



3rd International Training School on solid-state NMR

Decoupling of the homonuclear dipole-dipole interactions

by

Shimon Vega

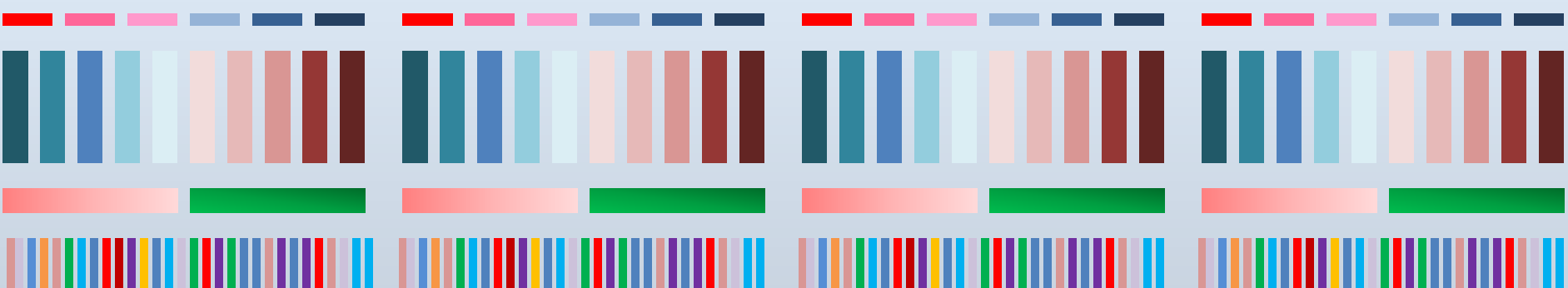
Weizmann Institute of Science

Rehovot, Israel

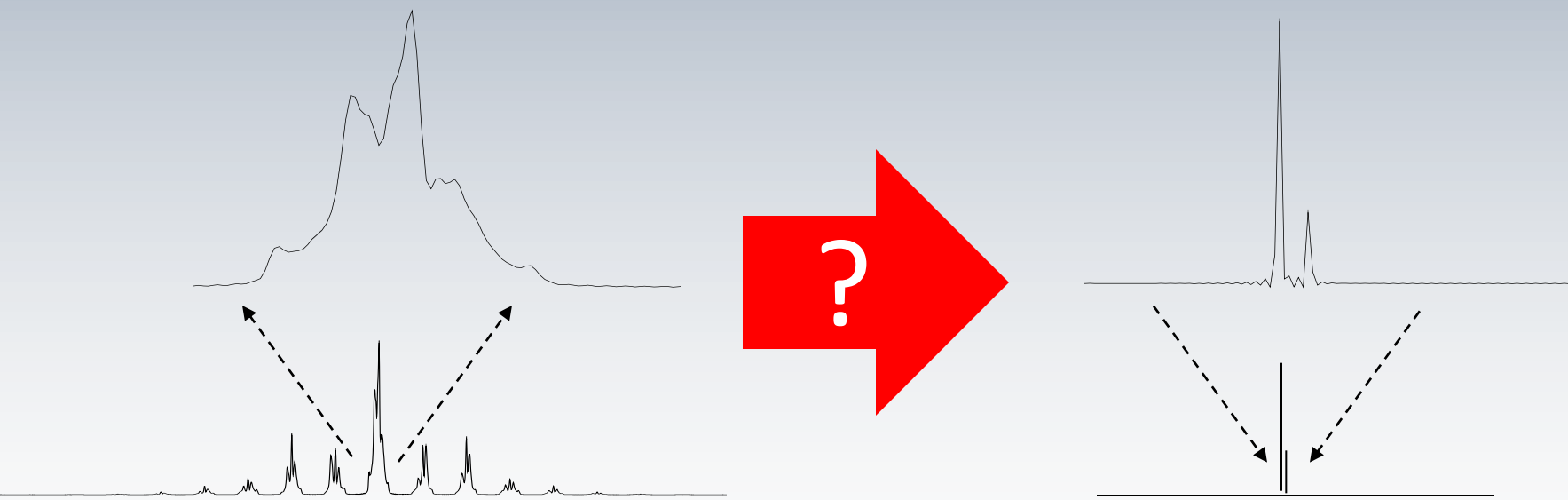


at the solid state NMR School
in Leiden, 2010





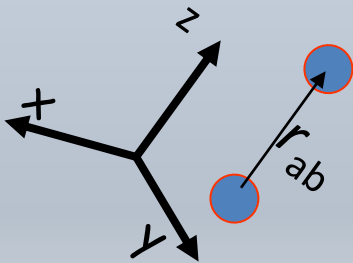
the objective is
to eliminate the influence of the strong dipole-dipole interactions
on the linewidths of the protons in a solid



$$H_D^{PAS} = \frac{\mu_0 \gamma_i \gamma_j}{4\pi(r_{ij})^3} (3(\bar{I}_a \cdot \bar{e}_{ab})(\bar{I}_b \cdot \bar{e}_{ab}) - \bar{I}_a \cdot \bar{I}_b) = \frac{\mu_0 \gamma_i \gamma_j}{4\pi(r_{ab})^3} (3I_{za}I_{zb} - \bar{I}_a \cdot \bar{I}_b)$$

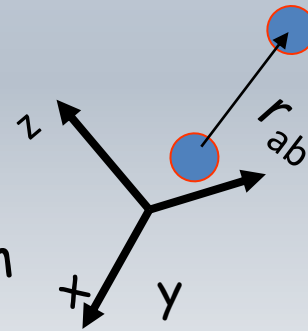
$$= A_{0,ij}^{(2)} T_{0ij}^{(2)}$$

Principle Axis System



$$A_{0,ij}^{(2)PAS} = \frac{\mu_0 \gamma_i \gamma_j}{2\pi(r_{ij})^3}$$

Any ROTOR Axis System



$$H_D = \sum_{m=-2,2} (-)^m A_{-m,ab}^{(2)}(\alpha_{ab}, \beta_{ab}, \gamma_{ab}) \times T_{m,ab}^{(2)}$$

$\sum_{a < b}$ are left out

Euler angles for frame transformations

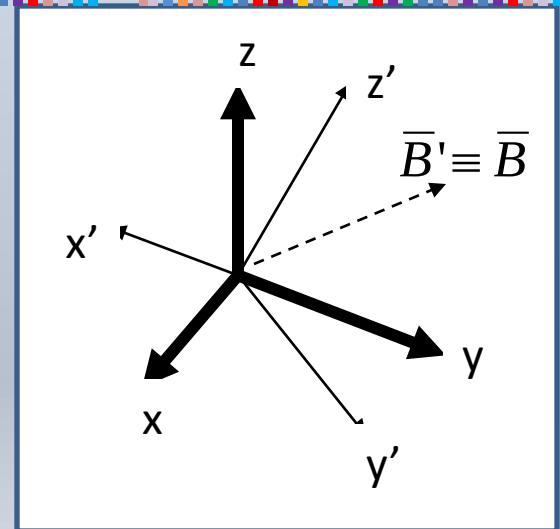
Rotation of a coordinate system

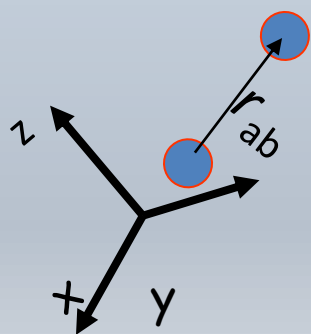
A rotation of a coordinate system is defined by three Euler angles:

- (i) a γ° rotation around the z-axis with $0 \leq \gamma < 360^\circ$
- (ii) a β° rotation around the y-axis with $0 \leq \beta \leq 180^\circ$
- (iii) a α° rotation around the z-axis with $0 \leq \alpha < 360^\circ$.

or the same

- (i) a α° rotation around z resulting in (x_1, y_1, z_1) with $z_1 = z$
- (ii) a β° rotation around y_1 resulting in (x_2, y_2, z_2) with $y_2 = y_1$
- (iii) a γ° rotation around z_2 resulting in (x', y', z') with $z' = z_2$





$$T_0^1 = I_{za}$$

$$T_{+1}^1 = I_a^+$$

$$T_{-1}^1 = I_a^-$$

$$T_0^2 = \frac{1}{2} (3I_{za}I_{zb} - \bar{I}_a \cdot \bar{I}_b)$$

$$T_{\pm 1}^2 = \frac{\mp 1}{2} (I_{za}[I_b^{\pm}] + [I_a^{\pm}]I_{zb})$$

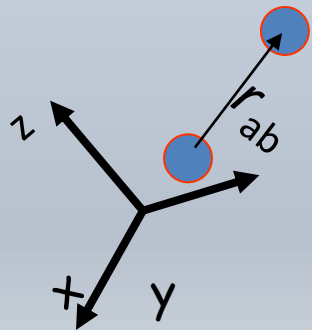
$$T_{\pm 2}^2 = \frac{1}{2} [I_a^{\pm}][I_b^{\pm}]$$

Irreducible second rank tensor components

$$H_D^{ROT} = \sum_{m=-2,2} (-)^m A_{-m,ab}^{(2)ROT}(\alpha, \beta, \gamma) \times T_{m,ab}^{(2)}$$

$$d_{m,n}^{(2)}(\beta)$$

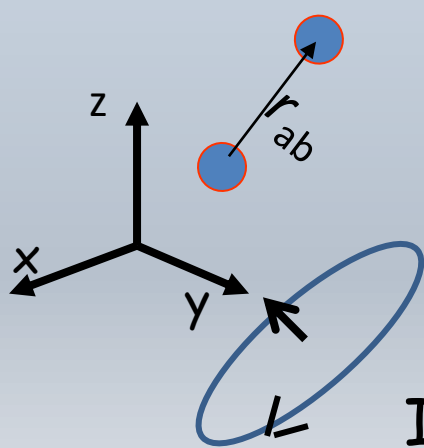
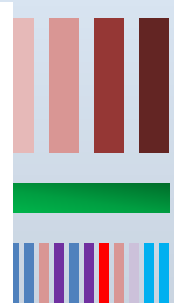
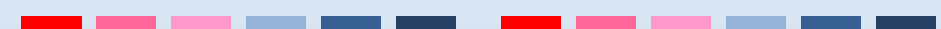
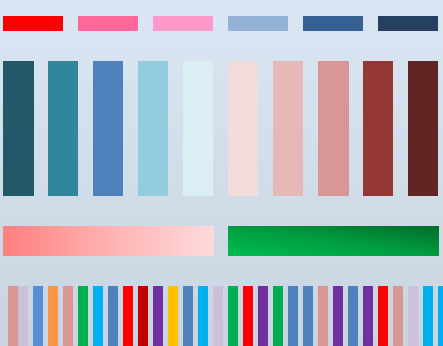
$\begin{smallmatrix} n \\ m \end{smallmatrix}$	2	1	0	-1	-2
2	$\cos^+(\beta/2)$	$-\frac{1}{2}(1 + \cos\beta)\sin\beta$	$\sqrt{3/8}\sin^2\beta$	$\frac{1}{2}(\cos\beta - 1)\sin\beta$	$\sin^+(\beta/2)$
1	$\frac{1}{2}\sin\beta(\cos\beta + 1)$	$\cos^2\beta - \frac{1}{2}(1 - \cos\beta)$	$-\sqrt{3/2}\sin\beta\cos\beta$	$\frac{1}{2}(1 + \cos\beta) - \cos^2\beta$	$\frac{1}{2}\sin\beta(\cos\beta - 1)$
0	$\sqrt{3/8}\sin^2\beta$	$\sqrt{3/8}\sin(2\beta)$	$\frac{1}{2}(3\cos^2\beta - 1)$	$-\sqrt{3/8}\sin(2\beta)$	$\sqrt{3/8}\sin^2\beta$
-1	$-\frac{1}{2}(\cos\beta - 1)\sin\beta$	$\frac{1}{2}(1 + \cos\beta) - \cos^2\beta$	$\sqrt{3/2}\sin\beta\cos\beta$	$\cos^2\beta - \frac{1}{2}(1 - \cos\beta)$	$-\frac{1}{2}(1 + \cos\beta)\sin\beta$
-2	$\sin^+(\beta/2)$	$-\frac{1}{2}(\cos\beta - 1)\sin\beta$	$\sqrt{3/8}\sin^2\beta$	$\frac{1}{2}(1 + \cos\beta)\sin\beta$	$\cos^+(\beta/2)$



Irreducible second rank tensor components

$$A_m^{(2)ROT}(0, \beta, \gamma) = A_0^{(2)PAS} d_{0m}^{(2)}(\beta) e^{-im\gamma}$$

$$H_D^{ROT} = \sum_{m=-2,2} (-)^m A_{-m,ab}^{(2)ROT}(\alpha_{ab}, \beta_{ab}, \gamma_{ab}) \times T_{m,ab}^{(2)}$$



$$d_{m,n}^{(2)}(\beta)$$

$\begin{smallmatrix} n \\ m \end{smallmatrix}$	2	1	0	-1	-2
2	$\cos^4(\beta/2)$	$-\frac{1}{2}(1 + \cos\beta)\sin\beta$	$\sqrt{3/8}\sin^2\beta$	$\frac{1}{2}(\cos\beta - 1)\sin\beta$	$\sin^4(\beta/2)$
1	$\frac{1}{2}\sin\beta(\cos\beta + 1)$	$\cos^2\beta - \frac{1}{2}(1 - \cos\beta)$	$-\sqrt{3/2}\sin\beta\cos\beta$	$\frac{1}{2}(1 + \cos\beta) - \cos^2\beta$	$\frac{1}{2}\sin\beta(\cos\beta - 1)$
0	$\sqrt{3/8}\sin^2\beta$	$\sqrt{3/8}\sin(2\beta)$	$\frac{1}{2}(3\cos^2\beta - 1)$	$-\sqrt{3/8}\sin(2\beta)$	$\sqrt{3/8}\sin^2\beta$
-1	$-\frac{1}{2}(\cos\beta - 1)\sin\beta$	$\frac{1}{2}(1 + \cos\beta) - \cos^2\beta$	$\sqrt{3/2}\sin\beta\cos\beta$	$\cos^2\beta - \frac{1}{2}(1 - \cos\beta)$	$-\frac{1}{2}(1 + \cos\beta)\sin\beta$
-2	$\sin^4(\beta/2)$	$-\frac{1}{2}(\cos\beta - 1)\sin\beta$	$\sqrt{3/8}\sin^2\beta$	$\frac{1}{2}(1 + \cos\beta)\sin\beta$	$\cos^4(\beta/2)$

Irreducible second rank tensor components

$$A_{m,ab}^{(2)LAB}(0, \beta_{ab}, \gamma_{ab}, -\omega_r t, \theta_M, 0) = \sum_{m'=-2}^2 A_{0,ab}^{(2)PAS} d_{0m'}^{(2)}(\beta_{ab}) e^{-im'\gamma_{ab}} e^{im'\omega_r t} d_{m'm}(\theta_M)$$

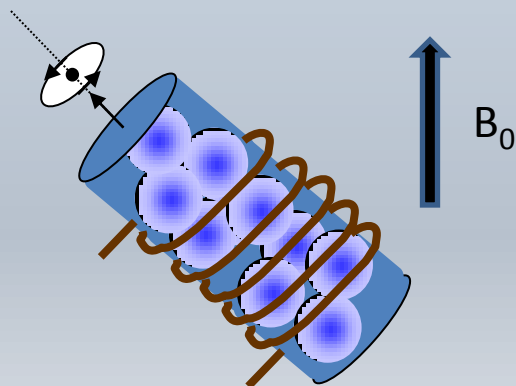
$$H_D^{LAB}(t) = \sum_{m=-2,2} (-)^m A_{-m,ab}^{(2)LAB}(\alpha_{ab}, \beta_{ab}, \gamma_{ab}; -\omega_r t, \theta_M, 0) \times T_{m,ab}^{(2)}$$

Abraqam's definitions

$$H = A + B + C + D + E + F$$

$$A + B \equiv A_0^{(2)} T_0^{(2)} \quad C \equiv -A_{-1}^{(2)} T_1^{(2)} \quad D \equiv -A_1^{(2)} T_{-1}^{(2)}$$

$$E \equiv -A_{-2}^{(2)} T_2^{(2)} \quad F \equiv -A_2^{(2)} T_{-2}^{(2)}$$

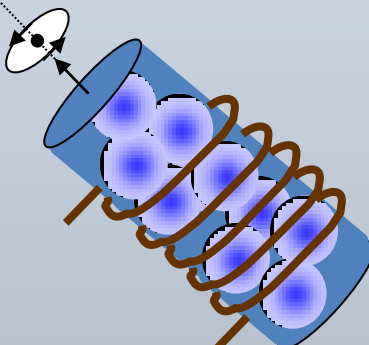


$$A_{m,ab}^{(2)LAB}(0, \beta_{ab}, \gamma_{ab}, -\omega_r t, \theta_M, 0) = \sum_{m'=-2}^2 A_{0,ab}^{(2)PAS} d_{0m'}^{(2)}(\beta_{ab}) e^{-im'\gamma_{ab}} e^{im'\omega_r t} d_{m'm}(\theta_M)$$

$$H_D^{LAB}(t) = \sum_{m=-2,2} (-)^m A_{-m,ab}^{(2)LAB}(\alpha_{ab}, \beta_{ab}, \gamma_{ab}; \omega_r t, \theta_M, 0) \times T_{m,ab}^{(2)}$$

The truncation of the dipolar Hamiltonian at high fields:

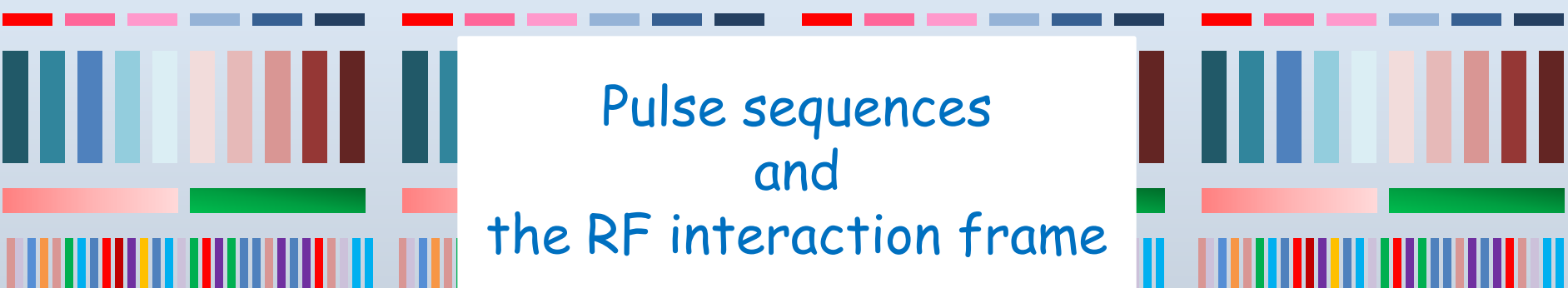
MAS NMR



$$\theta_M = 54.7^\circ : d_{00}(\theta_M) = 0 \quad ; \quad [I_z, T_m^{(2)}] \neq 0, m \neq 0$$

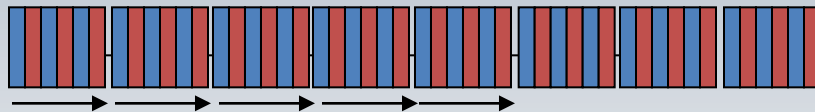
in the rotating frame

$$H_D(t) = \sum_{n=2,1,-2,-2} G_n(\alpha_{ab}, \beta_{ab}, \gamma_{ab}; \theta_M) \times T_{0,ab}^{(2)} e^{in\omega_r t}$$



Pulse sequences and the RF interaction frame

$$H(t) = \sum_{n=2,1,-2,-2} G_{n,ab} \times T_{0ab}^{(2)} e^{in\omega_r t} + H_{RF}(t)$$

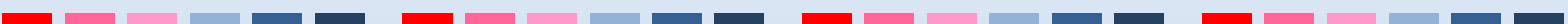


$$t_c = 2\pi / \omega_c$$

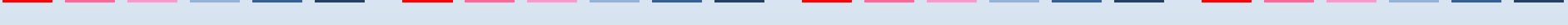
$$U_{RF}(t) = T \exp\{-iH_{RF}(t)\}$$

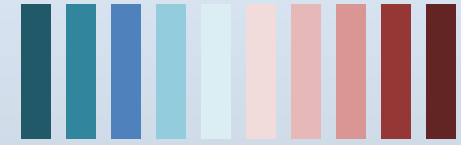
$$U_{RF}(t_c) = 1$$

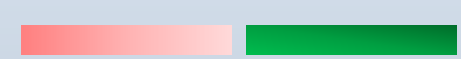
$$H^{\text{int}}(t) = \sum_{n=2,1,-2,-2} G_{n,ab} \times U_{RF}^{-1}(t) T_{0,ab}^{(2)} U_{RF}(t) e^{in\omega_r t}$$



Pulse sequences and the interaction frame

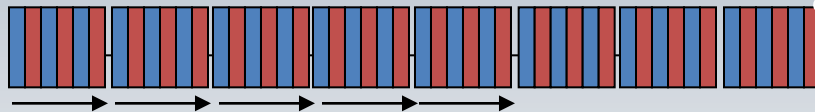








$$H_D^{\text{int}}(t) = \sum_{\substack{n=-2 \\ n \neq 0}}^2 \sum_{k=-\infty}^{\infty} G_{n,ab} \times \sum_{m=-2}^2 d_{m,k} T_{m,ab}^{(2)} e^{in\omega_r t} e^{ik\omega_c t}$$

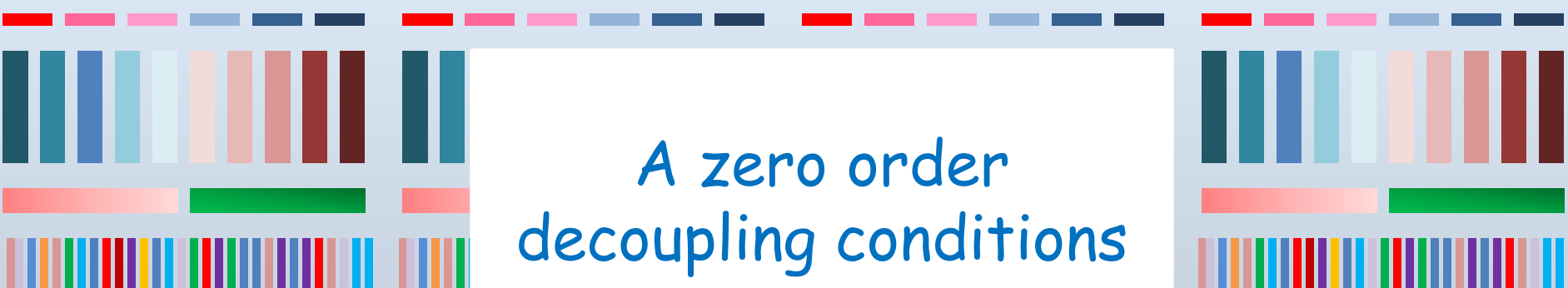


$$t_c = 2\pi / \omega_c$$

$$U_{RF}(t) = T \exp\{-iH_{RF}(t)\}$$

$$U_{RF}(t_c) = 1$$

$$H_D^{\text{int}}(t) = \sum_{n=2,1,-2,-2} G_{n,ab} \times U_{RF}^{-1}(t) T_{0,ab}^{(2)} U_{RF}(t) e^{in\omega_r t}$$

A series of color calibration bars are positioned along the top and sides of the slide. These include a row of small colored squares at the top, vertical bars of various colors on the left and right, and horizontal bars of different colors below the vertical ones.

A zero order decoupling conditions

$$G_0 = 0 :$$

$$\int_0^{t_c} dt H_D^{\text{int}}(t) = 0$$

Is it possible, necessary or even sufficient when

$$d_{m0} = 0, \forall_m$$



The Floquet representation

$$H_D(t) = \sum_{n,k} H_{nk} e^{ik\omega_c t} e^{in\omega_r t}$$

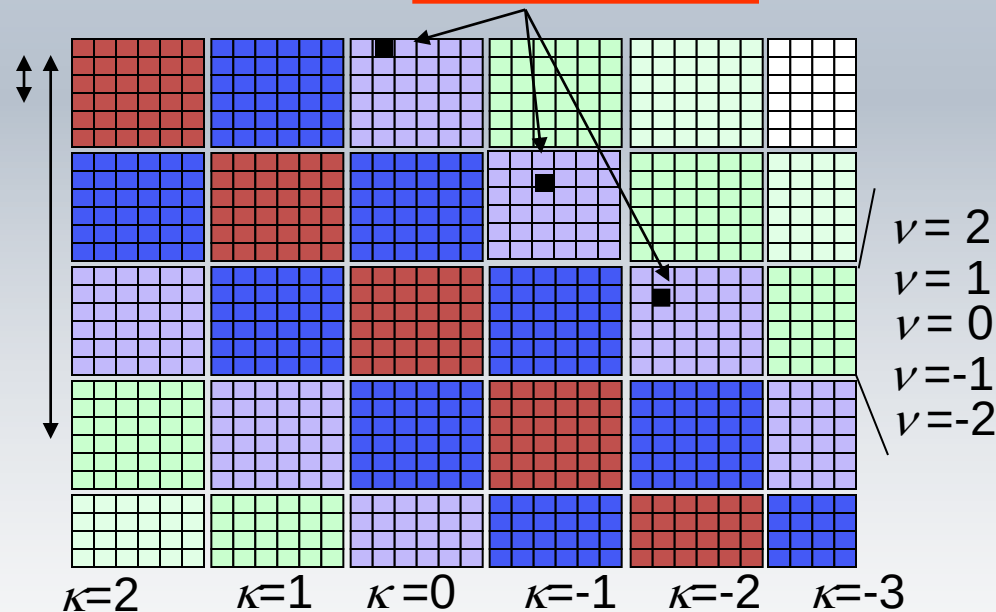
$$H_F^D = \sum_{n,k} H_{nk} F_n^r F_k^c + \omega_r N^r + \omega_c N^c$$

$$H_{n,k} = G_{n,ab} \times \sum_{m=-2}^2 d_{m,k} T_{m,ab}^{(2)} \quad n = -2, -1, 1, 2; \forall_k$$

The Floquet representation

$$\langle \varphi_i, \nu + n, \kappa + k | H_{n,k} F_n^r F_k^c | \varphi_j, \nu, \kappa \rangle$$

$|\varphi, \nu, \kappa \rangle$:

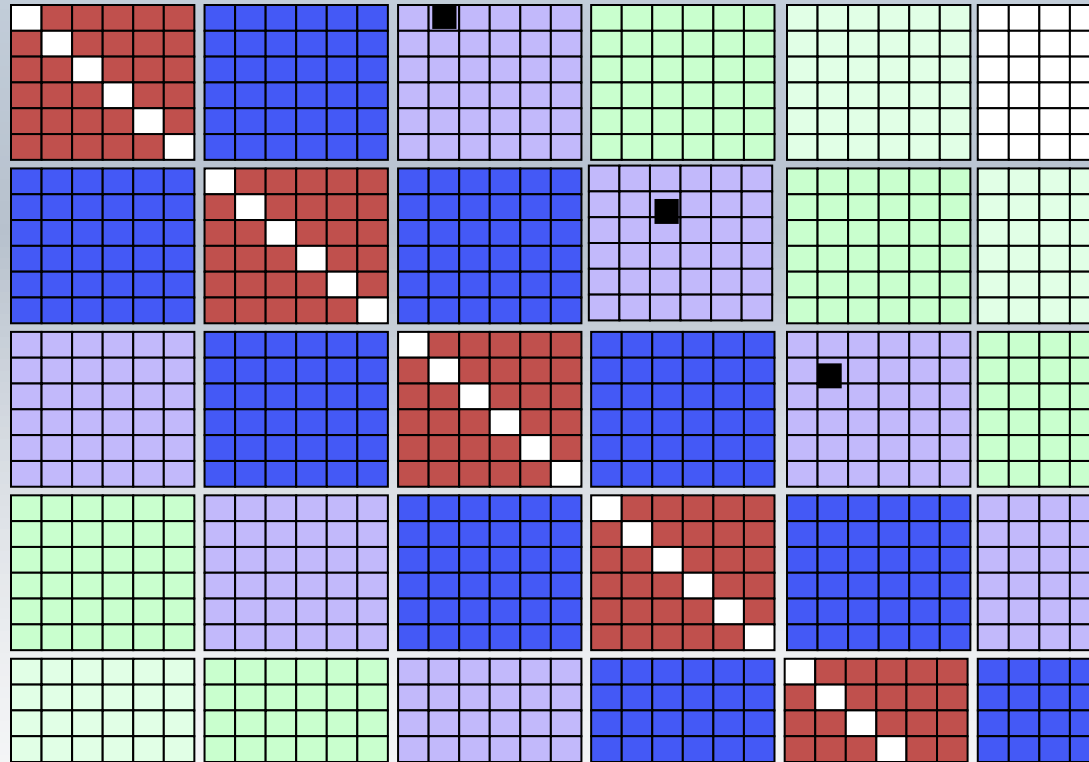


$$\{ \langle \varphi_i | H_{n,k} | \varphi_j \rangle \}$$

$$\nu, \kappa = -\infty, \dots, -2, -1, 0, 1, 2, \dots, \infty$$

The Floquet representation

$$H_{00} + v\omega_r I + \kappa\omega_c I$$



$$N^{r,c} \equiv F_z^{r,c}$$

$$H_{00}F_0^r F_0^c + \omega_r N^r + \omega_c N^c$$

The van Vleck transformation

Each (“non-degenerate”) off-diagonal block can be transformed by the van Vleck transformation to diagonal and off-diagonal blocks

$$e^S H_F^D e^{-S} = H_{0,0} F_0^r F_0^c - \frac{1}{2} \sum_{n,k \neq 0,0} \sum_{n',k' \neq 0,0} \frac{[H_{n,k}, H_{n',k'}]}{n' \omega_r + k' \omega_c} F_{n+n'}^r F_{k+k'}^c + \dots + \omega_r N^r + \omega_c N^c$$

$$\{e^S H_F^D e^{-S}\}_{0,0} = H_{0,0} F_0^r F_0^c - \frac{1}{2} \sum_{n,k \neq 0,0} \sum_{n',k' \neq 0,0} \frac{[H_{n,k}, H_{-n,-k}]}{n \omega_r + k \omega_c} F_0^r F_0^c + \omega_r N^r + \omega_c N^c$$

$$- \frac{1}{2} \sum_{n,k \neq 0,0} G_{n,ab} G_{-n,bc} \sum_{m,m'} \frac{d_{m,k} d_{m',-k}}{n \omega_r + k \omega_c} [T_{m,ab}^{(2)}, T_{m',bc}^{(2)}] F_0^r F_0^c$$

The effective Hamiltonian

$$H_{D,eff} = -\frac{1}{2} \omega_{ab} \omega_{bc} \sum_{n,k \neq 0,0} G_{n,ab} G_{-n,bc} \sum_{m,m'} \frac{d_{m,k} d_{m',-k}}{n\omega_r + k\omega_c} [T_{m,ab}^{(2)}, T_{m',bc}^{(2)}]$$

but in the degenerate case

$$n_d \omega_r + k_d \omega_c = 0$$

The terms connect degenerate blocks!

$$\{e^S H_F^D e^{-S}\} \cong H_{n_d, k_d} F_{n_d}^r F_{k_d}^c - \frac{1}{2} \sum_{\substack{n,k \neq 0,0 \\ n,k \neq n_d, k_d}} \frac{[H_{n,k}, H_{-n,-k}]}{n\omega_r + k\omega_c} F_0^r F_0^c + \omega_r N^r + \omega_c N^c$$

DECOUPLING

minimize

$$\Delta_{m,m'}^n = \sum_{m,m'} \sum_k \frac{d_{m,k} d_{m',-k}}{n\omega_r + k\omega_c}$$

Stay away from

$$n_d \omega_r + k_d \omega_c = 0$$

$$n_d = 1, 2$$

$$n_d = 3, 4$$

The isotropic
chemical shift
in the RF interaction frame

$$H_{CS}^{LAB} = \sigma_a I_{za}$$

$$\begin{aligned} H_{CS}^{\text{int}}(t) &= \sigma_a U_{RF}^{-1}(t) I_{za} U_{RF}(t) \\ &= \sigma_a \sum_k \left\{ s_{x,k} I_{xa} + s_{y,k} I_{ya} + s_{z,k} I_{za} \right\} e^{ik\omega_c t} \end{aligned}$$

in the Floquet representation

$$H_{F,00}^{\text{int},CS} + H_{F,00}^{\text{int},D} = \sigma_a \left\{ s_{x,0} I_{xa} + s_{y,0} I_{ya} + s_{z,0} I_{za} \right\} F_0^r F_0^c$$

the effective CS Hamiltonian

Multiple-Pulse- CRAMPS History

'65

'70

'75

'80

'85

'90

'95

LG Lee,Goldburg

WHH4 Haeberlen,Huber,Waugh; Mehring

MREV8 Vaughan et al.,Mansfield

CRAMPS Gerstein et al**

BR24 Burum,Rhim

BLEW12 Burum,Linder,Ernst

FSLG Bielecki,Kolbert,Levitt

CORY24 Cory

'95

'00

'05

'10

WHH4 Demco,Hafner,Spiess

MSHOT-3 Nielsen et al.

PMLG Vinogradov, Madhu

DUMBO Emsley et al.

R-symmetry Levitt et al.

w-PMLG5 Vinogradov,Madhu

w-eDUMBO Elena et al.

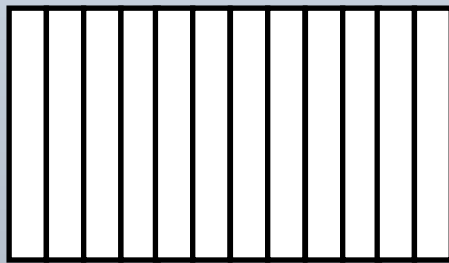
w-PMLG superc. Leskes,Madhu

SAM Amoureux

RN Madhu

Examples of pulse sequences

$x \ y \bar{x} \bar{x} \bar{y} \bar{x} \ x \ y \ x \ x \ \bar{y} \bar{x}$

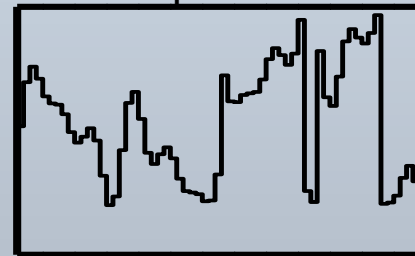


BLEW-12

Burum, Linder, Ernst (1981)

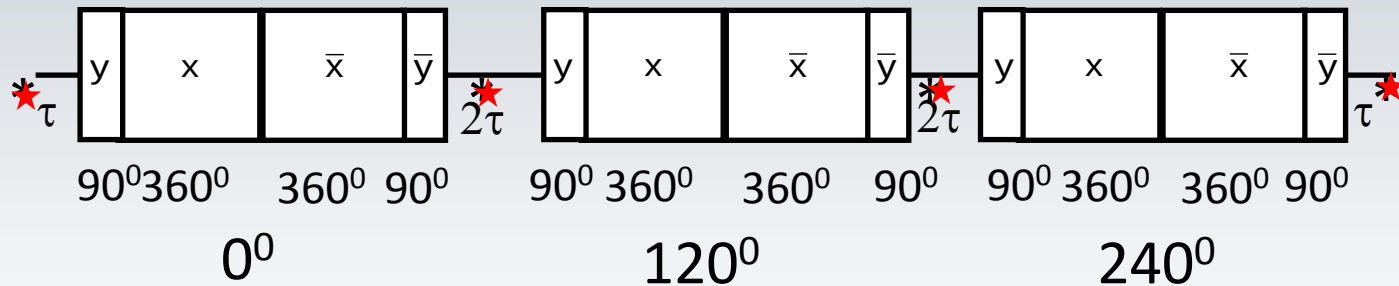
optimized 7 Fourier components

64 pulses



DUMBO

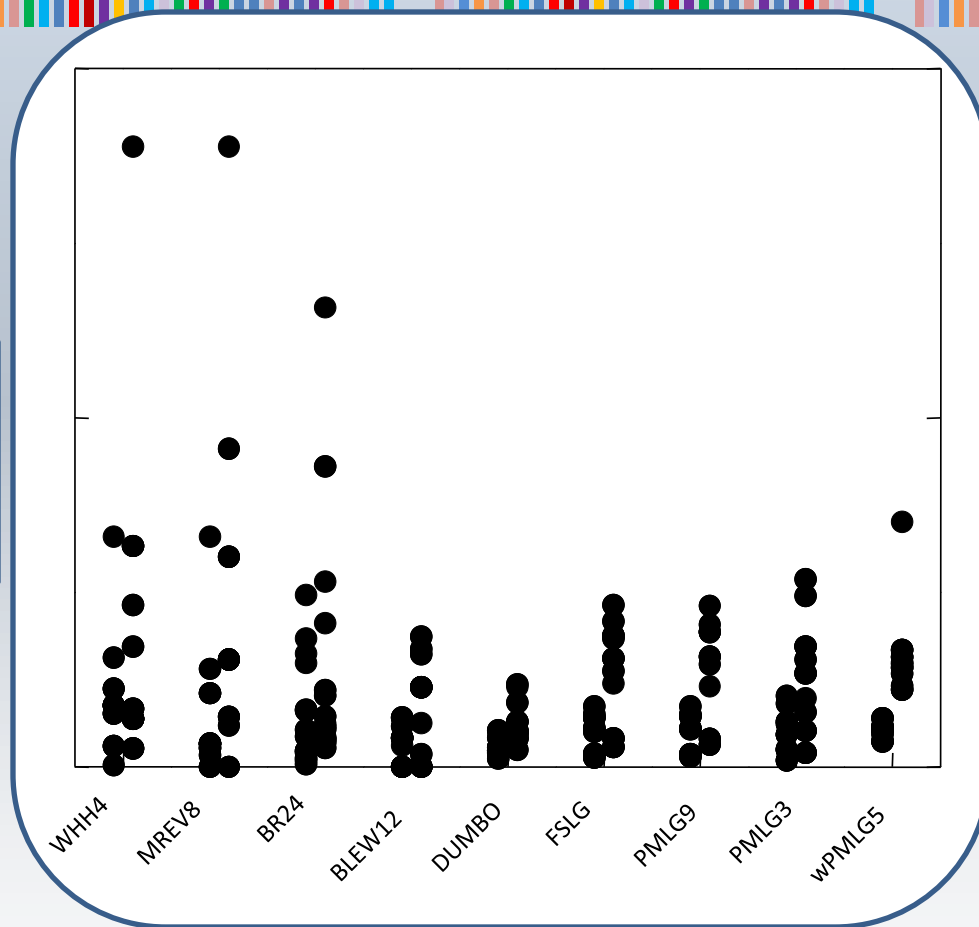
Emsley et al., (2000)



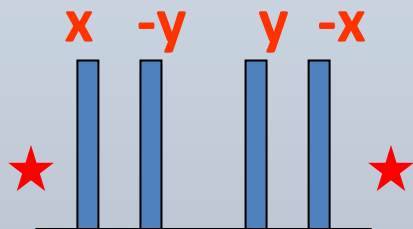
MSHOT-3

Nielsen et al. (1998)

$$\left| \Delta_{m,m'}^n \right|$$



WAHUHA (1967) MREV-8



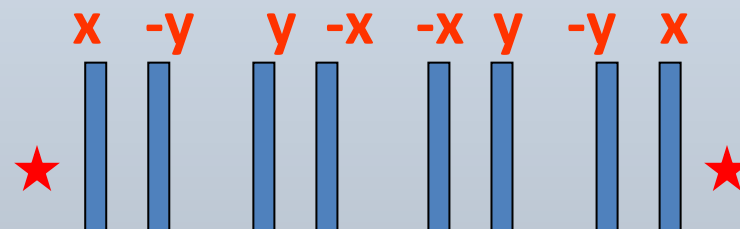
" I_z "

in the RF interaction frame



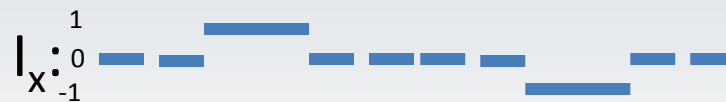
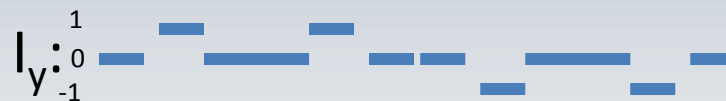
$$H_{CS}^{(0)} = \sqrt{\frac{1}{3}} \Delta\omega \left(\frac{I_z + I_x + I_y}{\sqrt{3}} \right)$$

$$\begin{aligned} H_D^{(0)} &= 0 \\ H_{F,00} &= 0 \end{aligned}$$



" I_z "

in the RF interaction frame



$$\begin{aligned} H_D^{(1)}(\omega_r = 0) &= 0 \\ H_{F,00}^{D(1)}(\omega_r \neq 0) &\neq 0 \end{aligned}$$

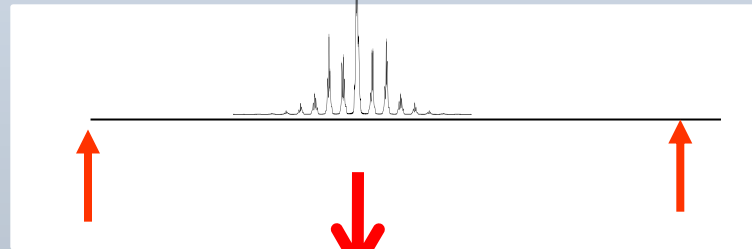
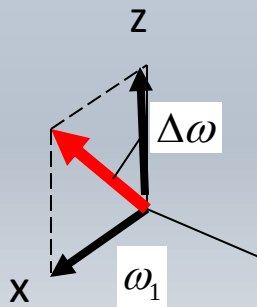
$$H_{CS}^{(0)} = \frac{1}{3} \Delta\omega I_z$$

The basic sequence of Lee-Godburg (1965)

1972's field switching, Mehring

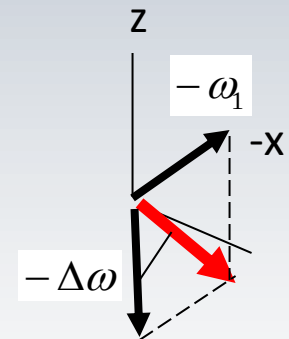
1991's frequency switching, Bielecki, Kolbert, Levitt

$$\omega_1 I_x + \Delta\omega I_z + \delta\omega I_z$$



$$\cos\theta_M = \frac{\omega_1}{\sqrt{\omega_1^2 + \Delta\omega^2}} = \sqrt{\frac{1}{3}}$$

$$H_D : d_{00} = (3\cos^2\theta_M - 1)$$



" I_z in the RF interaction frame"?

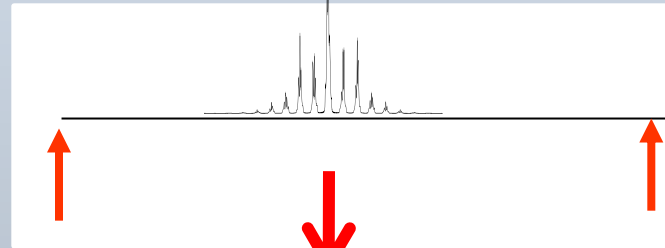
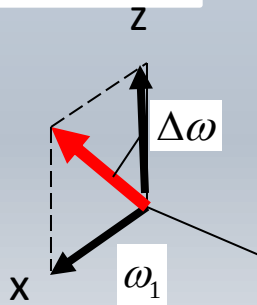
$$-\omega_1 I_x - \Delta\omega I_z + \delta\omega I_z$$

The basic sequence of Lee-Godburg (1965)

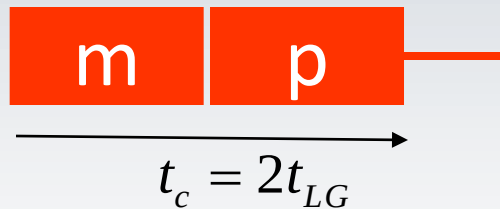
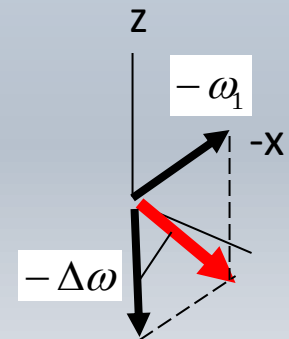
1972's field switching, Mehring

1991's frequency switching, Bielecki, Kolbert, Levitt

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



$$(\omega_1^2 + \Delta\omega^2)^{1/2} t_{LG} = 2\pi$$



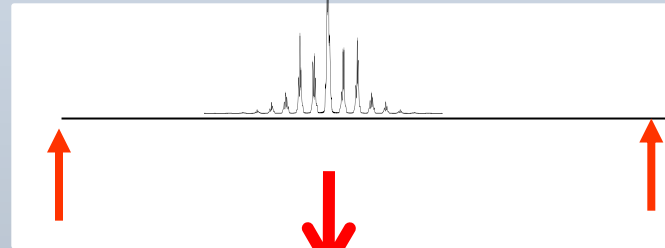
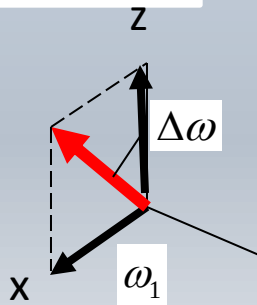
$$H_{eff}^{CS} = s\delta\omega(I_z \cos\theta_M + I_x \sin\theta_M)$$

The basic sequence of Lee-Godburg (1965)

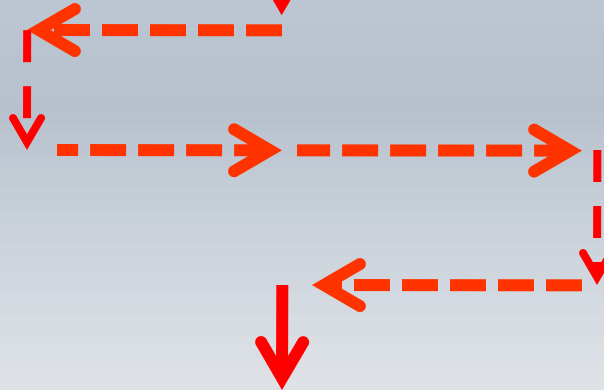
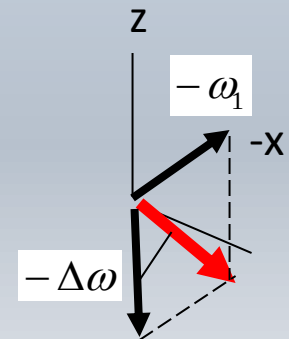
1972's field switching, Mehring

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



$$(\omega_1^2 + \Delta\omega^2)^{1/2} t_{LG} = 2\pi$$

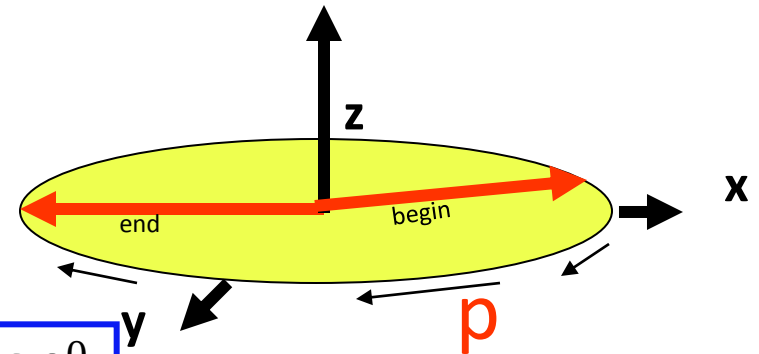
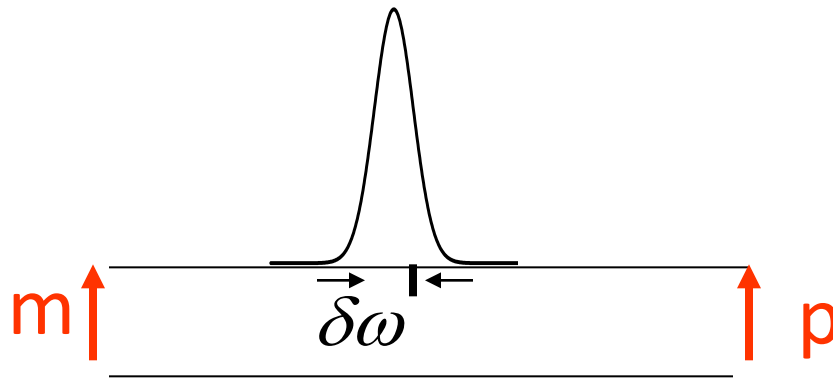
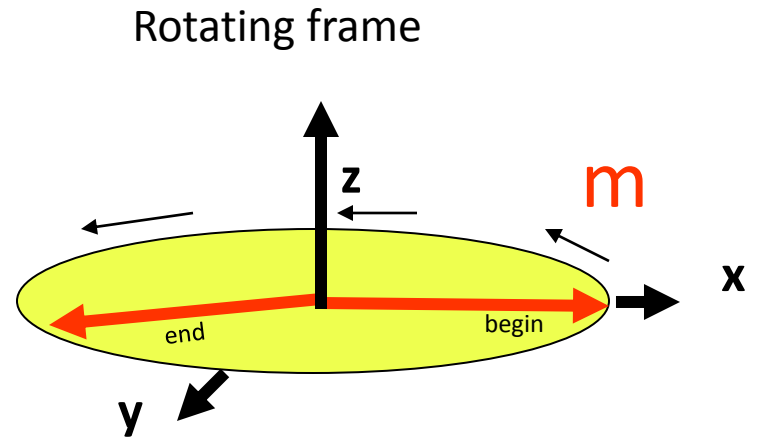


scale factor?

direction of CS Hamiltonian in the interaction frame?

Homonuclear proton decoupling

Bielecki, Kolbert, Levitt



$$\nu_{eff} = (\nu_1^2 + \delta\nu^2)^{1/2}$$

$$\nu_1 / \nu_{eff} = \cos\theta_M = \sqrt{1/3}$$

$$\nu_{eff} t_{LG} : 360^\circ$$

$$\nu_1 t_{LG} : 288^\circ$$

$$\Delta\omega t_{LG} : 208^\circ$$

wPMLG by Michal Leskes and P.K. Madhu



Some reviews:

Elena Vinogradov, P. K. Madhu, Shimon Vega,

“Strategies for high-resolution proton spectroscopy in solid state NMR”,

in: New Techniques in Solid-State NMR, Vol. 246 of Topics in Current Chemistry, 2004

Micahl Leskes, P. K. Madhu, Shimon Vega,

“Floquet Theory in Solid-State Nuclear Magnetic Resonance”

In: Progress in NMR Spectr. (2010) in press.

Ingo Scholz, Jacco van Beek, and Matthias Ernst

“Operator-Based Floquet Theory”

in: Solid-State NMR (2010) in press.

WP M L G5

x

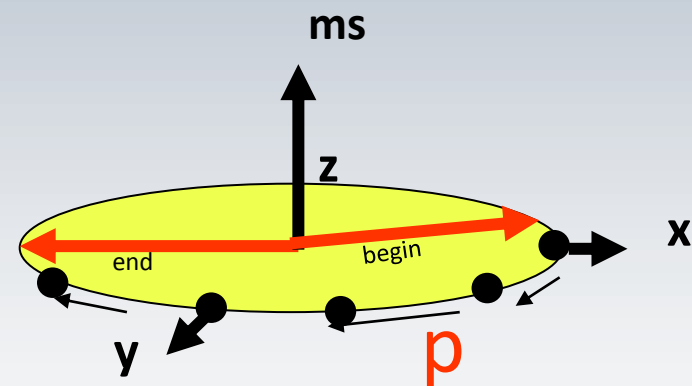
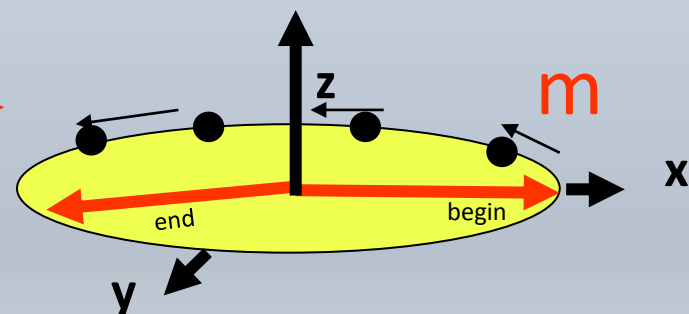
m

$\{5:m;x\}$

$\{5:m;x\}$

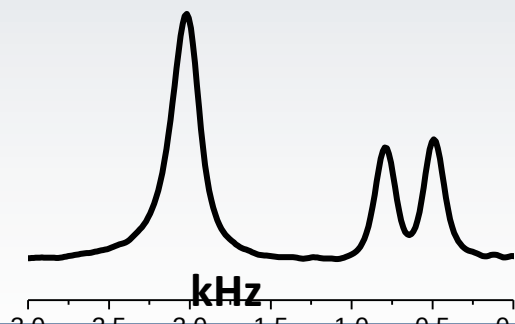
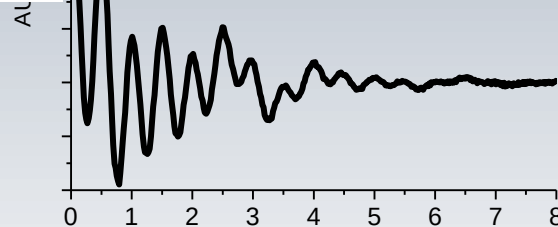
$4.5\mu\text{ses}$

Rotating frame

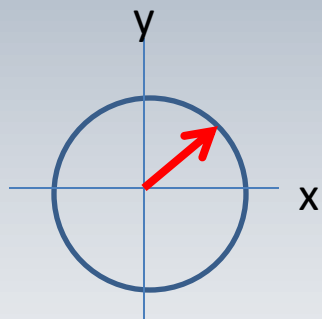


20.78, 62.34, 103.9, 145.46, 187.02
7.02, 325.46, 283.39, 242.34, 200.78

FID



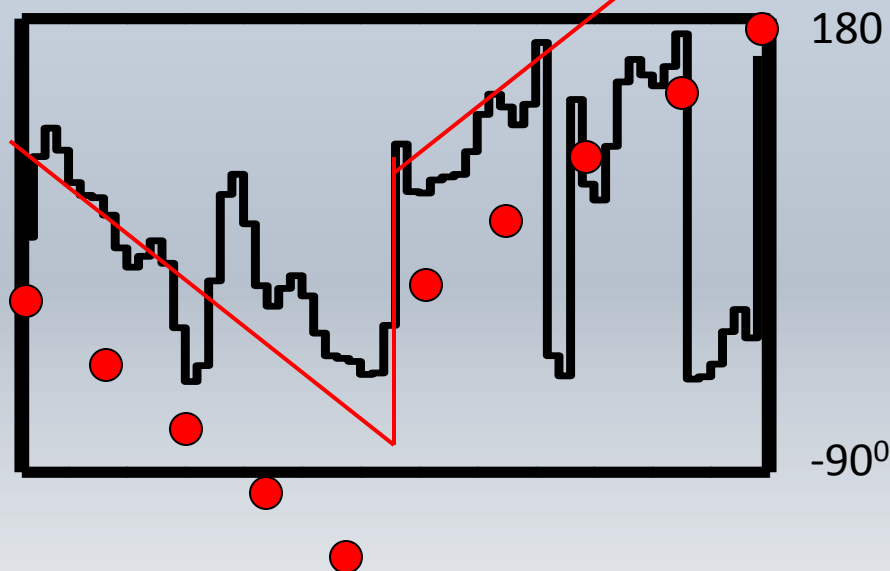
(e)DUMBO



$$\overline{\omega}_1(t)$$

in the rotating frame

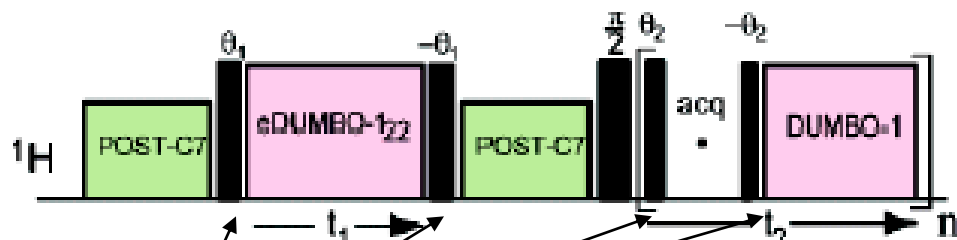
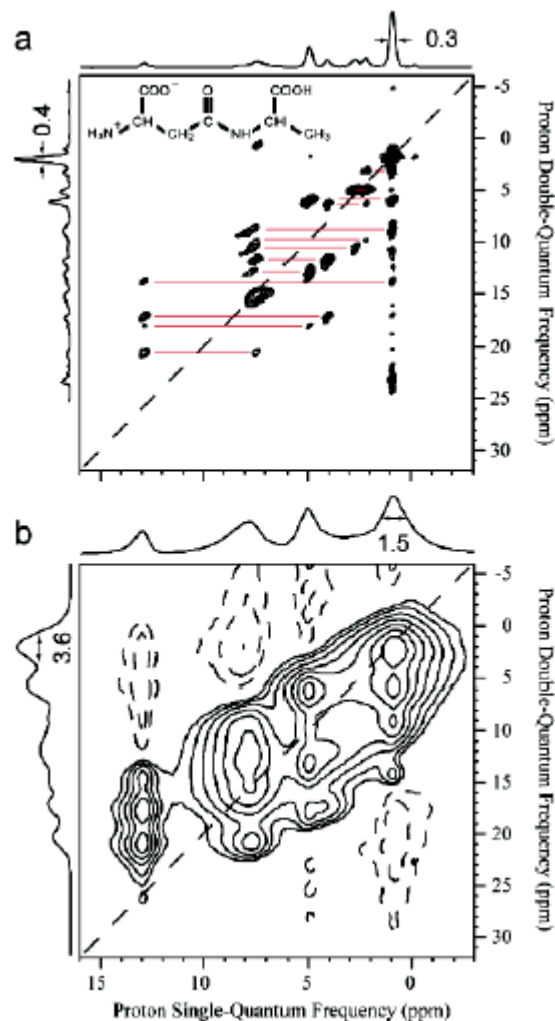
φ



optimized 7 Fourier components in 64 pulses

A. Lesage, D. Sakellariou, S. Hedier, B. Elena,
P. Charmont, S. Steuernagel, L. Emsley,
J. Magn. Reson. 163 (2003) 105.

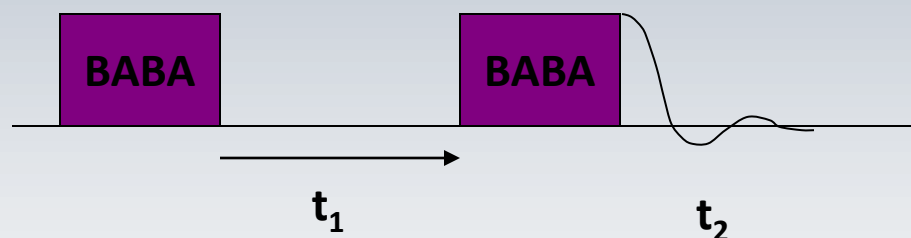
β -AspAla



Two-Dimensional ^1H - ^1H Double-Quantum CRAMPS NMR Spectroscopy

Steven P. Brown, Anne Lesage, Benedicte Elena, and Lyndon Emsley

J. AM. CHEM. SOC. 2004, 126, 13230-13231



For BABA see: Schnell, I.; Spiess, H. W. *J. Magn. Reson.* 2001, 151, 153.

Powder Crystallography by Proton Solid-State NMR Spectroscopy

Bénédicte Elena and Lyndon Emsley*

J. AM. CHEM. SOC. 2005, 127, 9140–9146

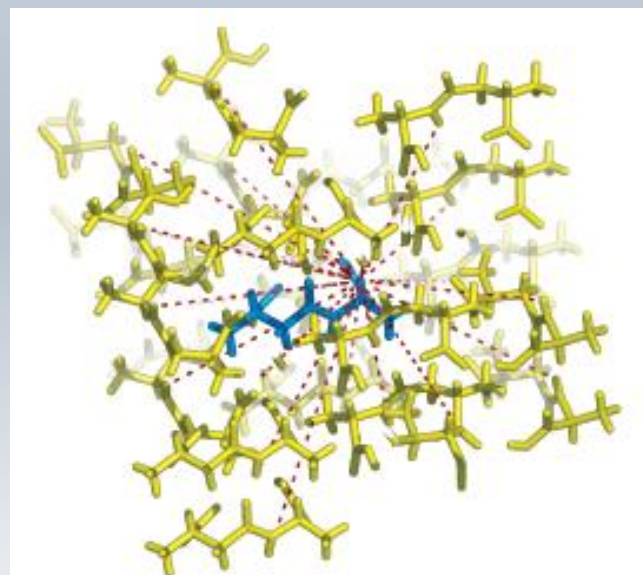


Figure 4. Representation of the NMR observed dipolar contacts corresponding to a single NH-CH₃ correlation peak from 2D spin-diffusion spectra. A single molecule (blue) is depicted in its crystalline environment (yellow). Mixed intra- and intermolecular contacts (dashed) are relevant for interpretation of ¹H-¹H spin-diffusion correlation peaks.

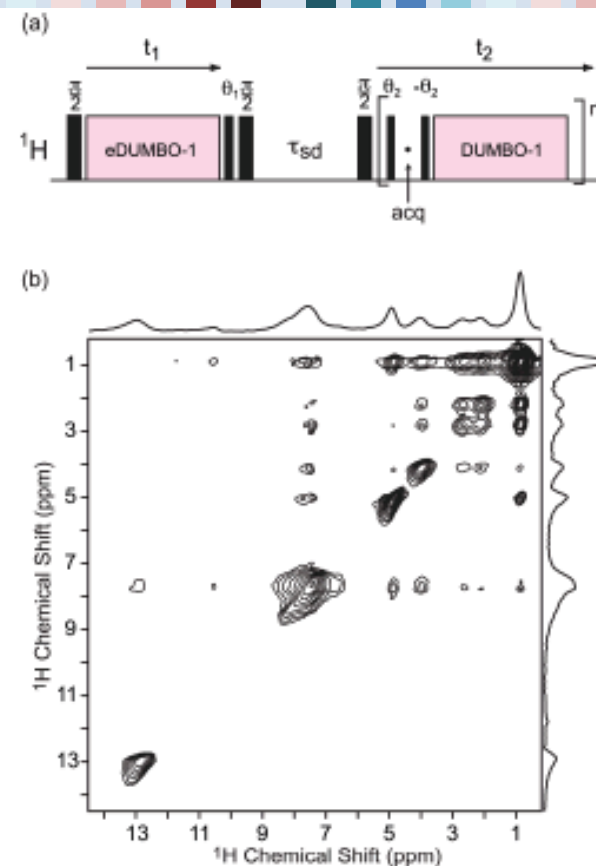
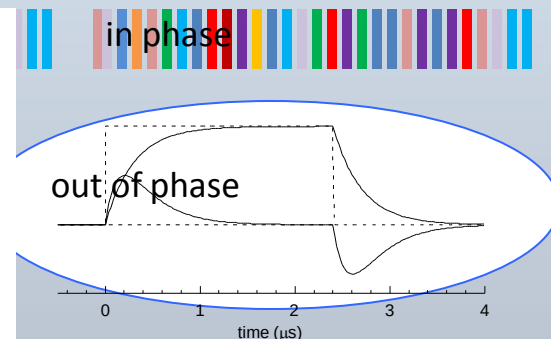
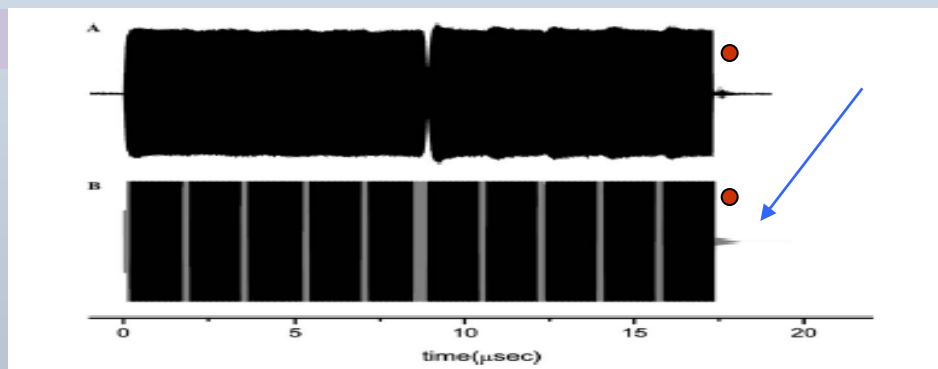


Figure 1. (a) Pulse sequence for the ¹H-¹H spin-diffusion CRAMPS detected experiment. The pulse program is available from our web site³⁶ or upon request. (b) 500 MHz 2D ¹H-¹H spin-diffusion spectrum of (1) acquired with a MAS frequency of 22 kHz, a mixing time $\tau_{sd} = 220 \mu s$, and a radio frequency field amplitude $\nu_1 \approx 100$ kHz. 16 transients were added with a 2.5 s repetition delay for each of the 180 complex t_1 points (96 μs t_1 increment), acquired using a States quadrature detection scheme on the second 90° pulse. The total experimental time was 2 h. For proton homonuclear dipolar decoupling during t_1 an intermediate version from the eDUMBO-1 decoupling schemes family³⁶ defined by Fourier coefficients $\{a_0 = 0; b_1 = 0.18, b_2 = 0.21, b_3 = 0.03, b_4 = 0.12, b_5 = -0.08, b_6 = 0.125\}$ was implemented, and $\theta_1 = 1.45 \mu s$. During t_2 , 6.3 μs windows were inserted for detection of a point every three cycles of the original DUMBO-1 decoupling scheme,^{11,31} as well as short θ_2 pulses (0.5 μs) to suppress quadrature images in F_2 . The total dwell time was 103.3 μs . In both dimensions, the decoupling cycles were defined with 64 phase steps of 500 ns each.

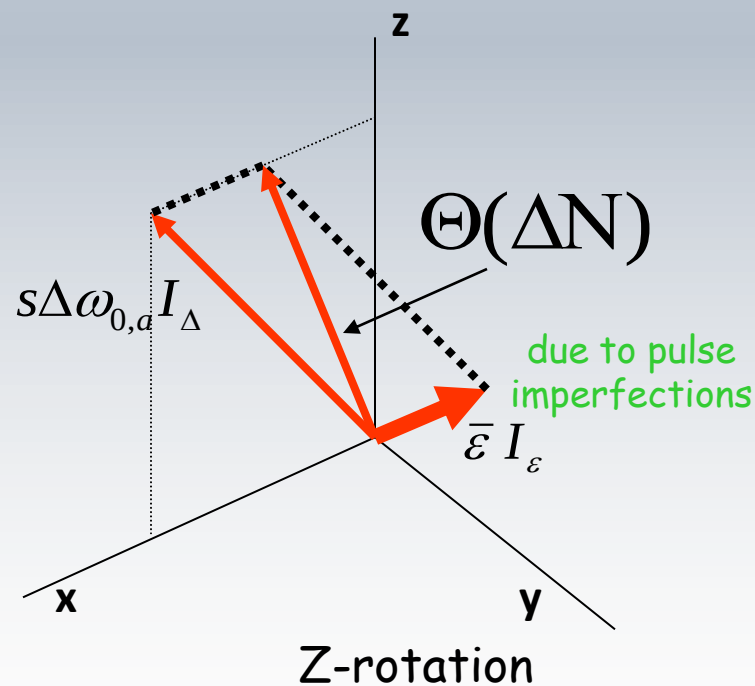
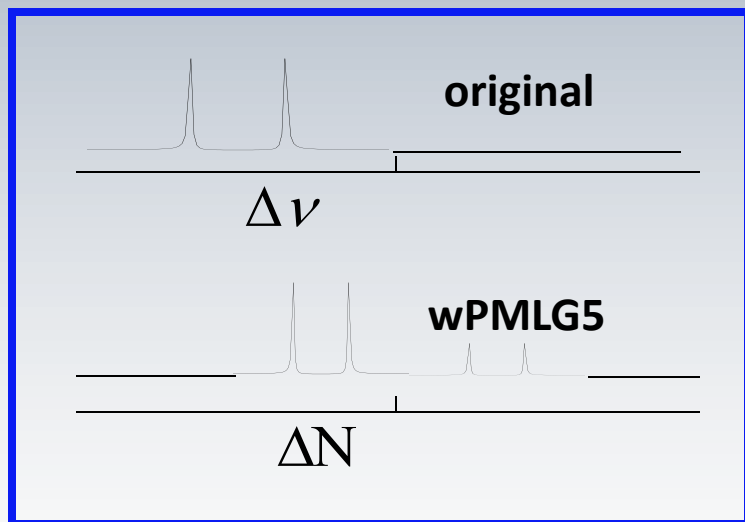
w P M L G 5

on the scope:

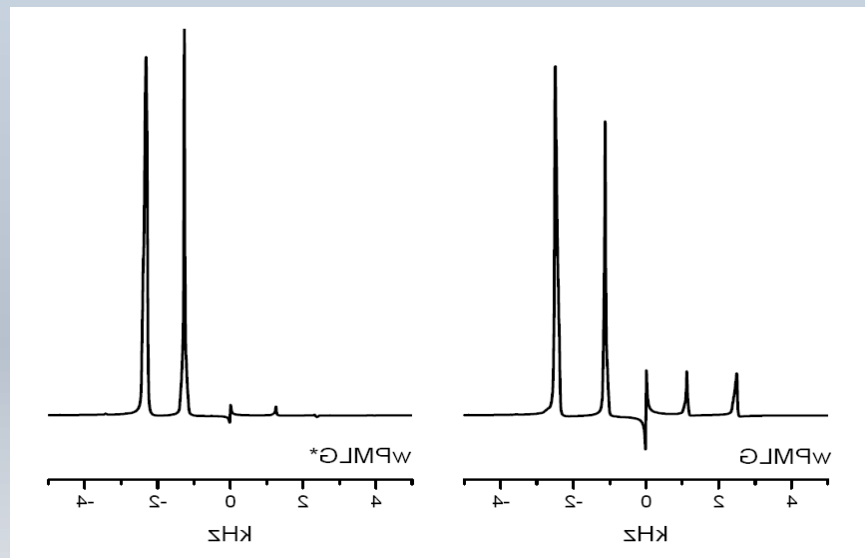
for simulations:



A.J. Vega, JMR (2005)

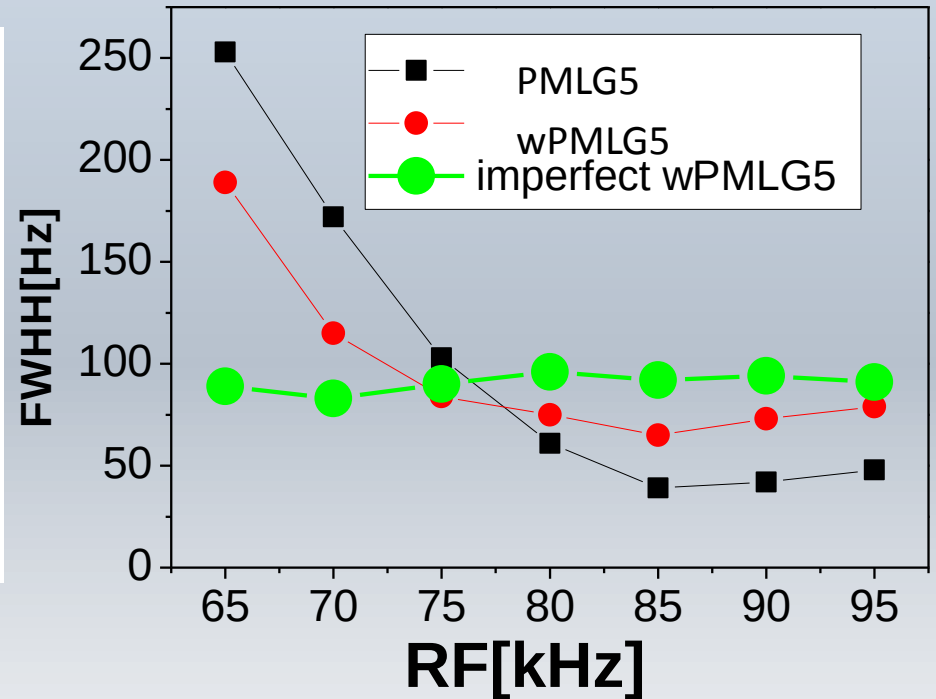


z-rotation of wPMLG



imp-wPMLG5

wPMLG



A simulated comparison between PMLG5, wPMLG5, imp-w-PMLG5

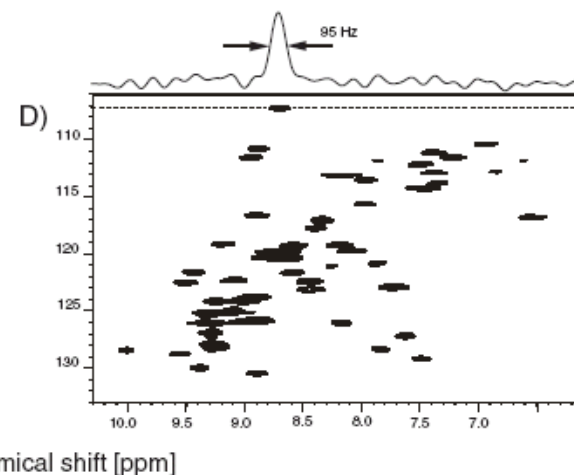
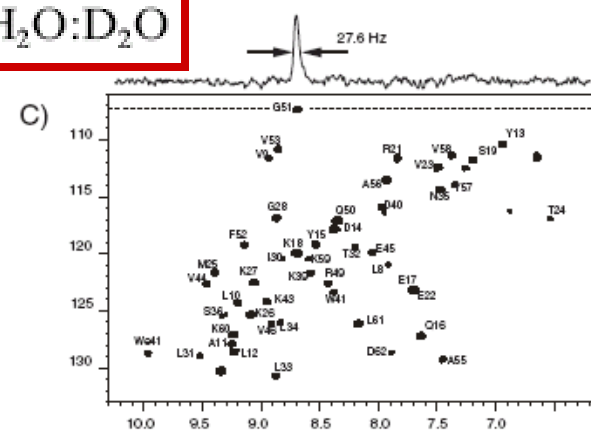
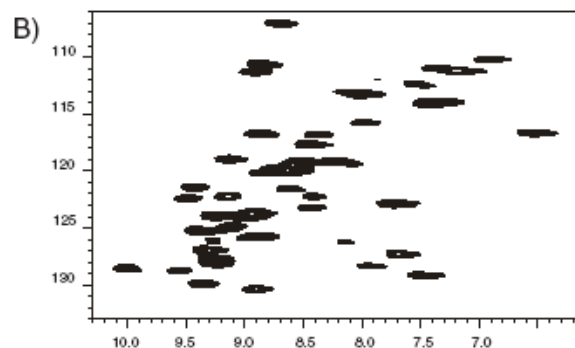
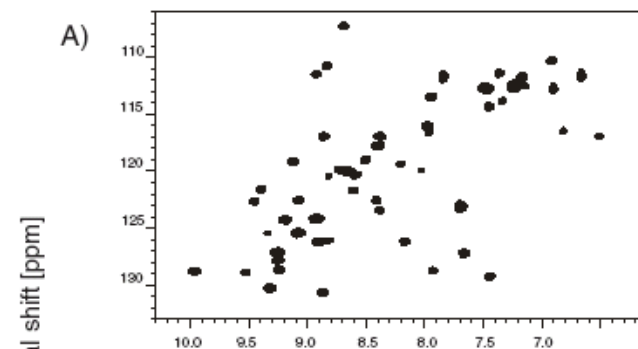
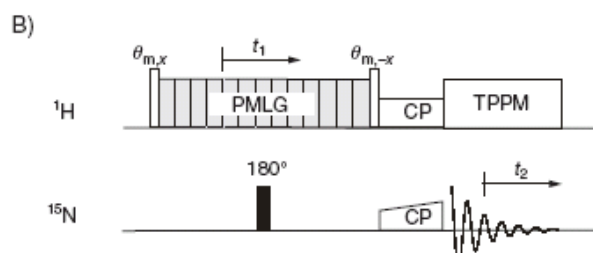
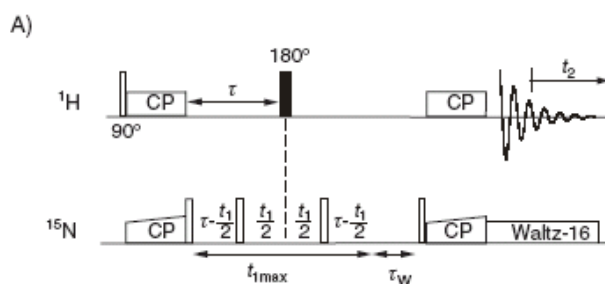
H_2 -H spin system

Ultrahigh Resolution in Proton Solid-State NMR Spectroscopy at High Levels of Deuteration**

Veniamin Chevelkov, Kristina Rehbein, Anne Diehl,
and Bernd Reif*

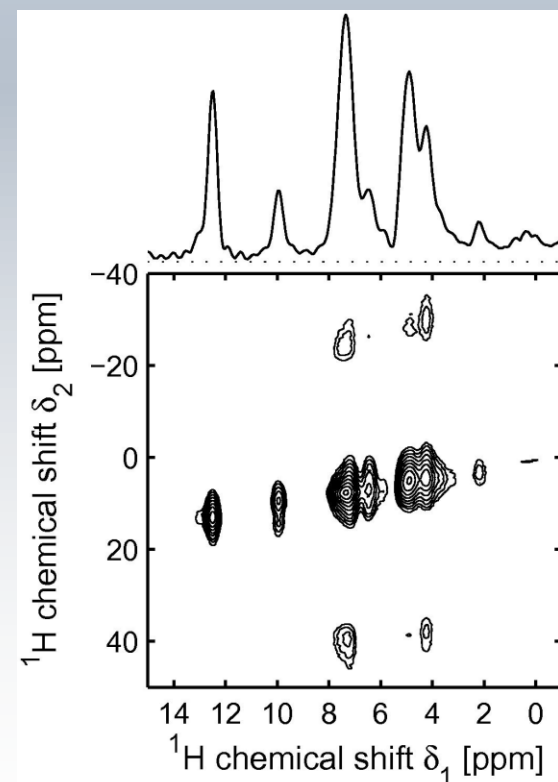
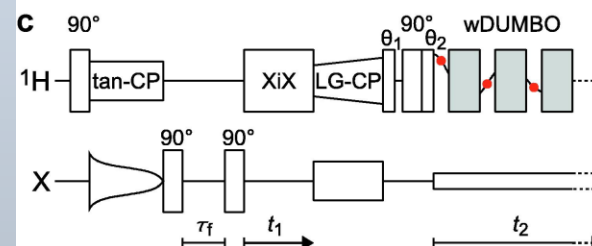
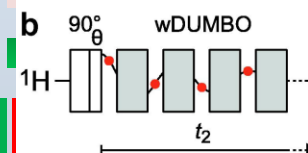
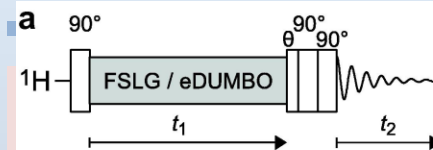
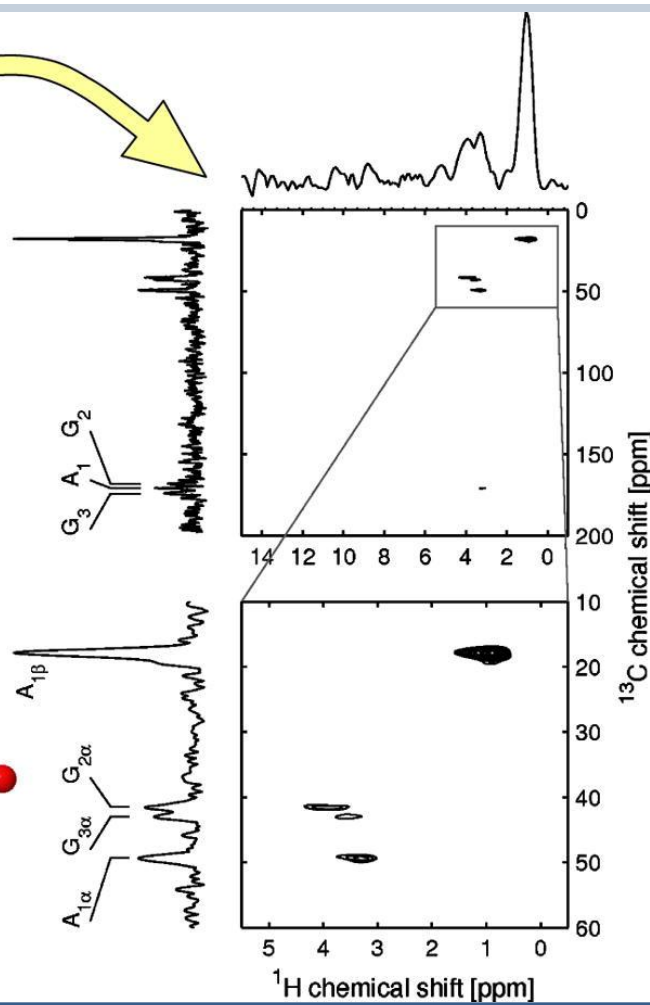
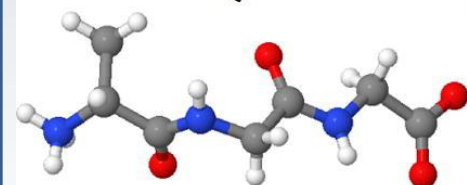
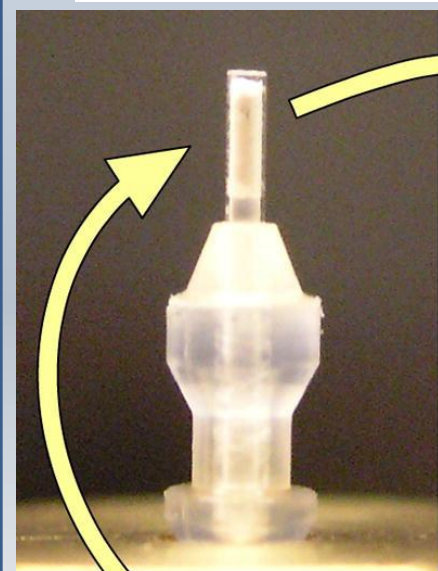
Angew. Chem. Int. Ed. 2006, 45, 3878–3881

10:90 H₂O:D₂O





Proton micro-magic-angle-spinning NMR spectroscopy of nanoliter samples

Andreas Brinkmann^{a,b,*}, Suresh Kumar Vasa^a, Hans Janssen^a, Arno P.M. Kentgens^{a,*}^aPhysical Chemistry/Solid State NMR, Institute for Molecules and Materials, Radboud University Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands^bStracie Institute for Molecular Sciences, National Research Council, 1200 Montreal Road, M-40 Ottawa, Ontario, Canada K1A 0R6

Nanochannels of Two Distinct Cross-Sections in a Porous Al-Based Coordination Polymer

Angiolina Comotti,^{*,†} Silvia Bracco,[†] Piero Sozzani,[†] Satoshi Horike,[‡] Ryotaro Matsuda,[§] Jinxi Chen,^{‡,||} Masaki Takata,[⊥] Yoshiki Kubota,[#] and Susumu Kitagawa[‡]

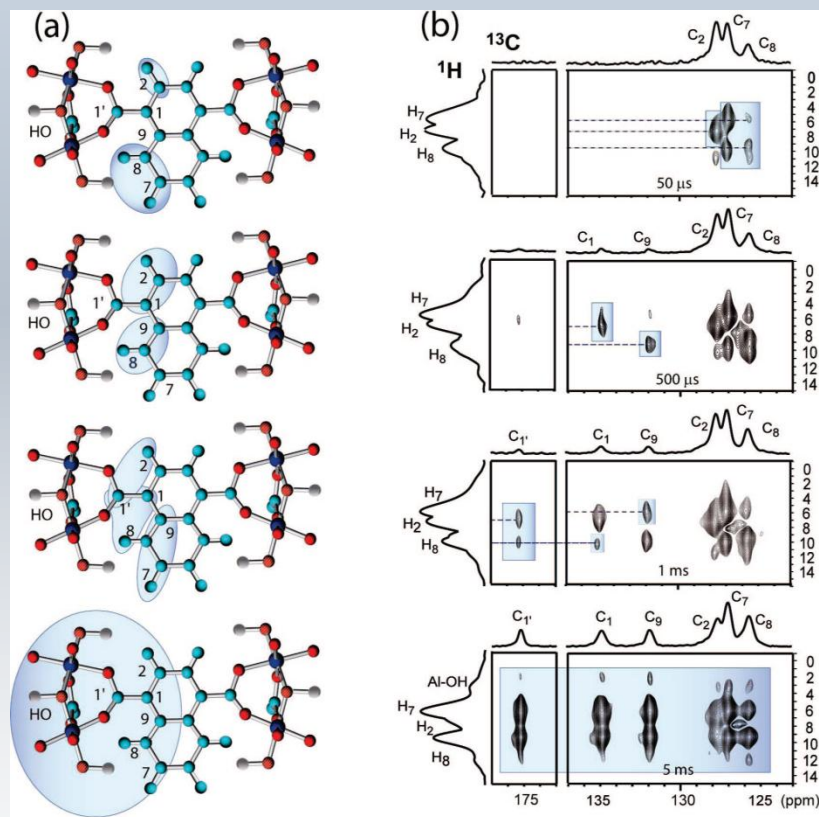
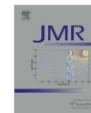


Figure 3. (a) Structural motif of the nanoporous Al(OH)(1,4-NDC) compound showing the Al-OH-Al chains interconnected by the 1,4-naphthalenedicarboxylate groups. The hydrogens of OH groups are modeled according to the geometry of the Al-OH-Al chains. The areas, highlighted blue, show the interaction sphere of hydrogens with the neighboring carbons at mixing times of 50 s, 500 s, 1 ms, and 5 ms of 2D NMR experiments. (b) 2D ¹H-¹³C Lee-Goldburg heterocorrelated NMR spectra of the nanoporous compound at different mixing times.



Communication

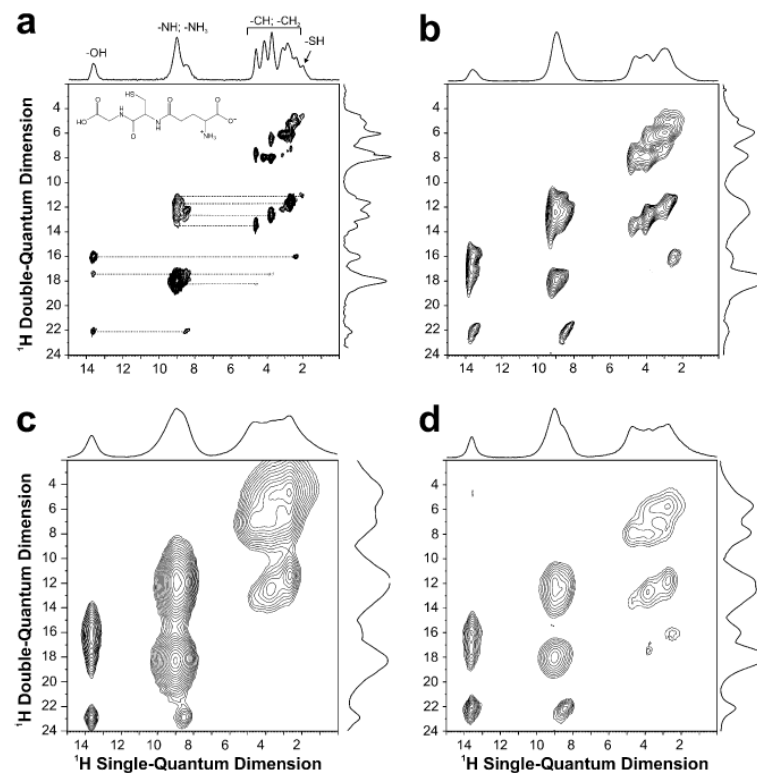
High-resolution ^1H homonuclear dipolar recoupling NMR spectra of biological solids at MAS rates up to 67 kHzLuis Mafrá^{a,*}, Renée Siegel^a, Christian Fernandez^b, Denis Schneider^c, Fabien Aussenac^d, João Rocha^a^a Department of Chemistry, University of Aveiro, CICECO, Campus de Santiago, 3810-193 Aveiro, Portugal^b Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 Bd. du Maréchal Juin, 14050 Caen, France^c Bruker-Biospin GmbH, 76287 Rheinstetten, Germany^d Bruker Biospin SA, 67166 Wissembourg, France

Fig. 4. 2D ^1H – ^1H DQ–SQ spectra of GSH using the R12_2^5 symmetry acquired (a and c) with DUMBO decoupling during t_1 and t_2 according to Fig. 1 (DUMBO shape pulse length = 16 and 15 μs ; decoupling power = 150 and 198 kHz for (a and c), respectively) and (b and d) without CRAMPS decoupling. 2D spectra were recorded at MAS rates of 35 kHz using $\nu_1 = 105$ kHz and Larmor frequency of 800 MHz ($B_0 = 18.8$ T, Bruker standard-bore NMR spectrometer) for (a and d) and at MAS rates of 67 kHz using $\nu_1 = 201$ kHz and Larmor frequency of 600 MHz ($B_0 = 14.1$ T, Bruker wide-bore NMR spectrometer) for (c and d).

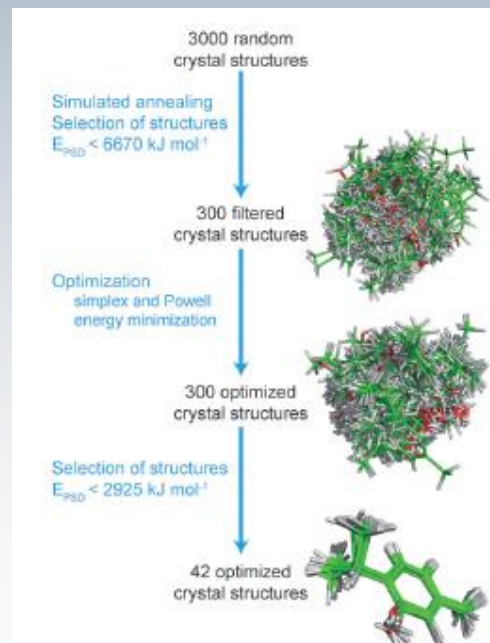
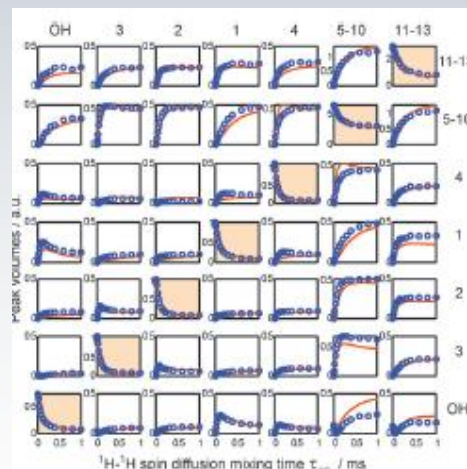
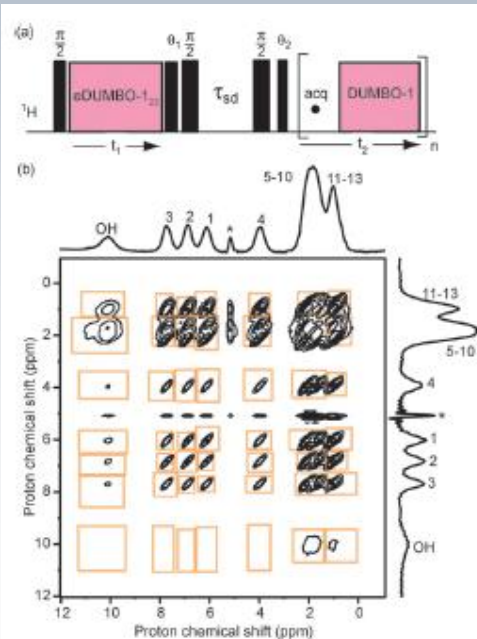
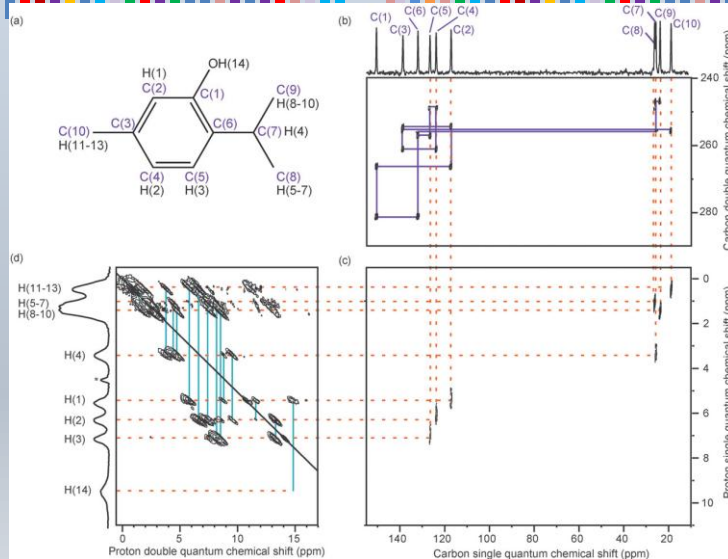
Powder NMR crystallography of thymol

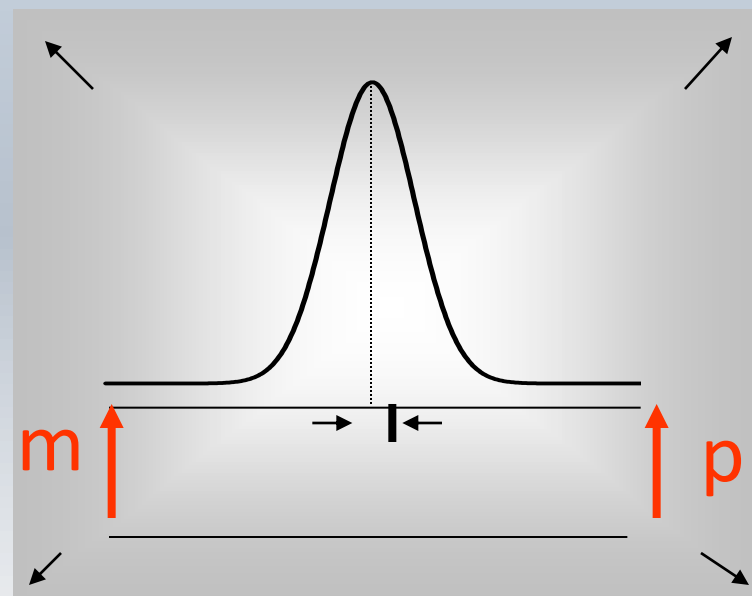
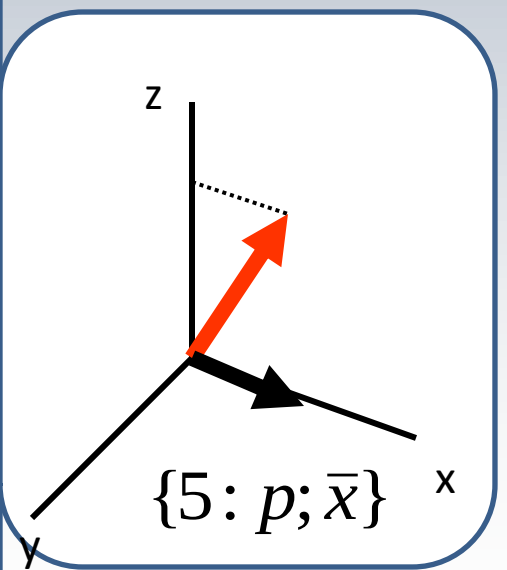
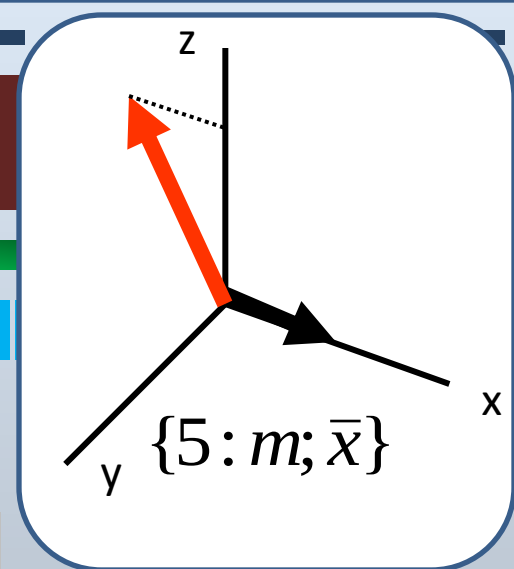
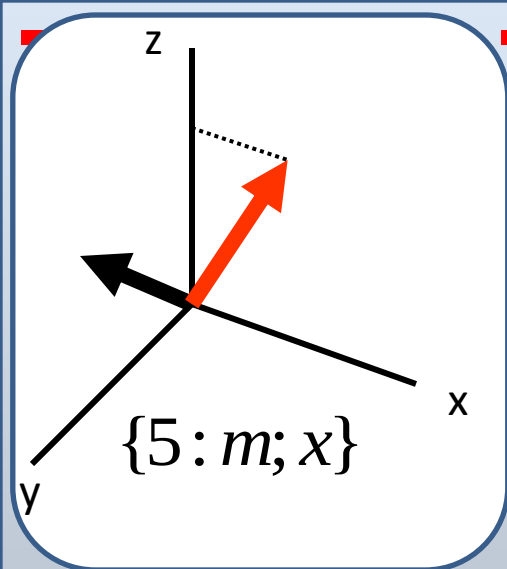
Elodie Salager,^a Robin S. Stein,^a Chris J. Pickard,^b Bénédicte Elena^a
and Lyndon Emsley^{*a}

Received 25th November 2008, Accepted 21st January 2009

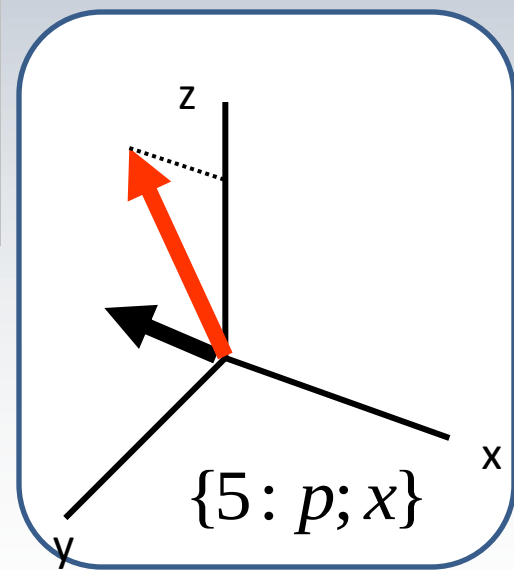
First published as an Advance Article on the web 25th February 2009

DOI: 10.1039/b821018g





$$\Delta\omega > 0$$



WP M L G5

x

x

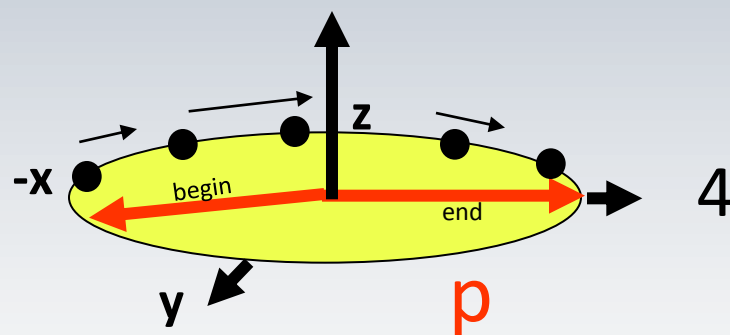
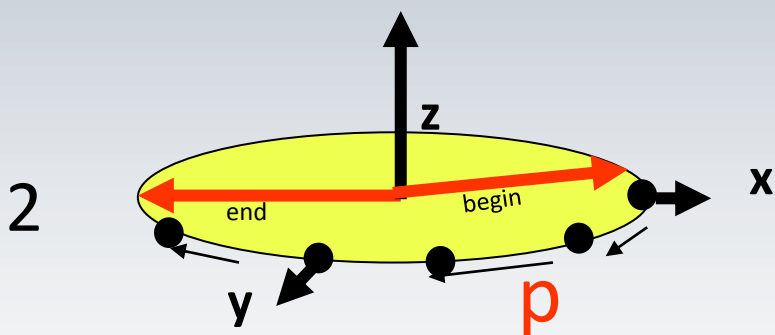
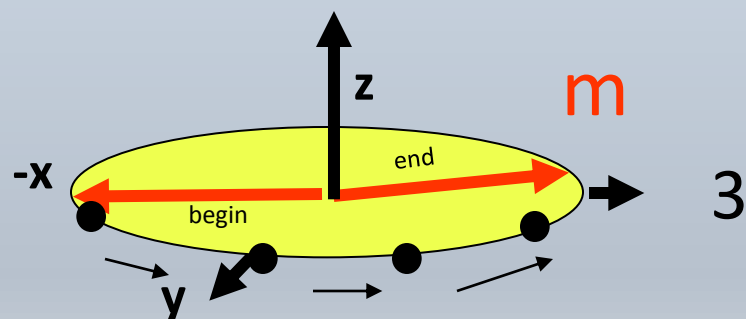
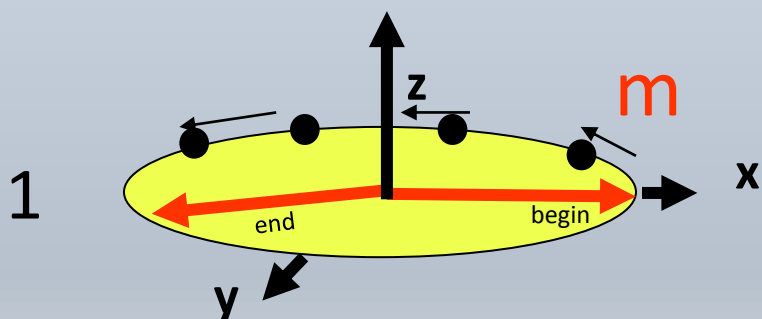
m

m

supercycle

Rotating frame

Rotating frame



mx

p

$m\bar{x}$

p

1

2

3

4

wP M L G5

x

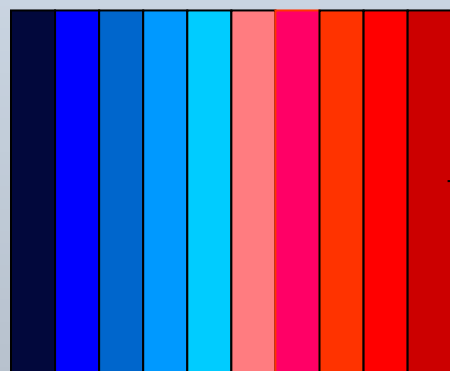
$\bar{x}$

m

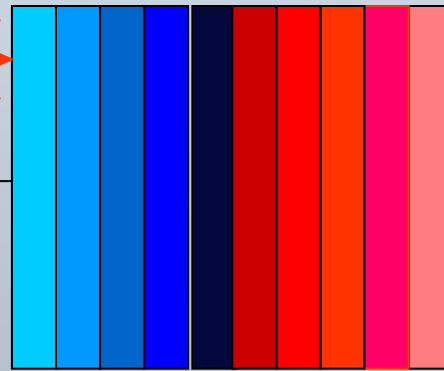
m

Supercycle

M. Leskes, P.K. Madhu, SV, [JCP \(2008\), 128\(5\)](#)



$\{5:m;x\}$



$\{5:m;\bar{x}\}$

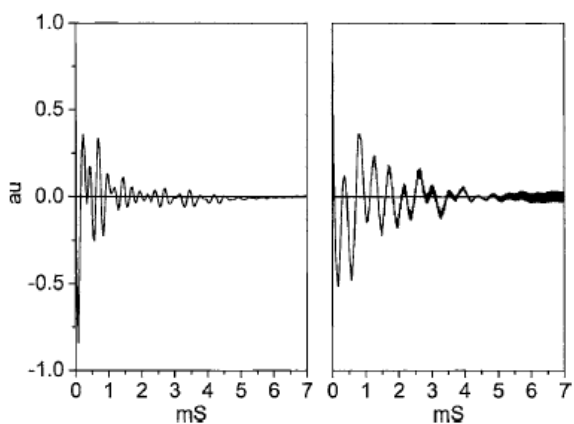


FIG. 7. The glycine time-domain signals acquired with wPMLG5 $\bar{x}$ when detected at every $\tau_c^{\bar{x}}$ (left) and τ_c^x (right). Different off-resonance values were used to emphasize the effect of nonsynchronized detection.

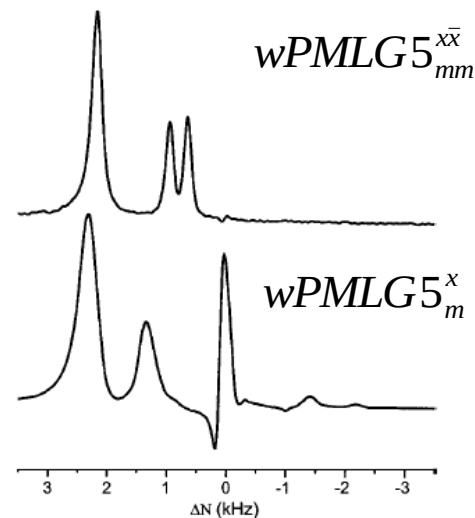


FIG. 6. Experimental glycine spectra obtained at 10 kHz spinning with wPMLG5 $\bar{x}$ (top) and wPMLG5 $_m^x$ (bottom). A pulse length of 1.4 μ s, window of 4.35 μ s, and a rf power of 95 kHz, optimized for the best performance of the $\bar{x}$ scheme, were chosen.

DQ-SQ Correlation

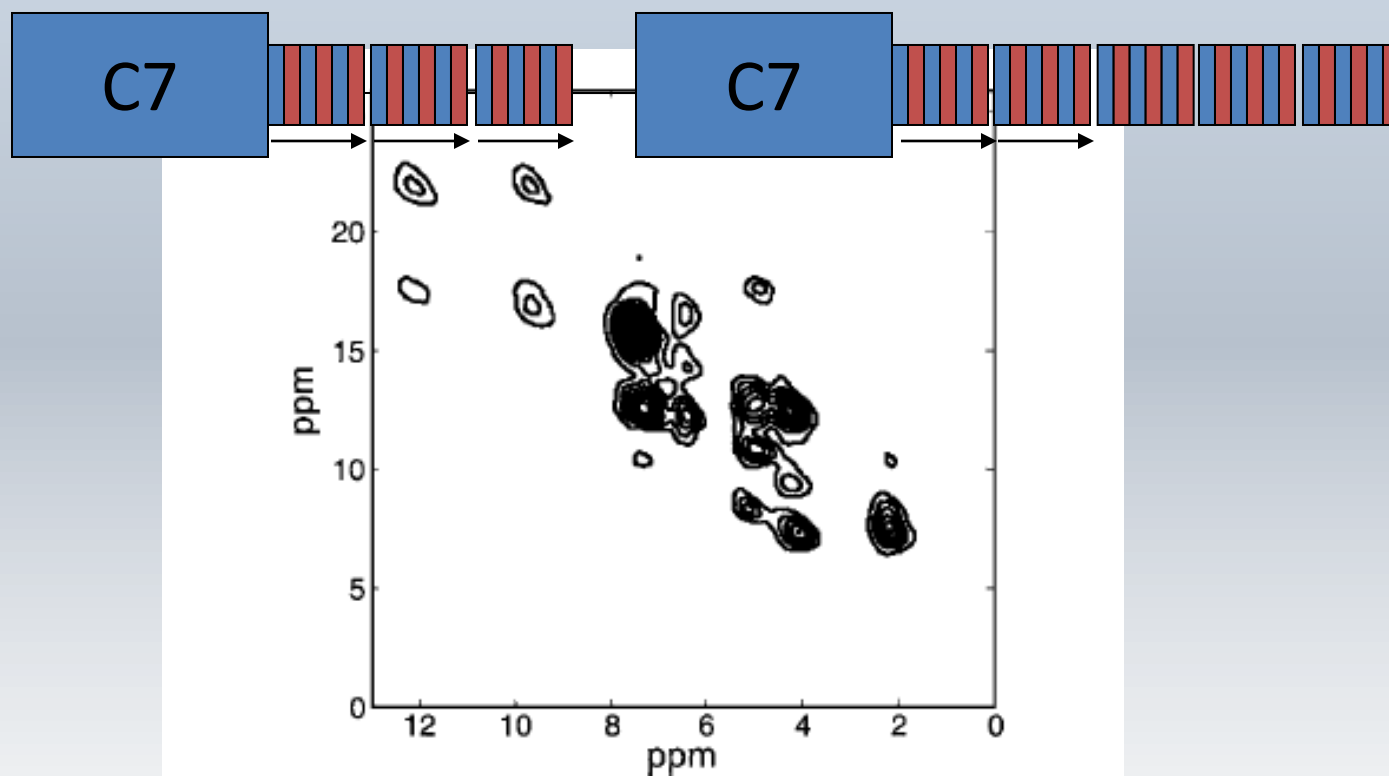
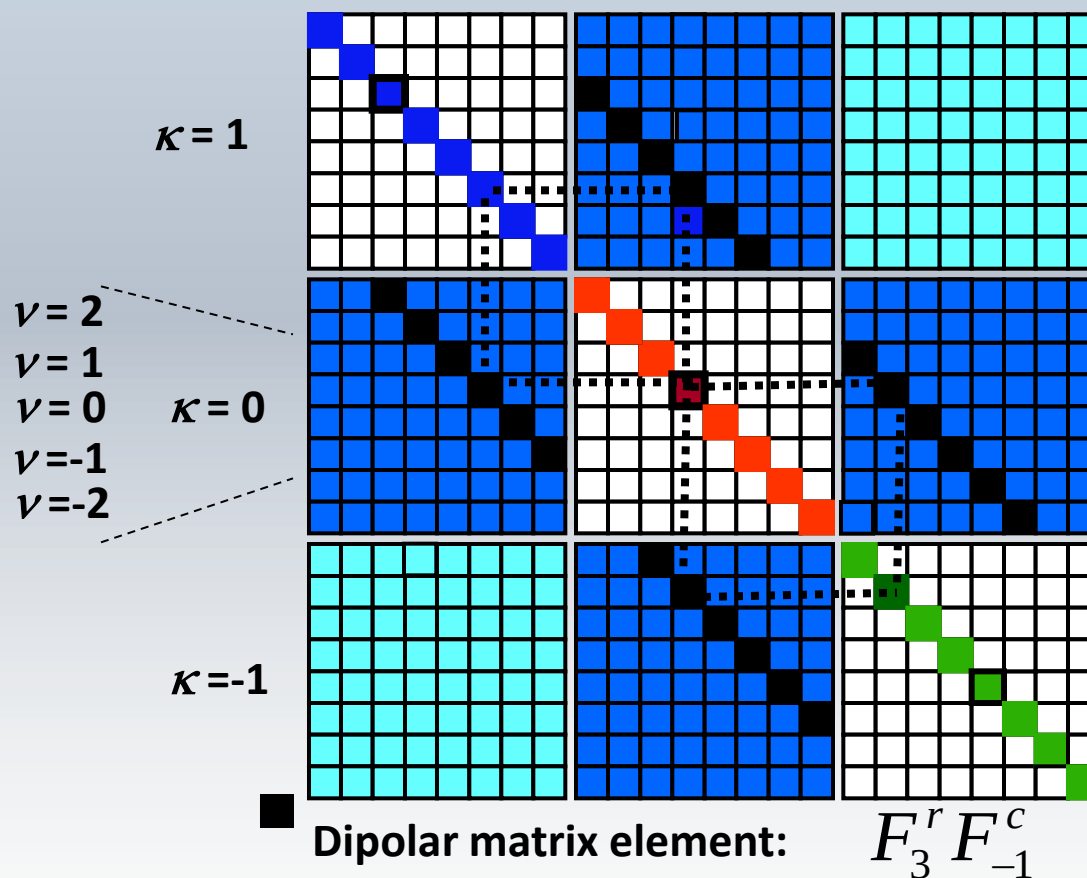


FIG. 10. DQ-SQ correlation spectrum of tyrosine HCl obtained using a one rotor period of $C7_1^3$ as the DQ excitation and reconversion pulse sequence and a data acquisition at a spinning frequency of 20 kHz using $wPMLG5_{mm}^{\bar{x}x}$ in both the time dimensions. DQ filter phase cycling and TPPI detection were used to select the desired DQ pathway and obtain frequency discrimination in the indirect dimension.

Example of accidental degeneracy

An example



$$\{n = 3 ; k = -1\}$$

Accidental degeneracy

An example

$$3\omega_r - \omega_c \neq 0$$

$$s\sigma I_z F_0^r F_0^c + \chi I_x H_{3,-1} F_3^r F_{-1}^c + \chi I_x F_{-3}^r F_1^c + \omega_r N^r + \omega_c N^c$$

$|\beta, 0, 0\rangle$

$|\beta, 3, -1\rangle$

$|\beta, 0, 0\rangle$

$$\begin{pmatrix} \frac{s\sigma}{2} & 0 \\ 0 & -\frac{s\sigma}{2} \end{pmatrix}$$

$$\begin{pmatrix} 0 & \frac{\chi}{2} \\ -\frac{\chi}{2} & 0 \end{pmatrix}$$

$|\beta, 3, -1\rangle$

$$\begin{pmatrix} 0 & \frac{\chi}{2} \\ -\frac{\chi}{2} & 0 \end{pmatrix}$$

$$\begin{pmatrix} \frac{s\sigma}{2} + 3\omega_r - \omega_c & 0 \\ 0 & -\frac{s\sigma}{2} + 3\omega_r - \omega_c \end{pmatrix}$$

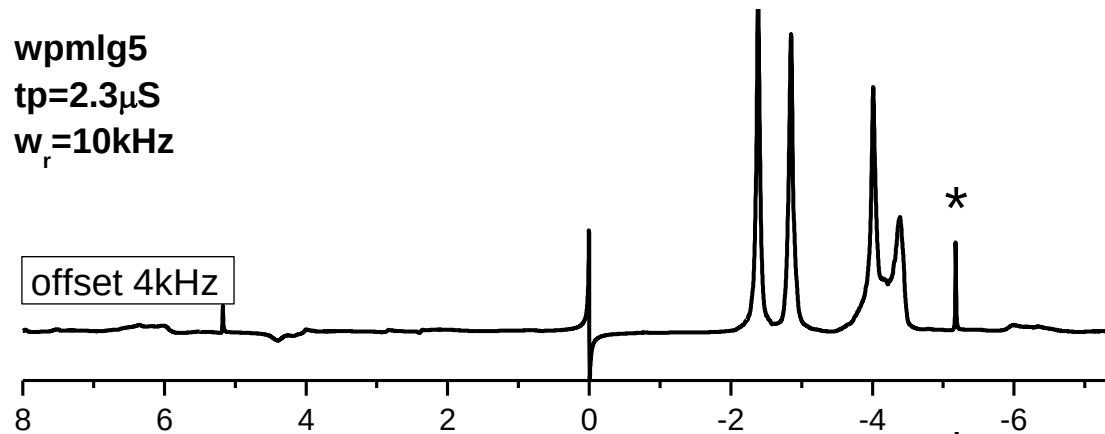
Example of accidental degeneracy

An example

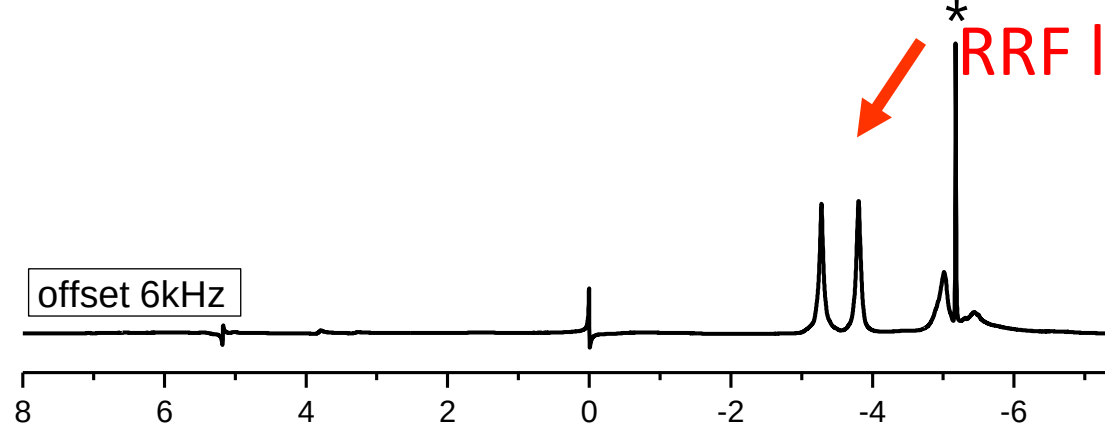
$$3\omega_r - \omega_c = s\sigma$$

wpm1g5
tp=2.3μS
w_r=10kHz

offset 4kHz



offset 6kHz

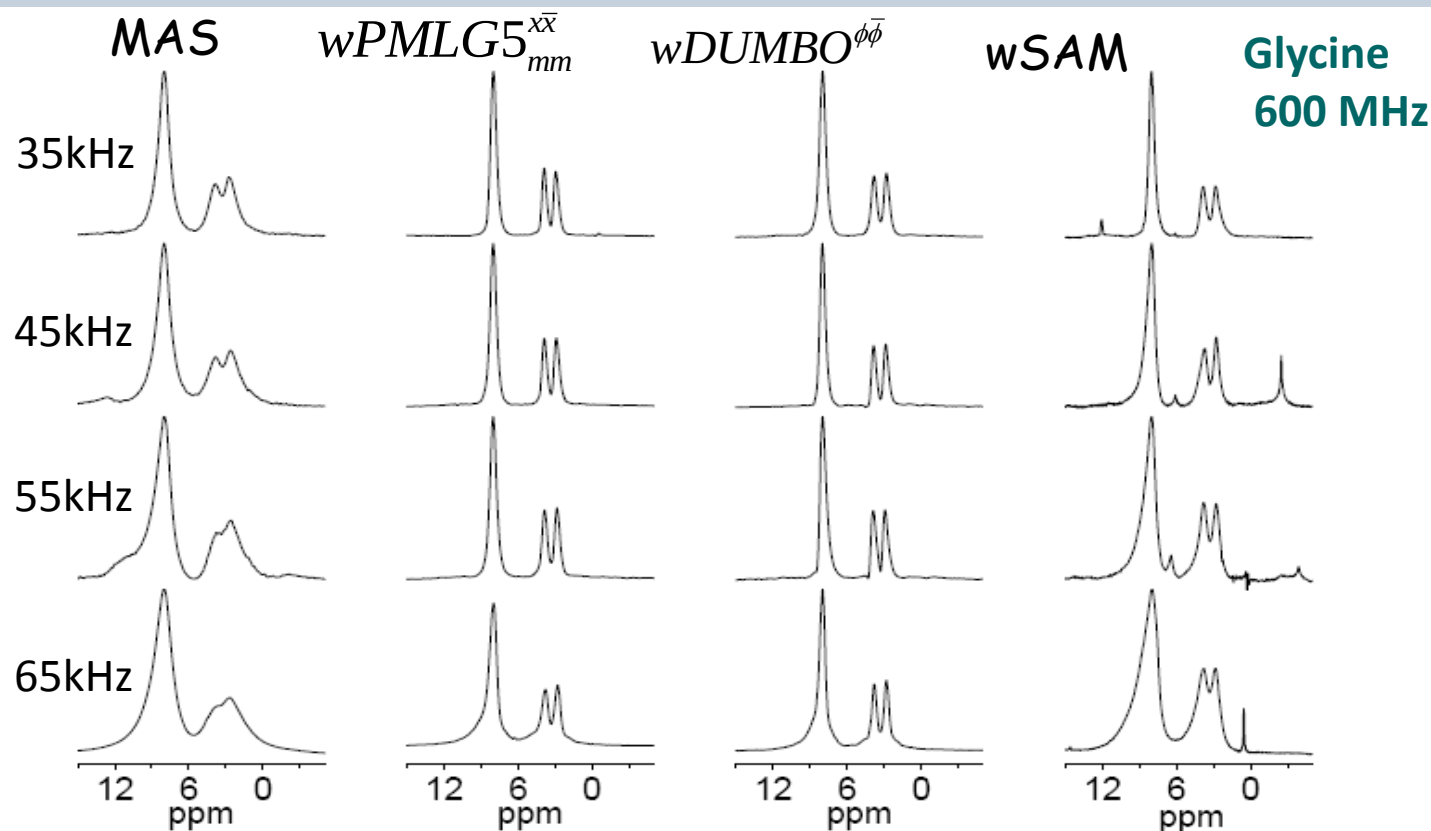


RRF lines

kHz

CRAMPS at high spinning frequencies

M. Leskes, S. Steuernagel, D. Schneider, P.K. Madhu, SV, CPL (2008)



DUMBO:

D. Sakellariou, A. Lesage,
P. Hodgkinson, L. Emsley,
Chem. Phys. Lett. 319
(2000) 253.

SAM:

J.P. Amoureux, B. Hu,
J. Trebosc,
J. Magn. Reson. 193
(2008) 305.

Table 1

Experimental parameters.

Pulse scheme	$\omega_r/2\pi$ (kHz)	35	45	55	65
wPMLG5 $_{mm}^{xx}$	τ_{rf} (μ s)	15.4	11.6	12	9.6
	$\omega_1/2\pi$ (kHz)	131	180	190	216
	$\omega_c/2\pi$ (kHz)	26.32	34.97	34.01	40.65
	s	0.44	0.45	0.43	0.48
wDUMBO $^{\phi\bar{\phi}}$	τ_{rf} (μ s)	15.4	12	12	9.6
	$\omega_1/2\pi$ (kHz)	196	232	226	254
	$\omega_c/2\pi$ (kHz)	26.32	34.01	34.01	40.65
	s	0.54	0.55	0.56	0.56
wSAM	τ_{rf} (μ s)	20	22.2	36.4	15.4
	τ_m (μ s)	6.67	7.41	5.2	5.13
	$\omega_1/2\pi$ (kHz)	124	137	183	194
	$\omega_c/2\pi$ (kHz)	42.37	40.1	25.6	55.3
	s	0.88	0.78	0.75	0.73
	w (μ s)	3.6	2.7	2.7	2.7

Remember: The effective dipolar Hamiltonian

$$\tilde{H}_{00} F_0^r F_0^c \cong \left\{ H_{00} - \frac{1}{2} \sum_{k,n;\neq 0,0} \frac{[H_{n,k}, H_{-n,-k}]}{n\omega_r + k\omega_c} \right\} F_0^r F_0^c$$

Avoid the degenerate resonance case

$$n\omega_r + k\omega_c = 0$$

$$H_F = \tilde{H}_{0,0} F_0^r F_0^c + \boxed{H_{n,k} F_n^r F_k^c} - \frac{1}{2} \sum_{\substack{n',n'' \\ k',k''}} \frac{[H_{n',k'}, H_{n'',k''}]}{n'\omega_r + k'\omega_c} F_{n'+n''}^r F_{k'+k''}^c + \omega_r N^r + \omega_c N^c$$

wPMLG at high spinning frequencies

M. Leskes, P.K. Madhu, SV, JMR (2009),

Minimize
Dipolar broadening

$$\sum_{n,k} \frac{[H_{nk}, H_{-n-k}]}{n\omega_r + k\omega_c} \propto \sum_{n,k} \frac{d_{nk}^{(2)} d_{-n-k}^{(2)}}{n\omega_r + k\omega_c}$$

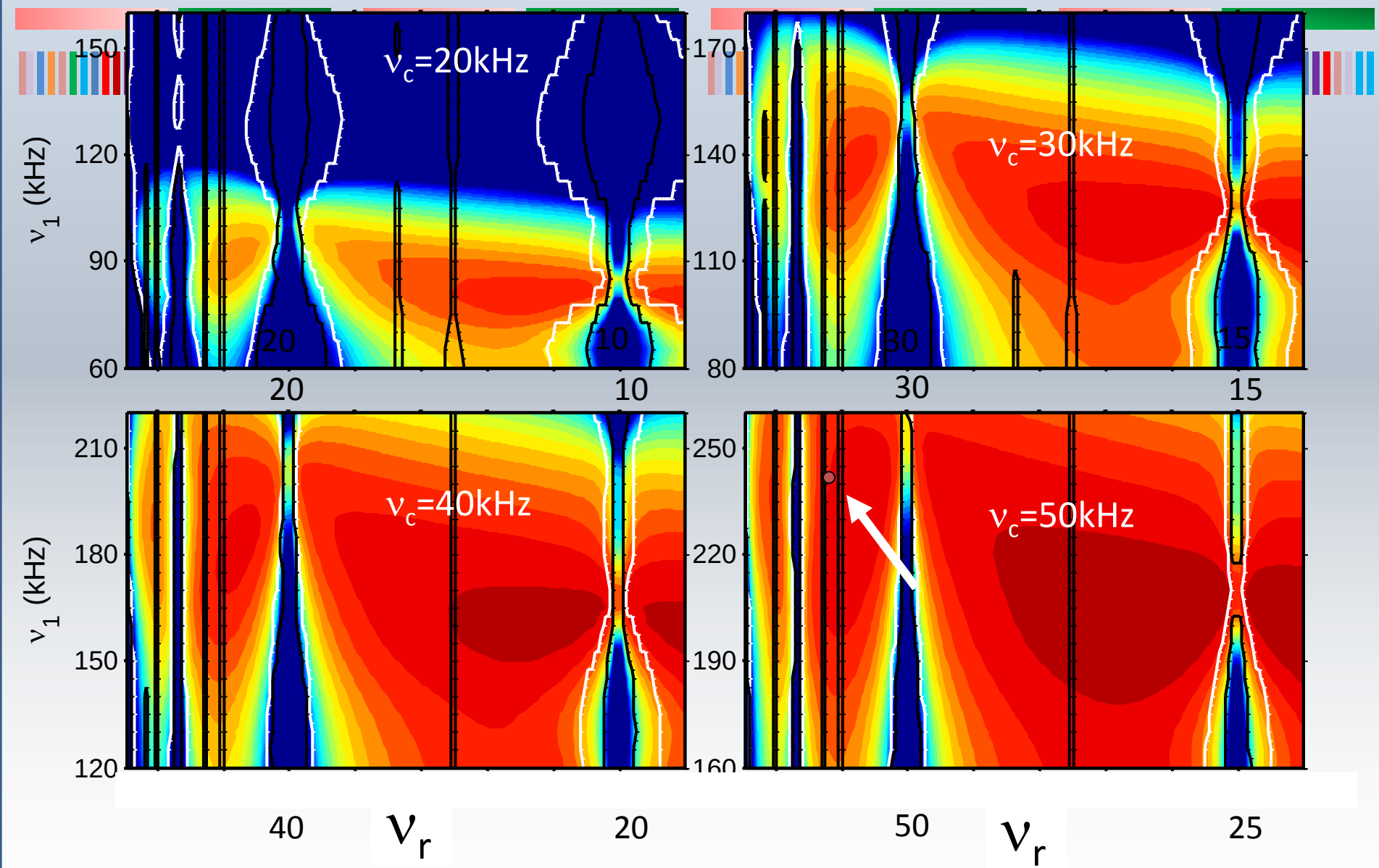
$$\chi^2 \equiv \frac{\sum_{n,m,m'} \left(\sum_k \frac{d_{mk}^{(2)} d_{m'-k}^{(2)}}{n\omega_r + k\omega_c} \right)^2}{\sum_m \left(\sum_k d_{mk}^{(1)} \right)^2}$$

Maximize
Chemical shift

$$H_{00} \propto \sum_k d_{mk}^{(1)}$$

WP M L G5

x x
mm



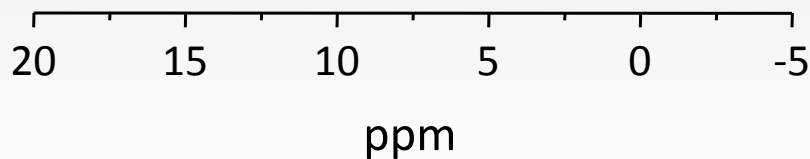
Fast MAS Experiments: Tyrosine.HCl at 600 MHz

MAS at 65 kHz

$$\psi = \omega_c / \omega_r = 0.63, \nu_{\text{nut}} = 216 \text{ kHz}$$

MAS at 10 kHz

$$\psi = \omega_c / \omega_r = 2.75, \nu_{\text{nut}} = 96 \text{ kHz}$$



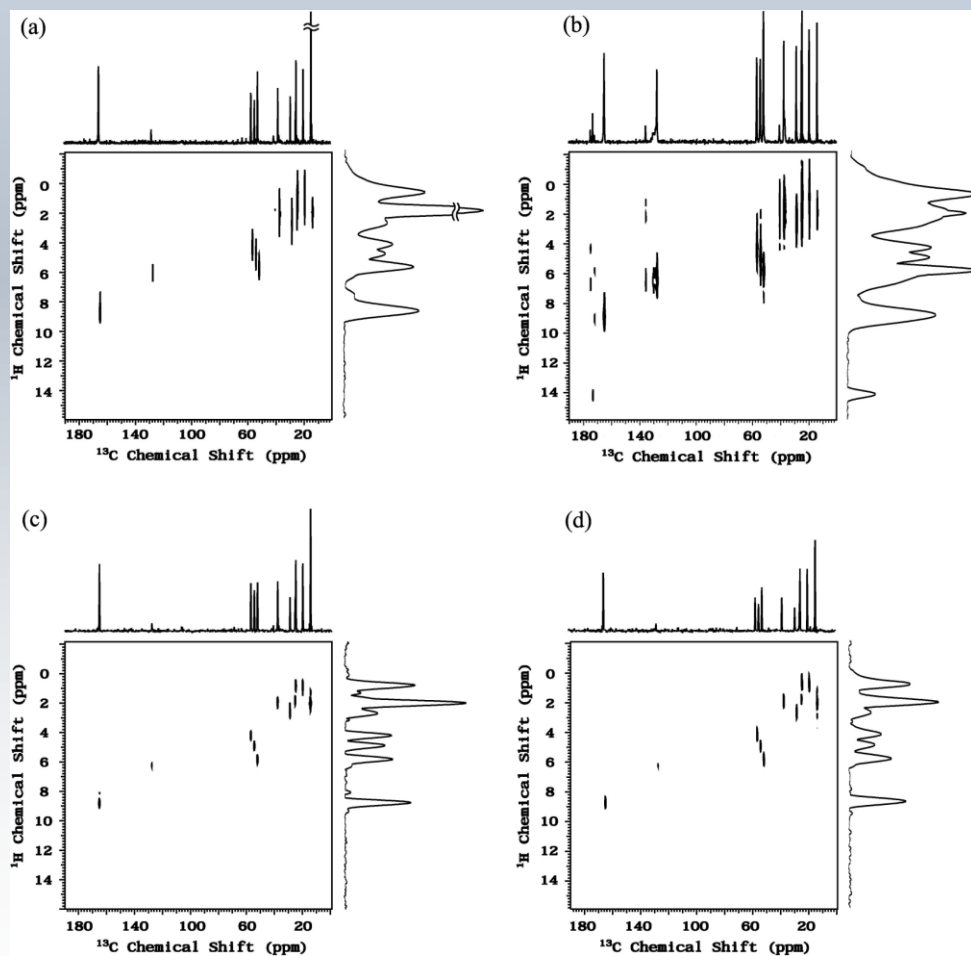
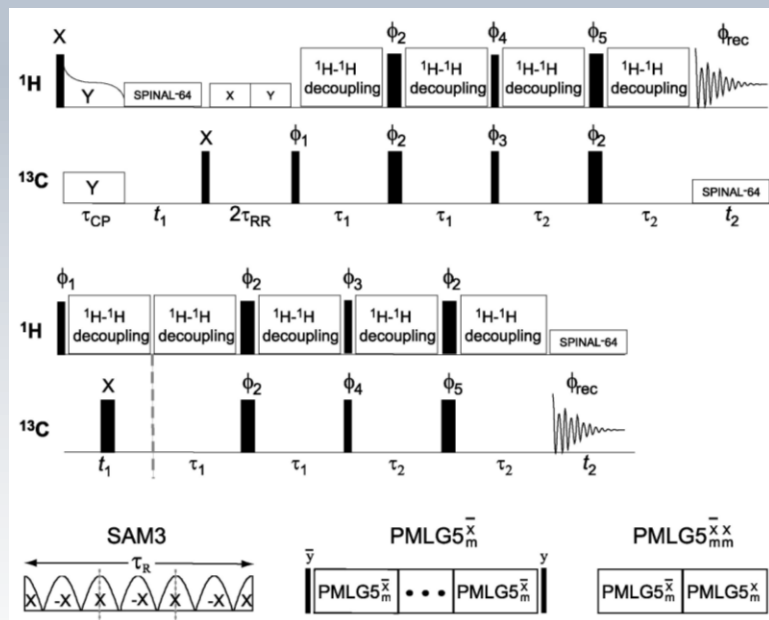


Directly and indirectly detected through-bond heteronuclear correlation solid-state NMR spectroscopy under fast MAS

Kanmi Mao, Marek Pruski *

Ames Laboratory, Iowa State University, Ames, IA 50011–3020, USA
Department of Chemistry, Iowa State University, Ames, IA 50011–3020, USA

$$f - MLF - OH$$

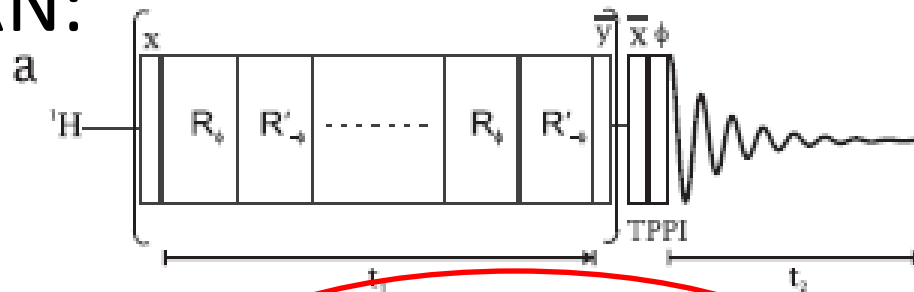


R-symmetry derived pulse sequences

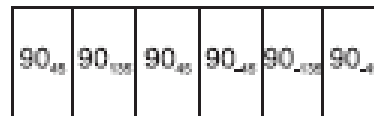
S. Paul, D. Schneider, P.K Madhu, JMP in press

2D-RN versus 2D-wPMLG at high spinning frequencies

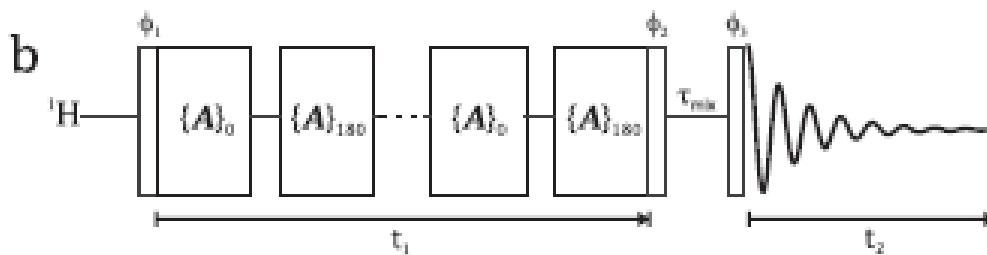
RN:



$\{R_y R'_y\} \equiv$

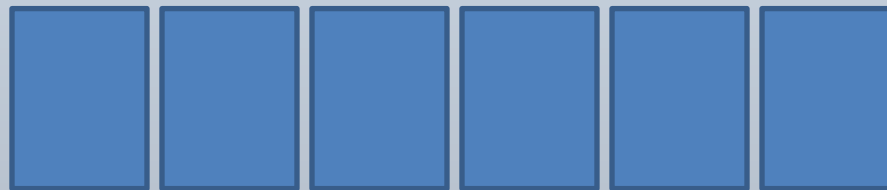


wPMLG:



Exercise : What is the interaction CS-Hamiltonian

90_0 90_{90} 90_0 90_{-90} 90_{-180} 90_{-90}



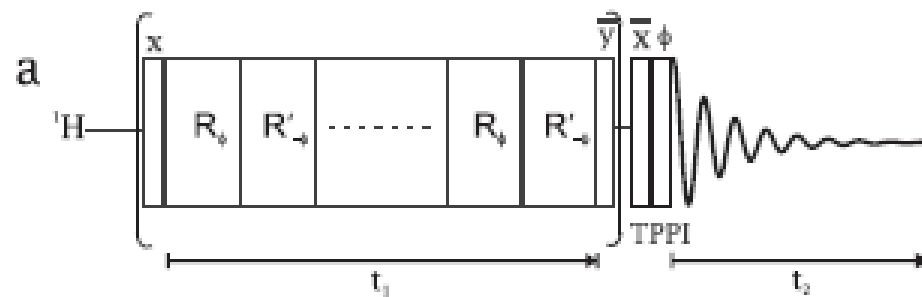
I_x	0	+	+	0	+	+
I_y	-	-		-	-	0
I_z	+	0	-	-	0	+

$$H_{CS}^{\text{int}(0)} = \frac{s}{\sqrt{2}} \sigma(I_x - I_y)$$

45^0

R-symmetry derived pulse sequences

S. Paul, D. Schneider, P.K. Paul, JMP in press



$$\{R_y R'_y\} \equiv \begin{array}{|c|c|c|c|c|c|} \hline 90_{45} & 90_{135} & 90_{45} & 90_{-45} & 90_{-135} & 90_{-45} \\ \hline \end{array}$$

$$H_{CS}^{\text{int}(0)} = s \sigma I_x$$

Remember for
DECOUPLING

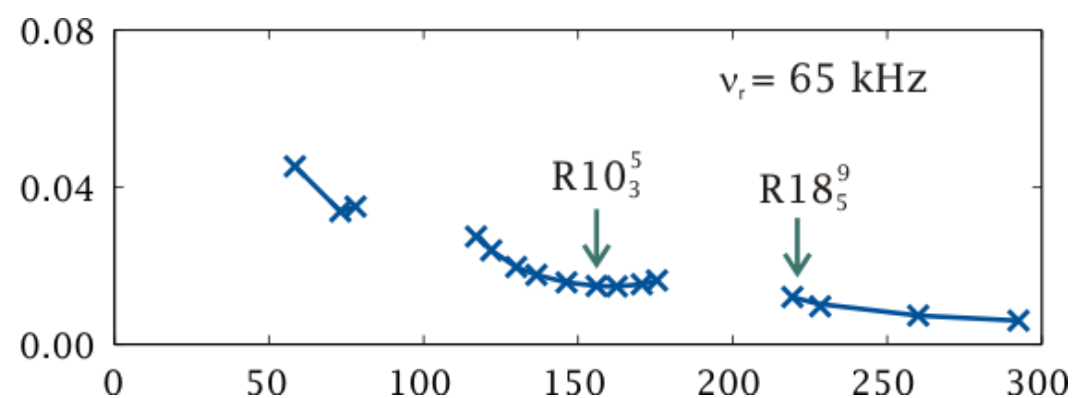
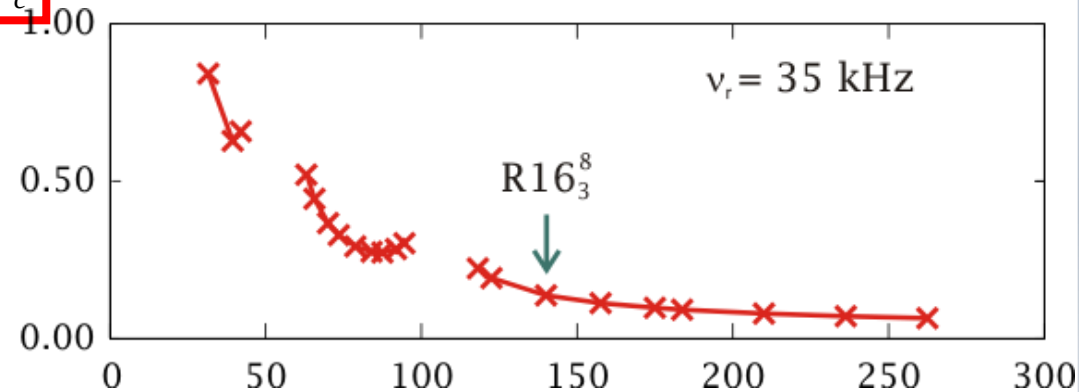
minimize

$$\Delta_{m,m'}^n = \sum_{m,m'} \sum_k \frac{d_{m,k} d_{m',-k}}{n\omega_r + k\omega_c}$$

Stay away from

$$n_d \omega_r + k_d \omega_c = 0$$

$$\sum_{n,k,m,m'} |\Delta_{m,m'}^{n,k}|$$



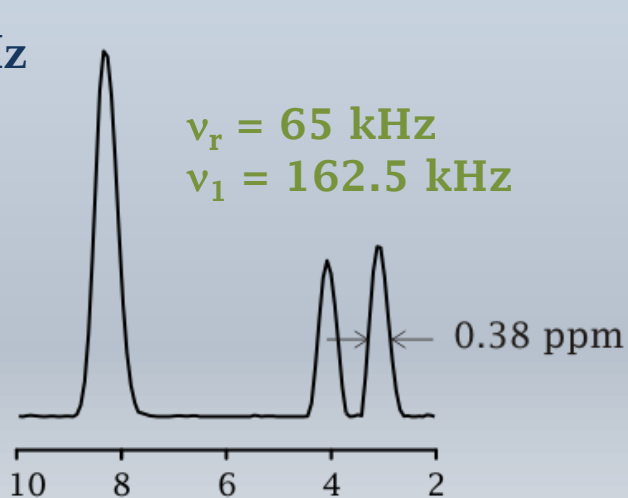
In the 2D mode

RN_n^ν

$wPMLG_{mm}^{\bar{x}x}$

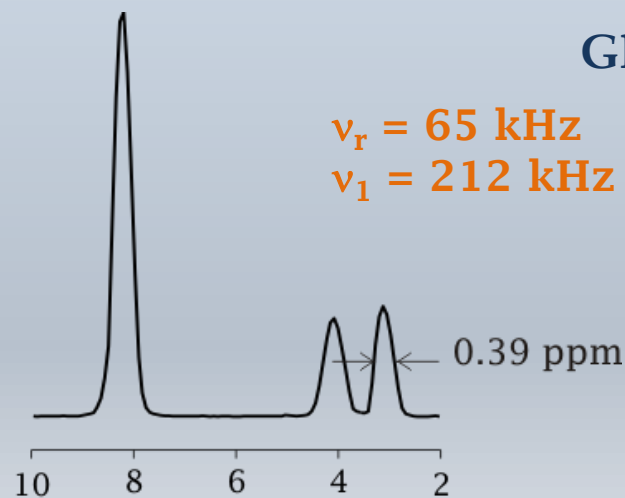
600 MHz

$\nu_r = 65 \text{ kHz}$
 $\nu_1 = 162.5 \text{ kHz}$

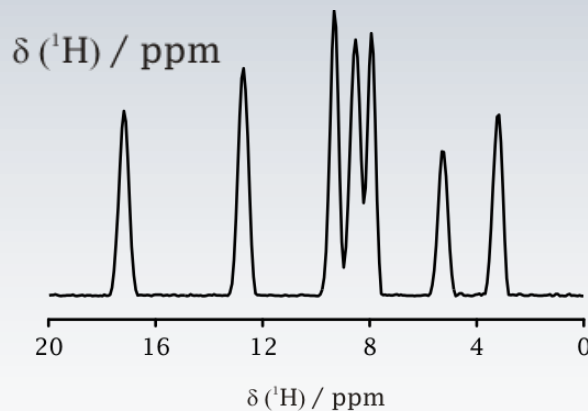


Glycine

$\nu_r = 65 \text{ kHz}$
 $\nu_1 = 212 \text{ kHz}$



$R10_3^5$



$U\text{-}^{13}\text{C}\text{-L-Histidine.HCl.H}_2\text{O}$