spinning

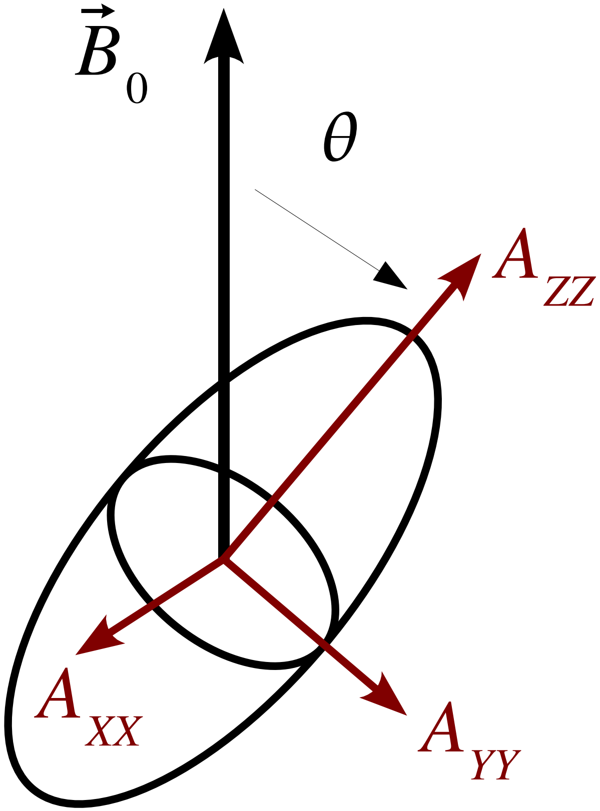
$$\boxed{\underbrace{R^D_{20}(\Omega)}_{\textit{Second Rank}} \propto 3\cos^2(\theta) - 1}$$

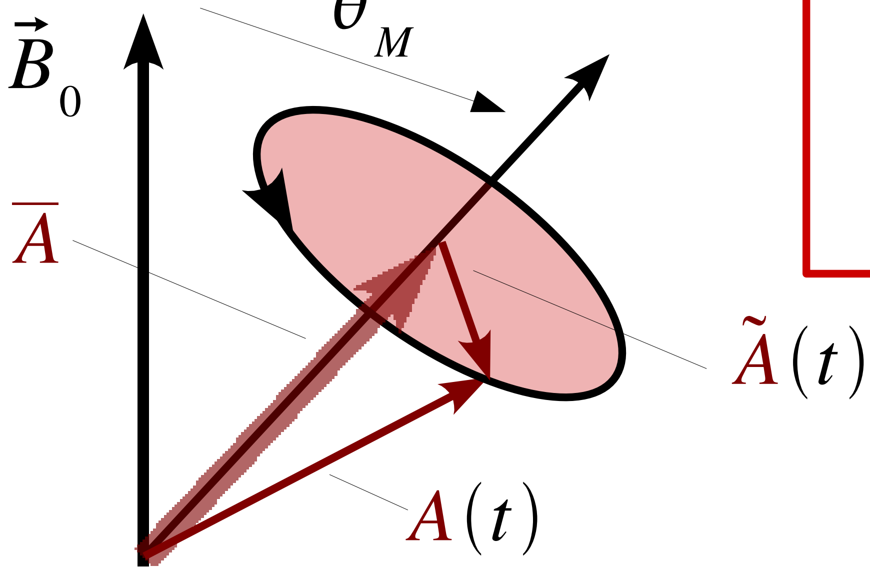


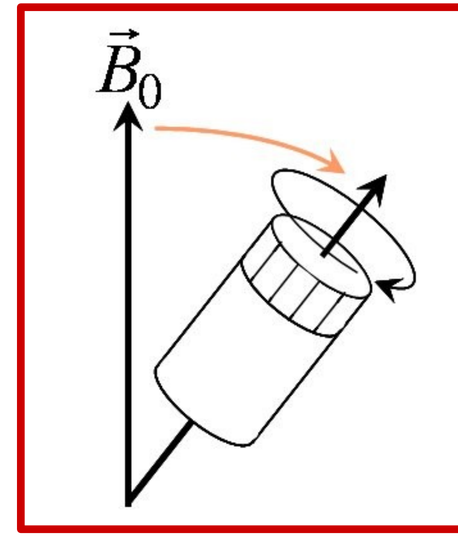


$$3\cos^2\theta_M - 1 = 0$$

Magic Angle Sample Spinning







$\overline{A}(\theta_M)=0 \quad \overline{\tilde{A}(t)}=0$

Like Brownian motion, a *coherent motion* can average NMR interaction to zero

Coherent Averaging

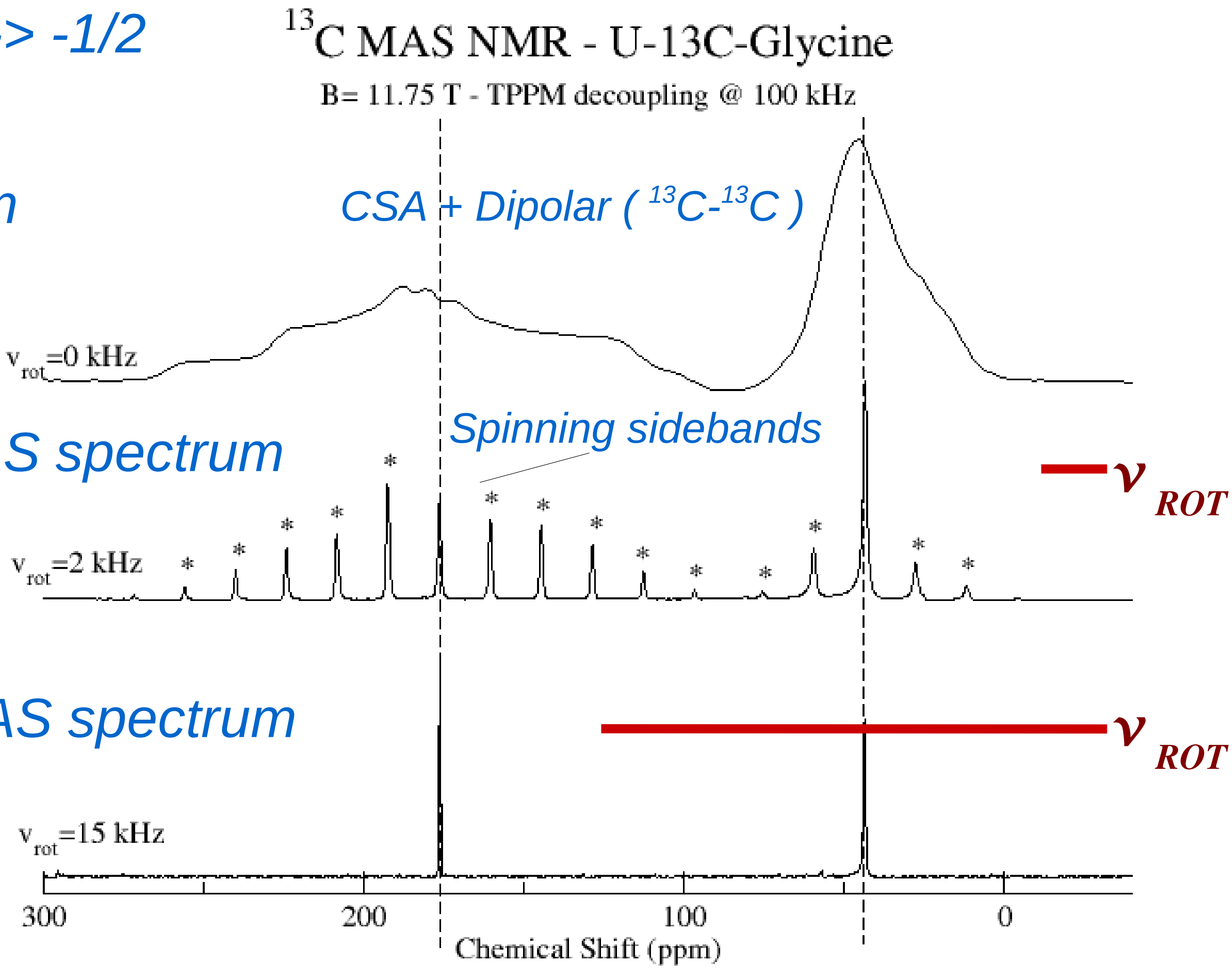
MAS at work $I = 1/2$

+1/2 <-> -1/2

Static spectrum

Low speed MAS spectrum

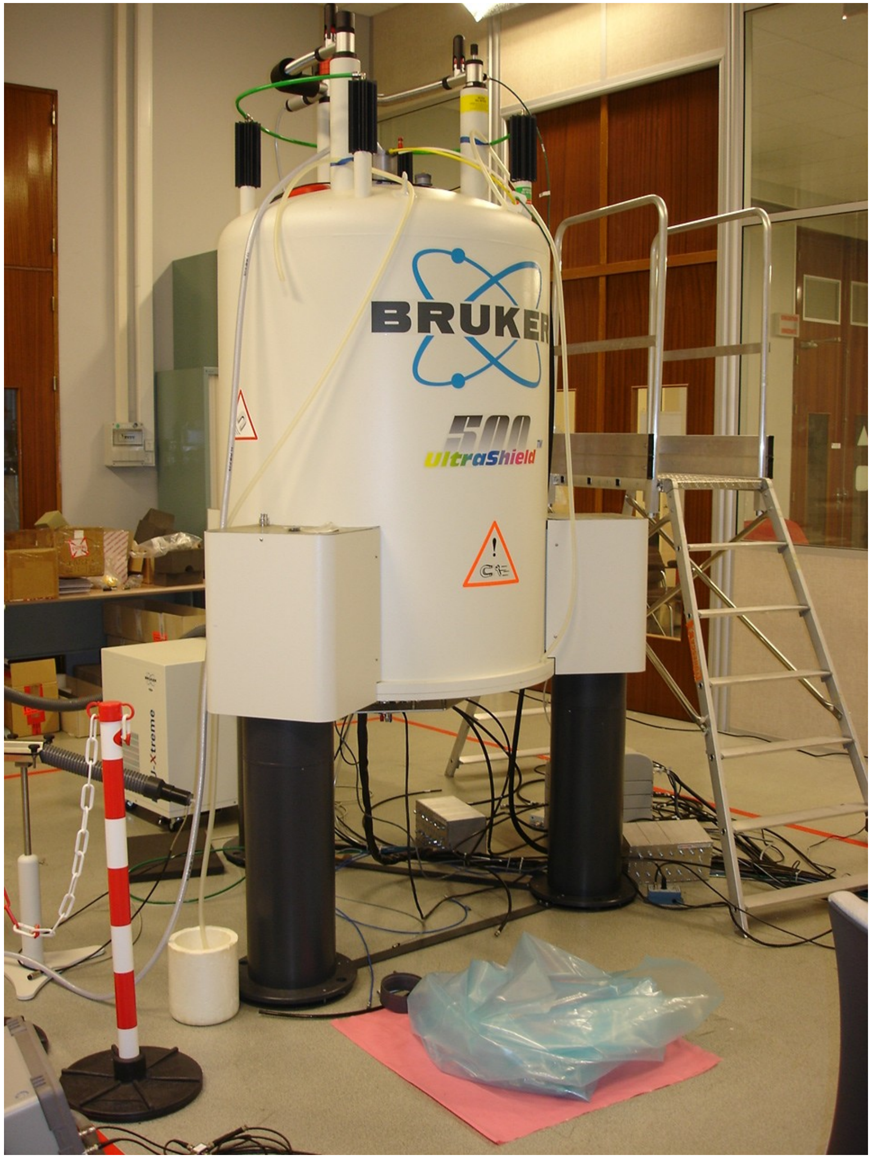
High speed MAS spectrum



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

The NMR Laboratory

torturing probe...



MAS probe

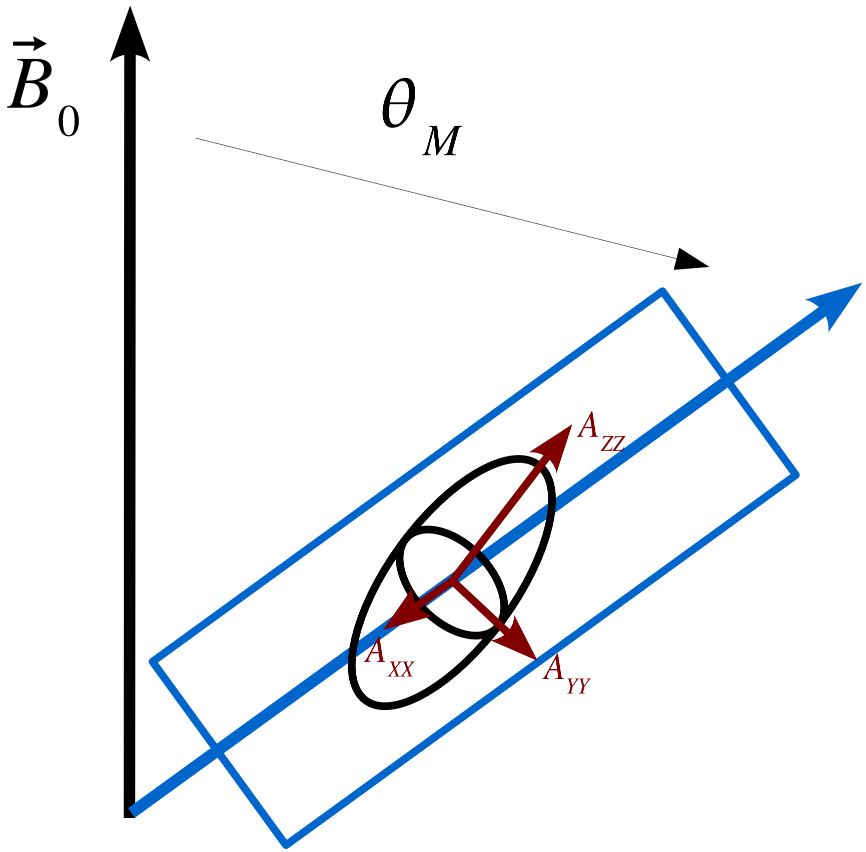
MAS Rotor

Superconducting magnet

The MAS NMR signal in theory

Time dependent Hamiltonian & frequencies

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



PAS

$\downarrow$

$$\left(\alpha_L(t), \beta_L(t), \gamma_L(t)\right)$$

$\downarrow$

LAB

PAS

$\downarrow$

$$\left(\alpha, \beta, \gamma\right)$$

$\downarrow$

ROTOR

$\downarrow$

$$\left(\omega_{ROT} t, \theta_M, 0\right)$$

$\downarrow$

LAB

$$D^k_{m,0}\left(\alpha_L(t), \beta_L(t), 0\right) = \sum_p D^k_{m,p}\left(\alpha, \beta, \gamma\right) \times D^k_{p,0}\left(\omega_{ROT} t, \theta, 0\right)$$

The MAS NMR signal in theory

Time-dependent transitions frequencies:

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

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

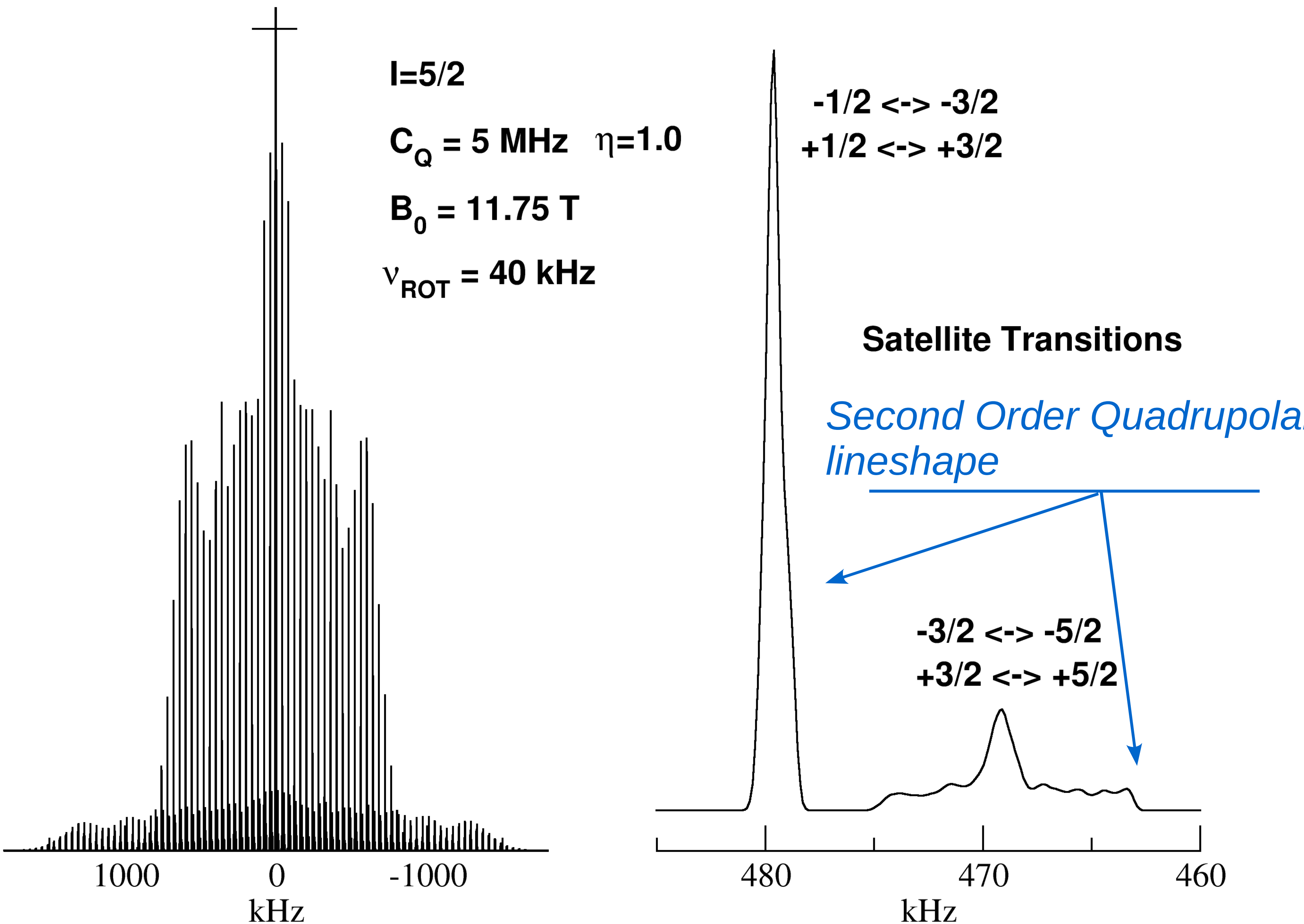
Origin of the spinning sidebands

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

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

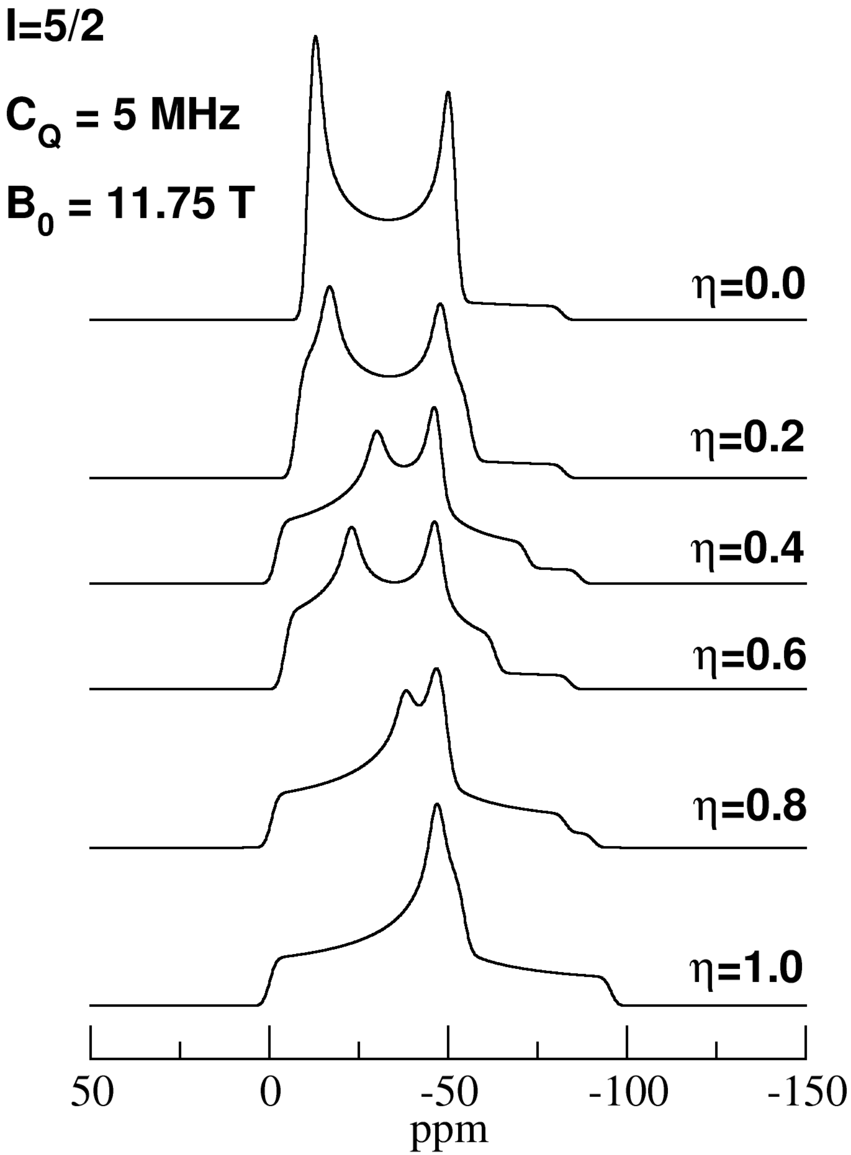
$$\left| I_k(\alpha,\beta) \right|^2:\ positive\ spinning\ sidebands$$

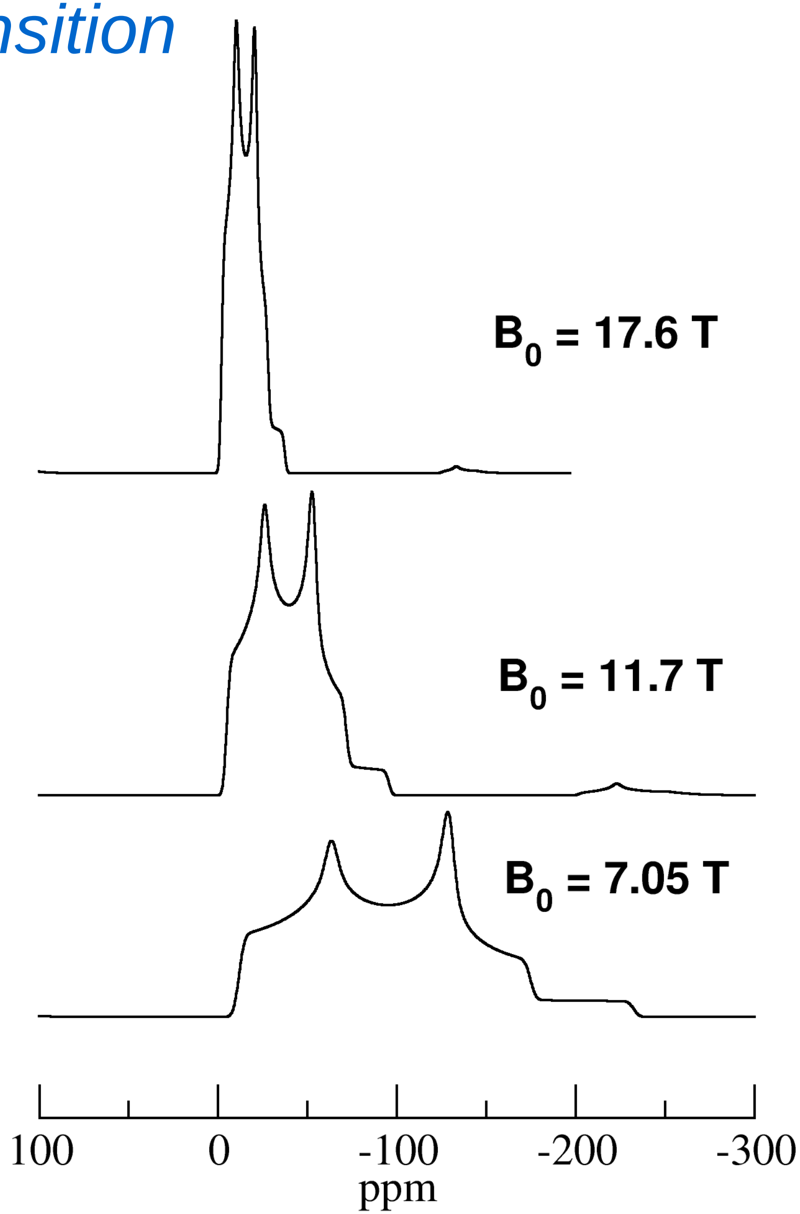
MAS NMR of quadrupolar nuclei



MAS NMR of quadrupolar nuclei

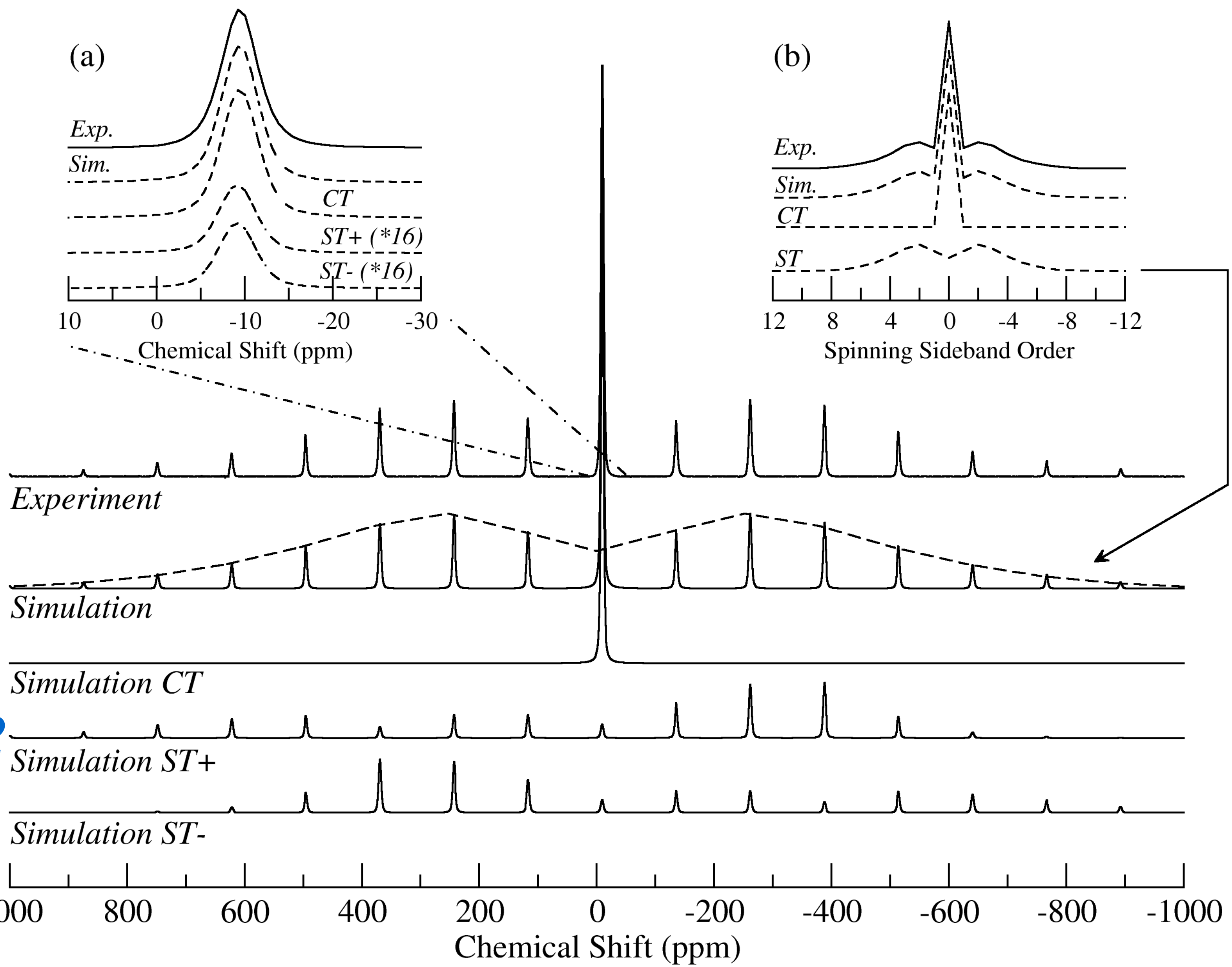
Central transition





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

$NaAlH_4$



+1/2 <-> -1/2

+3/2 <-> +1/2

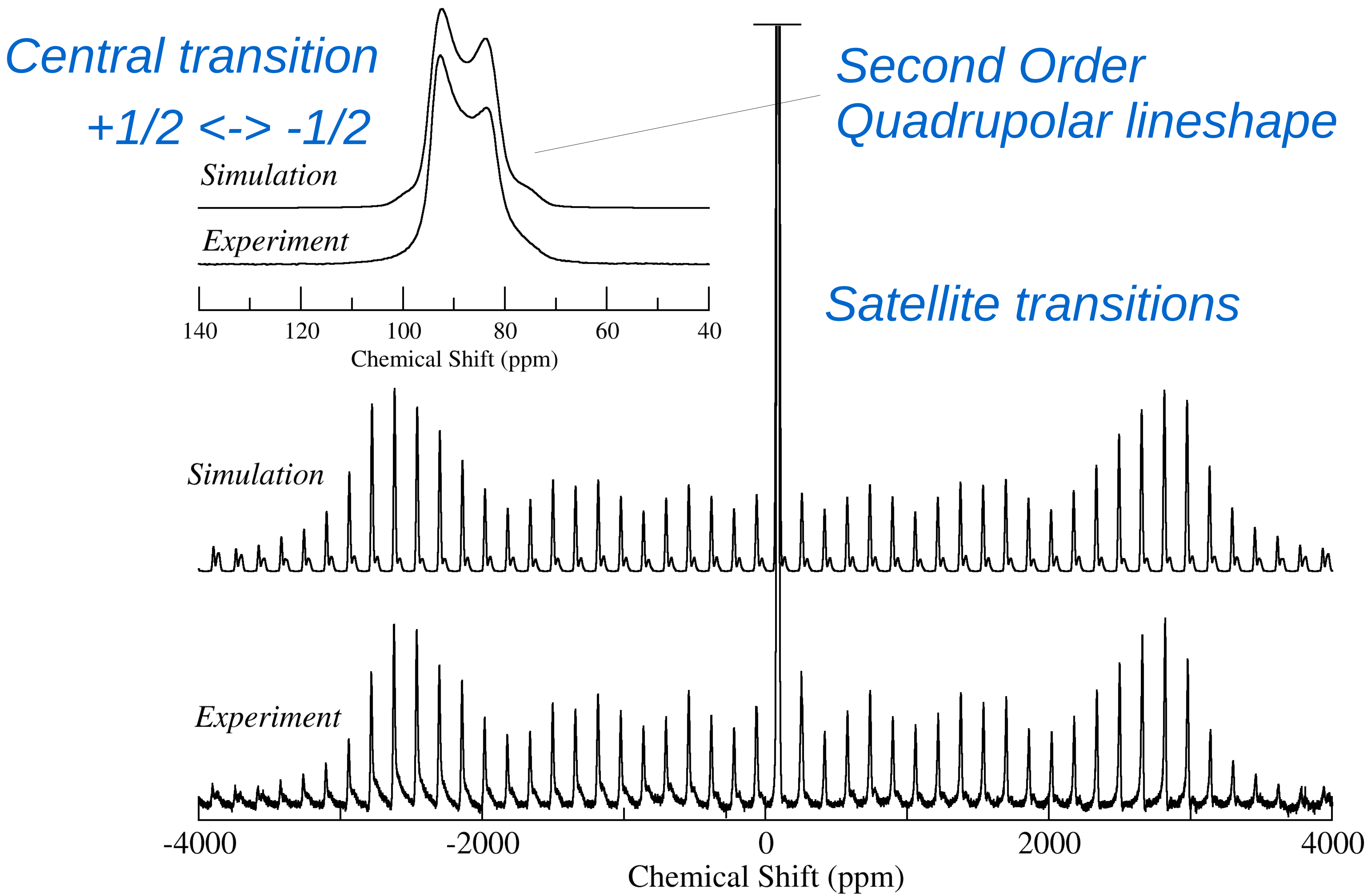
-3/2 <-> -1/2

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

MAS at work

$NaAlH_4$

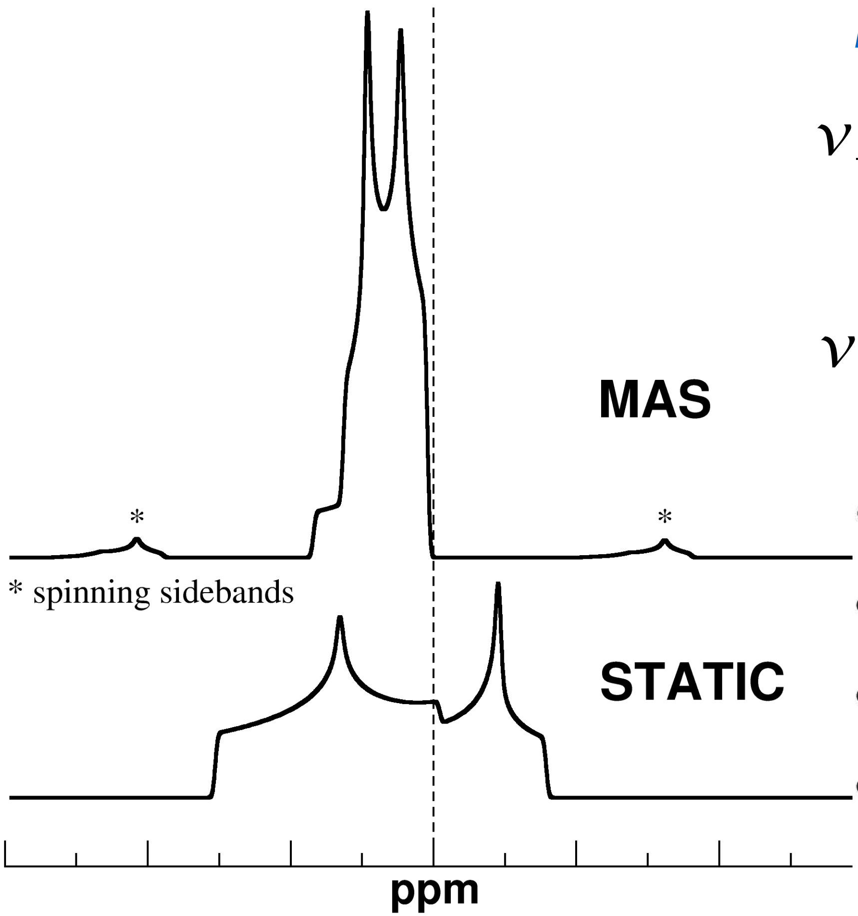
^{27}Al $I=5/2$



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

MAS NMR of quadrupolar nuclei

Central transition for half integer quadrupolar nuclei (I=3/2, 5/2, 7/2, 9/2 ...)

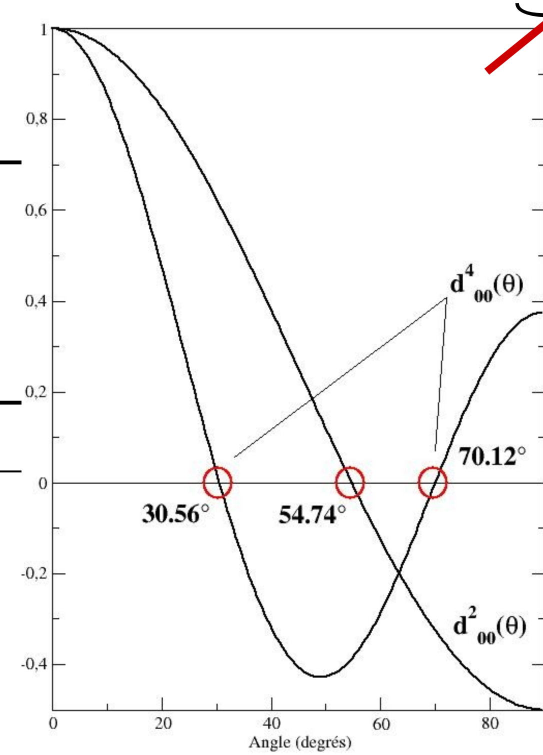


In non-spinning samples

$$\nu_{-1/2,-1/2}(\Omega)=a_0+a_2^S G_2(\Omega)+a_4^S G_4(\Omega)$$

Under MAS

$$\nu_{-1/2,-1/2}(\Omega)=a_0+\cancel{\underbrace{a_2^R G_2(\Omega)}_{=0\ MAS}}+a_4^R G_4(\Omega)$$

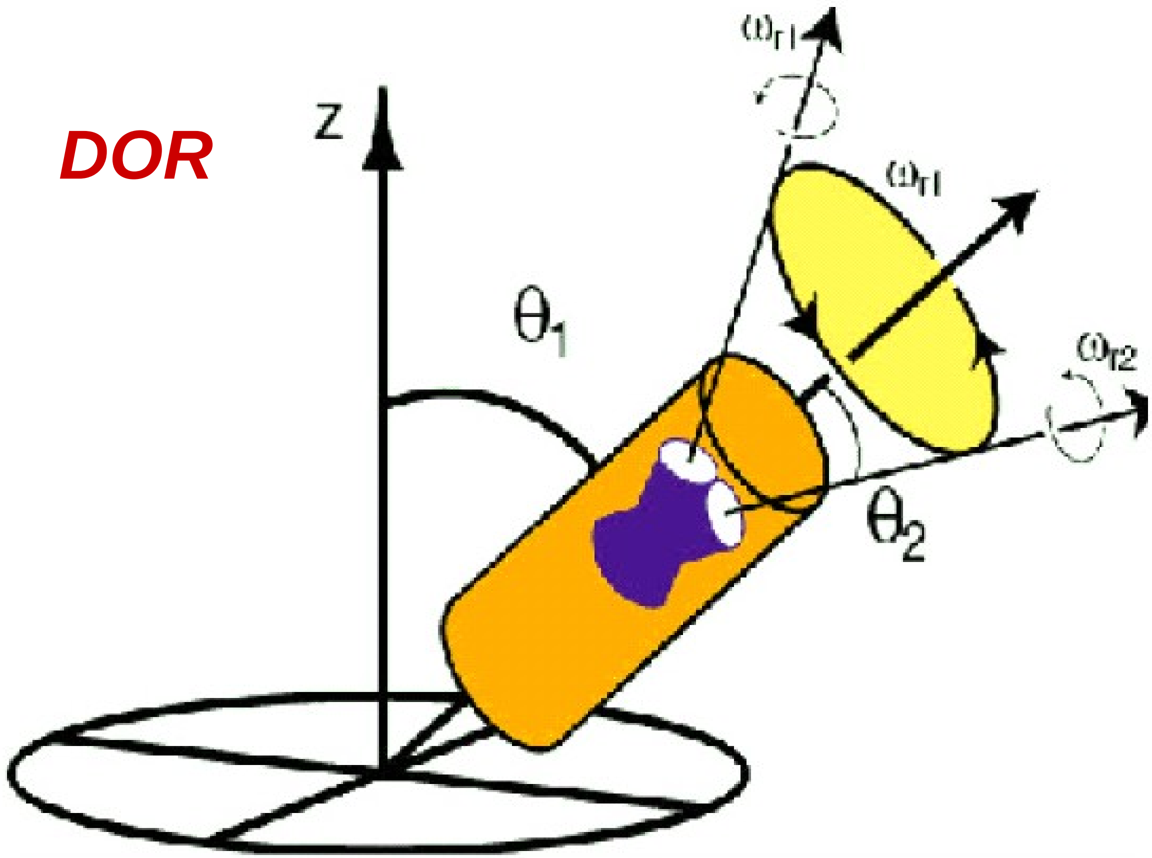


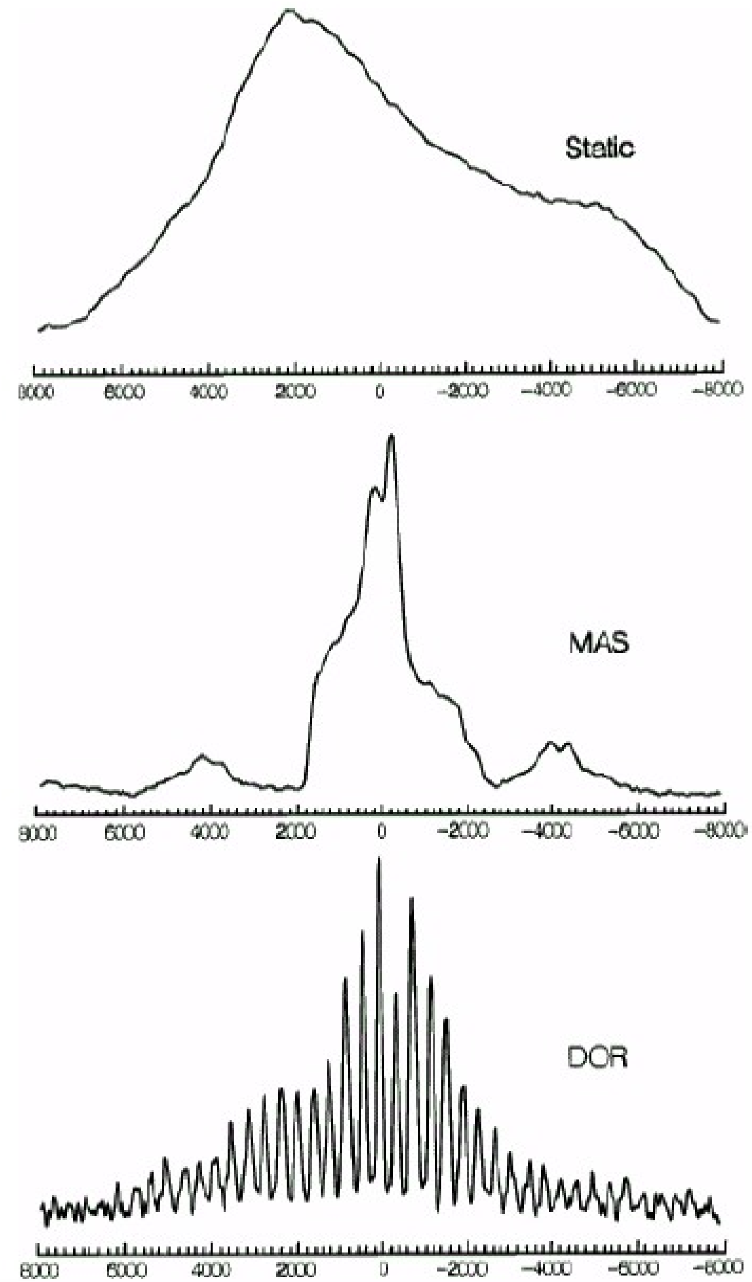
MAS can only average second-rank interaction !

High Resolution MAS NMR of quadrupolar nuclei

Double Rotation

DOR

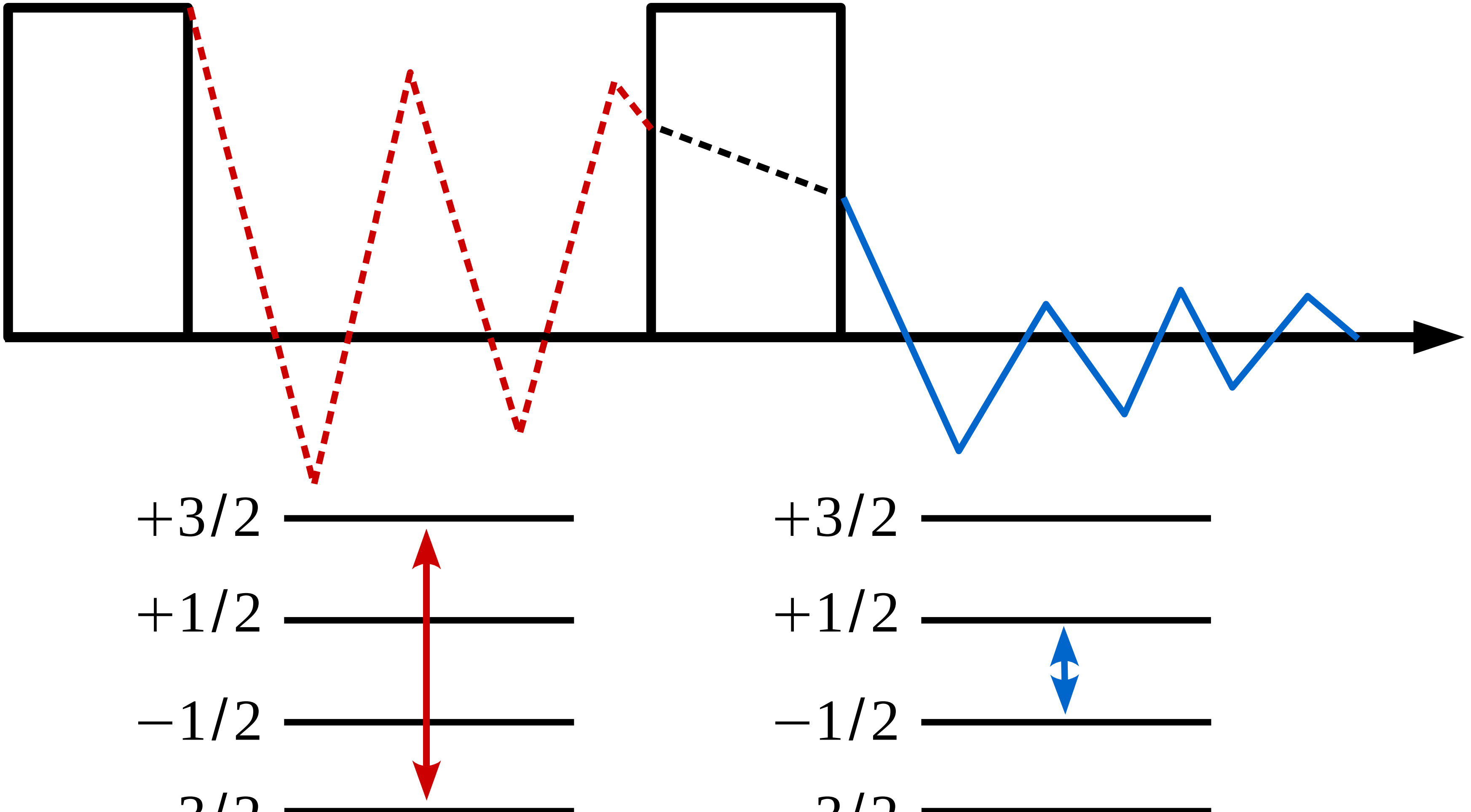




2:1 mixture of Na_2SO_4 and $Na_2C_2O_4$

High Resolution
MAS NMR of quadrupolar nuclei

Multiple Quantum MAS MQMAS - 2D NMR



Indirection detection of a multiple quantum transition

MQMAS (2D NMR) in theory

$$s(t_{1,} t_2) = \exp(-i\nu_{3Q} t_1) \times \exp(-i\nu_{1Q} t_2) = \exp\{-i\phi(t_{1,} t_2)\}$$

Coherence is not lost !

Total accumulated phase of the signal $\phi(t_{1,} t_2) = \nu_{3Q} t_1 + \nu_{1Q} t_2$

$$\nu_{3Q} t_1 = a_0(3Q) t_1 + \boxed{a_4(3Q) G_4(\Omega) t1}$$

$$\nu_{1Q} t_2 = a_0(1Q) t_2 + \boxed{a_4(1Q) G_4(\Omega) t2}$$

$$a_4(3Q) t_1 + a_4(1Q) t_2 = 0$$

Cancellation of the anisotropic contribution: refocusing

$$s(t_{1,} t_2) \xrightarrow{\text{2D FT}} s(\nu_{1,} \nu_2)$$

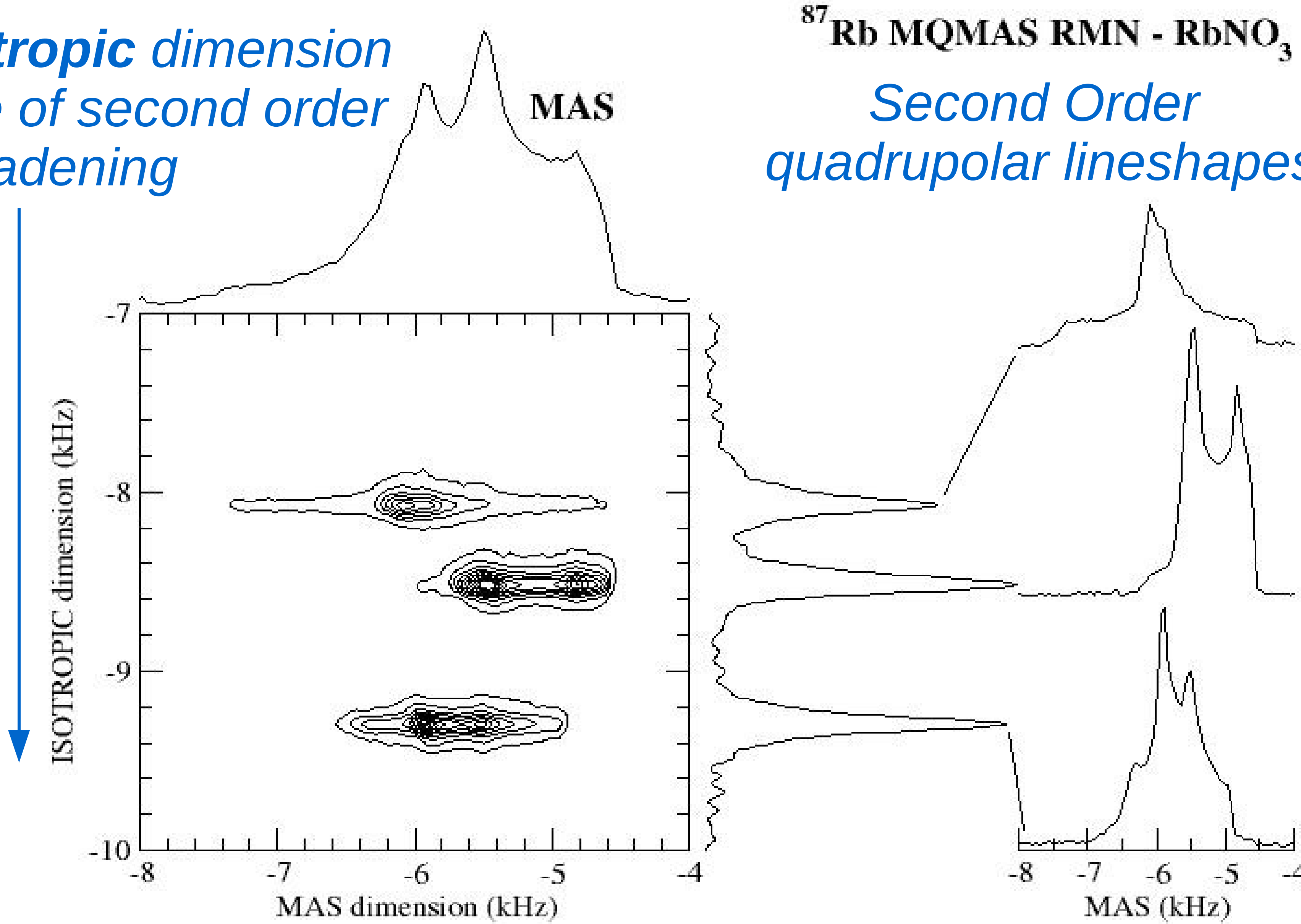
2D FID **2D Spectrum**

MQMAS at work

^{87}Rb $I = 3/2$

Isotropic *dimension free of second order broadening*

Second Order quadrupolar lineshapes

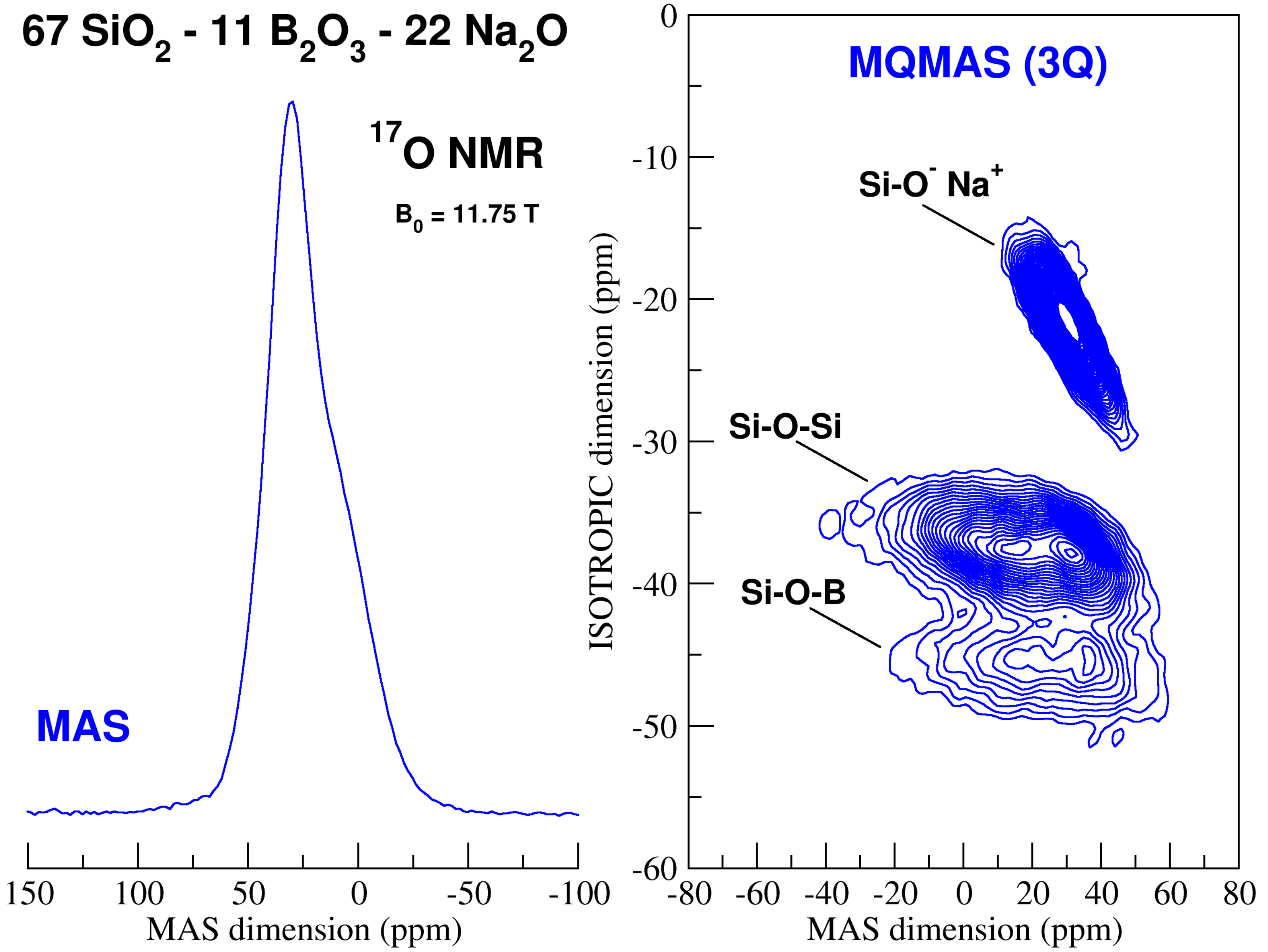


MAS dimension

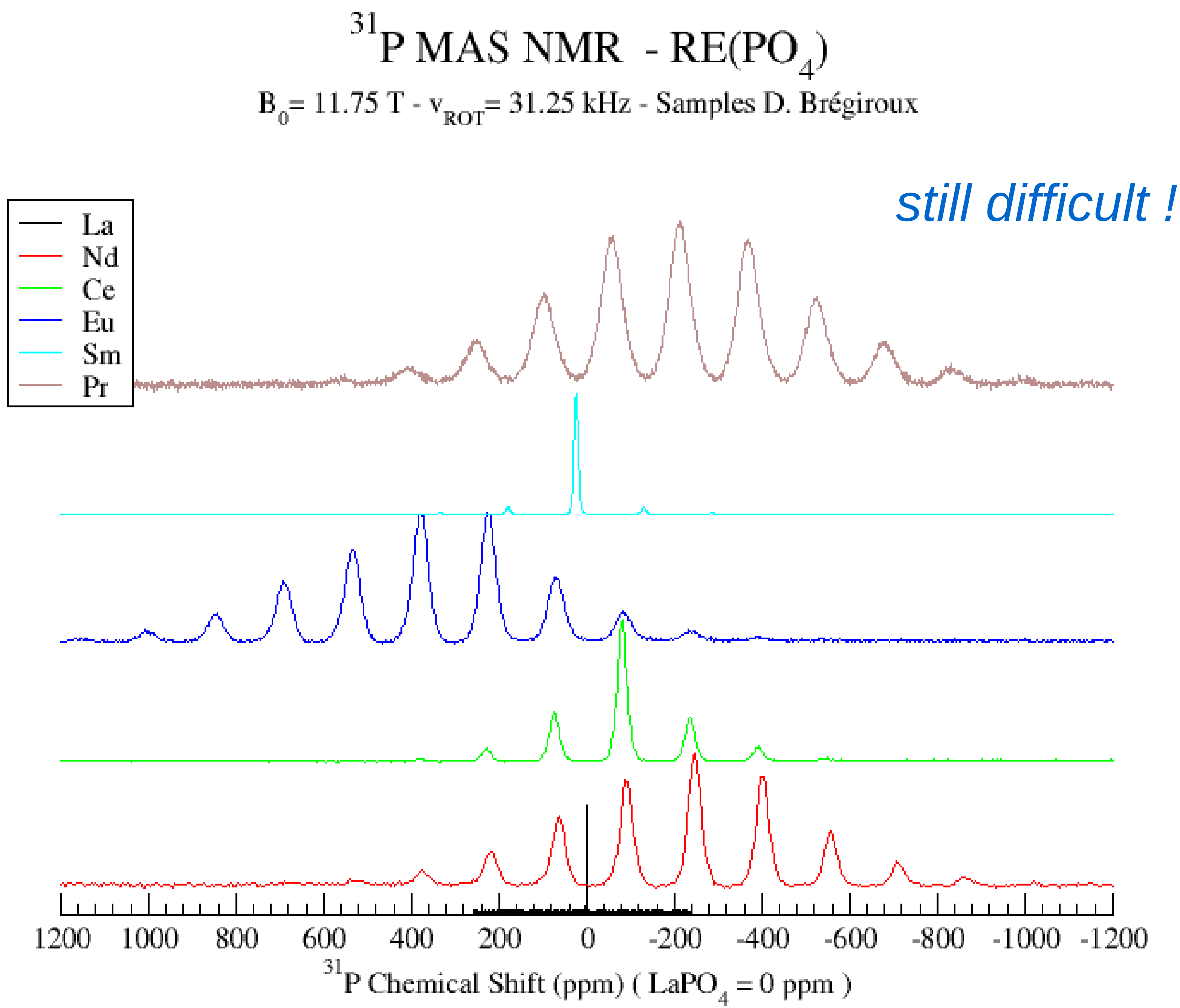
MQMAS at work

^{17}O $I = 5/2$

Amorphous materials



NMR of paramagnetic materials



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}

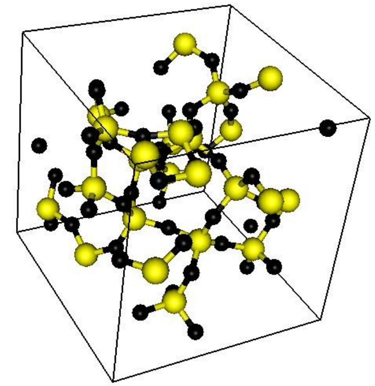
Relative orientation
of CSA PAS in Quad. PAS
(Three Euler angles) $\left(\alpha_{CSA,Q}, \beta_{CSA,Q}, \gamma_{CSA,Q}\right)$

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

Many 1D-2D NMR approches

STATIC, MAS, MQMAS, STMAS, DOR, DAS, MQDOR...

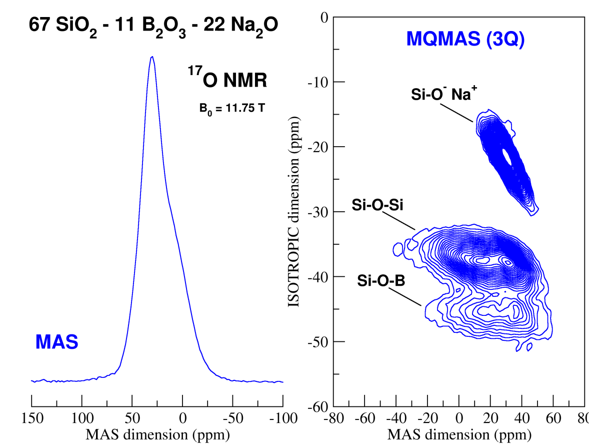
DFT Calculations



Structure

NMR Hamiltonian

NMR Simulations



DFT vs Experiments

Many 1D-2D NMR approches

STATIC, MAS, MQMAS, STMAS, DOR, DAS, MQDOR...