

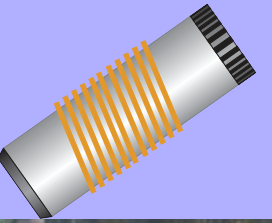
NMR Experimental Building Blocks in Solid-State NMR

Matthias Ernst

*Institute for Molecular Physical Sciences, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland
NMR Meets Biology 6, Samrudhii Resort, Gorkana, India, 26.1.2026*

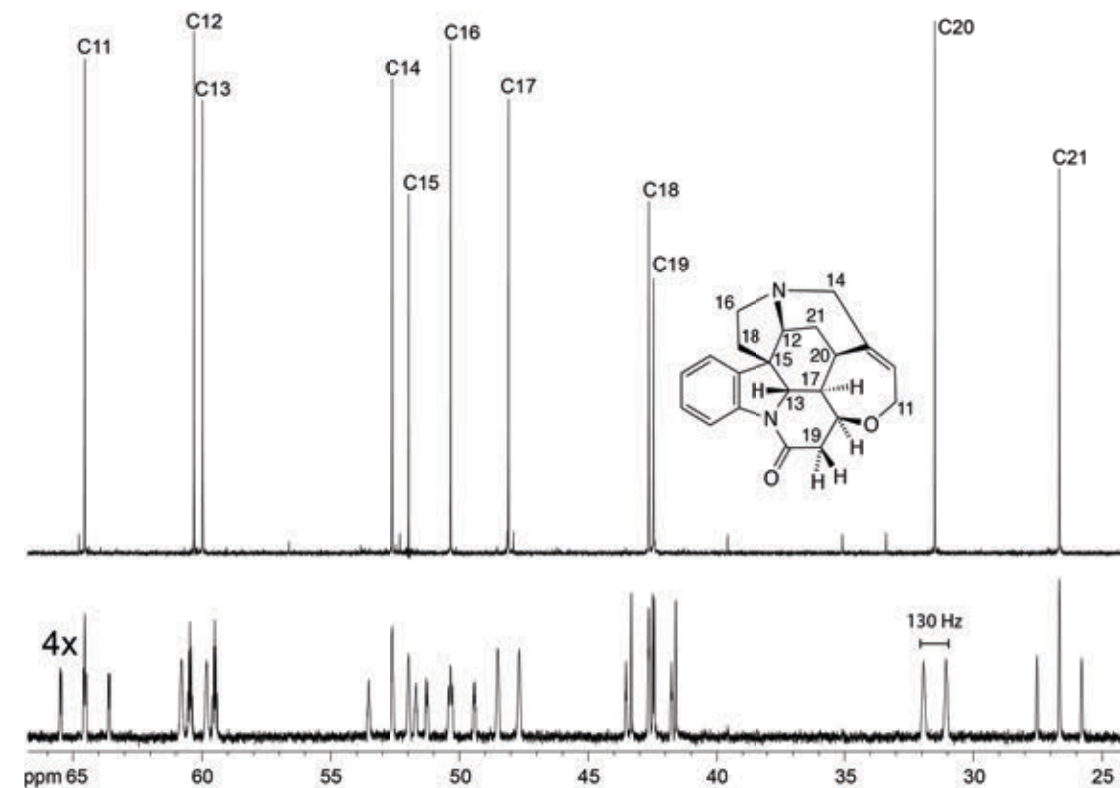
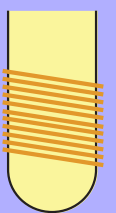


Introduction and Overview

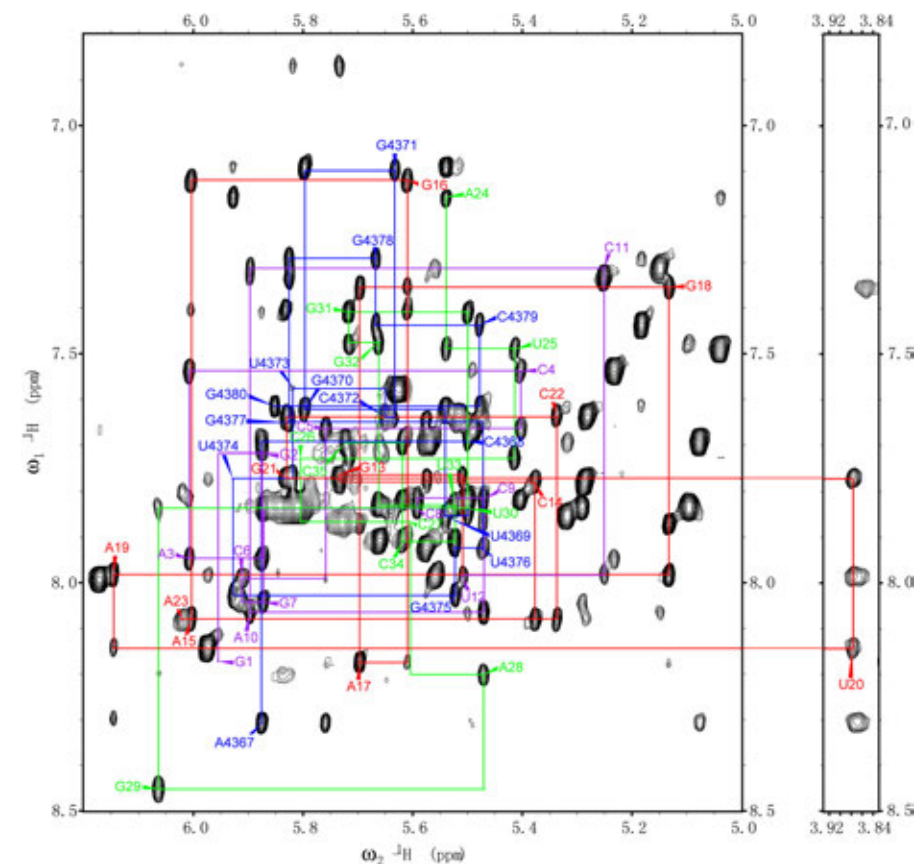


Hampi, 2022

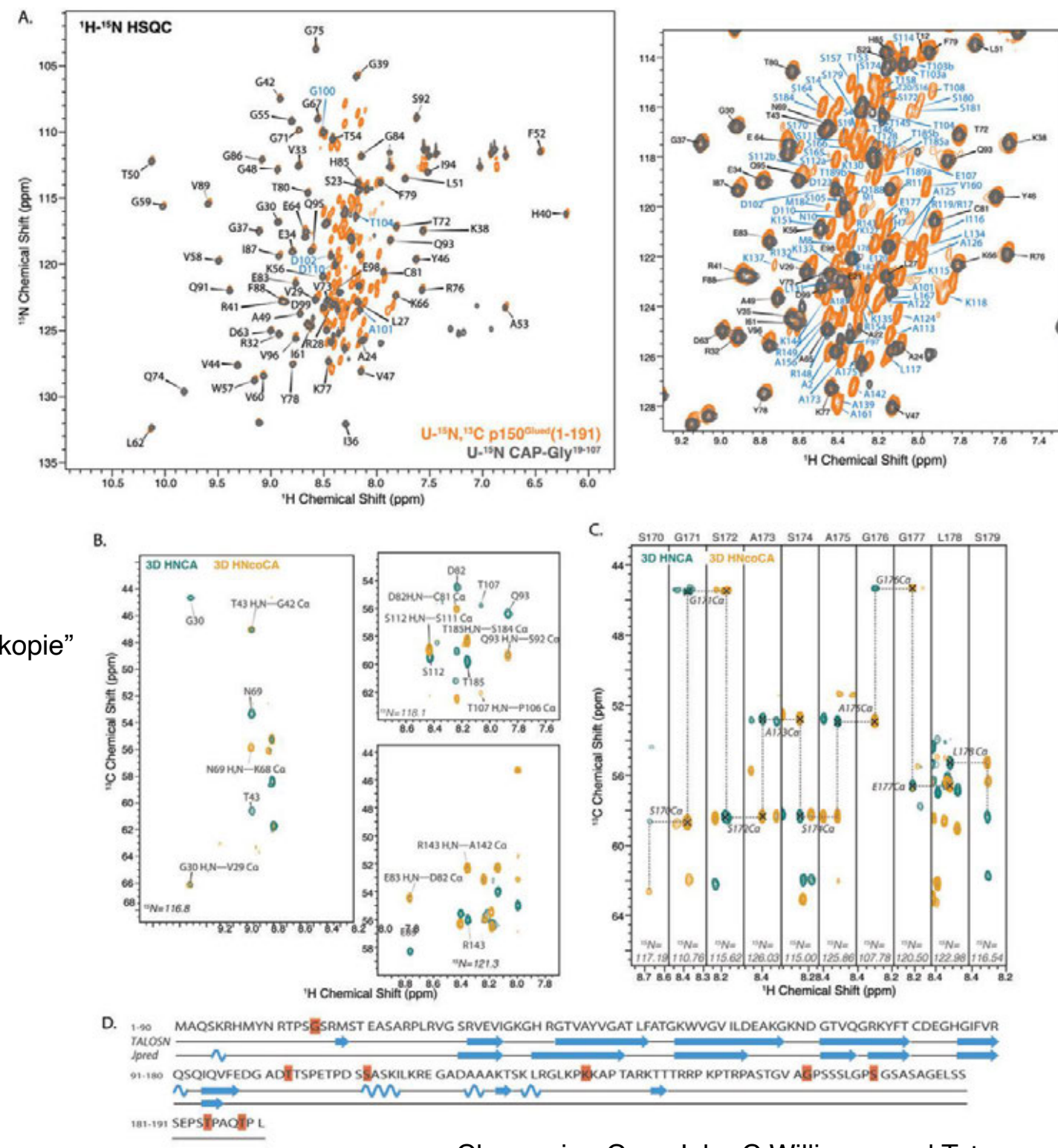
Liquid-State NMR - High Spectral Resolution



M.O. Ebert, Skript zur Vorlesung "Analytische Chemie I & II NMR-Spektroskopie"

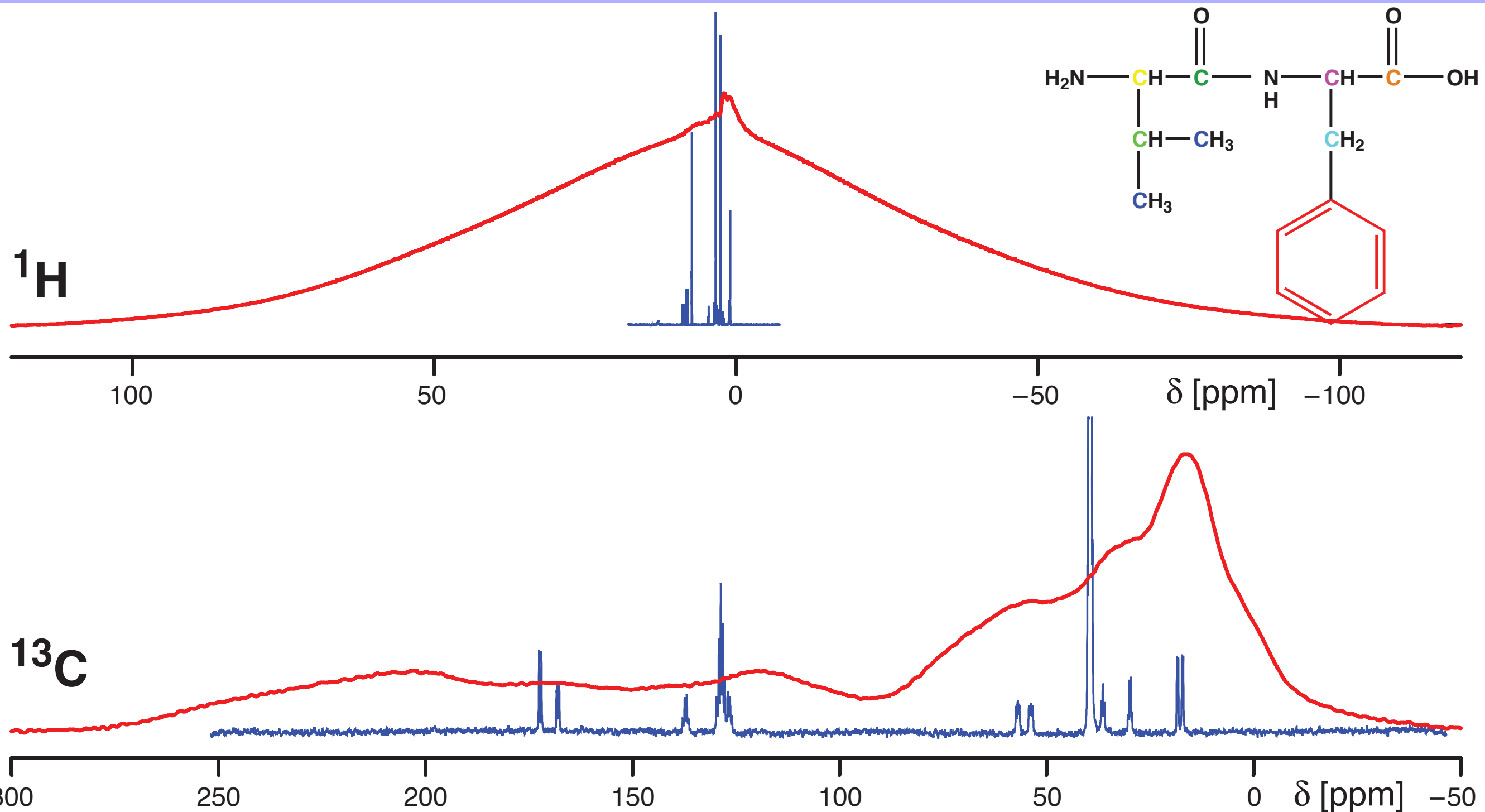
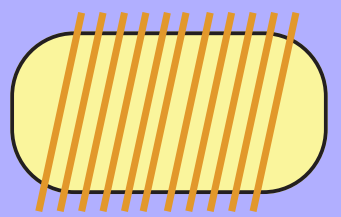


<http://publish.illinois.edu/hongjinlab/gallery-and-movies/> - NOESY Spectrum of HJ3



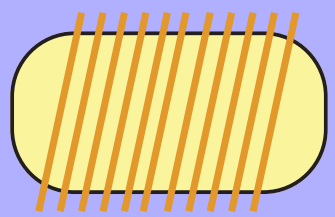
Changmiao Guo, John C. Williams, and Tatyana Polenova, Biophys J. 117, 938-949 (2019)

Solution-State and Solid-State NMR Spectra

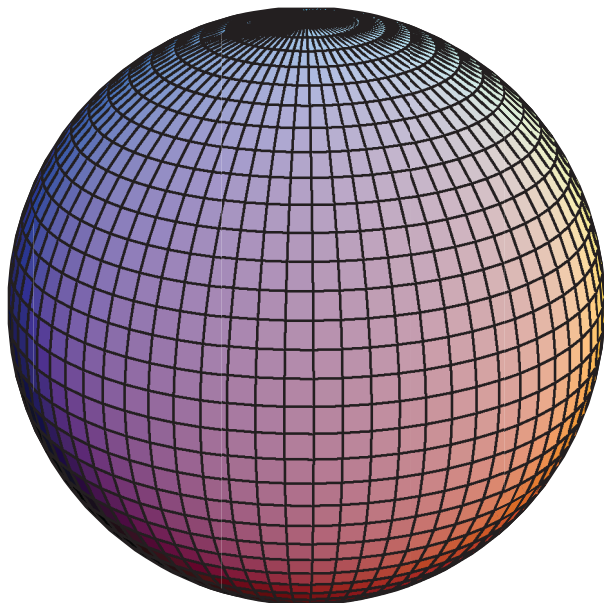


- ❑ Static solid-state NMR spectra of powdered samples are very broad compared to solution-state NMR spectra.
- ❑ This is due to the anisotropic interactions.

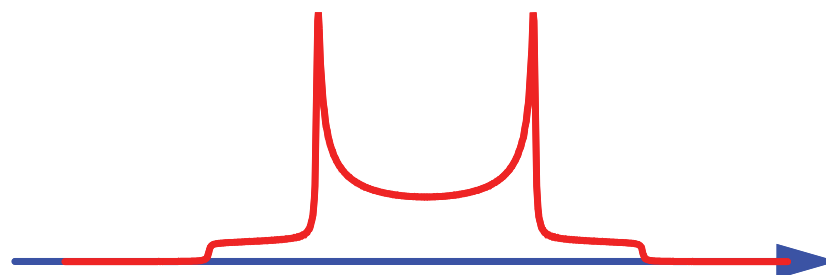
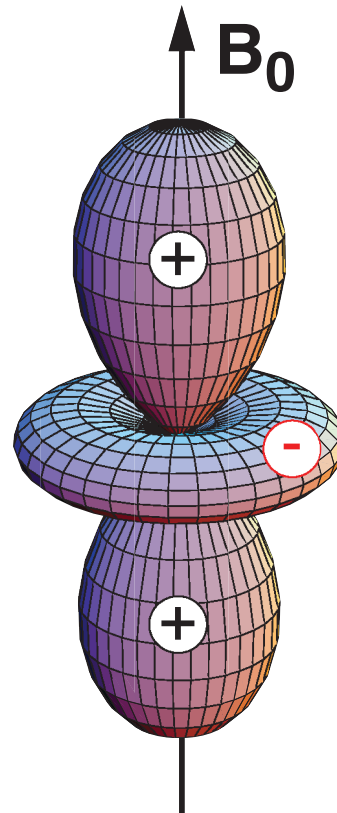
Source of Anisotropy



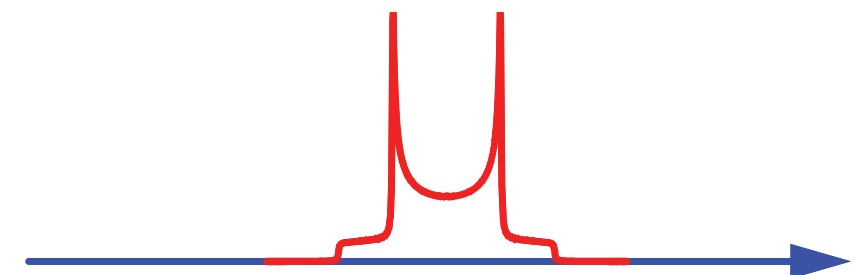
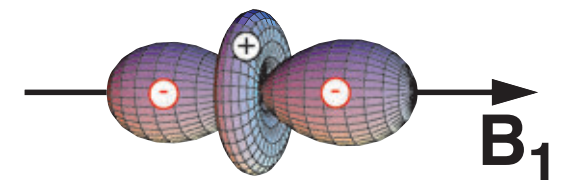
Without an external field, the dipolar-coupling Hamiltonian is isotropic.



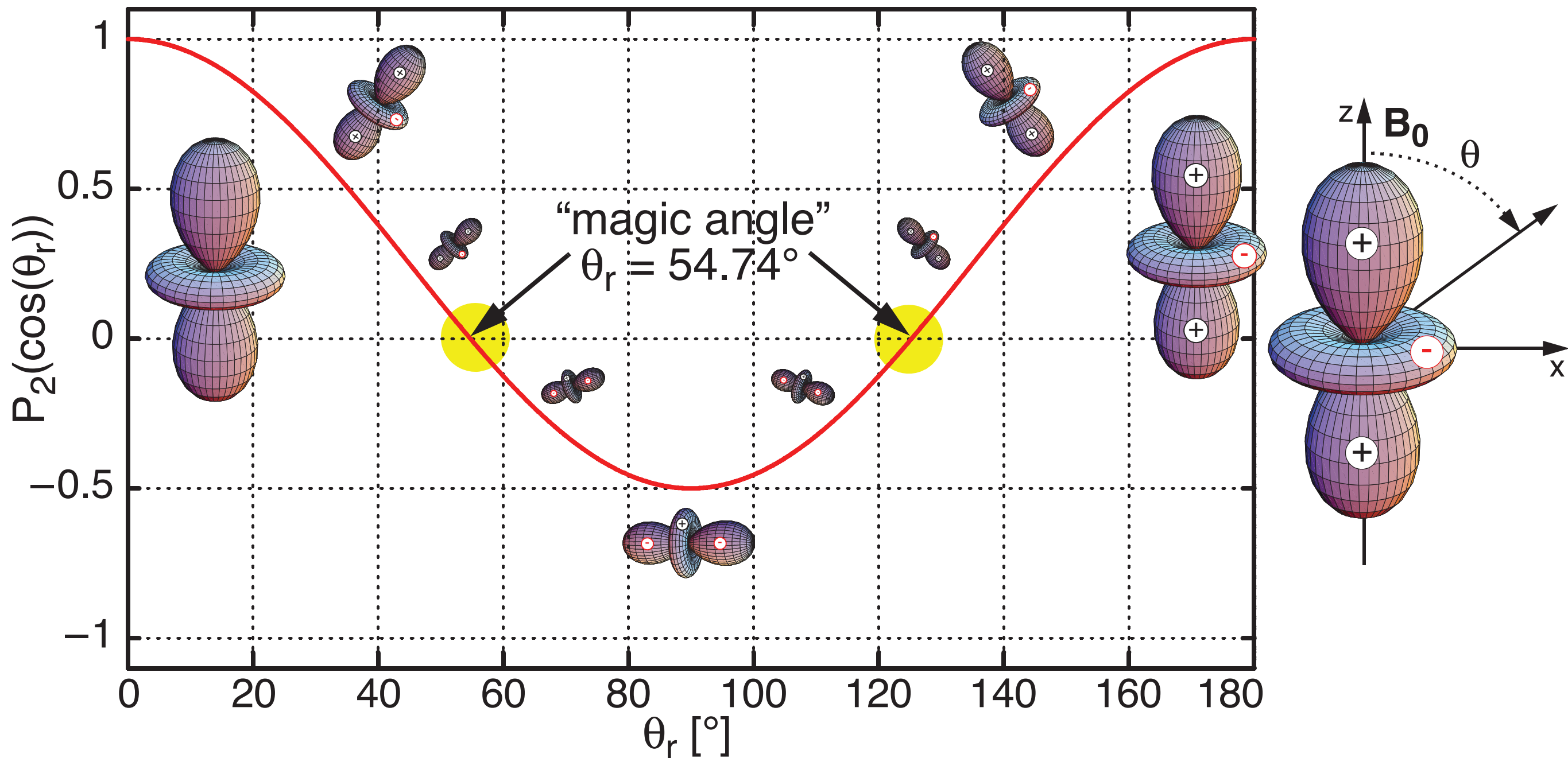
The static magnetic field B_0 truncates the dipolar-coupling Hamiltonian.



An applied rf field B_1 truncates the dipolar-coupling Hamiltonian again.

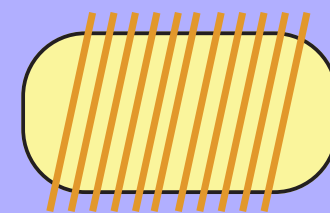


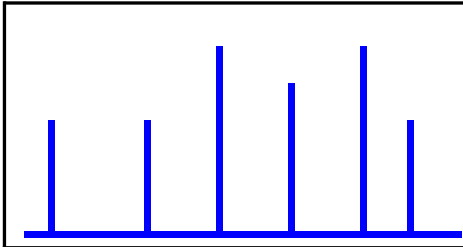
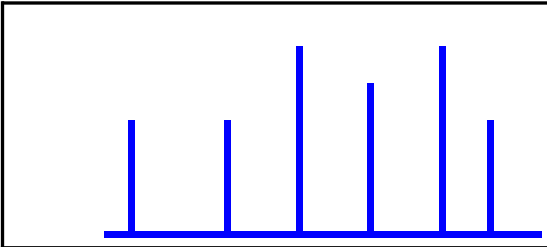
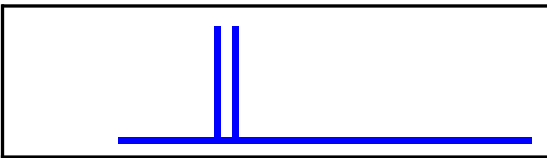
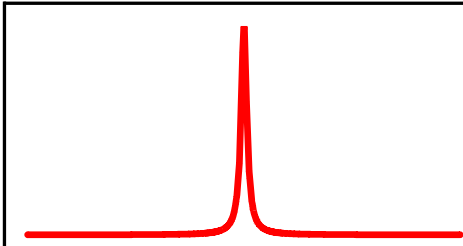
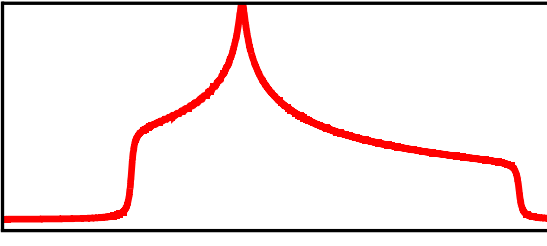
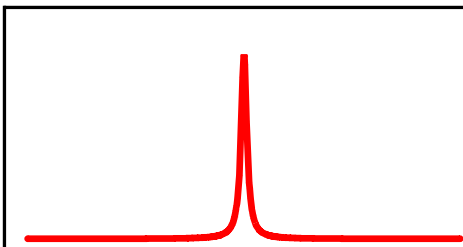
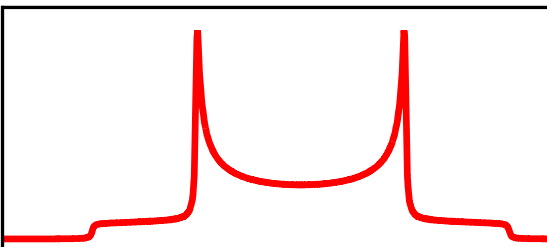
Averaging of Anisotropic Interactions



- ❑ The spatial part of the anisotropic part of the Hamiltonian is a second-rank tensor and has an orientation dependence of $(3 \cos^2(\theta) - 1)/2$.
- ❑ Rotation of the sample about an axis θ_r leads to a scaling of the tensor by $(3 \cos^2(\theta_r) - 1)/2$.

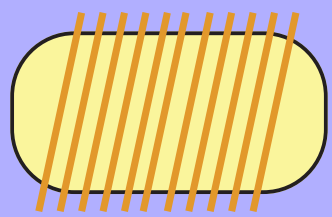
Isotropic and Anisotropic Interactions



Interaction	Liquid-State NMR	Solid-State NMR
chemical shift (20000 Hz)	differentiation between different atoms 	differentiation between different atoms 
J-coupling (100 Hz)	splittings 	splittings 
chemical-shift tensor (20000 Hz)	relaxation: line broadening 	anisotropic powder line shape 
dipolar coupling (50000 Hz)	relaxation: line broadening 	anisotropic powder line (Pake pattern) 

- ❑ Broad powder lines are the source of many technical difficulties in solid-state NMR.
- ❑ High spectral resolution is important to distinguish different lines and match them to atoms in the molecule.

Isotropic and Anisotropic Interactions



Interaction

chemical shift
(20000 Hz)

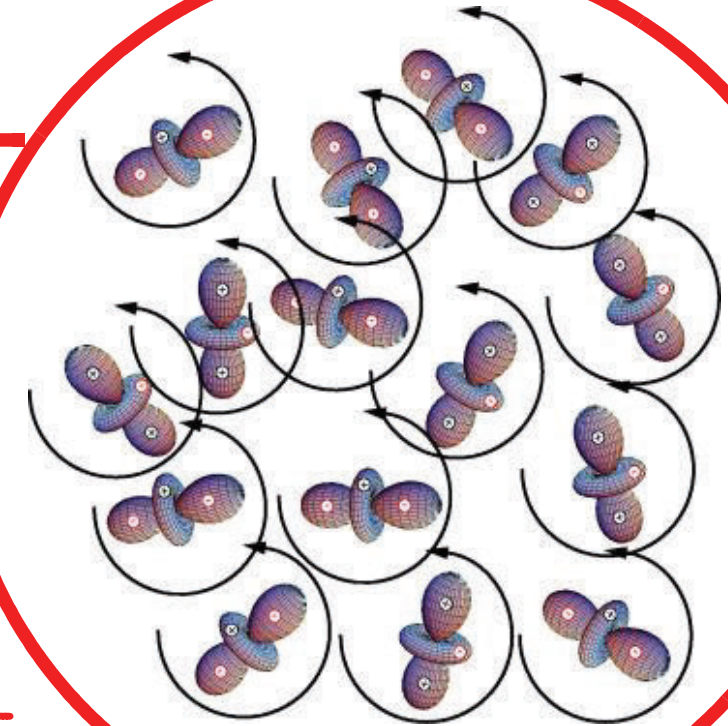
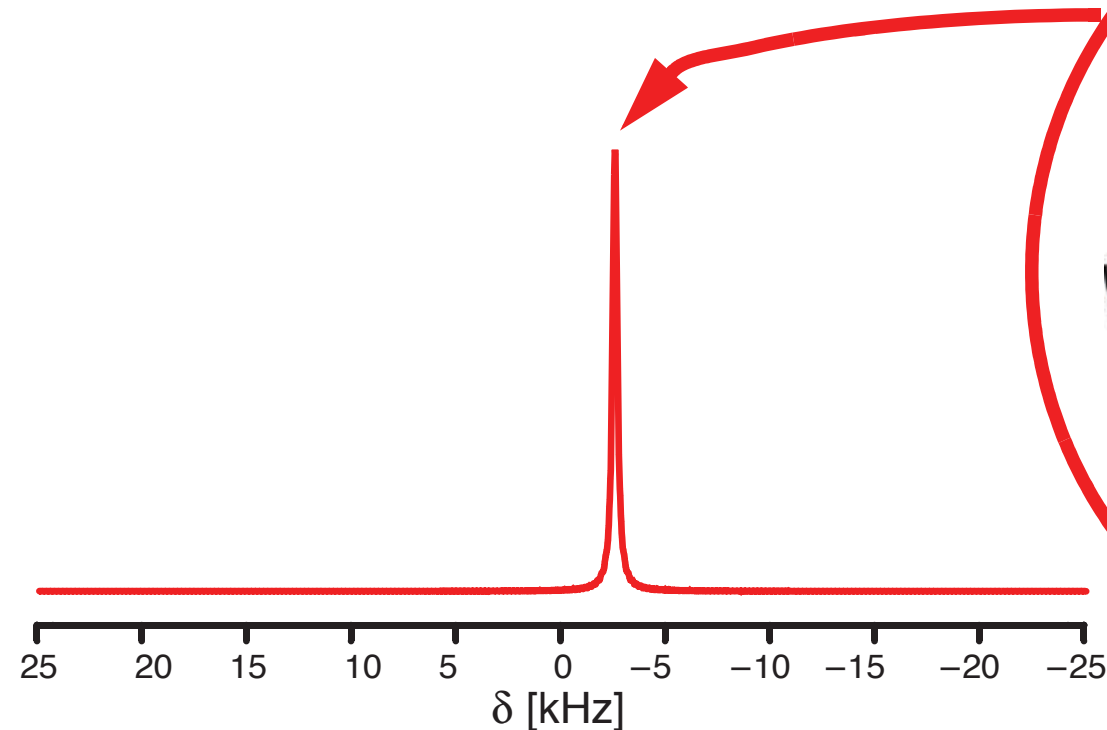
J-coupling
(100 Hz)

chemical-shift tensor
(20000 Hz)

dipolar coupling
(50000 Hz)

Liquid State NMR

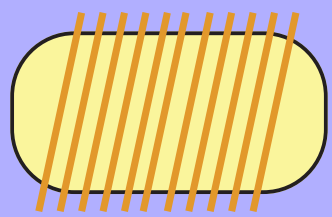
Solid State NMR



- ❑ Molecular tumbling leads to an averaging of the anisotropic interaction.
- ❑ Anisotropy is only manifest through line broadening by relaxation processes.

- ❑ Broad powder pattern
- ❑ High spectral resolution in the molecule.

Isotropic and Anisotropic Interactions



Interaction

chemical shift
(20000 Hz)

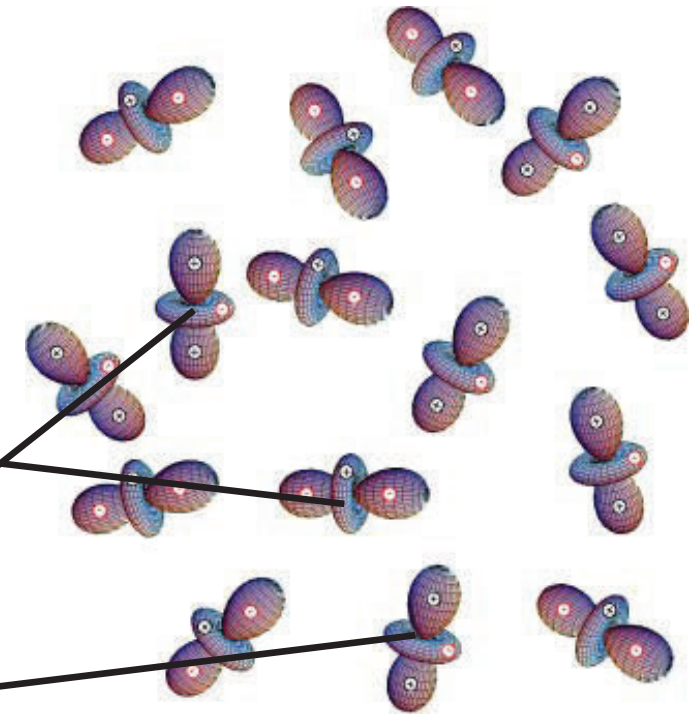
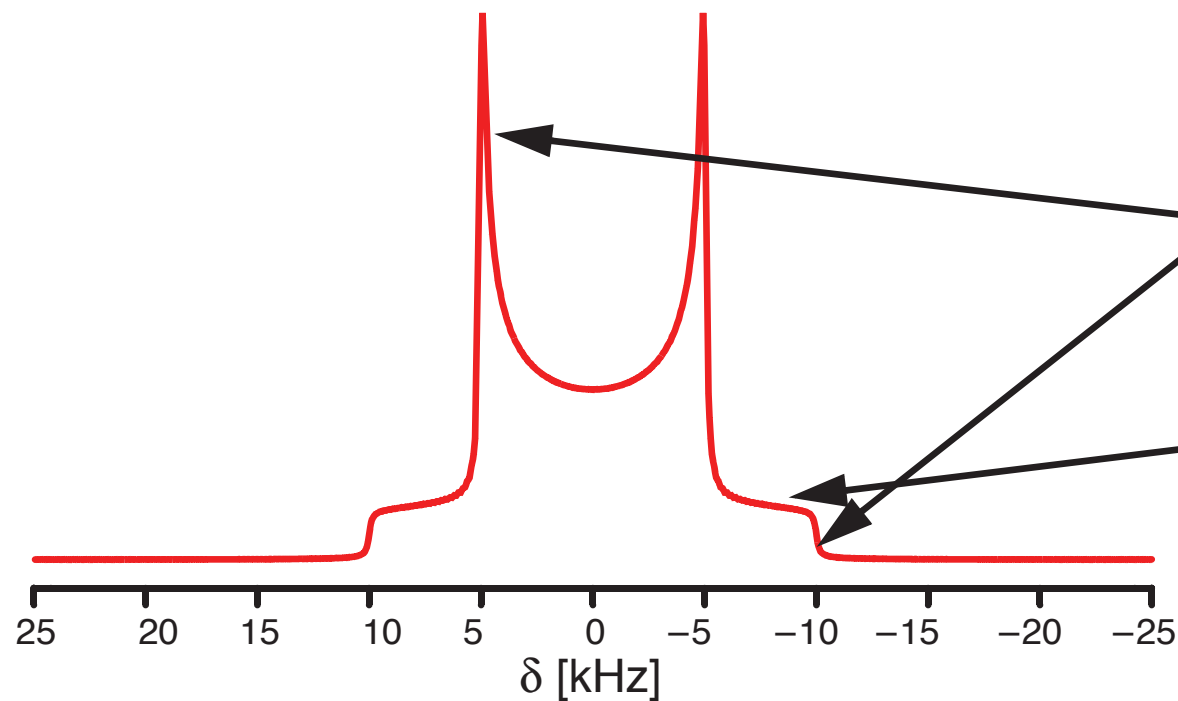
J-coupling
(100 Hz)

chemical-shift tensor
(20000 Hz)

dipolar coupling
(50000 Hz)

Liquid State NMR

Solid State NMR

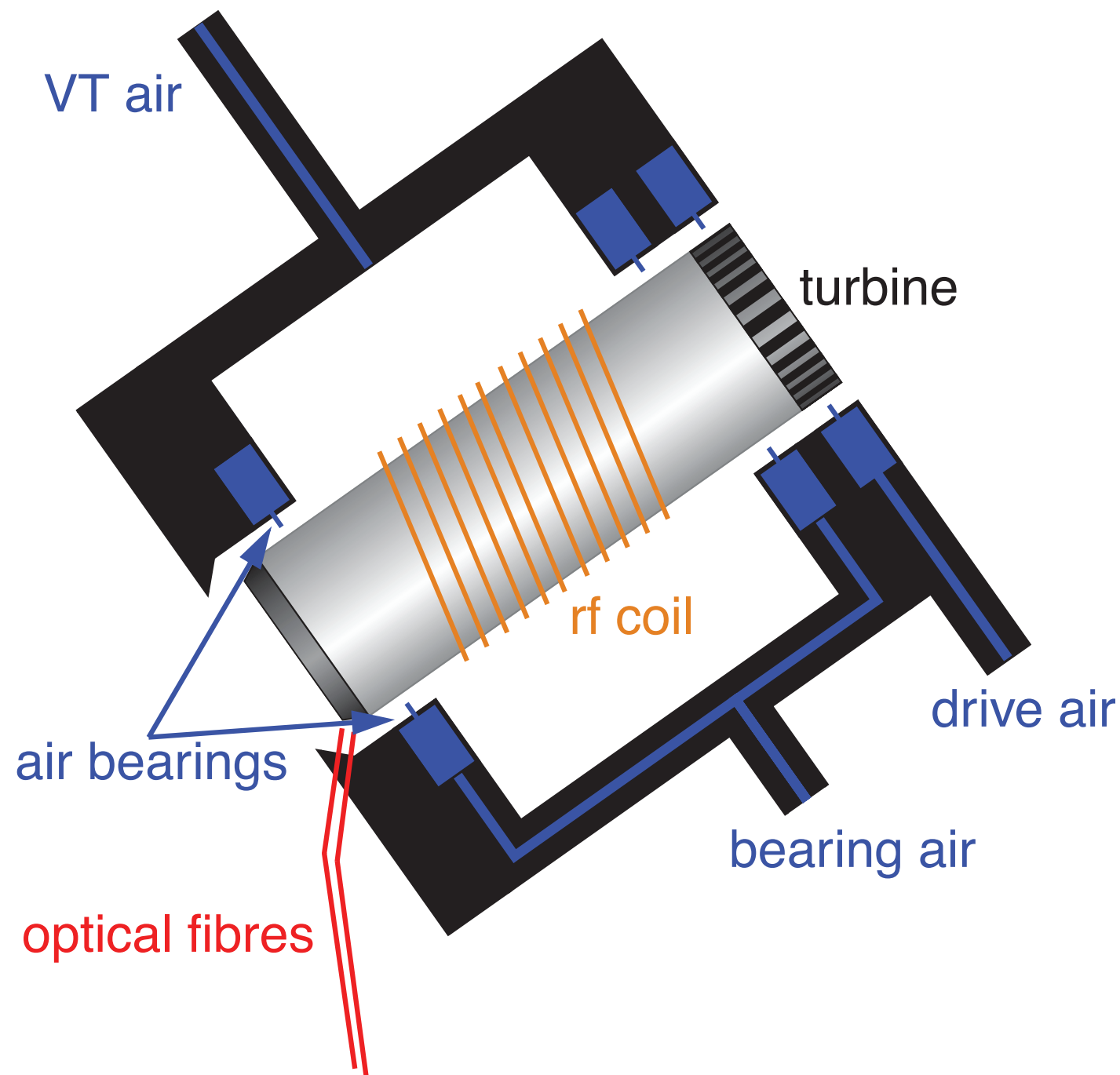


- ❑ Different crystallite orientations contribute to different positions in the powder line shape.
- ❑ Anisotropy is manifest through broad lines.

❑ Broad powder lines

❑ High spectral resolution is required to resolve anisotropic interactions in the molecule.

Magic-Angle Spinning



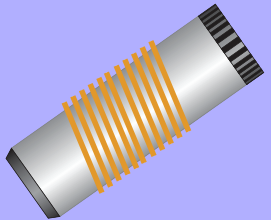
1.8 mm MAS probe (50 kHz)

(A. Samoson et al. J. Magn. Reson. 149, 264 (2001))

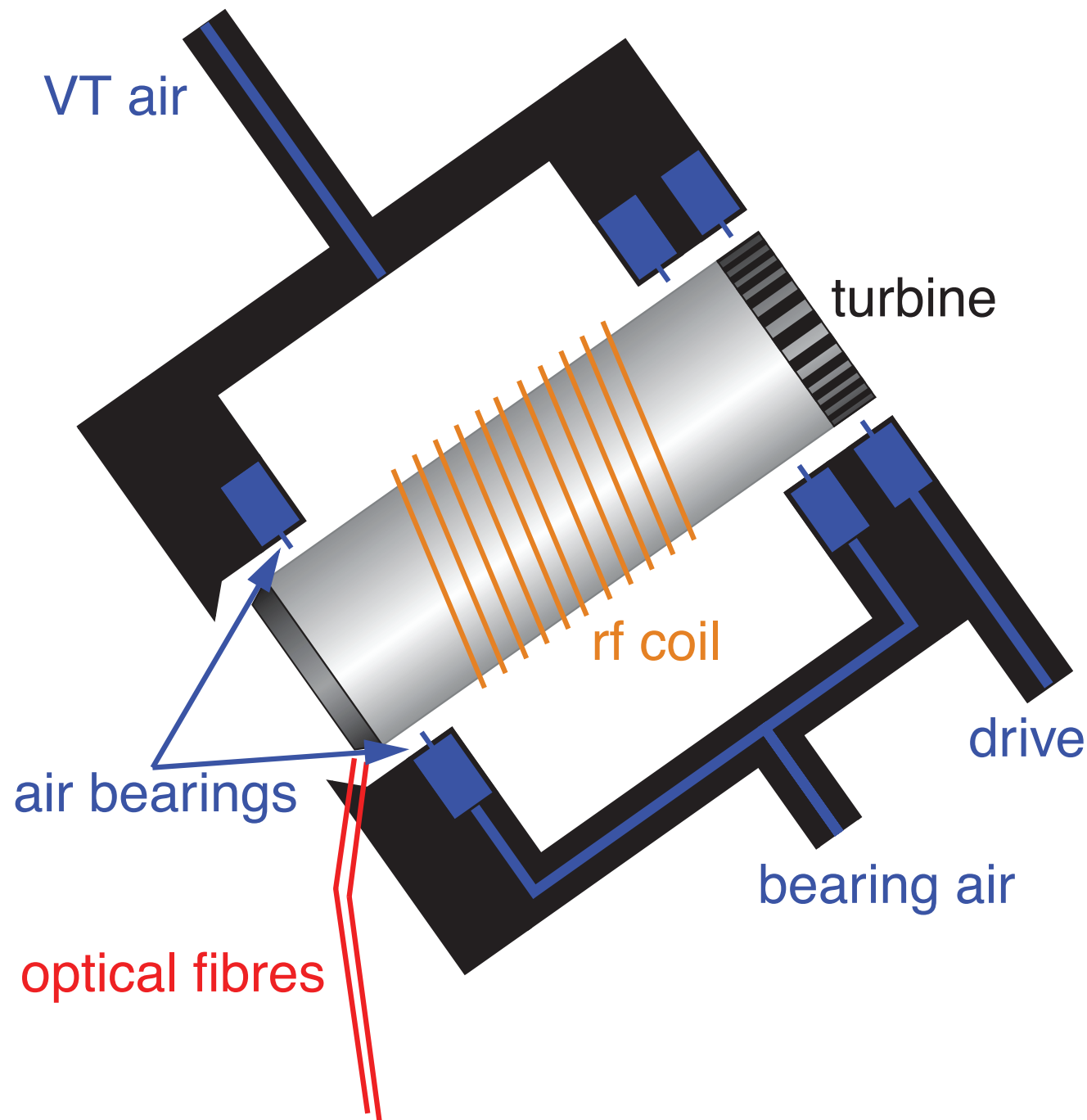


- ❑ Outer diameter of MAS rotor determines maximum rotation frequency: 6 mm - 8 kHz, 4 mm - 15 kHz, 2.5 mm - 30 kHz, 1.8 mm - 50 kHz, 1.3 mm - 70 kHz, 0.5 mm - 170 kHz.
- ❑ Sample volume depends on (inner diameter).
- ❑ Higher MAS frequencies allow the implementation of different types of experiments.

Magic-Angle Spinning

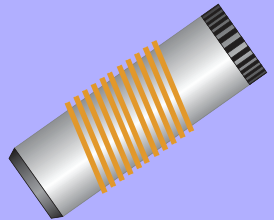


<http://www2.warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/equipment/>

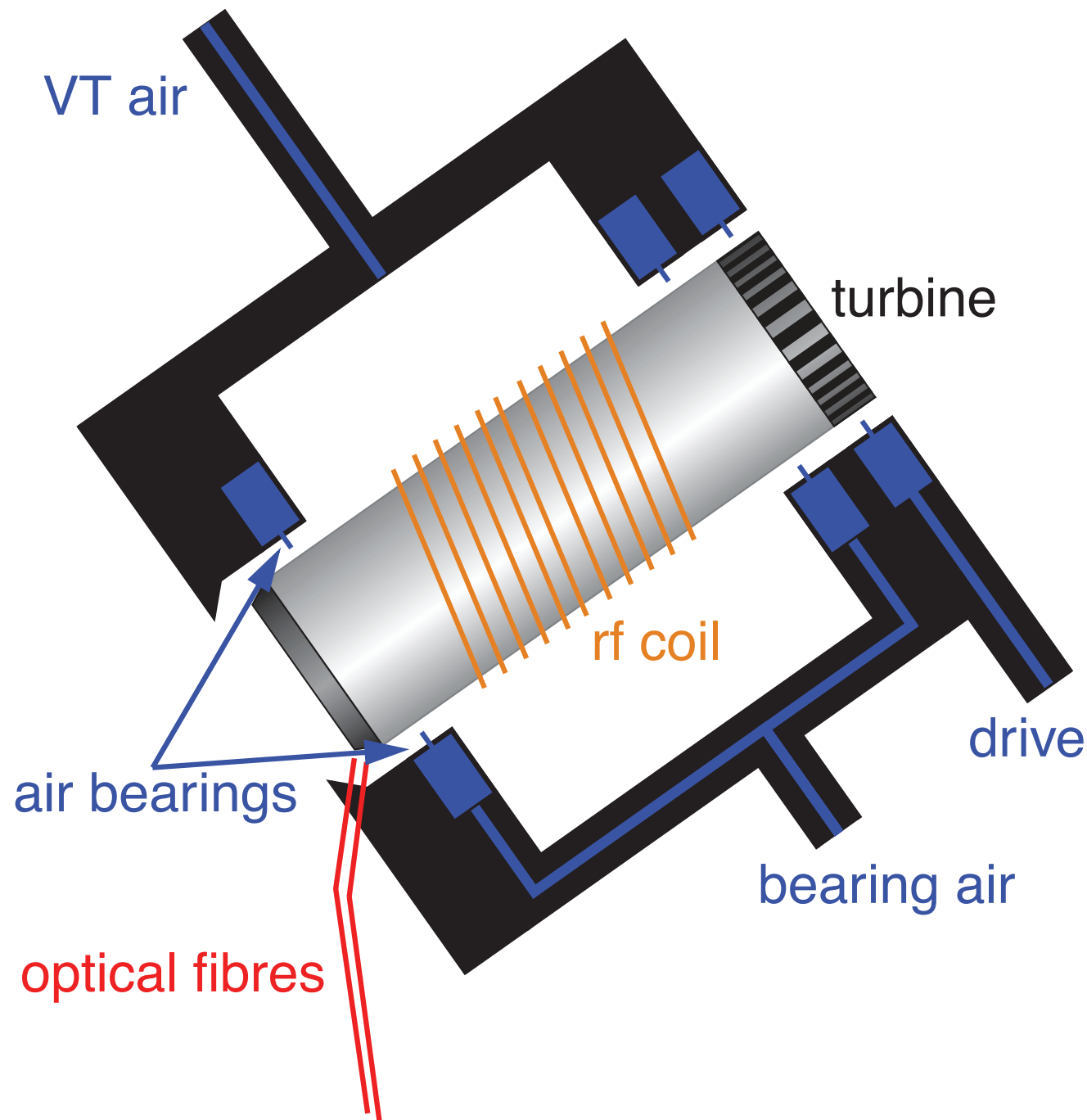


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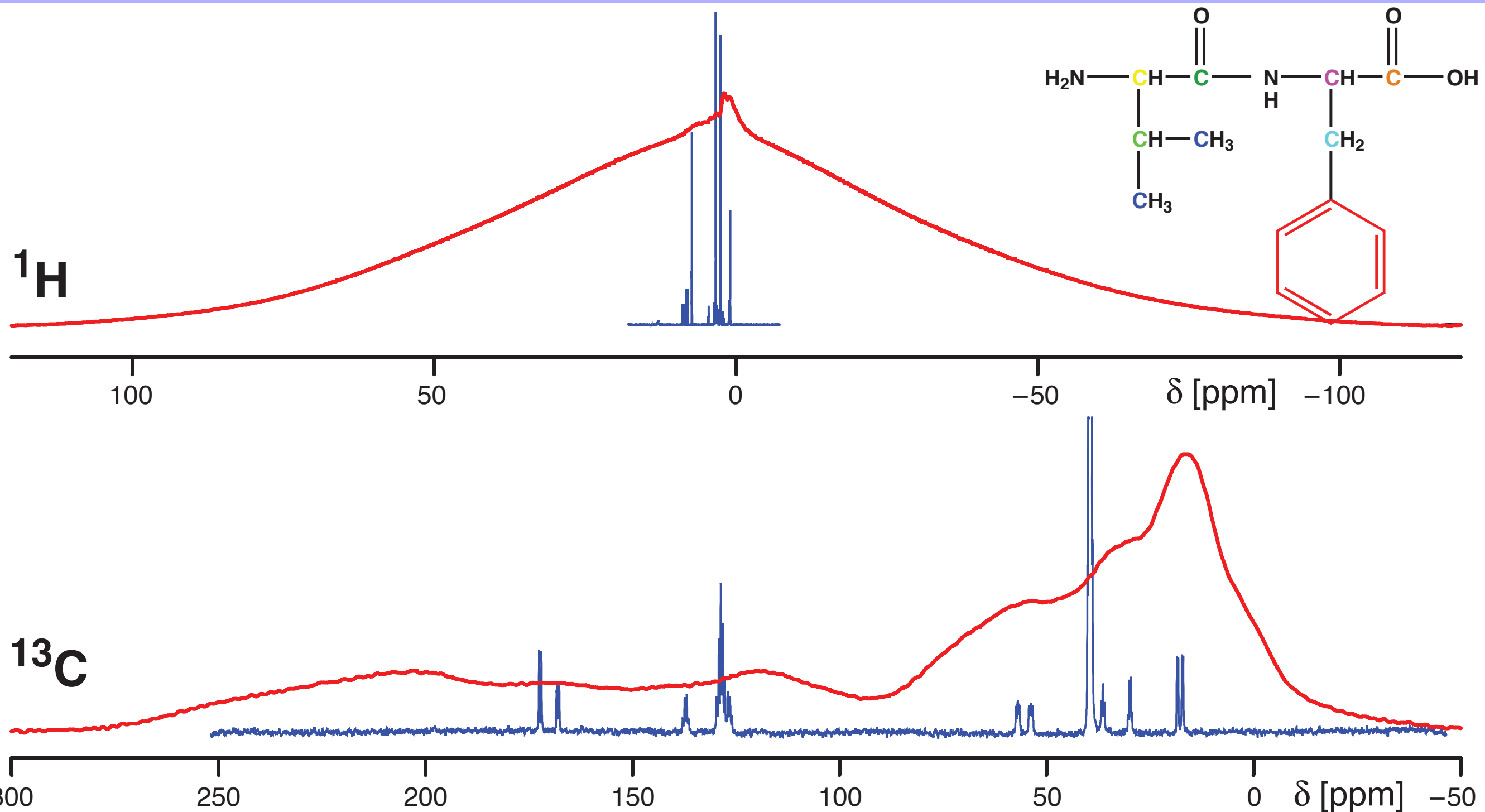
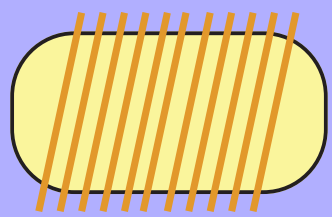
<http://www2.warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/equipment/>



† It was at the Ampere Congress in Pisa in 1960, where we presented some of our results, that the late Professor C. J. Gorter of Leiden asked a question about the ‘magic’ properties of this angle which led us to use this terminology thereafter.

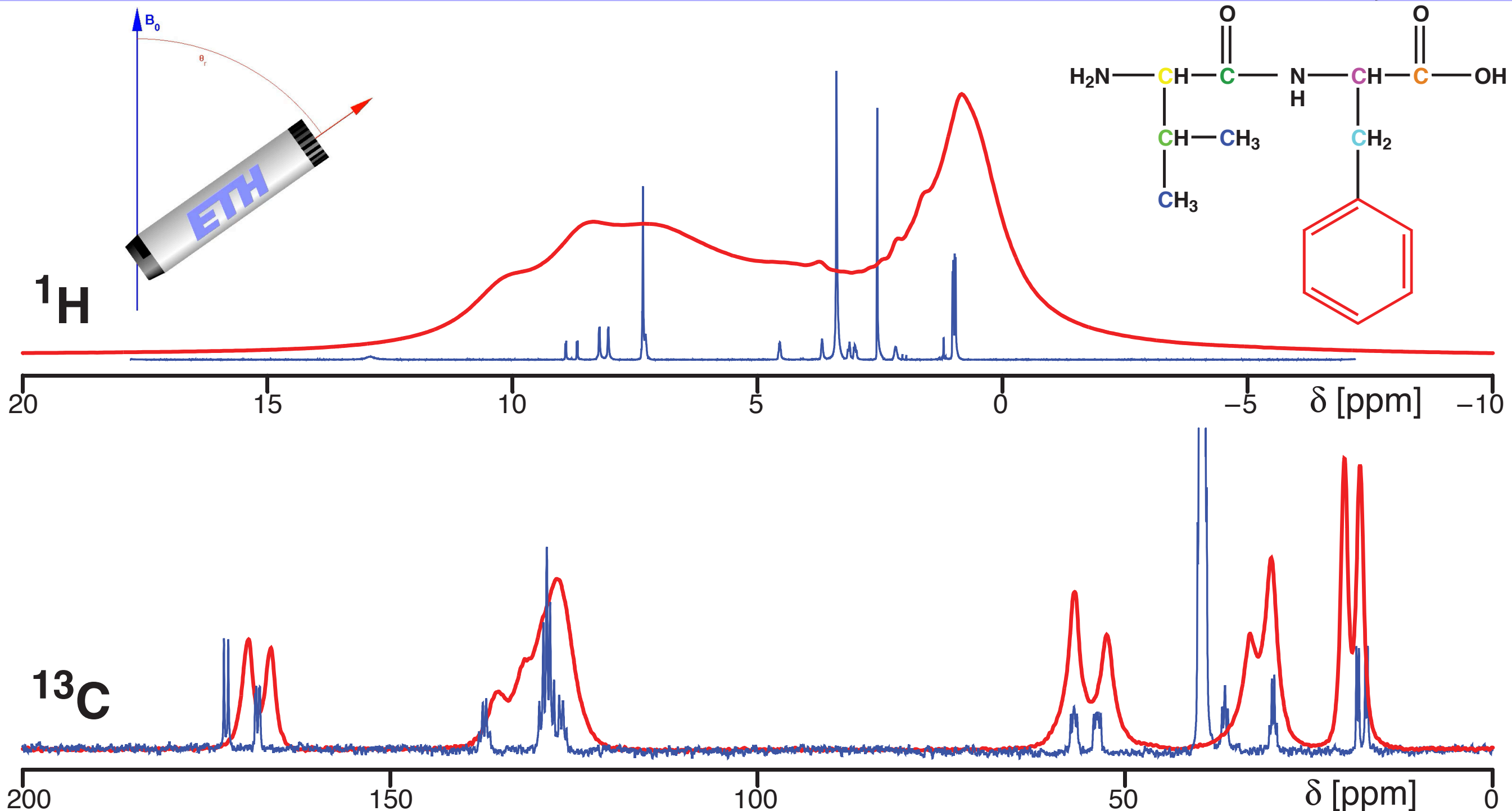
E.R. Andrew, Magic angle spinning in solid state n.m.r. spectroscopy, Philos. Trans. R. Soc. Lond. Ser. A, Math. Phys. Sci. 299 (1981) 505–520. <https://doi.org/10.1098/rsta.1981.0032>.

Solution-State and Solid-State NMR Spectra



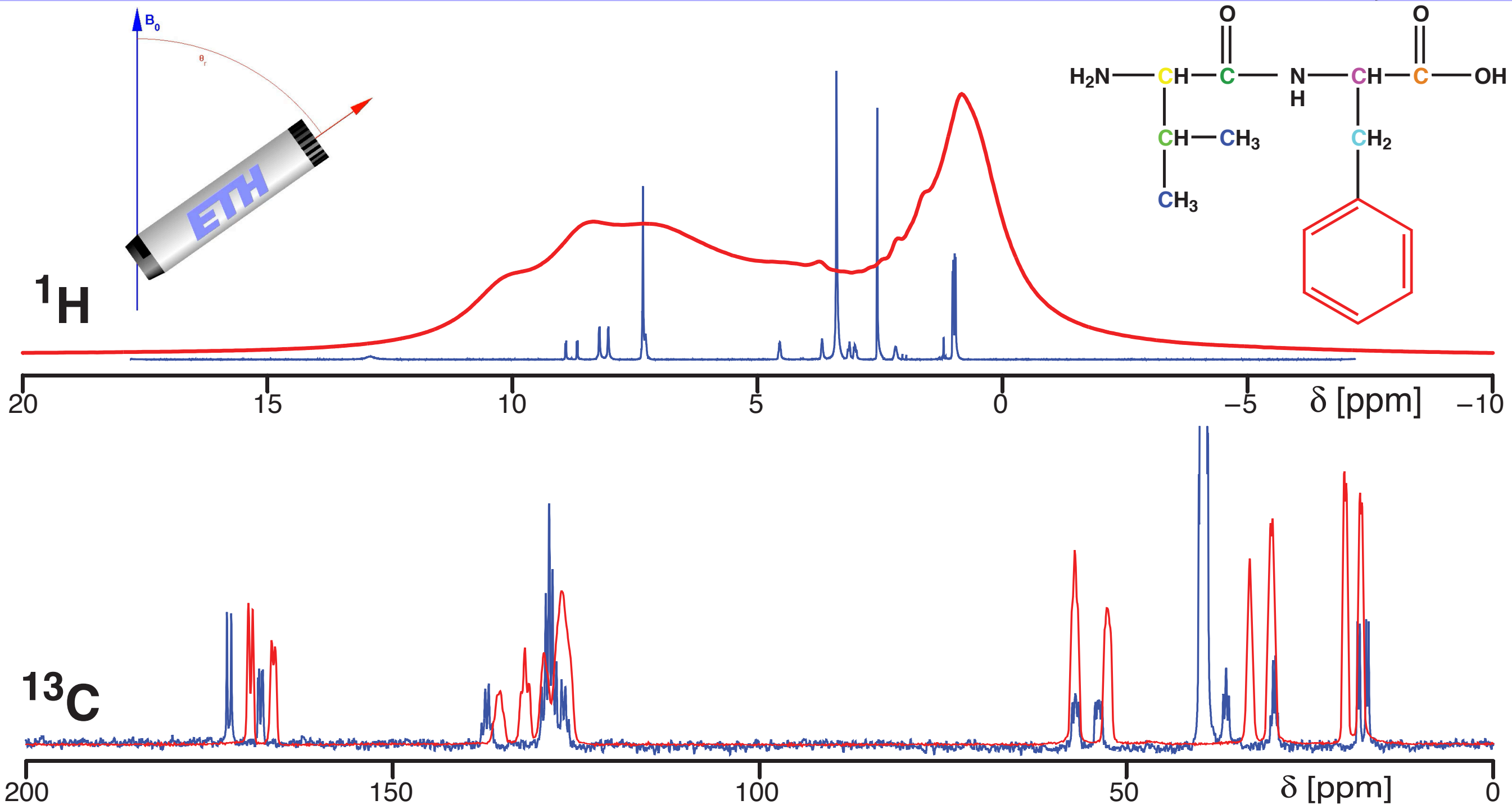
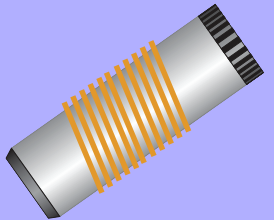
- ❑ Static solid-state NMR spectra of powdered samples are very broad compared to solution-state NMR spectra.
- ❑ This is due to the anisotropic interactions.

Solution-State and Solid-State NMR Spectra



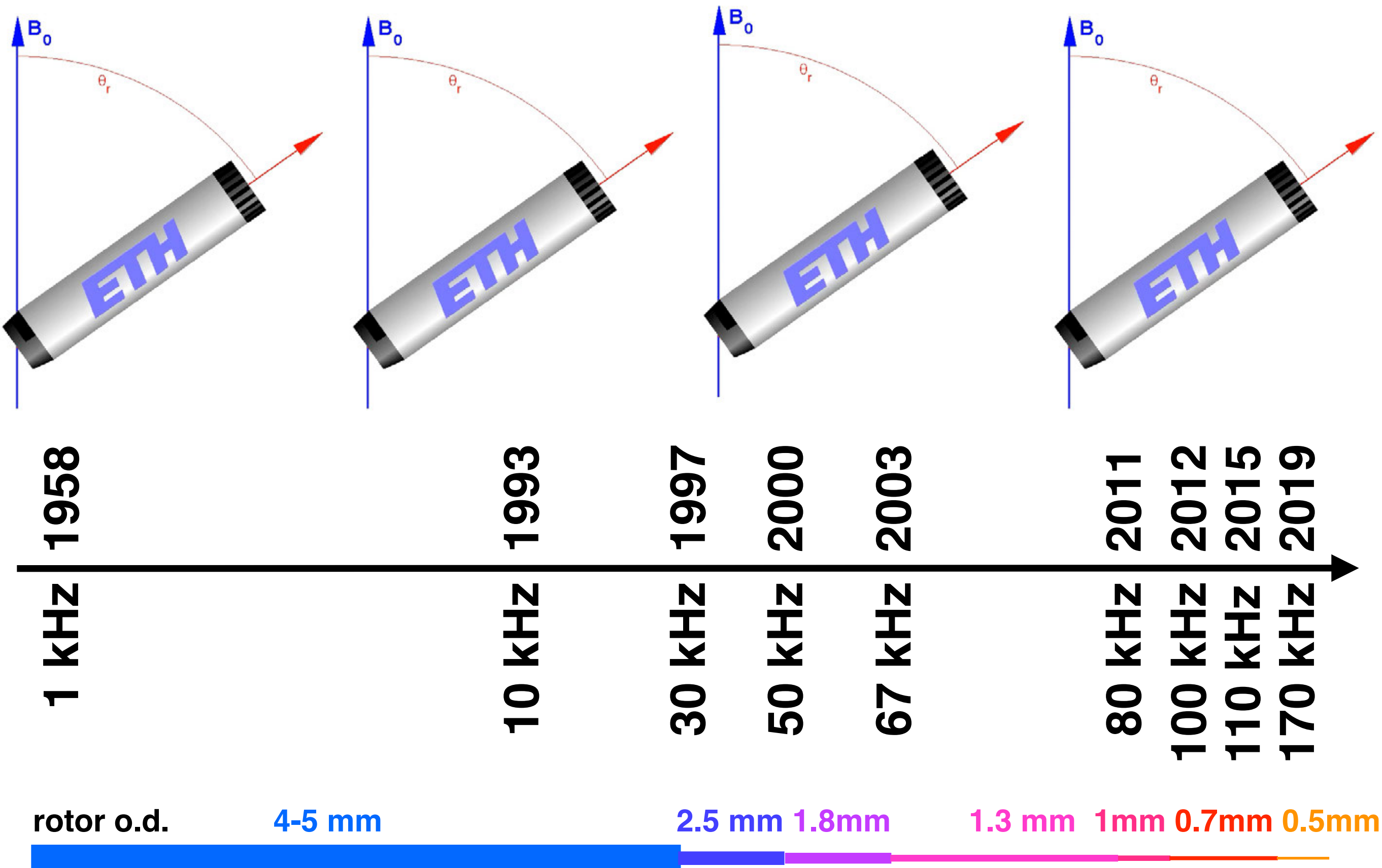
- Under fast MAS (30 kHz), the proton spectrum is still mostly featureless, while the carbon spectrum shows significant improvement in resolution.
- Using advanced decoupling methods, one can obtain spectra with narrow lines.
- Improving the ^1H spectrum is difficult (homonuclear decoupling, isotope dilution using ^2H).

Solution-State and Solid-State NMR Spectra

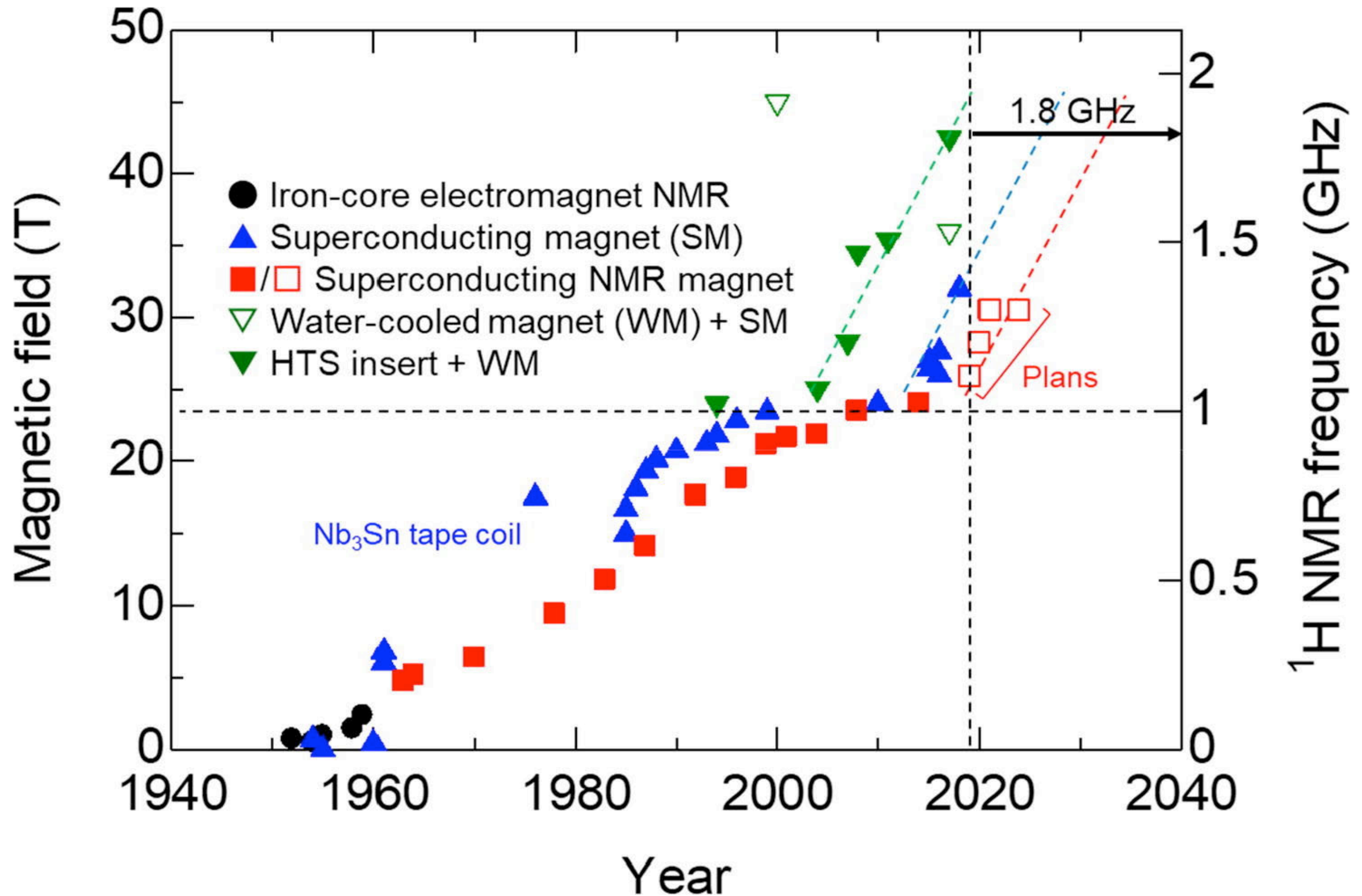
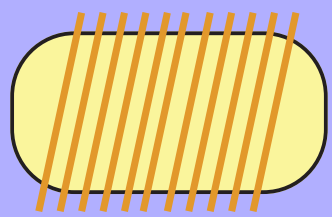


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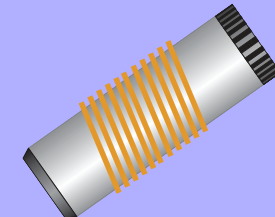
Timeline of MAS Developments



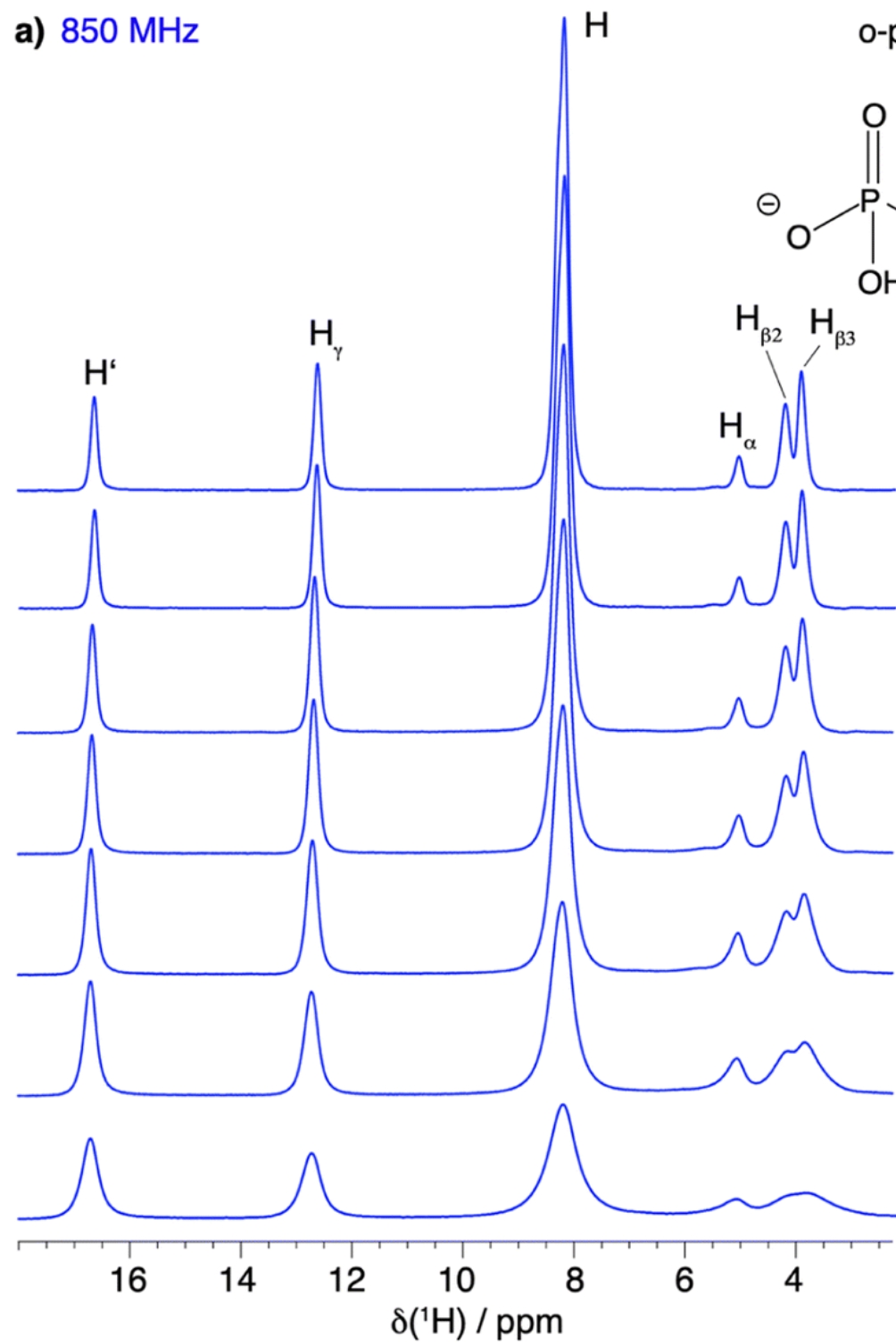
High-Field Magnet Development



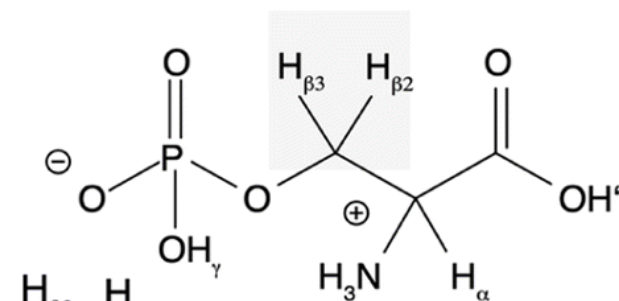
Proton Spectra at Faster MAS



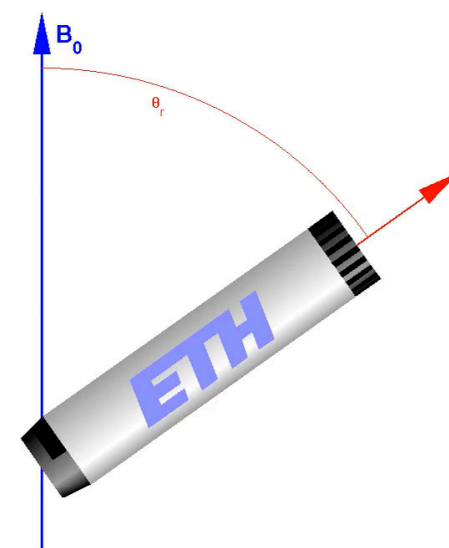
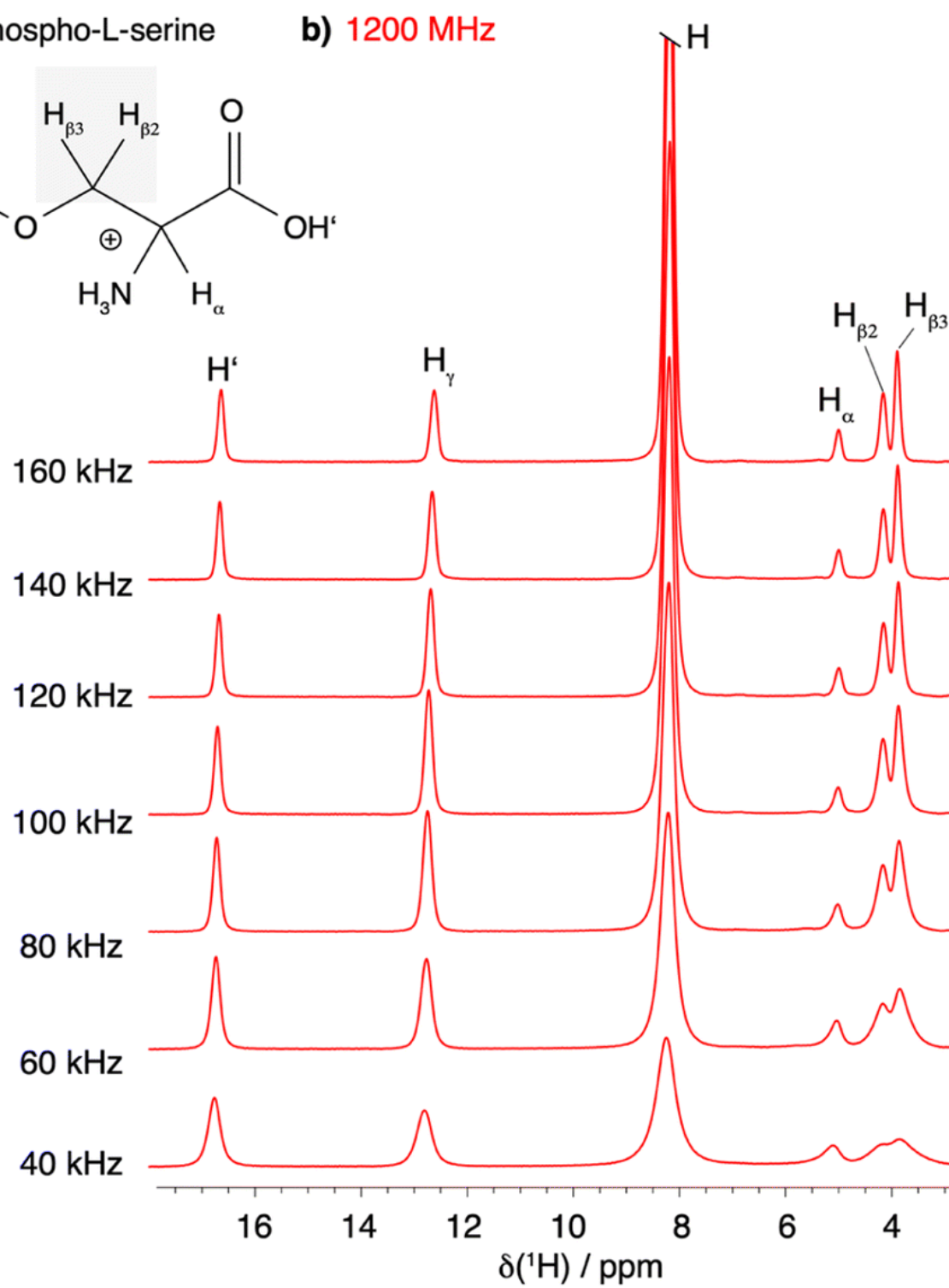
a) 850 MHz



o-phospho-L-serine



b) 1200 MHz



M. Callon, D. Luder, A.A. Malär, T. Wiegand, V. Římal, L. Lecoq, A. Böckmann, A. Samoson, B.H. Meier, High and fast: NMR protein–proton side-chain assignments at 160 kHz and 1.2 GHz, Chem. Sci. 14 (2023) 10824–10834. <https://doi.org/10.1039/d3sc03539e>.

~~interaction-frame transformation~~



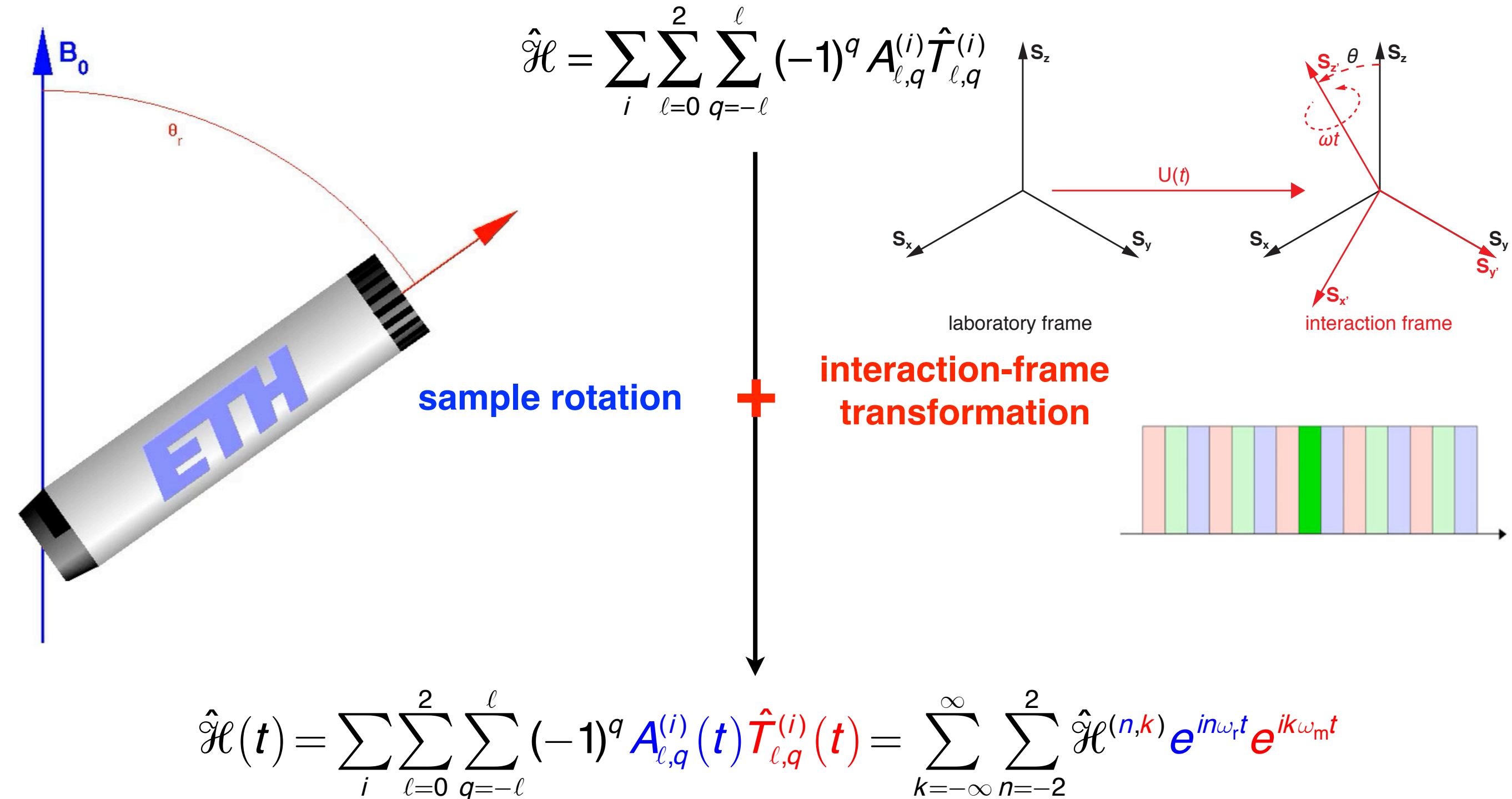
$$\hat{\mathcal{H}}(t) = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q A_{\ell,q}^{(i)} \hat{T}_{\ell,q}^{(i)}(t)$$

[

Time-Dependent Hamiltonians

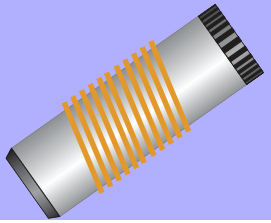


□ The internal spin-system Hamiltonian in the laboratory frame is static if the molecule is static.

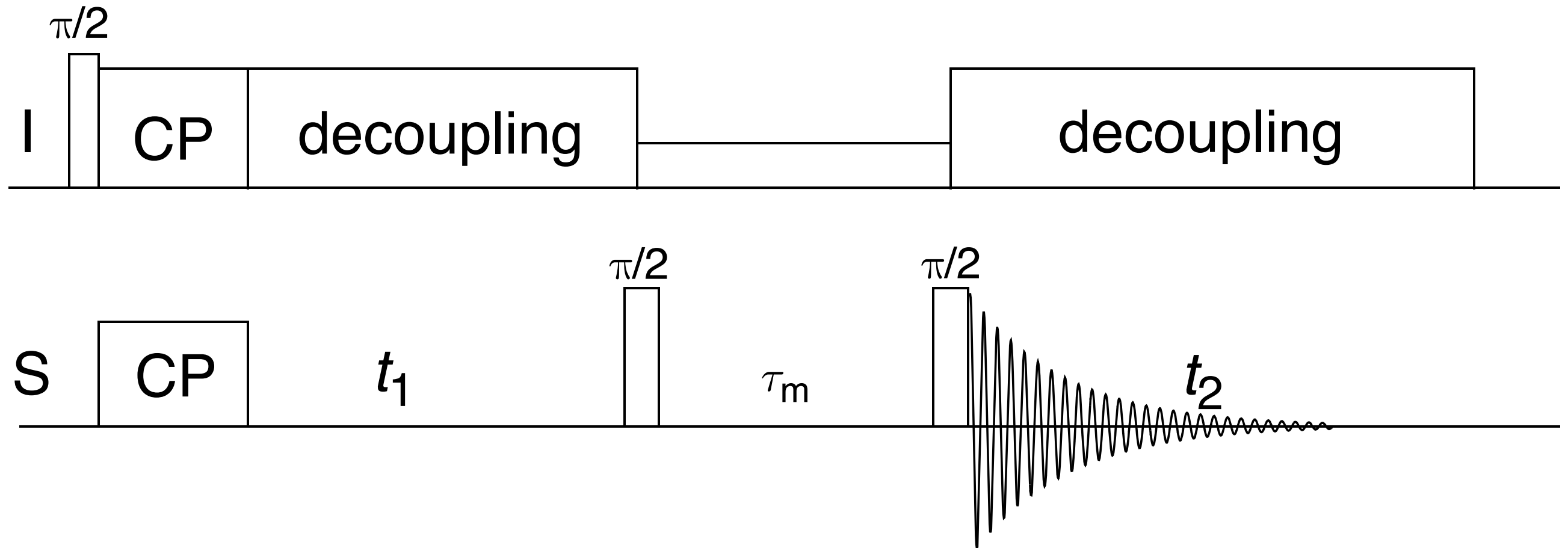


□ Hamiltonian in solid-state NMR has often multiple time dependencies!

Time-Dependent and Effective Hamiltonians



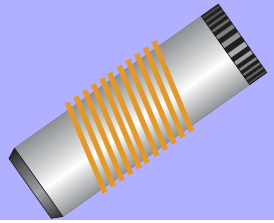
□ A simple solid-state NMR experiment: Proton-Driven Spin Diffusion under MAS (PDSD)



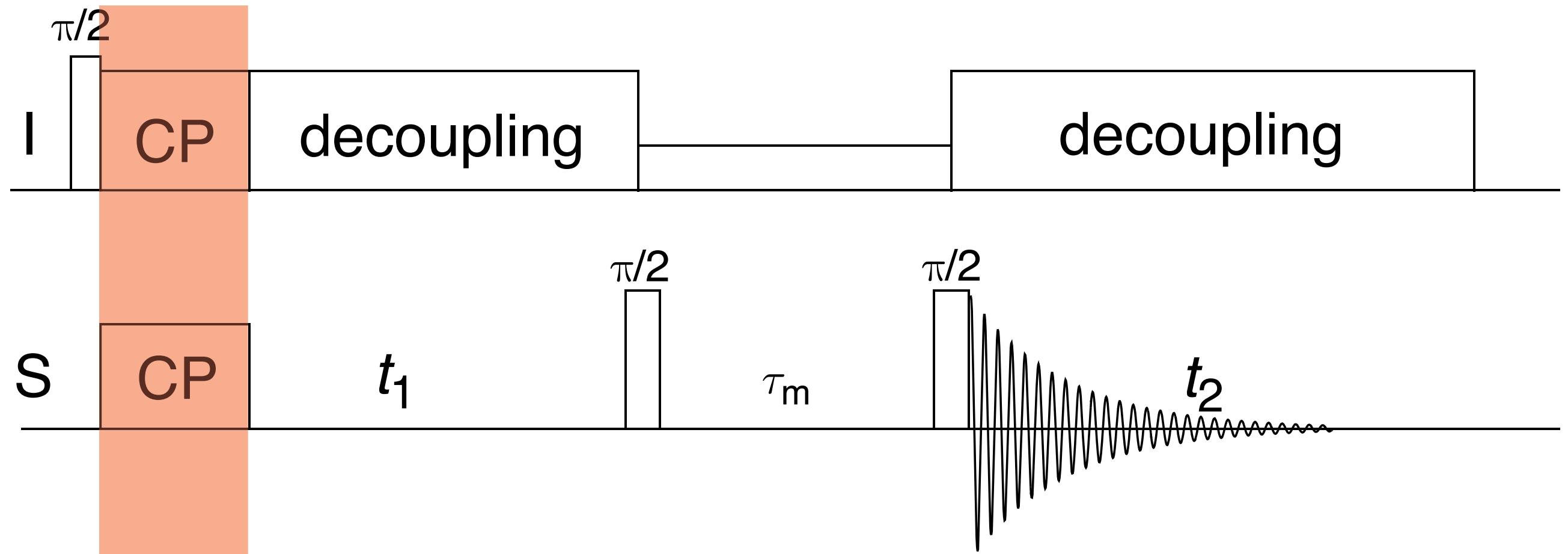
□ The time-dependent Hamiltonian with the exception of the radio-frequency part is the same during all times of the experiment:

$$\hat{\mathcal{H}}(t) = \sum_i \sum_{\ell=0}^2 \mathbf{A}_{\ell,0}^{(i)}(t) \hat{\mathbf{T}}_{\ell,0}^{(i)} + \hat{\mathcal{H}}_{\text{rf}}(t) = \hat{\mathcal{H}}_{\text{D}}(t) + \hat{\mathcal{H}}_{\text{CS}}(t) + \hat{\mathcal{H}}_{\text{J}}(t) + \hat{\mathcal{H}}_{\text{rf}}(t)$$

Time-Dependent and Effective Hamiltonians



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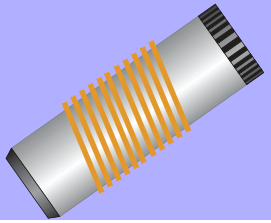


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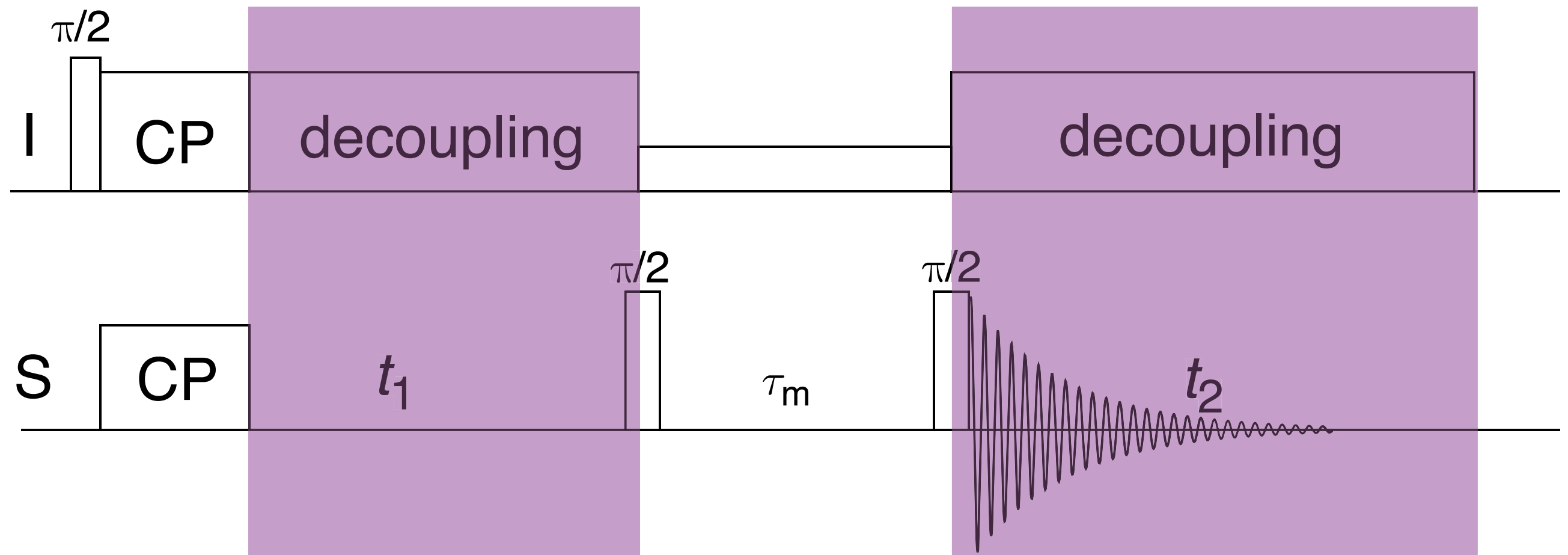
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□ Effective Hamiltonian during Hartmann-Hahn cross polarization: heteronuclear zero-quantum Hamiltonian: $\hat{\mathcal{H}} \approx \omega_{\text{IS}}^{(\text{eff})} (\hat{I}^+ \hat{S}^- + \hat{I}^- \hat{S}^+)$

Time-Dependent and Effective Hamiltonians



- A simple solid-state NMR experiment: Proton-Driven Spin Diffusion under MAS (PDSD)

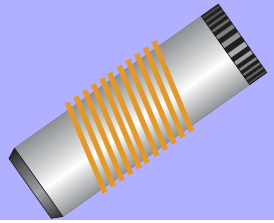


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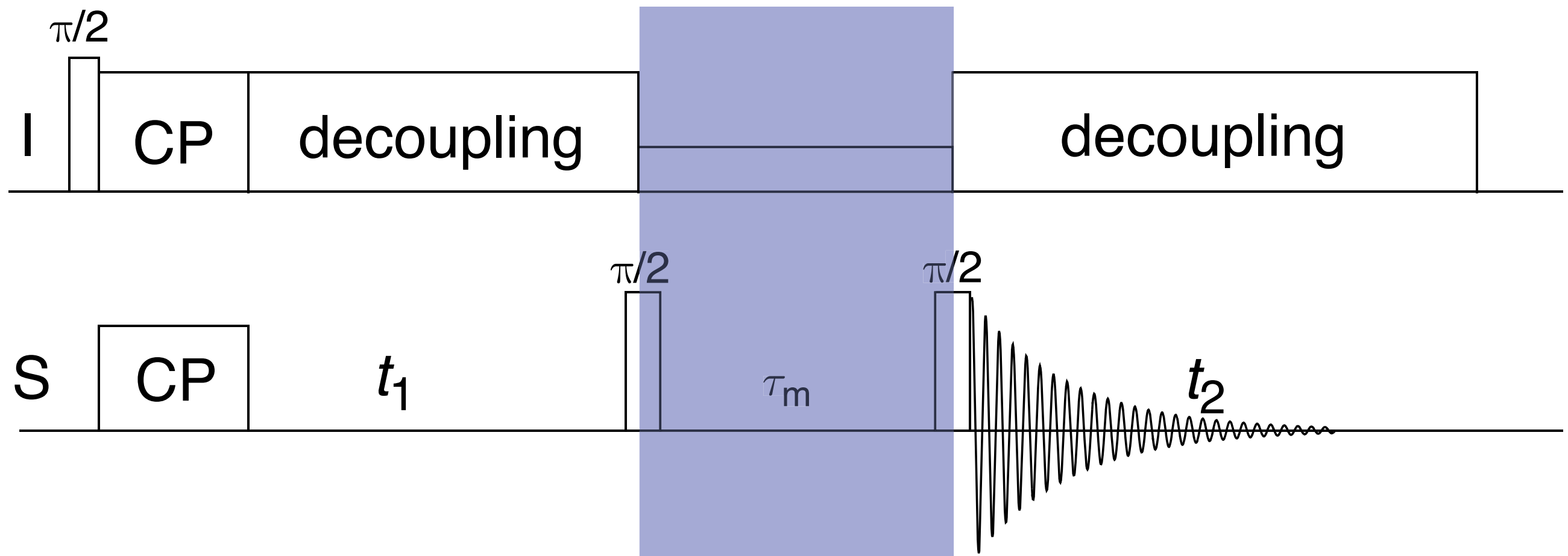
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- Effective Hamiltonian during free evolution (t_1 and t_2): S-spin isotropic chemical-shift Hamiltonian: $\hat{\mathcal{H}} \approx \omega_{\text{S}}^{(\text{iso})} \hat{\mathbf{S}}_z$

Time-Dependent and Effective Hamiltonians



■ A simple solid-state NMR experiment: Proton-Driven Spin Diffusion under MAS (PDSD)



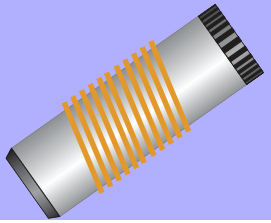
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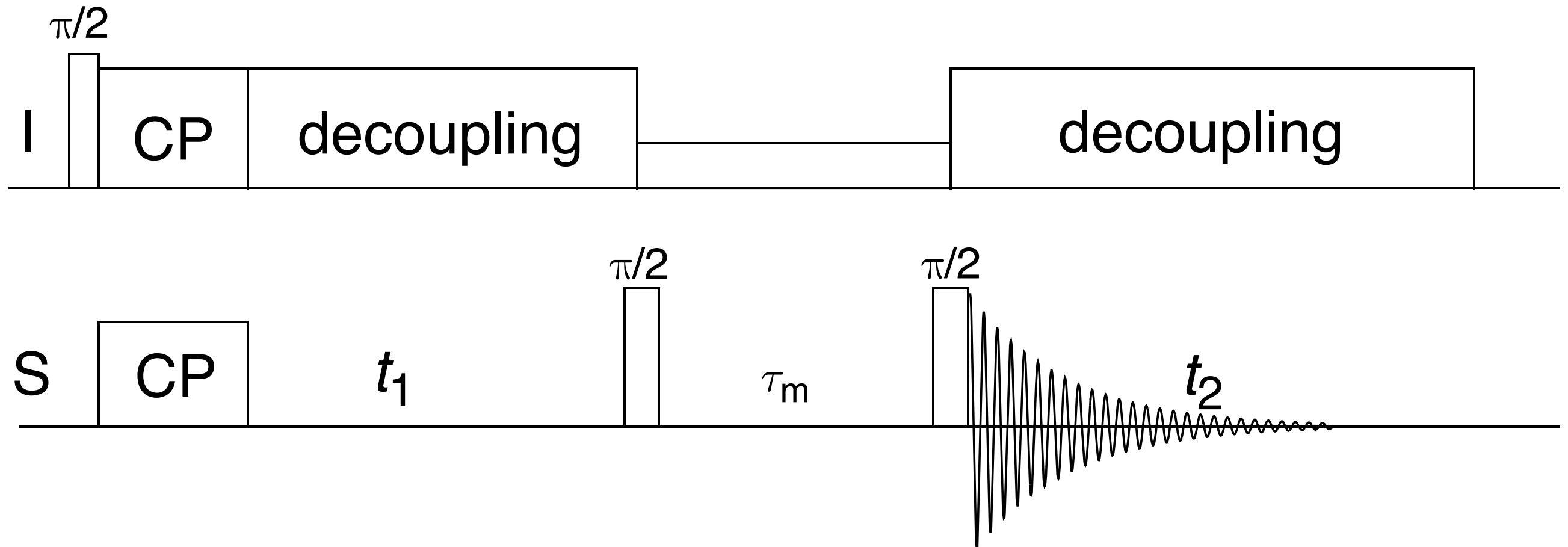
■ Effective Hamiltonian during spin-diffusion mixing time: homonuclear zero-quantum

Hamiltonian: $\hat{\mathcal{H}} \approx \omega_{\text{II}}^{(\text{eff})} (\hat{\mathbf{S}}_1^+ \hat{\mathbf{S}}_2^- + \hat{\mathbf{S}}_1^- \hat{\mathbf{S}}_2^+) \hat{I}_z$

Time-Dependent and Effective Hamiltonians



- A simple solid-state NMR experiment: Proton-Driven Spin Diffusion under MAS (PDSD)

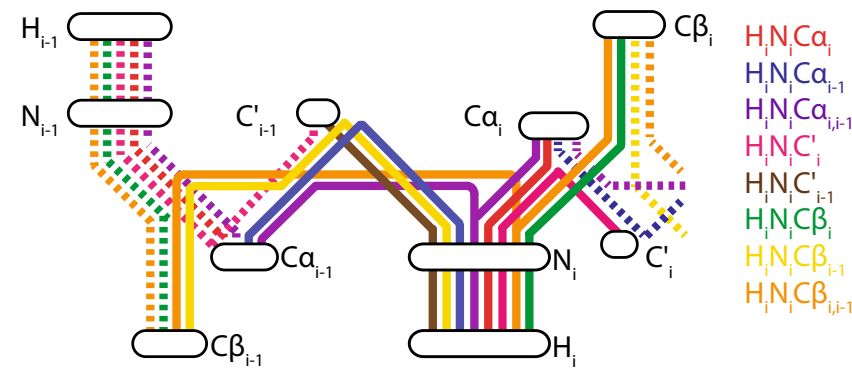
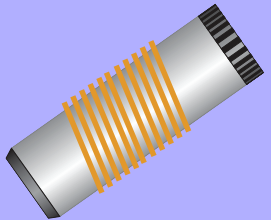


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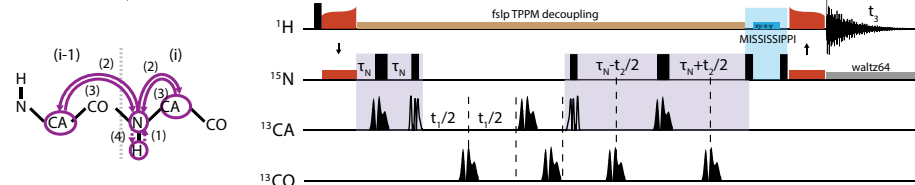
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- The combination of magic-angle spinning and time-dependent radio-frequency irradiation allows us to generate different effective Hamiltonians during the course of an experiment.

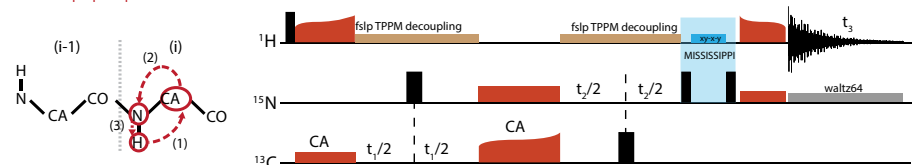
Typical NMR Experiments in Biological Solids



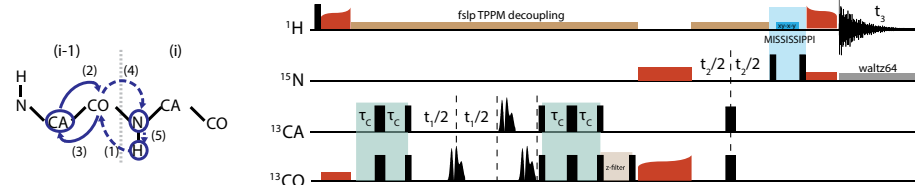
(a) $H_i N_i C_{\alpha i-1}$ correlation: (HN)CANH



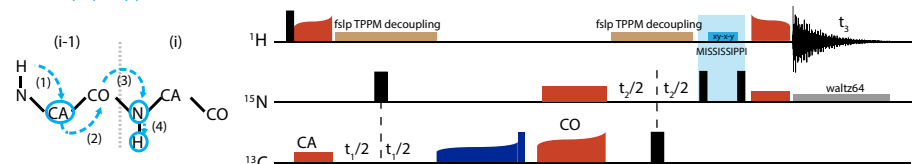
(b) $H_i N_i C_{\alpha i}$ correlation: (H)CANH



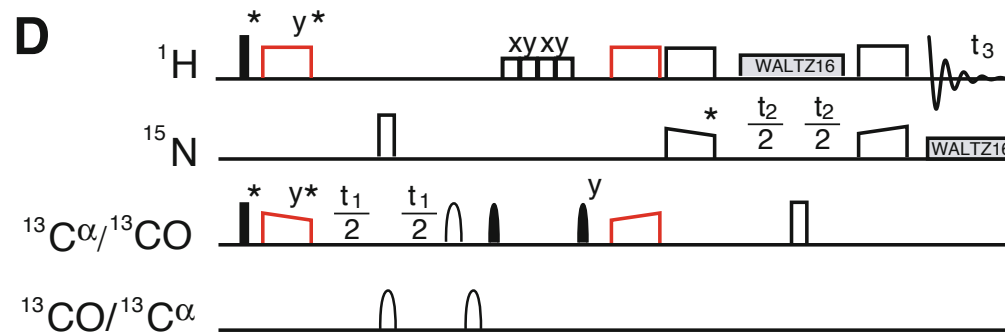
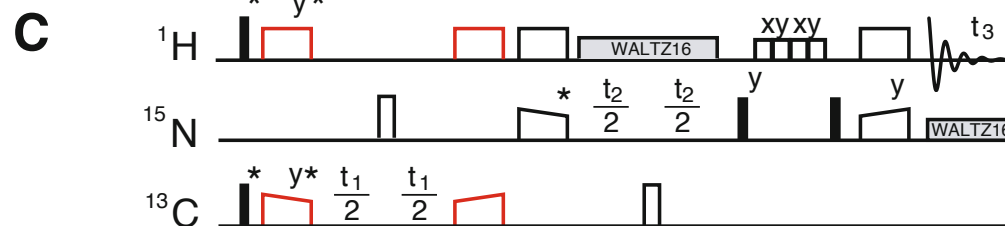
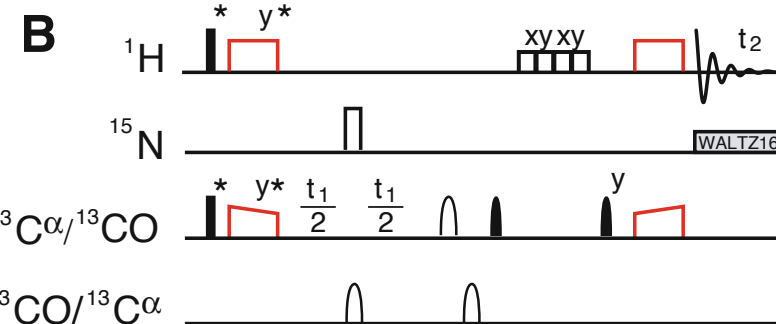
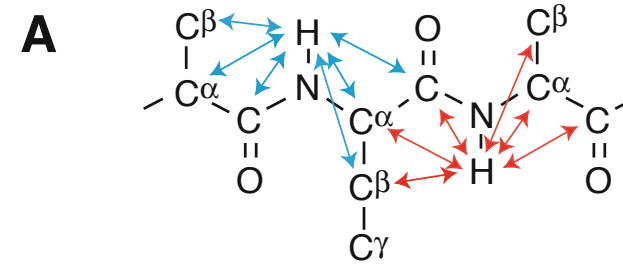
(c) $H_i N_i C_{\alpha i-1}$ correlation: (HCO)CA(CO)NH



(d) $H_i N_i C_{\alpha i-1}$ correlation: (H)CA(CO)NH



S. Penzel et al., J. Biomol. NMR **63**, 165 (2015)



R. Linser, J. Biomol. NMR **52**, 151 (2011)

DREAM DRAWS

C7 SPC5

AM-MIRROR

PDSD

SPINAL

R³

PARIS TPPM

SHANGHAI

R²

REDOR

PMLG

DANTE

RFDR

PAIN

PISSARRO

CORD

PAR

XiX

TOBSY

MIRROR

□ All pulse sequences use rf-irradiation schemes that lead to time-dependent Hamiltonians for decoupling or recoupling purposes.

Instrumentation

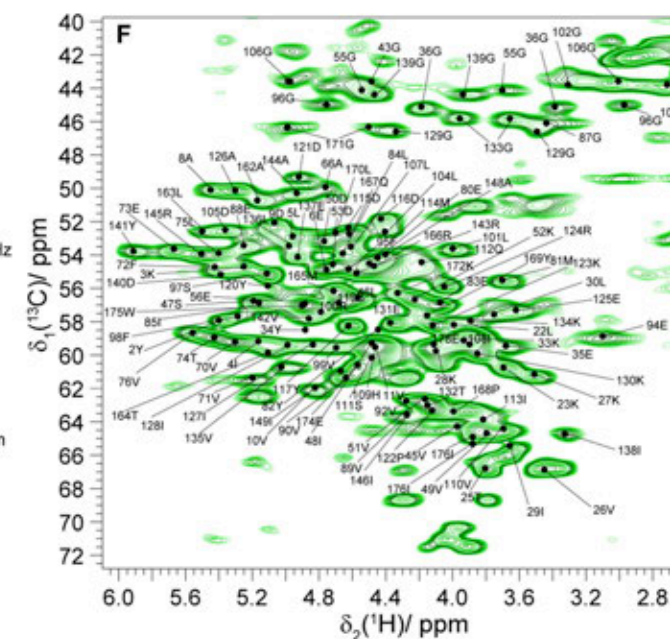
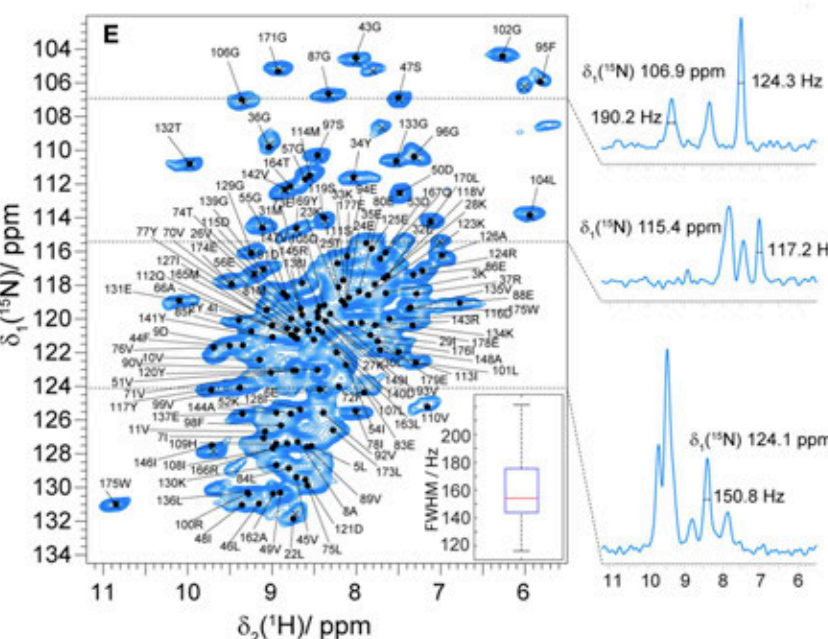
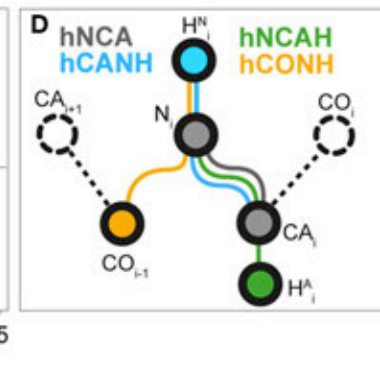
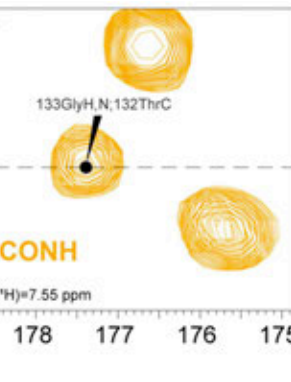
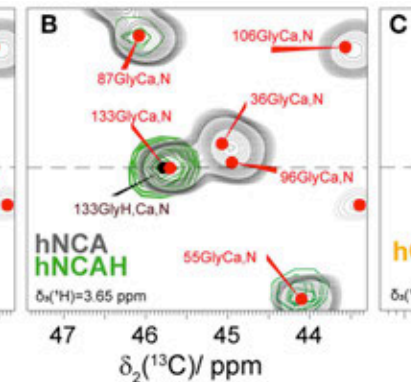
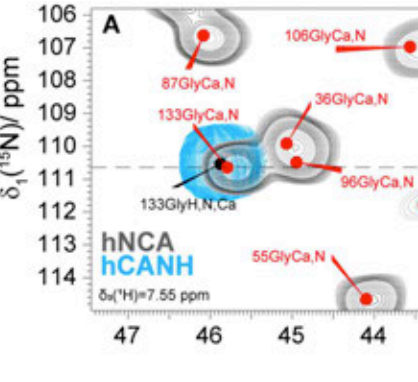
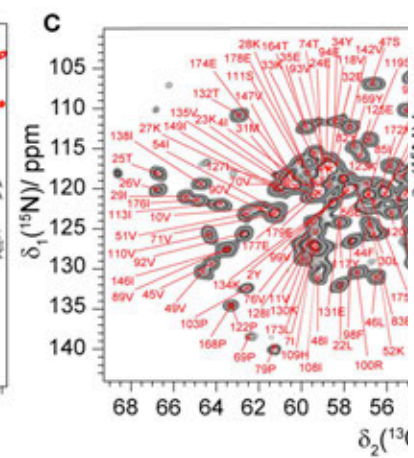
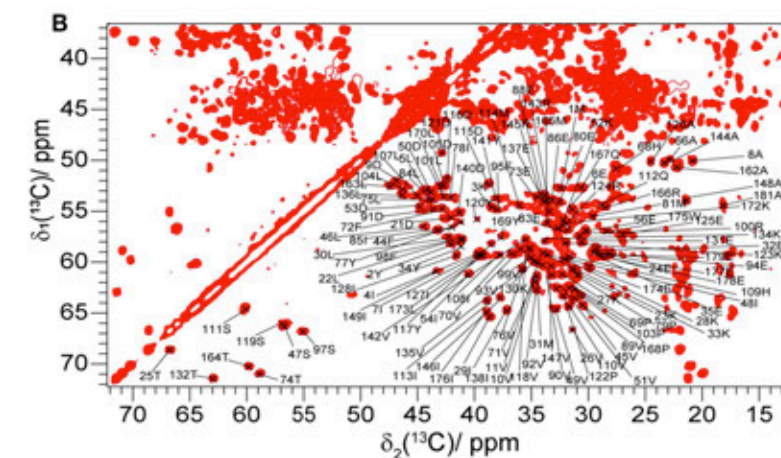
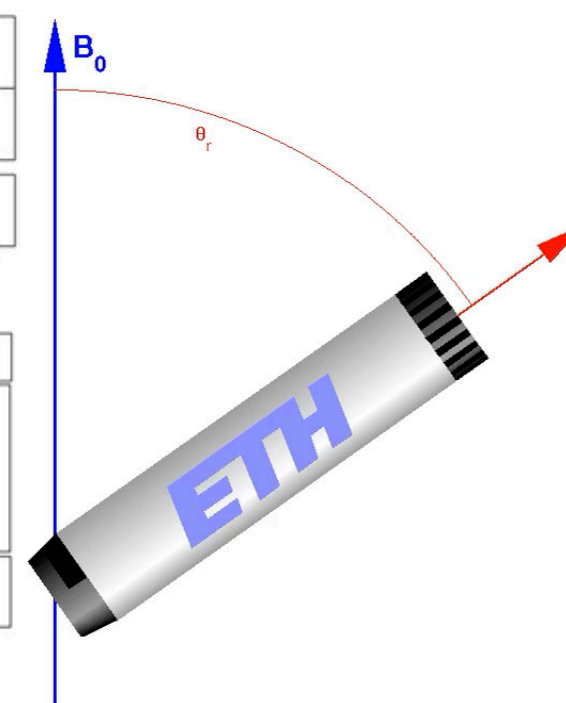
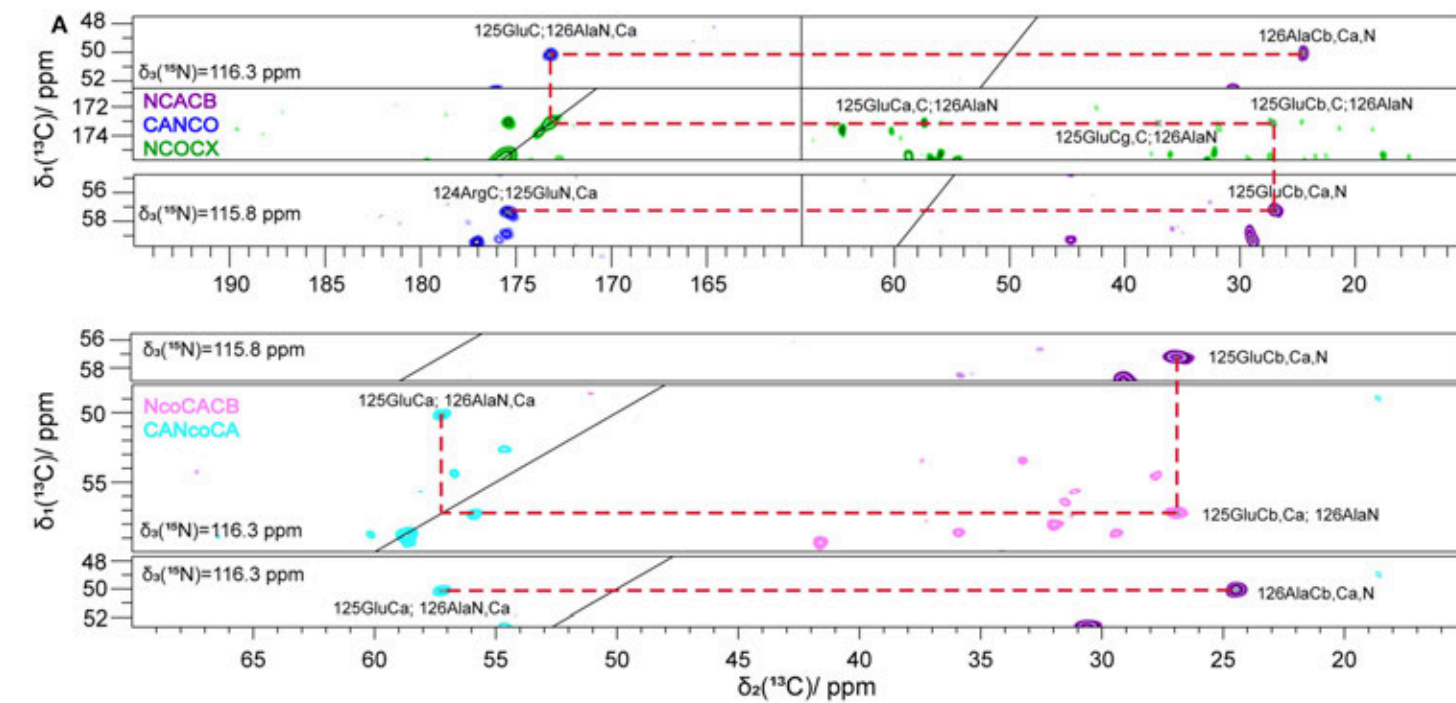


Time-lapse photography by M. Batel and A. Hunkeler



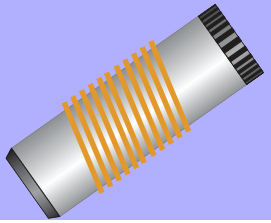
- ❑ High-field magnets are essential for solid-state NMR - a 1200 MHz standard-bore magnet has been available since a few years.
- ❑ Probes for fast MAS (up to 160 kHz) with multiple rf channels and high sensitivity.

High-Resolution Solid-State NMR



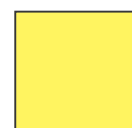
A. Torosyan, T. Wiegand, M. Schledorn, D. Klose, P. Güntert, A. Böckmann, B.H. Meier, Including Protons in Solid-State NMR Resonance Assignment and Secondary Structure Analysis: The Example of RNA Polymerase II Subunits Rpo4/7, *Front. Mol. Biosci.* 6 (2019) 36–8. doi:10.3389/fmolb.2019.00100.

Periodic Table: Quadrupolar Nuclei



IA																	VIIIA
H												IIIA	IVA	VA	VIA	VIIA	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	IIIB	IVB	VB	VIB	VIIB	VIII B			IB	IIB	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	‡Ac	Rf	Ha	Sg	Ns	Hs	Mt									

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



$S=1/2$

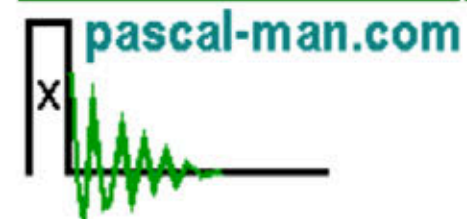


$S>1/2$

Periodic Table

Navigation bar with browser address bar showing www.pascal-man.com/periodic-table/periodictable.shtml and various icons. Below the address bar are several bookmark folders: Comics, CH, ETH, Books, Kinder, Google, softfactors Recruti..., map.geo.admin.ch, Texolit - Erzeugnisse, Block SSH Brute For..., and Other Bookmarks.

Navigation menu with green buttons: About P. Man ▼, FAQ ▼, Periodic Table ▼, Related site ▼, I-Ching ▼, Site map



Standard Periodic Table for quadrupole nuclei with half-integer spins

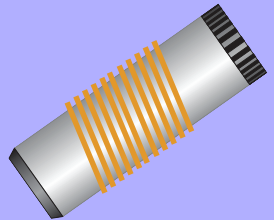
Navigation menu with green buttons: Download source code ▼, Phase cycling as Cogwheel, Pulse program ▼, Pulse sequence ▼, Quadrupole interaction ▼, Search NMR reference

[Home and Applets](#) > Standard Periodic Table

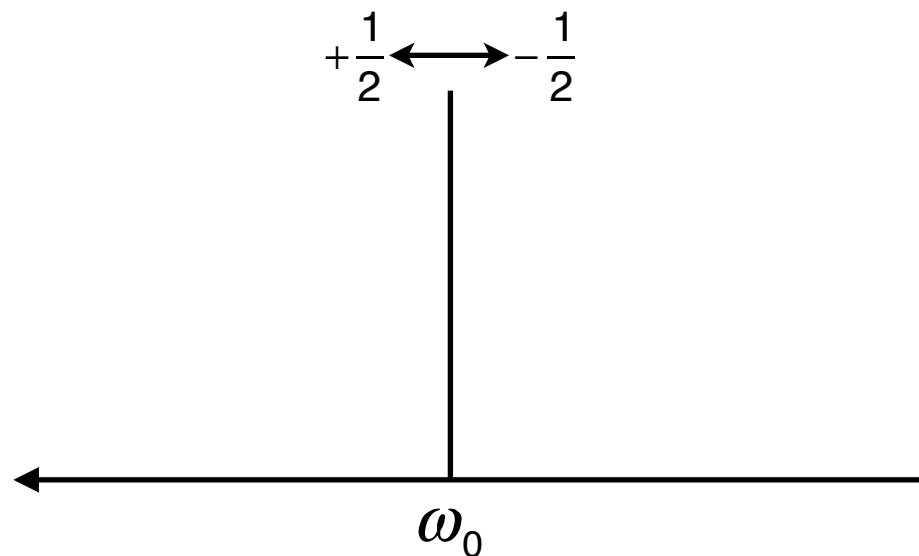
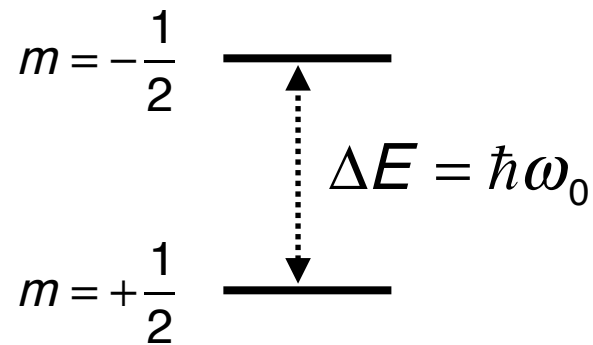
In the Periodic Table, **negative** NMR frequency describes **positive** gyromagnetic ratio:

Nucleus		Isotope	Spin	Natural abundance (%)		Quadrupole moment (10e-30 m.m)				Relative sensitivity		Absolute sensitivity		NMR frequency (MHz) at 2.3488T													
1																		18									
<u>H</u>	<u>D</u>	2											13		14	15		16	17	<u>He</u>							
<u>Li</u>	<u>Li</u>	<u>Be</u>											<u>B</u>	<u>B</u>	<u>C</u>	<u>N</u>	<u>N</u>	<u>O</u>	<u>F</u>	<u>Ne</u>							
<u>Na</u>		<u>Mg</u>	3	4	5	6	7	8	9	10	11	12	<u>Al</u>		<u>Si</u>	<u>P</u>	<u>S</u>	<u>Cl</u>	<u>Cl</u>	Ar							
<u>K</u>	<u>K</u>	<u>Ca</u>	<u>Sc</u>	<u>Ti</u>	<u>Ti</u>	<u>V</u>	<u>V</u>	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Cu</u>	<u>Zn</u>	<u>Ga</u>	<u>Ga</u>	<u>Ge</u>	<u>As</u>	<u>Se</u>	<u>Br</u>	<u>Br</u>	<u>Kr</u>				
<u>Rb</u>	<u>Rb</u>	<u>Sr</u>	<u>Y</u>	<u>Zr</u>	<u>Nb</u>	<u>Mo</u>	<u>Mo</u>	Tc	<u>Ru</u>	<u>Ru</u>	<u>Rh</u>	<u>Pd</u>	<u>Ag</u>	<u>Ag</u>	<u>Cd</u>	<u>Cd</u>	<u>In</u>	<u>In</u>	<u>Sn</u>	<u>Sn</u>	<u>Sb</u>	<u>Sb</u>	<u>Te</u>	<u>Te</u>	<u>I</u>	<u>Xe</u>	<u>Xe</u>
<u>Cs</u>		<u>Ba</u>	<u>Ba</u>	<u>La</u>	<u>La</u>	<u>Hf</u>	<u>Hf</u>	<u>Ta</u>	<u>W</u>	<u>Re</u>	<u>Re</u>	<u>Os</u>	<u>Os</u>	<u>Ir</u>	<u>Ir</u>	<u>Pt</u>	<u>Au</u>	<u>Hg</u>	<u>Hg</u>	<u>Tl</u>	<u>Tl</u>	<u>Pb</u>	<u>Bi</u>				
						Spin:		1/2	3/2	5/2	7/2	9/2	1	3	5	6											

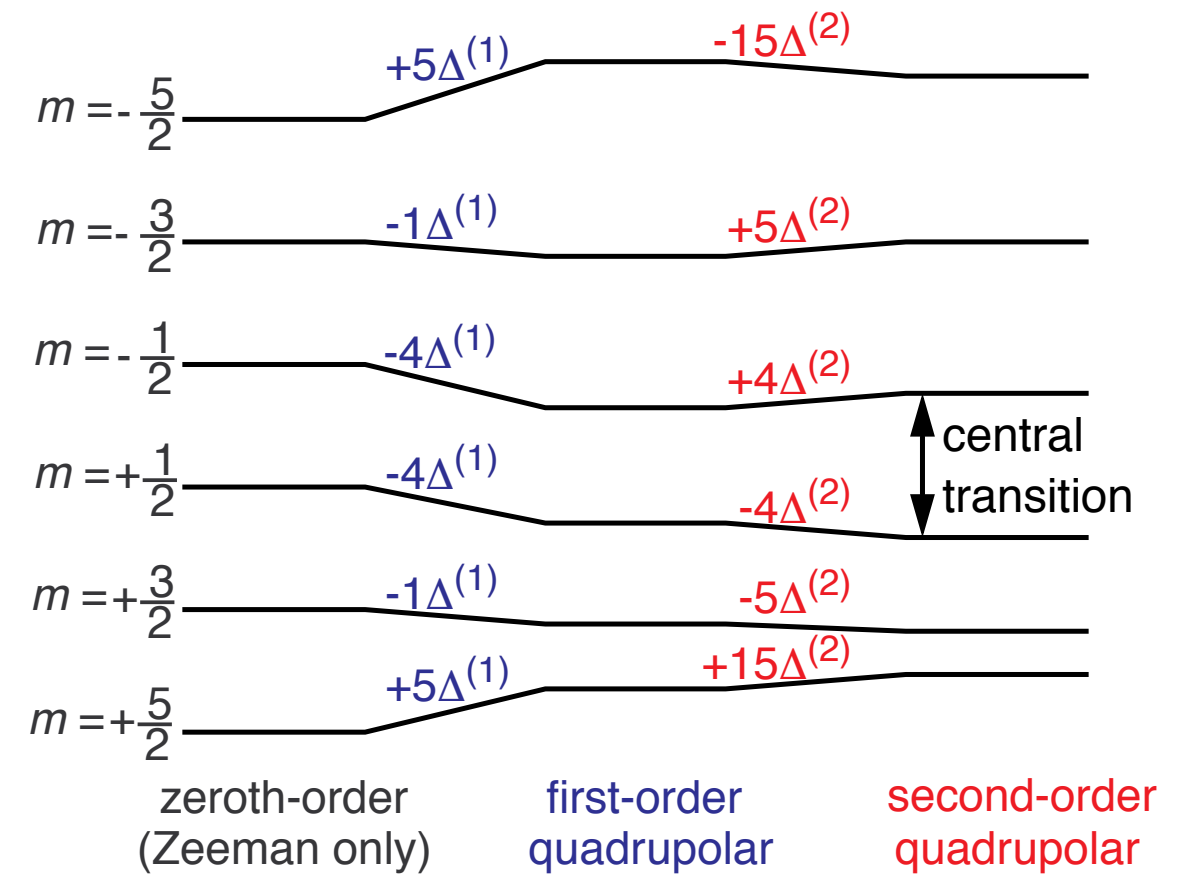
Spin-1/2 vs. Quadrupolar Nuclei



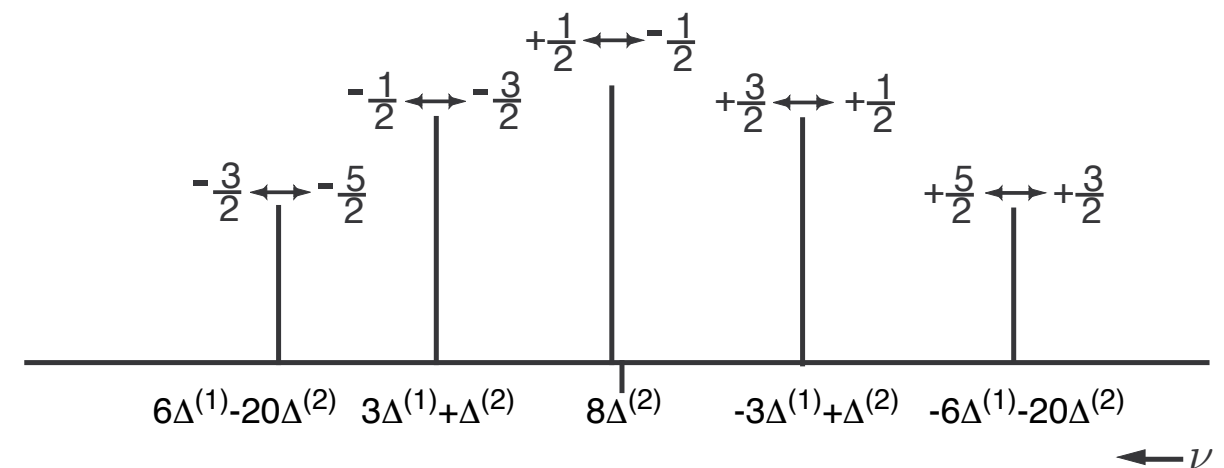
Spin $I = 1/2$



Spin $I > 1/2$



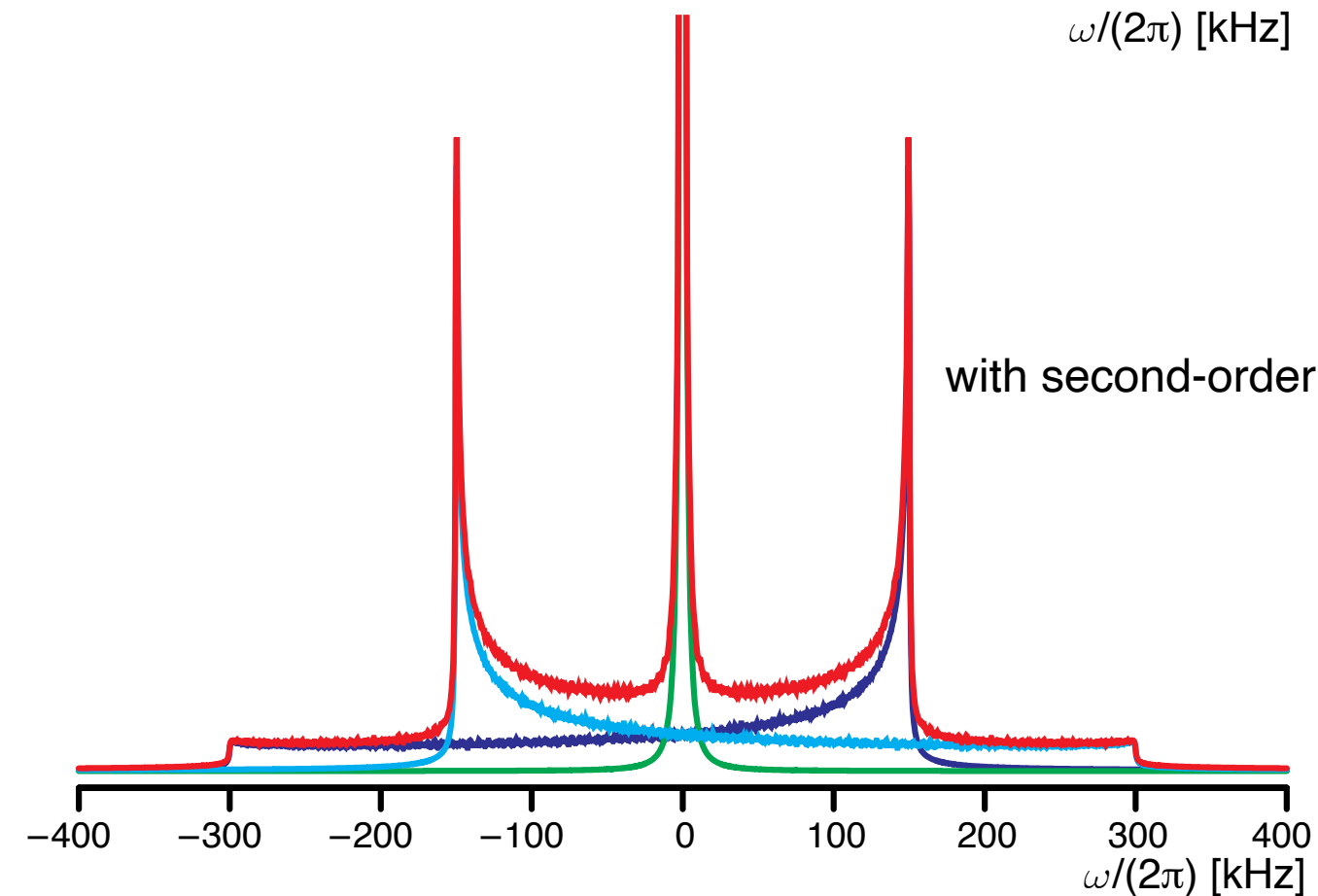
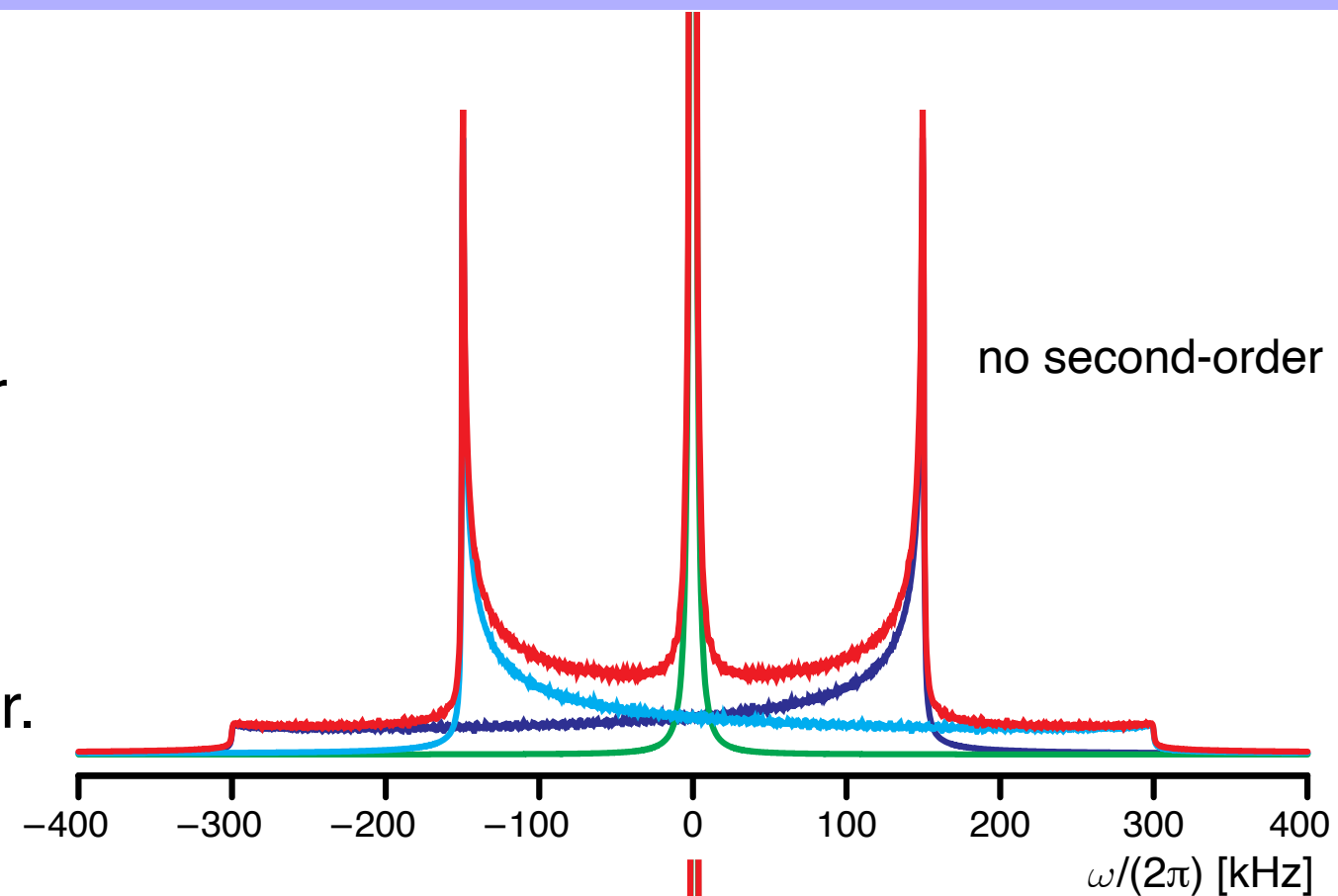
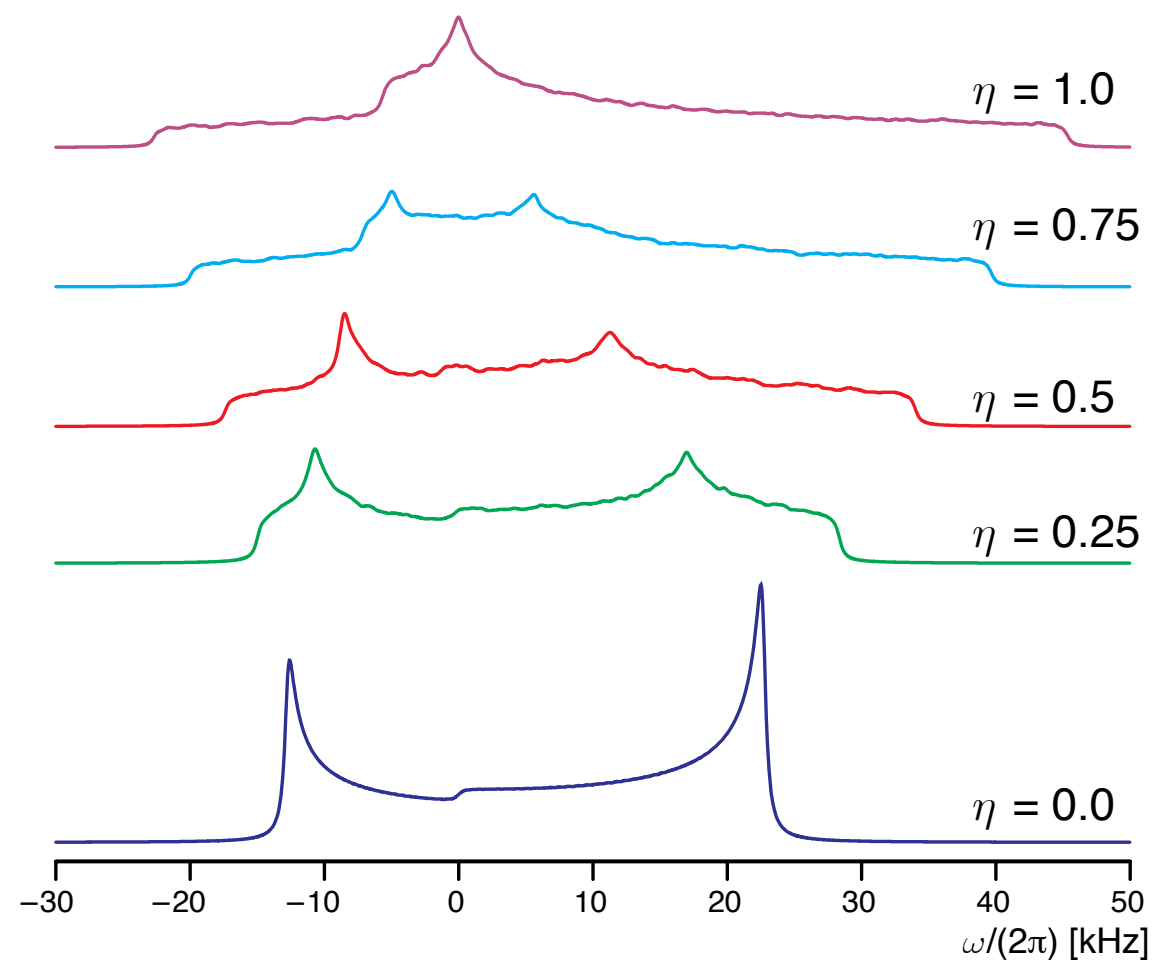
Line Spectrum for a Single Crystallite:



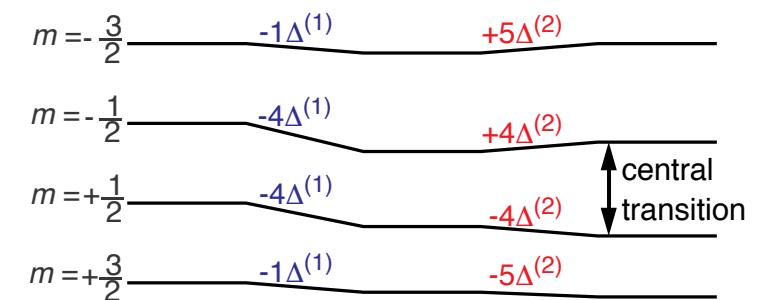
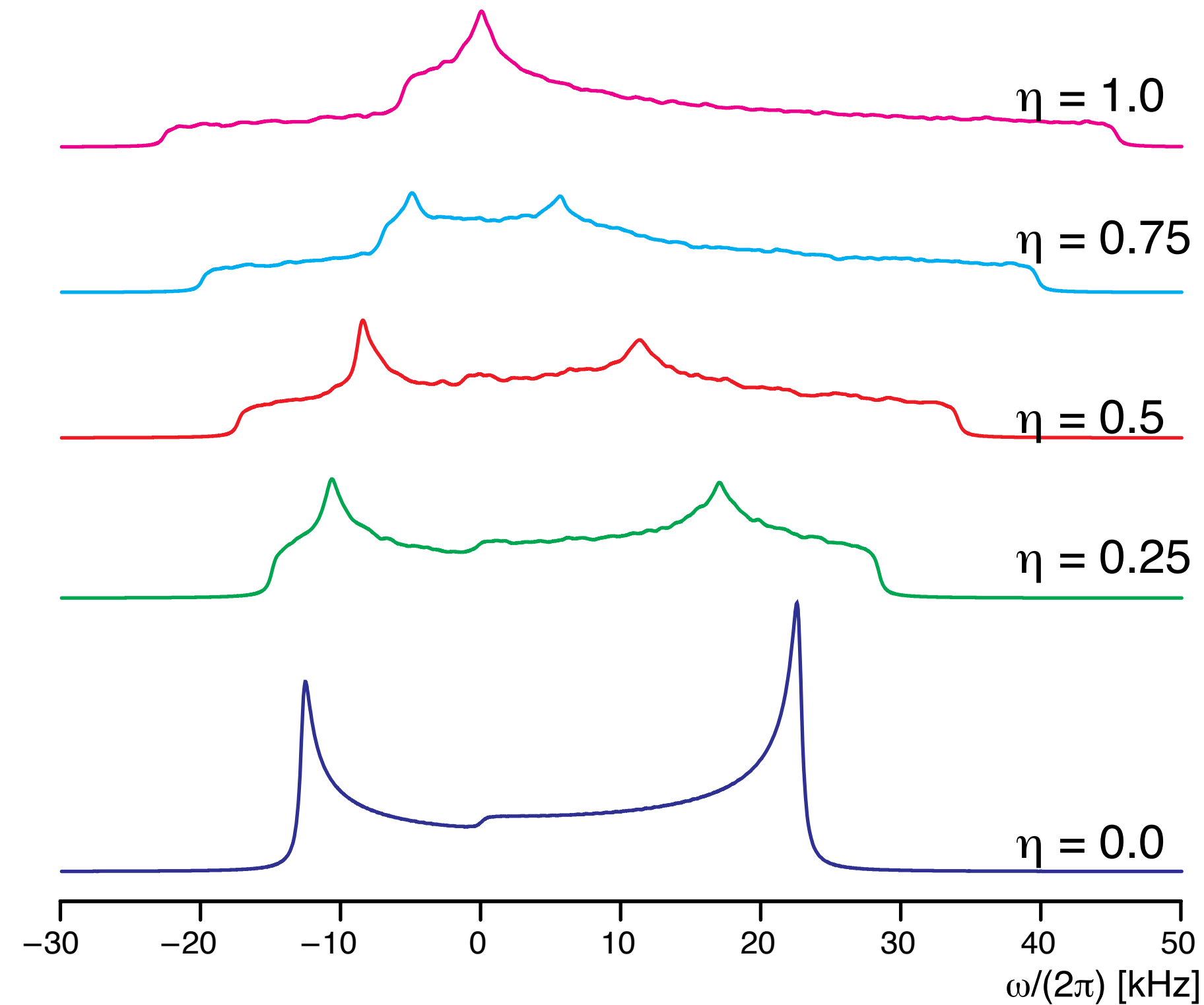
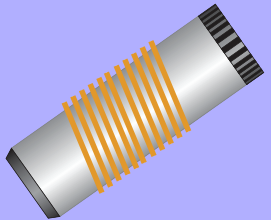
□ Quadrupolar nuclei have more than one transition frequency and, therefore, multiple lines in the spectrum.

Spectra of Quadrupolar Nuclei (Spin 3/2)

- ❑ Quadrupolar line shapes are very broad because of the satellite transitions that are shifted by the quadrupolar coupling.
- ❑ On the scale of the full line, the second-order contribution is not visible.
- ❑ If we zoom into the central transition, we see the line shape generated by the second order.

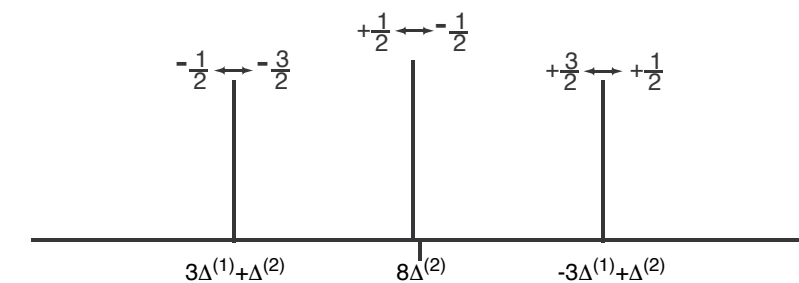


Magic-Angle Spinning of Quadrupolar Nuclei



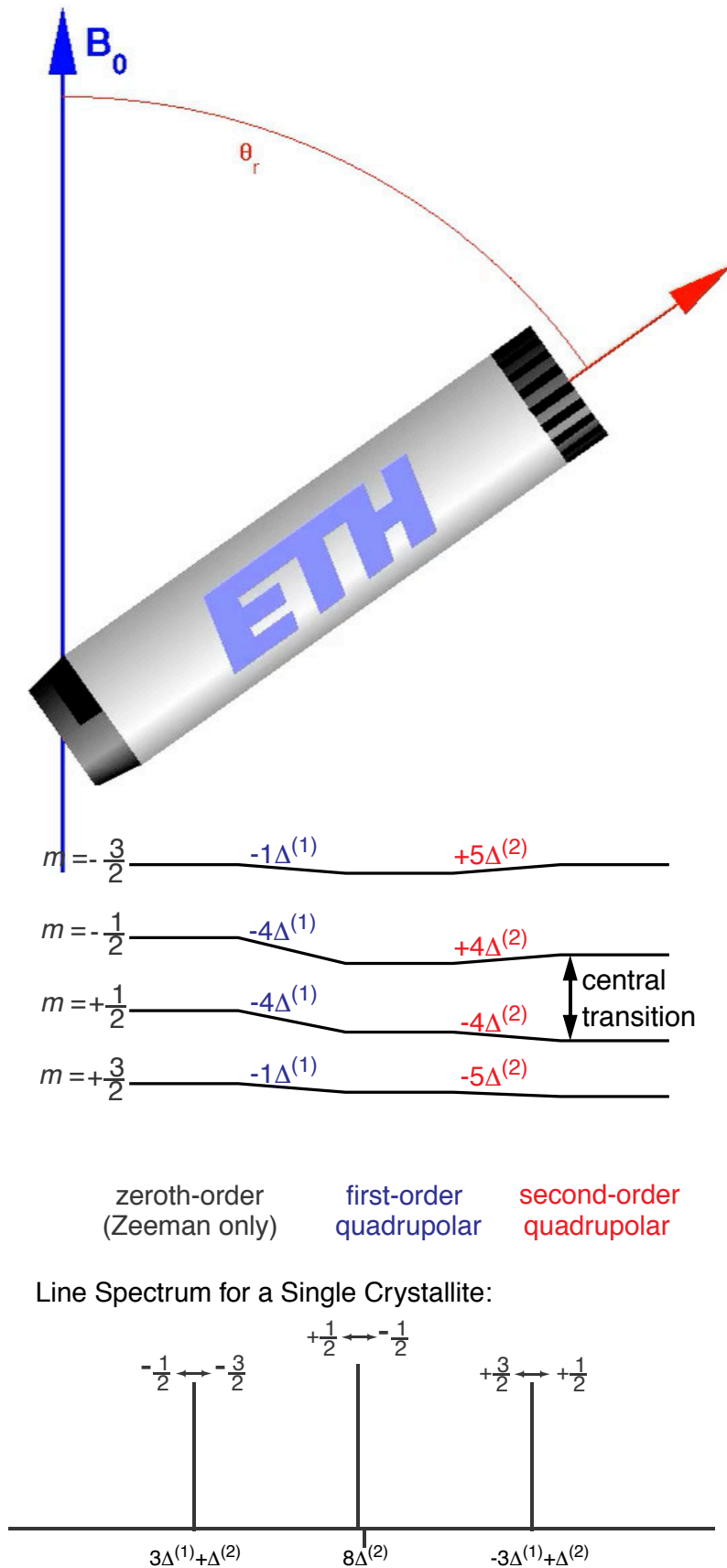
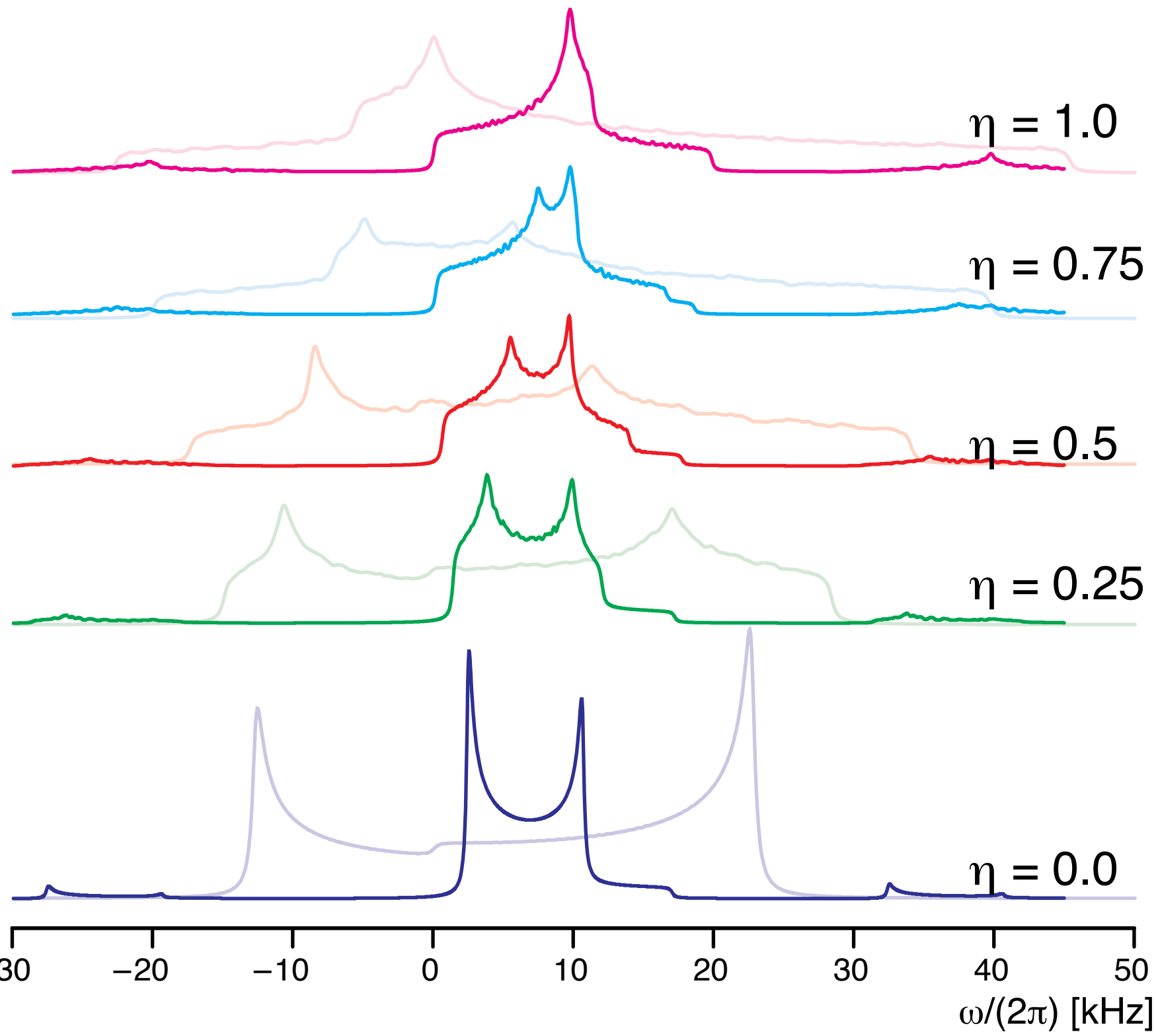
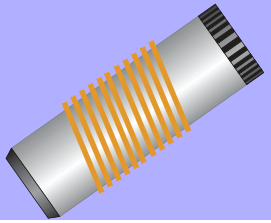
zeroth-order (Zeeman only) first-order quadrupolar second-order quadrupolar

Line Spectrum for a Single Crystallite:



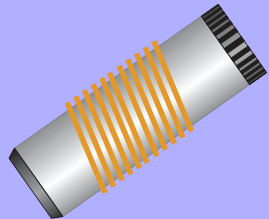
❑ MAS does not average the quadrupole lines completely.

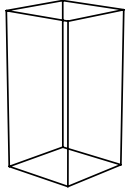
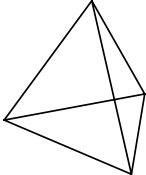
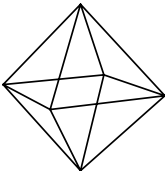
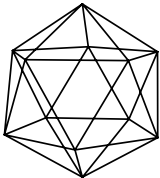
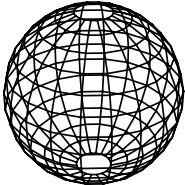
Magic-Angle Spinning of Quadrupolar Nuclei



❑ MAS does not average the quadrupole lines completely.

Tensor Symmetries Under Rotation

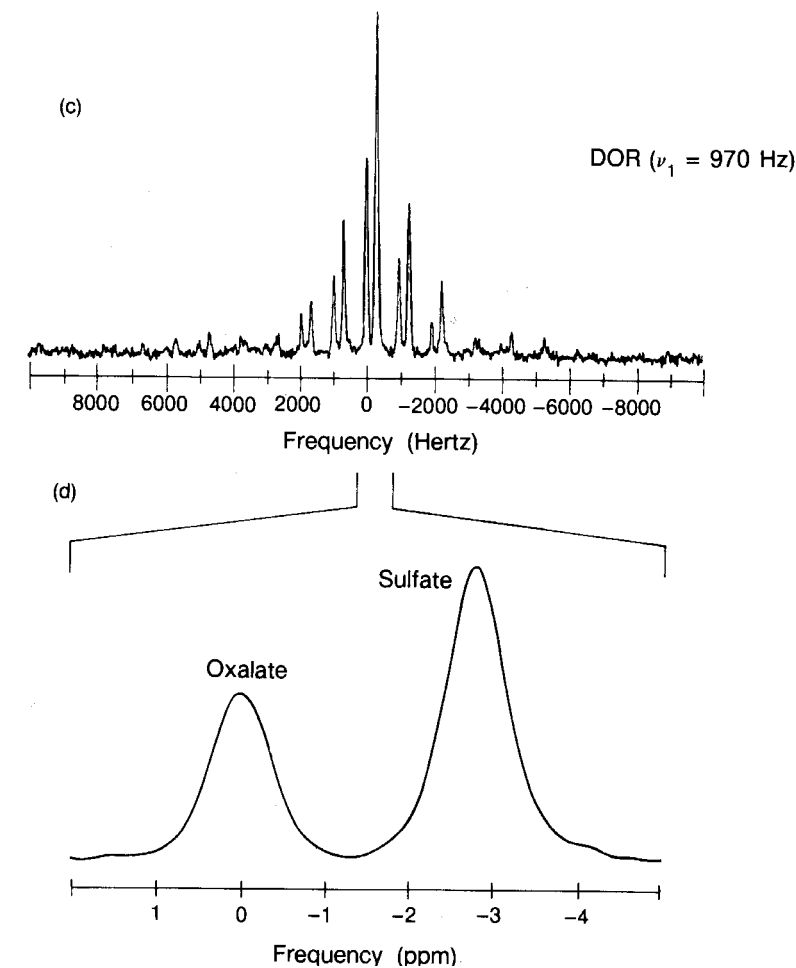
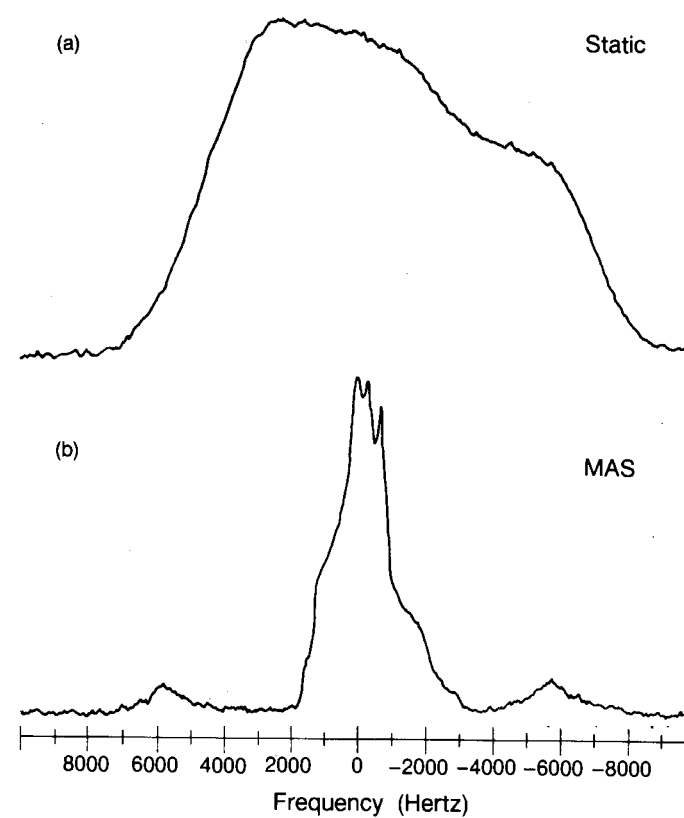
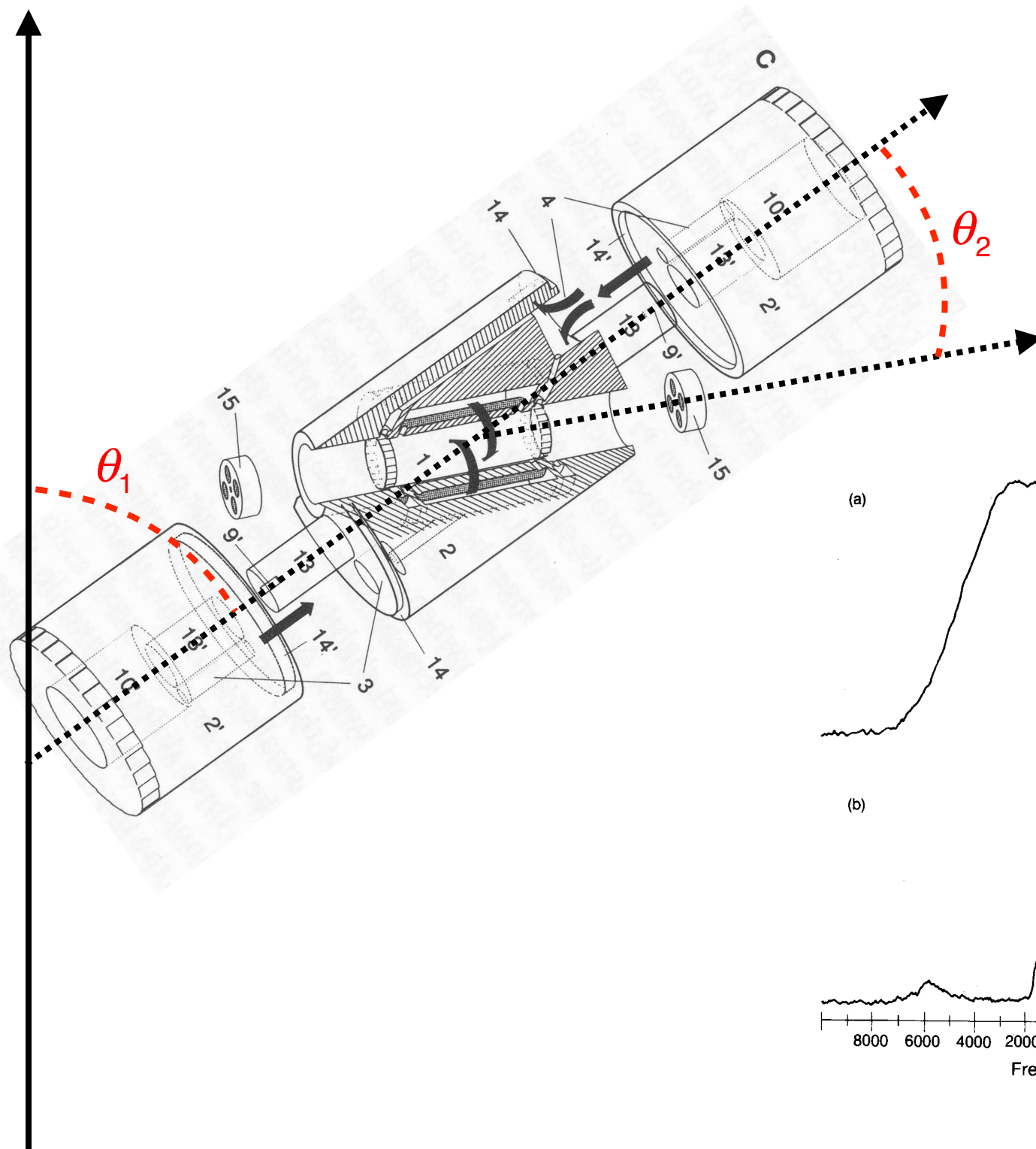


Symmetry		Possible Tensor Ranks										
Tetragonal 	D4	0		2		4	5	6	7	8	9	10
Tetrahedral 	T	0			3	4		6	7	8	9	10
Octahedral 	O	0				4		6		8	9	10
Icosahedral 	I	0						6				10
Spherical 	SO(3)	0										

Averaging Quadrupolar Couplings: Double Rotation

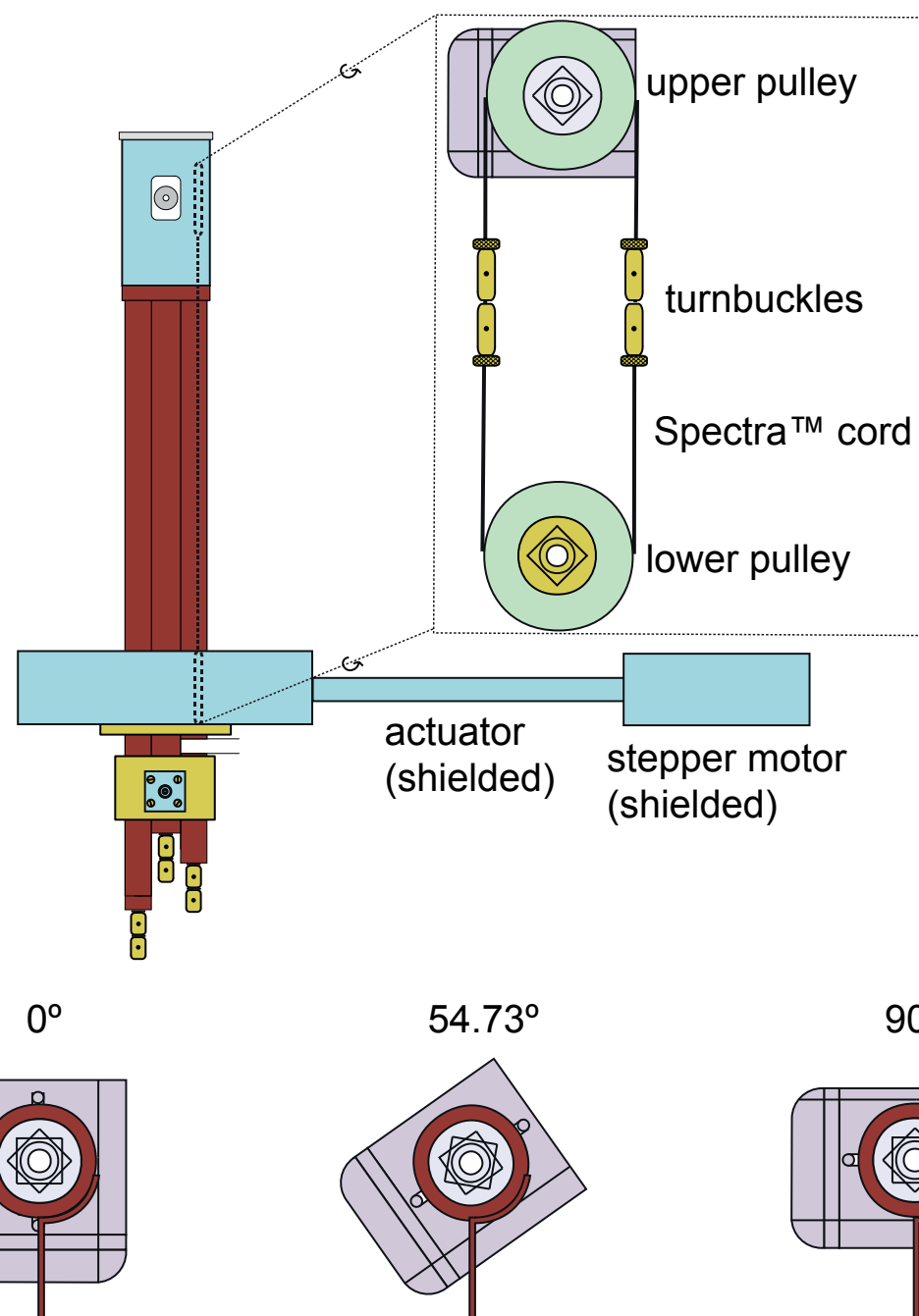
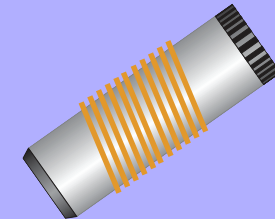


- Simultaneous rotation about two axes leads to a complete averaging of the quadrupole coupling.
- Example ^{23}Na : mixture of sodium oxalate and sodium sulfate.

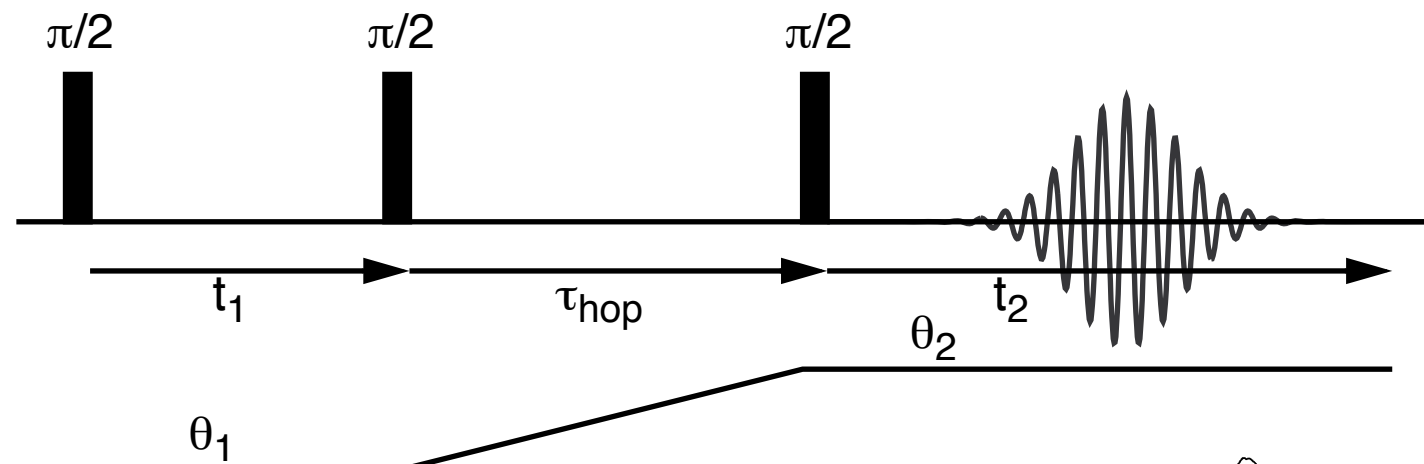


Copied from: Y. Wu, B.Q. Sun, A. Pines, A. Samoson, and E. Lippmaa, "NMR Experiments With a New Double Rotor", Journal of Magnetic Resonance 89, 297-309 (1990).

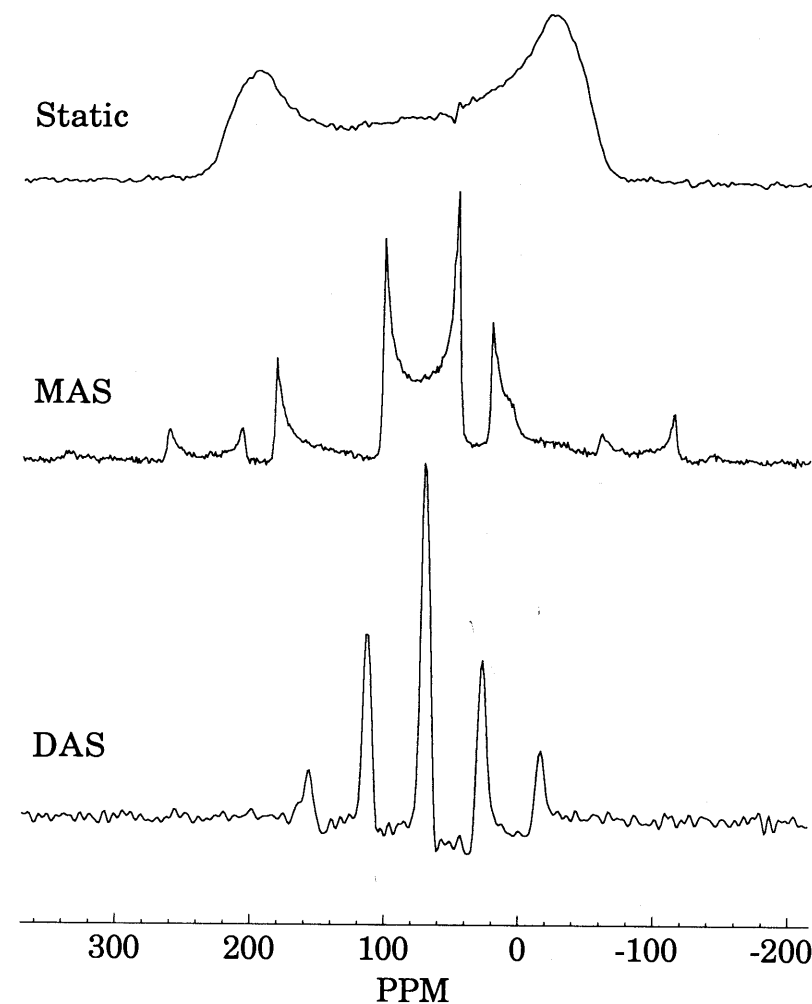
Averaging Quadrupolar Couplings: DAS



Dynamic-angle spinning (DAS) allows a fast reorientation of the spinning axis during the experiment.



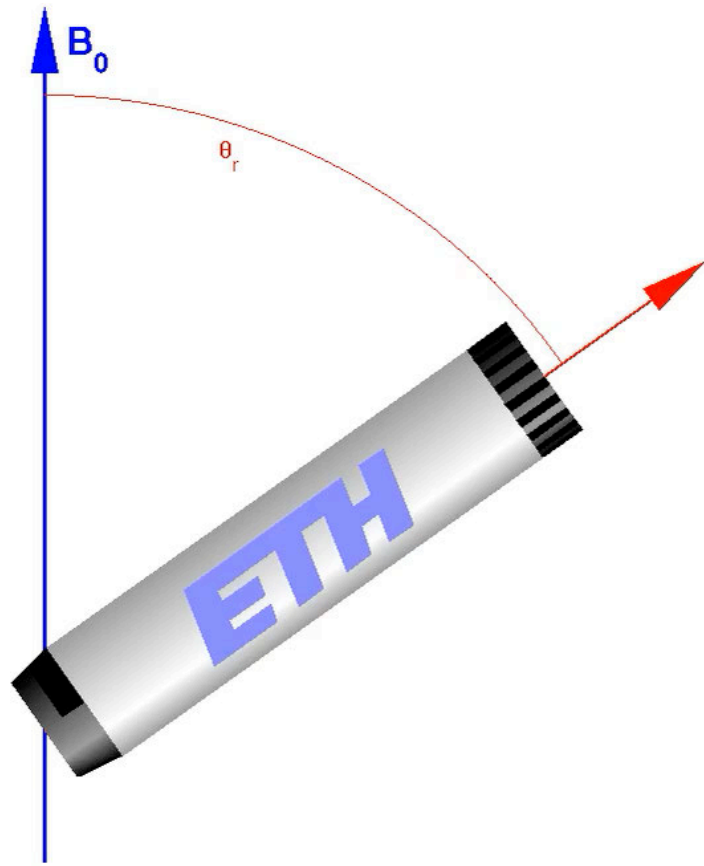
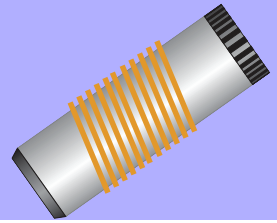
^{11}B spectra of boric acid



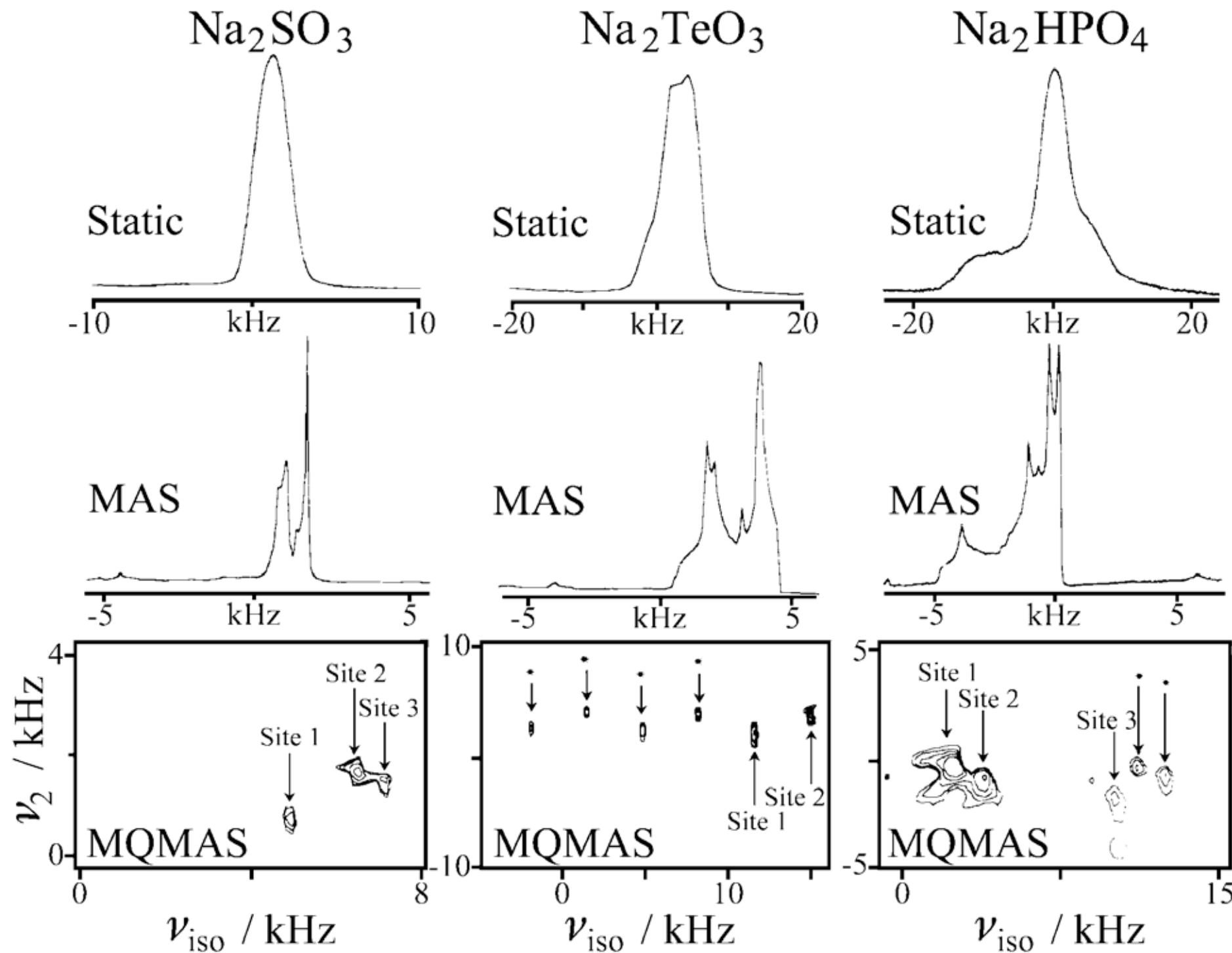
R.W. Martin, J.E. Kelly, K.A. Collier, Spatial reorientation experiments for NMR of solids and partially oriented liquids, Prog. NMR Spectr. 90-91 (2015) 92–122. doi:10.1016/j.pnmrs.2015.10.001.

M.A. Eastman, P.J. Grandinetti, Y.K. Lee, and A. Pines "Double-Tuned Hopping-Coil Probe for Dynamic-Angle Spinning NMR", Journal of Magnetic Resonance 98, 333-341 (1992)

Averaging Quadrupolar Couplings: MQMAS

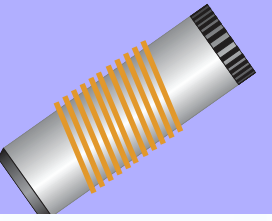


- MQMAS needs only a standard MAS probe.
- A special echo sequence leads to an averaging of the residual line broadening under MAS.
- Like DAS, this is a two-dimensional method.



A. Medek, L. Frydman, Multiple - quantum magic - angle spinning NMR: a new technique for probing quadrupolar nuclei in solids, J. Braz. Chem. Soc. 10 (1999) 1–16. doi:10.1590/S0103-50531999000400003.

Hamiltonians for Solid-State NMR



Mamallapuram, 2022

- Cartesian notation for Hamiltonians describing spin-field interactions:

$$\hat{\mathcal{H}}^{(k,B)} = \hat{\vec{I}}_k \mathbf{A}^{(k,B)} \vec{B} = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}$$

- Cartesian notation for Hamiltonians describing spin-spin interactions:

$$\hat{\mathcal{H}}^{(k,n)} = \hat{\vec{I}}_k \mathbf{A}^{(k,n)} \hat{\vec{I}}_n = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_{nx} \\ \hat{I}_{ny} \\ \hat{I}_{nz} \end{pmatrix}$$

- All Hamiltonian can be written in this notation.
- The coupling matrix $\mathbf{A}$ describes the spatial relationship between the two spins or the spin and the field.
- The coupling matrix $\mathbf{A}$ can be decomposed into three components:
 - trace of the matrix (isotropic component)
 - anti-symmetric part of the matrix (rank-1 component)
 - symmetric part of the matrix (rank-2 component)

Coupling Matrix A

□ A general matrix A can be decomposed into three parts: $A = A^{(0)} + A^{(1)} + A^{(2)}$

$$A^{(0)} = \begin{pmatrix} \bar{a} & 0 & 0 \\ 0 & \bar{a} & 0 \\ 0 & 0 & \bar{a} \end{pmatrix}$$

isotropic component
rank-zero component

$$A^{(1)} = \begin{pmatrix} 0 & \frac{a_{xy} - a_{yx}}{2} & \frac{a_{xz} - a_{zx}}{2} \\ \frac{a_{yx} - a_{xy}}{2} & 0 & \frac{a_{yz} - a_{zy}}{2} \\ \frac{a_{zx} - a_{xz}}{2} & \frac{a_{zy} - a_{yz}}{2} & 0 \end{pmatrix}$$

first-rank component
anti-symmetric matrix component

$$A^{(2)} = \begin{pmatrix} a_{xx} - \bar{a} & \frac{a_{xy} + a_{yx}}{2} & \frac{a_{xz} + a_{zx}}{2} \\ \frac{a_{xy} + a_{yx}}{2} & a_{yy} - \bar{a} & \frac{a_{yz} + a_{zy}}{2} \\ \frac{a_{xz} + a_{zx}}{2} & \frac{a_{yz} + a_{zy}}{2} & a_{zz} - \bar{a} \end{pmatrix}$$

second-rank component
symmetric matrix component

□ Rotations will not mix the three components!

Coupling Matrix A

□ A general matrix A can be decomposed into three parts: $A = A^{(0)} + A^{(1)} + A^{(2)}$

$$A^{(0)} = \begin{pmatrix} \bar{a} & 0 & 0 \\ 0 & \bar{a} & 0 \\ 0 & 0 & \bar{a} \end{pmatrix}$$

isotropic component
rank-zero component
Important for solution and solids

$$A^{(1)} = \begin{pmatrix} 0 & \frac{a_{xy} - a_{yx}}{2} & \frac{a_{xz} - a_{zx}}{2} \\ \frac{a_{yx} - a_{xy}}{2} & 0 & \frac{a_{yz} - a_{zy}}{2} \\ \frac{a_{zx} - a_{xz}}{2} & \frac{a_{zy} - a_{yz}}{2} & 0 \end{pmatrix}$$

first-rank component
anti-symmetric matrix component
does not play an important role in MR

$$A^{(2)} = \begin{pmatrix} a_{xx} - \bar{a} & \frac{a_{xy} + a_{yx}}{2} & \frac{a_{xz} + a_{zx}}{2} \\ \frac{a_{xy} + a_{yx}}{2} & a_{yy} - \bar{a} & \frac{a_{yz} + a_{zy}}{2} \\ \frac{a_{xz} + a_{zx}}{2} & \frac{a_{yz} + a_{zy}}{2} & a_{zz} - \bar{a} \end{pmatrix}$$

second-rank component
symmetric matrix component
**Important for solids
(and relaxation in liquids)**

□ Rotations will not mix the three components!

□ Cartesian notation for Hamiltonians describing spin-field interactions:

$$\hat{\mathcal{H}}^{(k,B)} = \hat{\vec{I}}_k \mathbf{A}^{(k,B)} \vec{B} = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix} = \hat{\vec{I}}^{(k,B)} \cdot \vec{A}^{(k,B)}$$

□ Cartesian notation for Hamiltonians describing spin-spin interactions:

$$\hat{\mathcal{H}}^{(k,n)} = \hat{\vec{I}}_k \mathbf{A}^{(k,n)} \hat{\vec{I}}_n = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_{nx} \\ \hat{I}_{ny} \\ \hat{I}_{nz} \end{pmatrix} = \hat{\vec{I}}^{(k,n)} \cdot \vec{A}^{(k,n)}$$

□ The **scalar-product notation** is equivalent to the vector/matrix/vector notation with the vectors $\vec{A}$, $\hat{\vec{I}}^{(k,B)}$, and $\hat{\vec{I}}^{(k,n)}$ defined by

$$\vec{A}^{(k,n)} = (a_{xx}, a_{xy}, a_{xz}, a_{yx}, a_{yy}, a_{yz}, a_{zx}, a_{zy}, a_{zz})$$

$$\hat{\vec{I}}^{(k,n)} = (\hat{I}_{kx}\hat{I}_{nx}, \hat{I}_{kx}\hat{I}_{ny}, \hat{I}_{kx}\hat{I}_{nz}, \hat{I}_{ky}\hat{I}_{nx}, \hat{I}_{ky}\hat{I}_{ny}, \hat{I}_{ky}\hat{I}_{nz}, \hat{I}_{kz}\hat{I}_{nx}, \hat{I}_{kz}\hat{I}_{ny}, \hat{I}_{kz}\hat{I}_{nz})$$

$$\hat{\vec{I}}^{(k,B)} = (\hat{I}_{kx}B_x, \hat{I}_{kx}B_y, \hat{I}_{kx}B_z, \hat{I}_{ky}B_x, \hat{I}_{ky}B_y, \hat{I}_{ky}B_z, \hat{I}_{kz}B_x, \hat{I}_{kz}B_y, \hat{I}_{kz}B_z)$$

Rotation of Spatial Tensors

□ Spatial rotations can be implemented by rotation matrices in both representations.

□ $\mathbf{A}^{(\text{new})} = \mathbf{R}(\alpha, \beta, \gamma) \mathbf{A}^{(\text{old})} \mathbf{R}^{-1}(\alpha, \beta, \gamma)$

□ $\vec{A}^{(\text{new})} = \tilde{\mathbf{R}}(\alpha, \beta, \gamma) \vec{A}^{(\text{old})}$ with $\tilde{\mathbf{R}}(\alpha, \beta, \gamma) = \mathbf{R}(\alpha, \beta, \gamma) \otimes \mathbf{R}(\alpha, \beta, \gamma)$.

□ We can block diagonalize the rotation matrix in the scalar-product representation of the Hamiltonian which makes rotations more efficient.

□ This block diagonalization uses the separation of $\mathbf{A} = \mathbf{A}^{(0)} + \mathbf{A}^{(1)} + \mathbf{A}^{(2)}$

□ Spherical tensors are a special symmetry adapted basis where the different ranks are separated and the rotations are described by the Wigner rotation matrices.

□ A spherical tensor of rank ℓ has $2\ell+1$ elements and can be written as a vector:

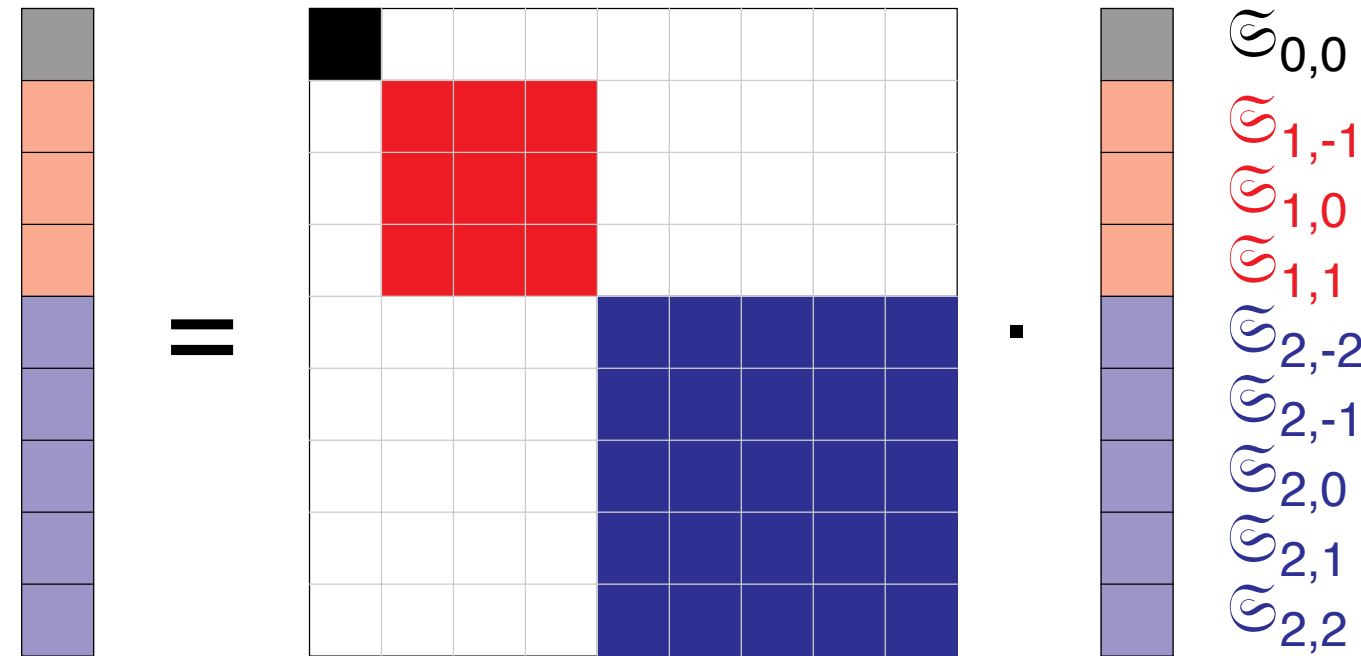
$$\mathfrak{S}_\ell = (\mathfrak{S}_{\ell,-\ell}, \mathfrak{S}_{\ell,-\ell+1}, \dots, \mathfrak{S}_{\ell,0}, \dots, \mathfrak{S}_{\ell,\ell-1}, \mathfrak{S}_{\ell,\ell})$$

□ The rotation of spherical tensors is given by

$$\mathfrak{S}_\ell^{(\text{new})} = \mathfrak{D}^\ell(\alpha, \beta, \gamma) \mathfrak{S}_\ell^{(\text{old})}$$

or written for the Wigner rotation matrix elements:

$$\mathfrak{S}_{\ell,m}^{(\text{new})} = \sum_{m'=-\ell}^{\ell} \mathfrak{D}_{m',m}^\ell(\alpha, \beta, \gamma) \mathfrak{S}_{\ell,m'}^{(\text{old})}$$



□ Note: The $\mathfrak{S}_\ell$ are matrices of dimension $2\ell+1$, the $\mathfrak{S}_{\ell,m}$ are complex numbers.

□ The Wigner rotation matrix elements are given by:

$$\mathfrak{D}_{m',m}^\ell(\alpha, \beta, \gamma) = e^{-im'\alpha} d_{m',m}^\ell(\beta) e^{-im\gamma}$$

□ The reduced Wigner rotation matrix elements $d_{m',m}^\ell(\beta)$ are tabulated or can be calculated using Mathematica or Matlab.

Spatial Tensors: PAS and Lab Frame

□ Cartesian representation of a pure second-rank tensor: a symmetric traceless 3x3 matrix:

PAS

$$\mathbf{A}^{\text{PAS}} = \begin{pmatrix} a_{xx} & 0 & 0 \\ 0 & a_{yy} & 0 \\ 0 & 0 & a_{zz} \end{pmatrix}$$

$$\text{tr}\{\mathbf{A}^{\text{PAS}}\} = a_{xx} + a_{yy} + a_{zz} = 0$$

Laboratory Frame

$$\mathbf{A}^{\text{LAB}} = R(\alpha, \beta, \gamma) \mathbf{A}^{\text{PAS}} R^{-1}(\alpha, \beta, \gamma) = \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{xy} & a_{yy} & a_{yz} \\ a_{xz} & a_{yz} & a_{zz} \end{pmatrix}$$

$$\text{tr}\{\mathbf{A}^{\text{LAB}}\} = a_{xx} + a_{yy} + a_{zz} = 0$$

□ Number of independent parameters: 5

2 tensor values and 3 Euler angles

5 tensor values (2 diagonal, 3 off diagonal)

□ For an axially symmetric tensor, we have $a_{xx}=a_{yy}$, i.e. only a single tensor value in the PAS.

□ Spherical Representation of a pure second-rank tensor:

$$\mathbf{A}_{2,0}^{(\text{PAS})} = \sqrt{\frac{3}{2}}\delta = \sqrt{\frac{3}{2}}a_{zz}$$

$$\mathbf{A}_{20} = \sqrt{\frac{3}{8}}\delta \left[(3\cos^2\beta - 1) - \eta\sin^2\beta\cos(2\alpha) \right]$$

$$\mathbf{A}_{2,\pm 1}^{(\text{PAS})} = 0$$

$$\mathbf{A}_{2\pm 1} = \pm \frac{\delta}{2} \sin\beta e^{\pm i\gamma} \left[(3 + \eta\cos(2\alpha))\cos\beta \mp i\eta\sin(2\alpha) \right]$$

$$\mathbf{A}_{2,\pm 2}^{(\text{PAS})} = -\frac{1}{2}\delta\eta = \frac{1}{2}(a_{xx} - a_{yy}) \quad \mathbf{A}_{2\pm 2} = \frac{\delta}{2} e^{\pm 2i\gamma} \left[\frac{3}{2}\sin^2\beta - \frac{\eta}{2}(1 + \cos^2\beta)\cos(2\alpha) \pm i\eta\cos\beta\sin(2\alpha) \right]$$

□ Relationship between Cartesian and spherical representation of a second-rank tensor:

$$A_{2,0} = \frac{1}{\sqrt{6}}(3a_{zz} - (a_{xx} + a_{yy} + a_{zz}))$$

$$A_{2,\pm 1} = \mp \frac{1}{2}(a_{xz} + a_{zx} \pm i(a_{zy} + a_{yz}))$$

$$A_{2,\pm 2} = \frac{1}{2}(a_{xx} - a_{yy} \pm i(a_{xy} - a_{xz}))$$

□ In the PAS, all off-diagonal elements of the Cartesian matrix are zero, in the laboratory frame all tensor elements are non zero:

$$A_{2,0}^{(\text{PAS})} = \frac{1}{\sqrt{6}}(3a_{zz} - (a_{xx} + a_{yy} + a_{zz})) = \sqrt{\frac{3}{2}}\delta$$

$$A_{2,\pm 1}^{(\text{PAS})} = 0$$

$$A_{2,\pm 2}^{(\text{PAS})} = \frac{1}{2}(a_{xx} - a_{yy}) = -\frac{1}{2}\delta\eta$$

$$A_{2,0}^{(\text{LAB})} = \frac{1}{\sqrt{6}}(3a_{zz} - (a_{xx} + a_{yy} + a_{zz}))$$

$$A_{2,\pm 1}^{(\text{LAB})} = \mp \frac{1}{2}(a_{xz} + a_{zx} \pm i(a_{zy} + a_{yz}))$$

$$A_{2,\pm 2}^{(\text{LAB})} = \frac{1}{2}(a_{xx} - a_{yy} \pm i(a_{xy} - a_{xz}))$$

□ Most common parametrisation of second-rank tensors in PAS:

$$\delta = a_{zz} - \bar{a}$$

$$\eta = \frac{a_{yy} - a_{xx}}{\delta}$$

$$|a_{zz} - \bar{a}| \geq |a_{xx} - \bar{a}| \geq |a_{yy} - \bar{a}|$$

□ Examples from solution-state NMR:

- Zeeman Hamiltonian:

$$\hat{\mathcal{H}}_Z = -\gamma \vec{B}_0 \cdot \hat{\vec{I}} = \hat{\vec{I}} \begin{pmatrix} -\gamma & 0 & 0 \\ 0 & -\gamma & 0 \\ 0 & 0 & -\gamma \end{pmatrix} \vec{B}_0 = -\gamma B_0 \hat{I}_z = \omega_0 \hat{I}_z$$

- Chemical-shift Hamiltonian:

$$\hat{\mathcal{H}}_{CS} = -\gamma \sigma_{iso} \vec{B}_0 \cdot \hat{\vec{I}} = \hat{\vec{I}} \begin{pmatrix} -\gamma \sigma_{iso} & 0 & 0 \\ 0 & -\gamma \sigma_{iso} & 0 \\ 0 & 0 & -\gamma \sigma_{iso} \end{pmatrix} \vec{B}_0 = -\gamma \sigma_{iso} B_0 \hat{I}_z = \Omega \hat{I}_z$$

- J -coupling Hamiltonian:

$$\hat{\mathcal{H}}_J = 2\pi J_{12} \hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2 = \hat{\vec{I}}_1 \begin{pmatrix} 2\pi J_{12} & 0 & 0 \\ 0 & 2\pi J_{12} & 0 \\ 0 & 0 & 2\pi J_{12} \end{pmatrix} \hat{\vec{I}}_2 = 2\pi J_{12} [\hat{I}_{1x} \hat{I}_{2x} + \hat{I}_{1y} \hat{I}_{2y} + \hat{I}_{1z} \hat{I}_{2z}]$$

□ All coupling matrices **A** are multiples of the identity matrix and, therefore, invariant under rotations.

□ All interactions are isotropic because the molecules tumble fast in solution.

Anisotropic-Chemical Shift

$$\hat{\mathcal{H}}(t)$$

- The induced field $\vec{B}_s$ due the electronic environment has an arbitrary orientation and is proportional to the external field $\vec{B}_0$.

$$\begin{pmatrix} B_{s,x} \\ B_{s,y} \\ B_{s,z} \end{pmatrix} = - \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}$$

- The chemical-shielding matrix (tensor) is a full 3x3 matrix.

- The chemical-shielding Hamiltonian is given by:

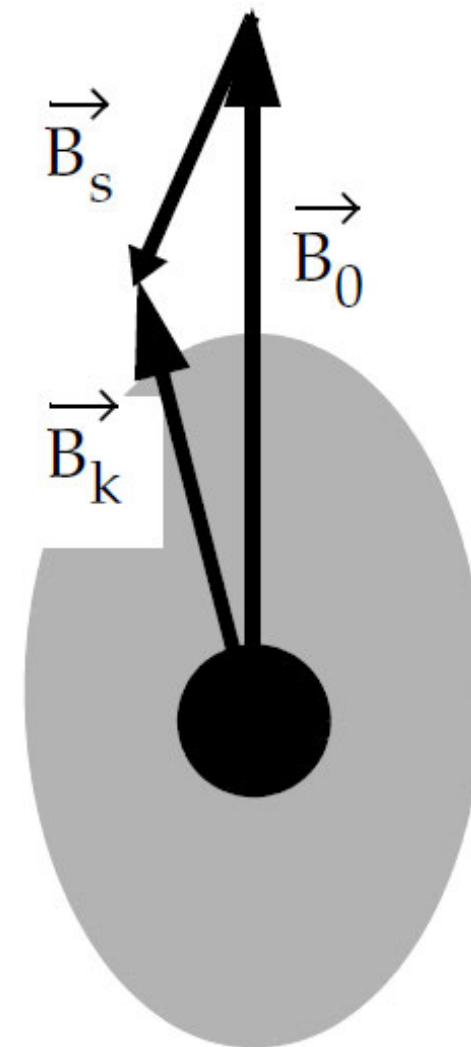
$$\begin{aligned} \hat{\mathcal{H}}^{(k,B)} &= \hat{I}_k (-\gamma) \vec{B}_s = \hat{I}_k \gamma \underline{\sigma}^{(k,B)} \vec{B} = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \gamma \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} \\ &= \gamma B_0 (\sigma_{xz} \hat{I}_x + \sigma_{yz} \hat{I}_y + \sigma_{zz} \hat{I}_z) \end{aligned}$$

- In the rotating frame, we get only the z-term: $\hat{\mathcal{H}}^{(k,B)} = \gamma B_0 \sigma_{zz} \hat{I}_z$

- The value of the chemical shielding depends on the orientation of the molecule relative to the static magnetic field.

- The isotropic chemical shielding that we see in solution-state NMR is given by:

$$\sigma_{\text{iso}} = \frac{1}{3} \underline{\sigma} = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

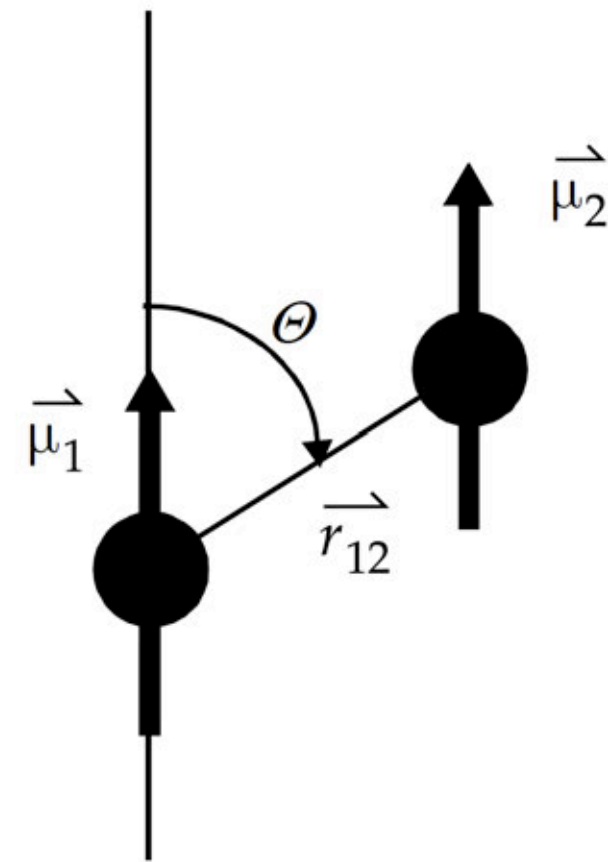


The Dipolar Interaction

$$\hat{\mathcal{H}}(t)$$

- ❑ The dipolar coupling is the direct through-space interaction between two spins.
- ❑ The dipolar coupling is anisotropic without an isotropic part. Therefore it is averaged to zero in solution.
- ❑ The laboratory-frame Hamiltonian is given by:

$$\hat{\mathcal{H}}^{(k,n)} = \hat{\vec{I}}_k \mathbf{D}^{(k,n)} \hat{\vec{I}}_n = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_{nx} \\ \hat{I}_{ny} \\ \hat{I}_{nz} \end{pmatrix}$$



- ❑ The matrix $\mathbf{D}^{(k,n)}$ is a symmetric and traceless matrix and the elements are given by:

$$(D^{(k,n)})_{\alpha,\beta} = \frac{\mu_0}{4\pi} \frac{\gamma_k \gamma_n \hbar}{r_{kn}^3} (\delta_{\alpha\beta} - 3e_\alpha e_\beta) \text{ with } \alpha, \beta \in \{x, y, z\}$$

- ❑ The e_α are the components of a unit vector along the internuclear vector $\vec{r}_{kn}$.

The Dipolar Interaction

□ The dipolar coupling is the direct through-space interaction between two spins.

□ The dipolar Hamiltonian can be written as: $\hat{\mathcal{H}}_D = -\frac{\mu_0}{4\pi} \frac{\hbar \gamma_1 \gamma_2}{r_{12}^3} [\hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} + \hat{F}]$

□ This is sometimes called the dipolar alphabet:

$$\hat{A} = 2\hat{I}_{1z}\hat{I}_{2z} \frac{3\cos^2\theta - 1}{2}$$

$$\hat{B} = -\frac{1}{2}(\hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+) \frac{3\cos^2\theta - 1}{2}$$

ZQ term - flip-flop term

$$\hat{C} = -(\hat{I}_1^+\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^+) \frac{3\cos\theta\sin\theta e^{-i\phi}}{2}$$

SQ terms

$$\hat{D} = -(\hat{I}_1^-\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^-) \frac{3\cos\theta\sin\theta e^{i\phi}}{2}$$

$$\hat{E} = -\hat{I}_1^+\hat{I}_2^+ \frac{3\sin^2\theta e^{-2i\phi}}{4}$$

DQ terms

$$\hat{F} = -\hat{I}_1^-\hat{I}_2^- \frac{3\sin^2\theta e^{2i\phi}}{4}$$

The Dipolar Interaction

- ❑ The dipolar coupling is the direct through-space interaction between two spins.
- ❑ The dipolar coupling is anisotropic without an isotropic part. Therefore it is averaged to zero in solution.
- ❑ The laboratory-frame Hamiltonian is given by: $\hat{\mathcal{H}}_D = -\frac{\mu_0}{4\pi} \frac{\hbar\gamma_1\gamma_2}{r_{12}^3} [\hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} + \hat{F}]$
- ❑ In the rotating frame we have:
 - $\hat{\mathcal{H}}_D = -\frac{\mu_0}{4\pi} \frac{\hbar\gamma_1\gamma_2}{r_{12}^3} \frac{3\cos^2\theta - 1}{2} \left(2\hat{I}_{1z}\hat{I}_{2z} - \frac{1}{2}(\hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+) \right)$ for a **homonuclear** spin pair
 - $\hat{\mathcal{H}}_D = -\frac{\mu_0}{4\pi} \frac{\hbar\gamma_1\gamma_2}{r_{12}^3} \frac{3\cos^2\theta - 1}{2} (2\hat{I}_{1z}\hat{I}_{2z})$ for a **heteronuclear** spin pair
- ❑ This is fully analogous to the J coupling where we also had different rotating-frame Hamiltonians for homonuclear and heteronuclear couplings.
- ❑ The constant $d = -\frac{\mu_0}{4\pi} \frac{\hbar\gamma_1\gamma_2}{r_{12}^3} \frac{3\cos^2\theta - 1}{2}$ is often called the dipolar coupling constant.

Representation of Hamiltonians

$$\hat{\mathcal{H}}(t)$$

□ Cartesian Representation:

$$\hat{\mathcal{H}}^{(k,n)} = \hat{\vec{I}}_k A^{(k,n)} \hat{\vec{I}}_n = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_{nx} \\ \hat{I}_{ny} \\ \hat{I}_{nz} \end{pmatrix}$$

$$\hat{\mathcal{H}}^{(k,B)} = \hat{\vec{I}}_k A^{(k,B)} \vec{B} = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}$$

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vector x matrix x vector

$$\hat{\mathcal{H}}^{(k,B)} = \hat{\vec{I}}_k A^{(k,B)} \vec{B} = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}$$

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vector x matrix x vector

Spatial Matrix:

$$\begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \xleftrightarrow[R^{-1}(\alpha, \beta, \gamma)]{R(\alpha, \beta, \gamma)} \begin{pmatrix} a_{xx} & 0 & 0 \\ 0 & a_{yy} & 0 \\ 0 & 0 & a_{zz} \end{pmatrix}$$

laboratory frame (LAB):
full matrix

required for the Hamiltonian

principal axes system (PAS):
diagonal matrix

**simple, known from spectra
or calculations**

Representation of Hamiltonians

$$\hat{\mathcal{H}}(t)$$

Cartesian Representation:

$$\hat{\mathcal{H}}^{(k,n)} = \hat{\vec{I}}_k \mathbf{A}^{(k,n)} \hat{\vec{I}}_n = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_{nx} \\ \hat{I}_{ny} \\ \hat{I}_{nz} \end{pmatrix}$$

$\hat{\mathcal{H}}^{(k,B)} = \hat{\vec{I}}_k \mathbf{A}^{(k,B)} \vec{B} = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}$

vector x matrix x vector

Spin or Magnetic Field Vector:

typically a Cartesian vector:

other single-spin bases are possible:

$$\vec{\hat{I}} = \begin{pmatrix} \hat{I}_x \\ \hat{I}_y \\ \hat{I}_z \end{pmatrix} \xleftrightarrow[\begin{matrix} R^{-1} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ -i/2 & i/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{matrix}]{\begin{matrix} R = \begin{pmatrix} 1 & i & 0 \\ 1 & -i & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{matrix}} \vec{\hat{I}} = \begin{pmatrix} \hat{I}^+ \\ \hat{I}^- \\ \hat{I}_z \end{pmatrix}$$

such a change of the basis will
also change the **A** matrix!

□ Spherical-Tensor Representation:

$$\mathcal{H} = \left\{ \sum_i \sum_{\ell_1=0}^2 \sum_{\ell_2=0}^2 \mathbf{A}_{\ell_1}^{(i)} \otimes \hat{\mathcal{T}}_{\ell_2}^{(i)} \right\}_{0,0} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q \mathbf{A}_{\ell,q}^{(i)} \hat{\mathcal{T}}_{\ell,-q}^{(i)} = \sum_i \sum_{\ell=0}^2 \vec{\mathbf{A}}_{\ell}^{(i)} \cdot \vec{\hat{\mathcal{T}}}_{\ell}^{(i)}$$

Representation of Hamiltonians

$$\hat{\mathcal{H}}(t)$$

□ Spherical-Tensor Representation:

$$\mathcal{H} = \left\{ \sum_i \sum_{\ell_1=0}^2 \sum_{\ell_2=0}^2 \mathbf{A}_{\ell_1}^{(i)} \otimes \hat{\mathcal{T}}_{\ell_2}^{(i)} \right\}_{0,0} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q \mathbf{A}_{\ell,q}^{(i)} \hat{\mathcal{T}}_{\ell,-q}^{(i)} = \sum_i \sum_{\ell=0}^2 \vec{\mathbf{A}}_{\ell}^{(i)} \cdot \vec{\hat{\mathcal{T}}}_{\ell}^{(i)}$$

□ Spatial Part:

$$\mathbf{A}_{00} = -\sqrt{3}\bar{a}$$

$$\mathbf{A}_{20} = \sqrt{\frac{3}{8}}\delta \left[(3\cos^2 \beta - 1) - \eta \sin^2 \beta \cos(2\alpha) \right]$$

$$\mathbf{A}_{2\pm 1} = \pm \frac{\delta}{2} \sin \beta e^{\pm i\gamma} \left[(3 + \eta \cos(2\alpha)) \cos \beta \mp i\eta \sin(2\alpha) \right]$$

$$\mathbf{A}_{2\pm 2} = \frac{\delta}{2} e^{\pm 2i\gamma} \left[\frac{3}{2} \sin^2 \beta - \frac{\eta}{2} (1 + \cos^2 \beta) \cos(2\alpha) \pm i\eta \cos \beta \sin(2\alpha) \right]$$

laboratory frame (LAB):

full matrix

required for the Hamiltonian

$$\begin{array}{c} \xleftarrow{R(\alpha, \beta, \gamma) = \mathcal{D}^{\ell}(\alpha, \beta, \gamma)} \\ \xrightarrow{R^{-1}(\alpha, \beta, \gamma)} \end{array}$$

$$\rho_{0,0} = \mathbf{A}_{0,0}^{(\text{PAS})} = -\sqrt{3}\bar{a}$$

$$\rho_{2,0} = \mathbf{A}_{2,0}^{(\text{PAS})} = \sqrt{\frac{3}{2}}\delta$$

$$\rho_{2,\pm 1} = \mathbf{A}_{2,\pm 1}^{(\text{PAS})} = 0$$

$$\rho_{2,\pm 2} = \mathbf{A}_{2,\pm 2}^{(\text{PAS})} = -\frac{1}{2}\delta\eta$$

principal axes system (PAS):

diagonal matrix

simple, known from spectra
or calculations

□ Spherical-Tensor Representation:

$$\mathcal{H} = \left\{ \sum_i \sum_{\ell_1=0}^2 \sum_{\ell_2=0}^2 \mathbf{A}_{\ell_1}^{(i)} \otimes \hat{\mathcal{T}}_{\ell_2}^{(i)} \right\}_{0,0} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q \mathbf{A}_{\ell,q}^{(i)} \hat{\mathcal{T}}_{\ell,-q}^{(i)} = \sum_i \sum_{\ell=0}^2 \vec{\mathbf{A}}_{\ell}^{(i)} \cdot \vec{\hat{\mathcal{T}}}_{\ell}^{(i)}$$

□ Spin-Spin or Spin-Field Part:

$$\hat{\mathcal{T}}_{0,0}^{(k,n)} = \frac{-1}{\sqrt{3}} \hat{\mathbf{I}}_k \cdot \hat{\mathbf{I}}_n$$

$$\hat{\mathcal{T}}_{1,0}^{(k,n)} = \frac{-1}{2\sqrt{2}} (\hat{I}_k^+ \hat{I}_n^- - \hat{I}_k^- \hat{I}_n^+)$$

$$\hat{\mathcal{T}}_{1,\pm 1}^{(k,n)} = \frac{-1}{2} (\hat{I}_k^{\pm} \hat{I}_{nz} - \hat{I}_{kz} \hat{I}_n^{\pm})$$

$$\hat{\mathcal{T}}_{2,0}^{(k,n)} = \frac{1}{\sqrt{6}} (3\hat{I}_{kz} \hat{I}_{nz} - \hat{\mathbf{I}}_k \cdot \hat{\mathbf{I}}_n)$$

$$\hat{\mathcal{T}}_{2,\pm 1}^{(k,n)} = \mp (\hat{I}_k^{\pm} \hat{I}_{nz} + \hat{I}_{kz} \hat{I}_n^{\pm})$$

$$\hat{\mathcal{T}}_{2,\pm 2}^{(k,n)} = \frac{1}{2} (\hat{I}_k^{\pm} \hat{I}_n^{\pm})$$

$$\hat{\mathcal{T}}_{0,0}^{(k,B)} = \frac{-1}{\sqrt{3}} \hat{\mathbf{I}}_k \cdot \vec{B}$$

$$\hat{\mathcal{T}}_{1,0}^{(k,B)} = \frac{-1}{2\sqrt{2}} (\hat{I}_k^+ B^- - \hat{I}_k^- B^+)$$

$$\hat{\mathcal{T}}_{1,\pm 1}^{(k,B)} = \frac{-1}{2} (\hat{I}_k^{\pm} B_z - \hat{I}_{kz} B^{\pm})$$

$$\hat{\mathcal{T}}_{2,0}^{(k,B)} = \frac{1}{\sqrt{6}} (3\hat{I}_{kz} B_z - \hat{\mathbf{I}}_k \cdot \vec{B}_n)$$

$$\hat{\mathcal{T}}_{2,\pm 1}^{(k,B)} = \mp (\hat{I}_k^{\pm} B_z + \hat{I}_{kz} B^{\pm})$$

$$\hat{\mathcal{T}}_{2,\pm 2}^{(k,B)} = \frac{1}{2} (\hat{I}_k^{\pm} B^{\pm})$$

□ Spherical-Tensor Representation:

$$\mathcal{H} = \left\{ \sum_i \sum_{\ell_1=0}^2 \sum_{\ell_2=0}^2 \mathbf{A}_{\ell_1}^{(i)} \otimes \hat{\mathcal{T}}_{\ell_2}^{(i)} \right\}_{0,0} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q \mathbf{A}_{\ell,q}^{(i)} \hat{\mathcal{T}}_{\ell,-q}^{(i)} = \sum_i \sum_{\ell=0}^2 \vec{\mathbf{A}}_{\ell}^{(i)} \cdot \vec{\hat{\mathcal{T}}}_{\ell}^{(i)}$$

□ Spin-Spin or Spin-Field Part:

$$\hat{T}_{0,0}^{(k,n)} = \frac{-1}{\sqrt{3}} \hat{\mathbf{I}}_k \cdot \hat{\mathbf{I}}_n$$

$$\hat{T}_{1,0}^{(k,n)} = \frac{-1}{2\sqrt{2}} (\hat{I}_k^+ \hat{I}_n^- - \hat{I}_k^- \hat{I}_n^+)$$

$$\hat{T}_{1,\pm 1}^{(k,n)} = \frac{-1}{2} (\hat{I}_k^{\pm} \hat{I}_{nz} - \hat{I}_{kz} \hat{I}_n^{\pm})$$

$$\hat{T}_{2,0}^{(k,n)} = \frac{1}{\sqrt{6}} (3\hat{I}_{kz} \hat{I}_{nz} - \hat{\mathbf{I}}_k \cdot \hat{\mathbf{I}}_n)$$

$$\hat{T}_{2,\pm 1}^{(k,n)} = \mp (\hat{I}_k^{\pm} \hat{I}_{nz} + \hat{I}_{kz} \hat{I}_n^{\pm})$$

$$\hat{T}_{2,\pm 2}^{(k,n)} = \frac{1}{2} (\hat{I}_k^{\pm} \hat{I}_n^{\pm})$$

$$\hat{T}_{0,0}^{(k,B)} = \frac{-1}{\sqrt{3}} \hat{\mathbf{I}}_k \cdot \vec{B}$$

$$\hat{T}_{1,0}^{(k,B)} = \frac{-1}{2\sqrt{2}} (\hat{I}_k^+ B^- - \hat{I}_k^- B^+)$$

$$\hat{T}_{1,\pm 1}^{(k,B)} = \frac{-1}{2} (\hat{I}_k^{\pm} B_z - \hat{I}_{kz} B^{\pm})$$

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$$\hat{T}_{2,\pm 1}^{(k,B)} = \mp (\hat{I}_k^{\pm} B_z + \hat{I}_{kz} B^{\pm})$$

$$\hat{T}_{2,\pm 2}^{(k,B)} = \frac{1}{2} (\hat{I}_k^{\pm} B^{\pm})$$

□ Cartesian Representation:

$$\hat{\mathcal{H}}^{(k,n)} = \hat{\vec{I}}_k A^{(k,n)} \hat{\vec{I}}_n = \begin{pmatrix} \hat{I}_{kx} & \hat{I}_{ky} & \hat{I}_{kz} \end{pmatrix} \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \begin{pmatrix} \hat{I}_{nx} \\ \hat{I}_{ny} \\ \hat{I}_{nz} \end{pmatrix}$$

□ Spherical-Tensor Representation:

$$\mathcal{H} = \left\{ \sum_i \sum_{\ell_1=0}^2 \sum_{\ell_2=0}^2 \mathbf{A}_{\ell_1}^{(i)} \otimes \hat{\mathcal{T}}_{\ell_2}^{(i)} \right\}_{0,0} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q \mathbf{A}_{\ell,q}^{(i)} \hat{\mathcal{T}}_{\ell,-q}^{(i)} = \sum_i \sum_{\ell=0}^2 \vec{\mathbf{A}}_{\ell}^{(i)} \cdot \vec{\hat{\mathcal{T}}}_{\ell}^{(i)}$$

□ Both representations are fully equivalent and can be converted into each other.

□ Certain transformations or operations can be simpler in one or the other representation:

- Rotations are often expressed more concise in the spherical-tensor notation.
- Commutators are much easier calculated using the Cartesian representation.
- Time evolution of the density operator is often simpler when using the Cartesian representation (product-operator formalism).
- For quadrupolar nuclei, the spherical-tensors representation offers a simple complete basis set.

Reference Frames and Time Dependence

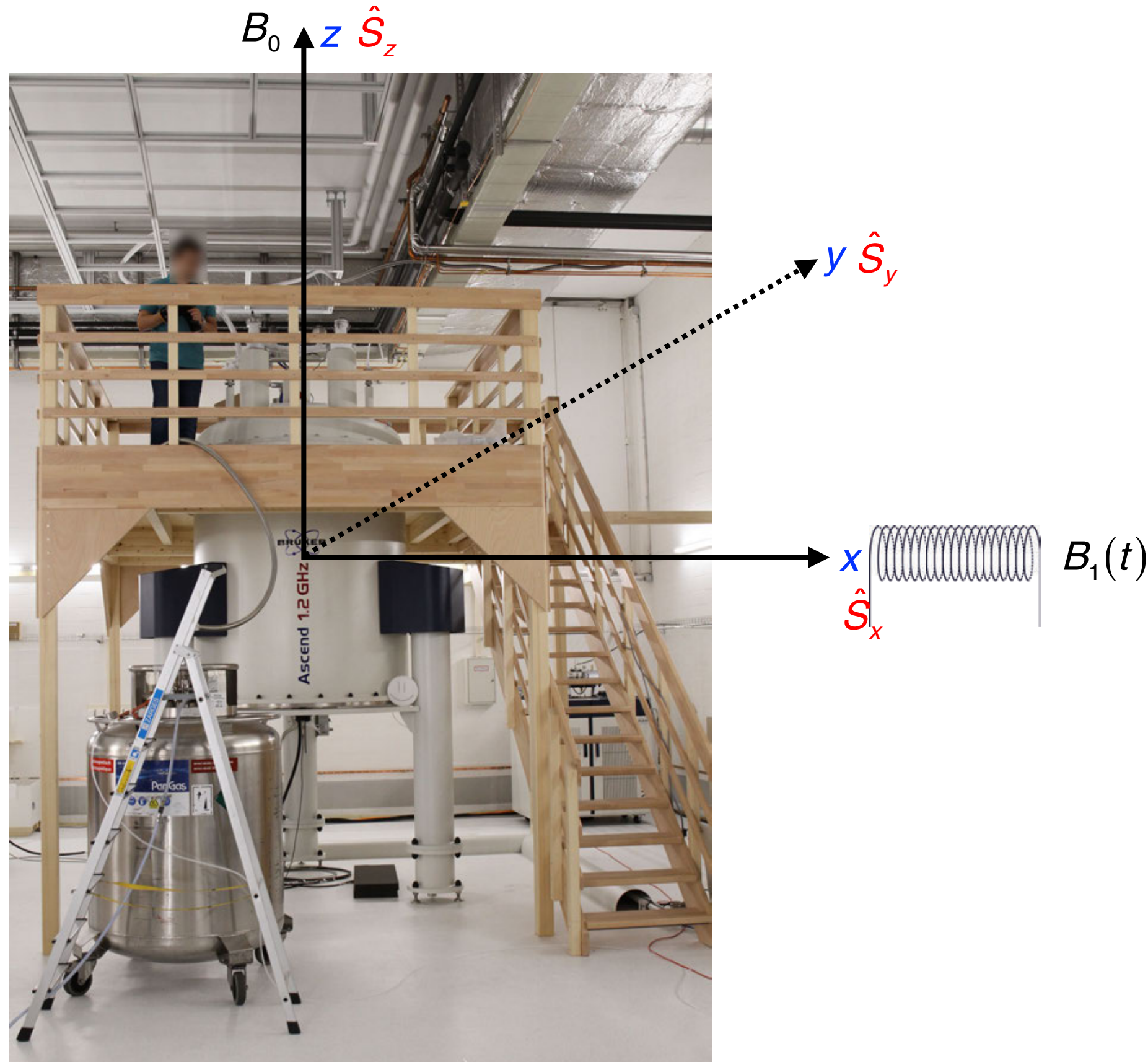
 $\hat{\mathcal{H}}(t)$ 

Khajuraho, 2018

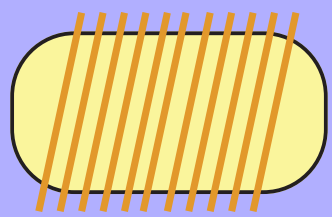
The Laboratory Frame

$$\hat{\mathcal{H}}(t)$$

- ❑ In the laboratory frame of reference, the Cartesian axes are well defined.
- ❑ The B_0 field direction determines the direction of the z axis.
- ❑ The B_1 field direction determines the direction of the x axis.
- ❑ The y axis points into the remaining orthogonal direction.
- ❑ All measurements are done in the laboratory frame of reference.



Radio-Frequency Irradiation



- Without any interference from the experimentalist, our Hamiltonian is static.
- We need radio-frequency fields in order to manipulate the magnetization.

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_Z + \hat{\mathcal{H}}_{CS} + \hat{\mathcal{H}}_D + \hat{\mathcal{H}}_J + \hat{\mathcal{H}}_{rf}(t)$$

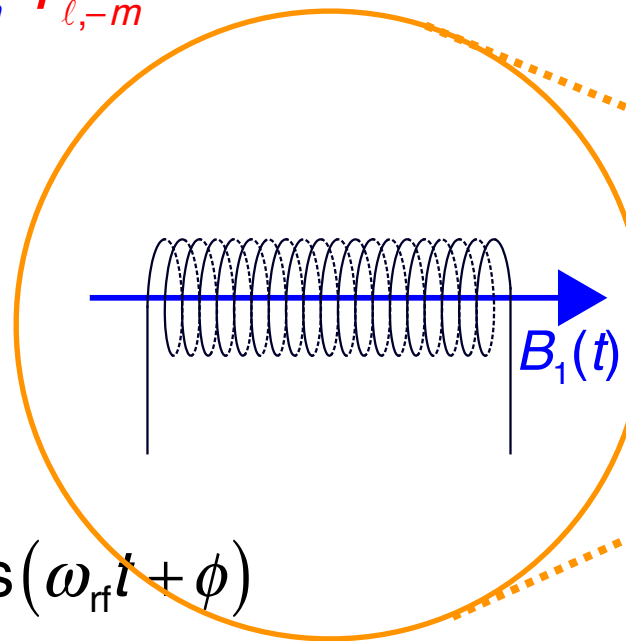
$$\hat{\mathcal{H}}_Z = A_{0,0}^{(Z)} \hat{T}_{0,0}^{(Z)}$$

$$\hat{\mathcal{H}}_{CS} = A_{0,0}^{(CS)} \hat{T}_{0,0}^{(CS)} + \sum_{\ell=1}^2 \sum_{m=-\ell}^{\ell} (-1)^m A_{\ell,m}^{(CS)} \hat{T}_{\ell,-m}^{(CS)}$$

$$\hat{\mathcal{H}}_D = \sum_{m=-2}^2 (-1)^m A_{2,m}^{(D)} \hat{T}_{2,-m}^{(D)}$$

$$\hat{\mathcal{H}}_J = A_{0,0}^{(J)} \hat{T}_{0,0}^{(J)}$$

$$\hat{\mathcal{H}}_{rf}(t) = -\gamma_k 2B_1(t) \hat{I}_{kx} = -2\omega_1 \hat{I}_{kx} \cos(\omega_{rf}t + \phi)$$



- The radio-frequency field Hamiltonian is time dependent!
- It represents a linear-polarized radio-frequency field.



The Laboratory-Frame Hamiltonian

$$\hat{\mathcal{H}}(t)$$

❑ The spin-system Hamiltonian in the *laboratory frame* is static and time independent:

$$\hat{\mathcal{H}} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q A_{\ell,q}^{(i)} \hat{T}_{\ell,-q}^{(i)}$$

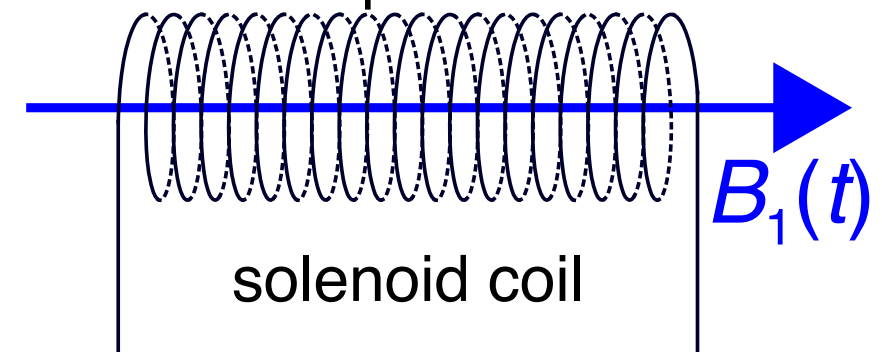
❑ We can write the spin-system Hamiltonian as a product of spherical **spatial** and **spin** terms.

❑ Example: homonuclear dipolar Hamiltonian: $\ell = 2$, $q = -2 \dots 2$, $(i) = (1,2)$

$$\hat{\mathcal{H}} = \sum_{q=-\ell}^{\ell} (-1)^q A_{2,q}^{(1,2)} \hat{T}_{2,-q}^{(1,2)} \left\{ \begin{array}{ll} \hat{T}_{2,0}^{(1,2)} = \frac{1}{\sqrt{6}} (3\hat{I}_{1z}\hat{I}_{2z} - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2) & A_{2,0}^{(1,2)} = \sqrt{\frac{3}{8}} \delta_D^{(1,2)} (3\cos^2(\beta) - 1) \\ \hat{T}_{2,\pm 1}^{(1,2)} = \mp (\hat{I}_1^{\pm} \hat{I}_{2z} + \hat{I}_{1z} \hat{I}_2^{\pm}) & A_{2,\pm 1}^{(1,2)} = \pm \frac{3}{4} \delta_D^{(1,2)} e^{\mp i\gamma} \sin(2\beta) \\ \hat{T}_{2,\pm 2}^{(1,2)} = \frac{1}{2} (\hat{I}_1^{\pm} \hat{I}_2^{\pm}) & A_{2,\pm 2}^{(1,2)} = \frac{3}{4} \delta_D^{(1,2)} e^{\mp i2\gamma} \sin^2(\beta) \end{array} \right.$$

❑ The radio-frequency Hamiltonian in the laboratory-frame is time dependent:

$$\begin{aligned} \hat{\mathcal{H}}_{\text{rf}}(t) &= -2\gamma B_1 \cos(\omega_{\text{rf}} t) \hat{I}_x \\ &= -\gamma B_1 (e^{i\omega_{\text{rf}} t} + e^{-i\omega_{\text{rf}} t}) \hat{I}_x \end{aligned}$$



❑ The **linear-polarized field** can be split into two circular-polarized fields, one rotating **clockwise**, the other **counterclockwise**.

The Laboratory-Frame Hamiltonian

$$\hat{\mathcal{H}}(t)$$

❑ The spin-system Hamiltonian in the *laboratory frame* is static and time independent:

$$\hat{\mathcal{H}} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q A_{\ell,q}^{(i)} \hat{T}_{\ell,-q}^{(i)}$$

❑ We can write the spin-system Hamiltonian as a product of spherical **spatial** and **spin** terms.

❑ Example: homonuclear dipolar Hamiltonian: $\ell = 2$, $q = -2 \dots 2$, $(i) = (1,2)$

$$\hat{\mathcal{H}} = \sum_{q=-\ell}^{\ell} (-1)^q A_{2,q}^{(1,2)} \hat{T}_{2,-q}^{(1,2)} \left\{ \begin{array}{ll} \hat{T}_{2,0}^{(1,2)} = \frac{1}{\sqrt{6}} (3\hat{I}_{1z}\hat{I}_{2z} - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2) & A_{2,0}^{(1,2)} = \sqrt{\frac{3}{8}} \delta_D^{(1,2)} (3\cos^2(\beta) - 1) \\ \hat{T}_{2,\pm 1}^{(1,2)} = \mp (\hat{I}_1^{\pm} \hat{I}_{2z} + \hat{I}_{1z} \hat{I}_2^{\pm}) & A_{2,\pm 1}^{(1,2)} = \pm \frac{3}{4} \delta_D^{(1,2)} e^{\mp i\gamma} \sin(2\beta) \\ \hat{T}_{2,\pm 2}^{(1,2)} = \frac{1}{2} (\hat{I}_1^{\pm} \hat{I}_2^{\pm}) & A_{2,\pm 2}^{(1,2)} = \frac{3}{4} \delta_D^{(1,2)} e^{\mp i2\gamma} \sin^2(\beta) \end{array} \right.$$

**Dipolar
Alphabet**

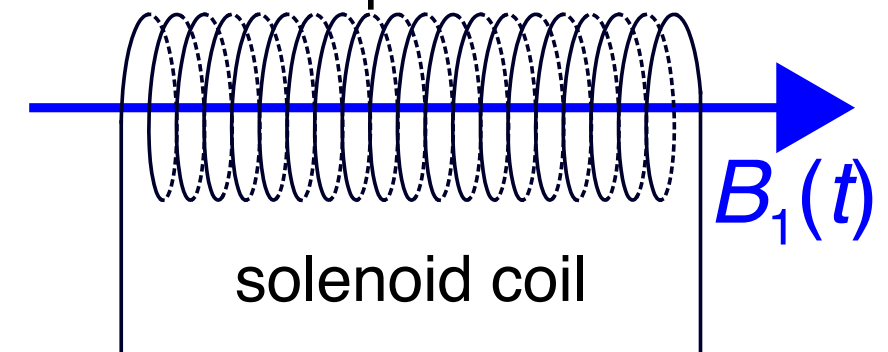
A+B

C+D

E+F

❑ The radio-frequency Hamiltonian in the laboratory-frame is time dependent:

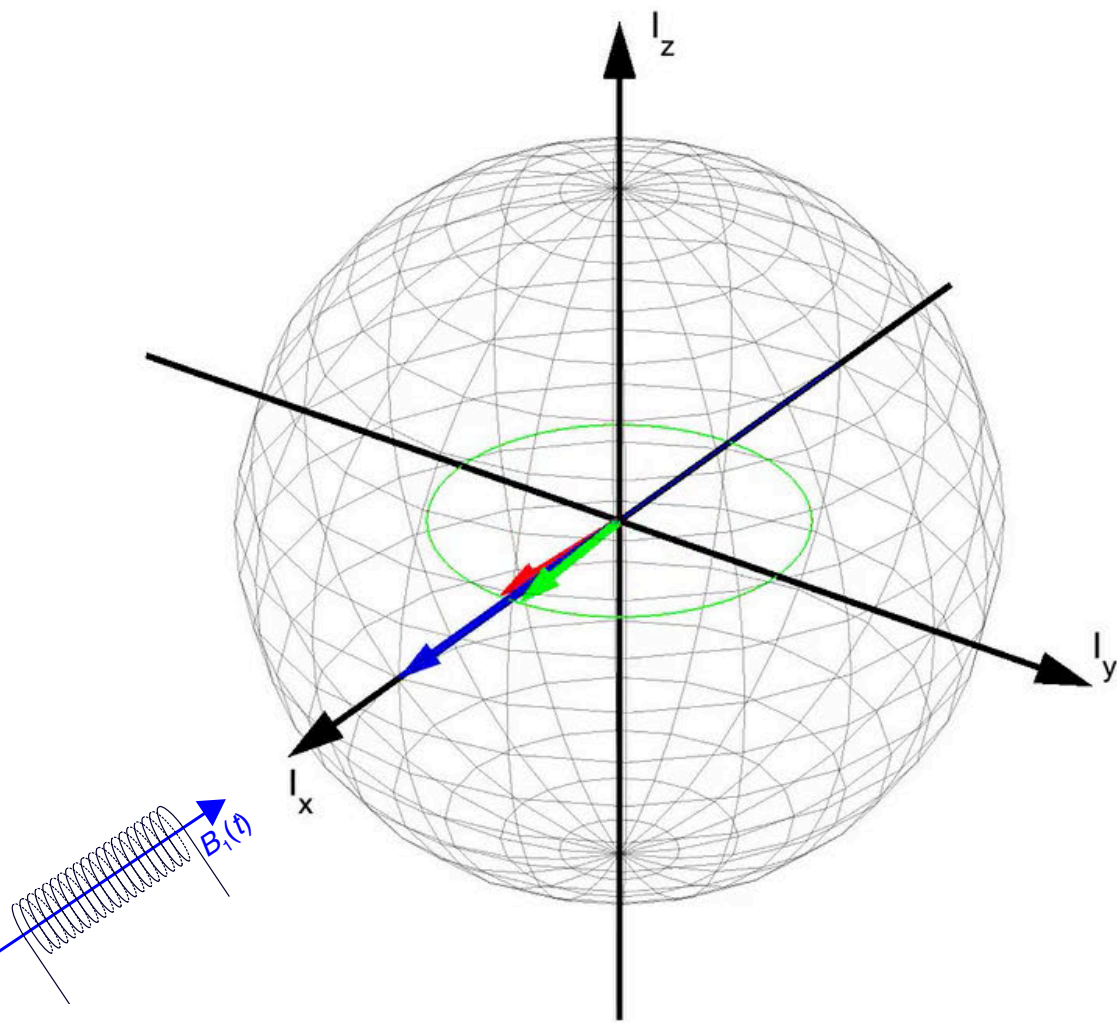
$$\begin{aligned} \hat{\mathcal{H}}_{\text{rf}}(t) &= -2\gamma B_1 \cos(\omega_{\text{rf}} t) \hat{I}_x \\ &= -\gamma B_1 (e^{i\omega_{\text{rf}} t} + e^{-i\omega_{\text{rf}} t}) \hat{I}_x \end{aligned}$$



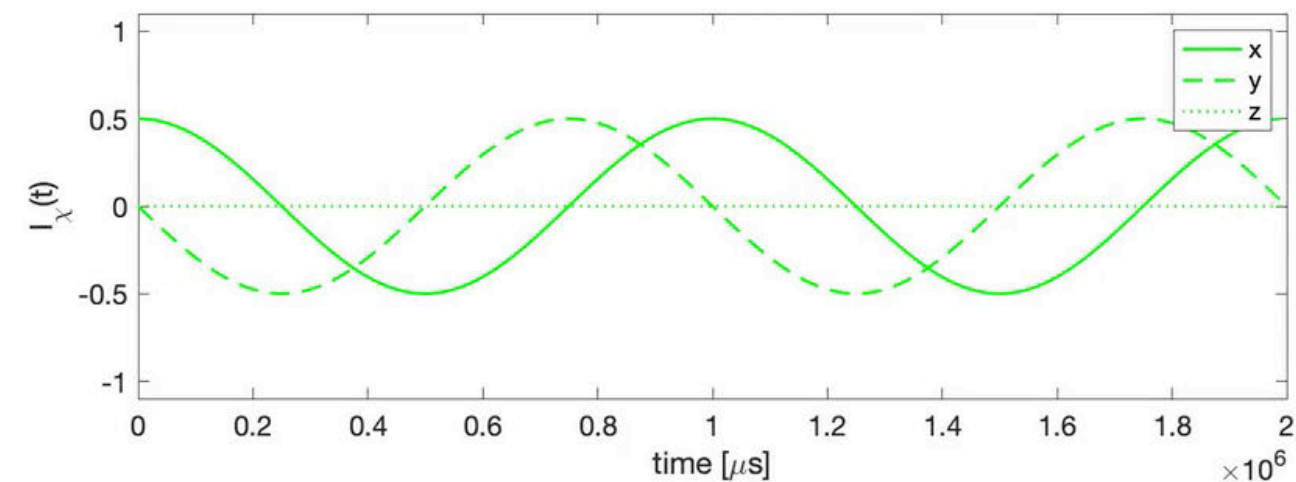
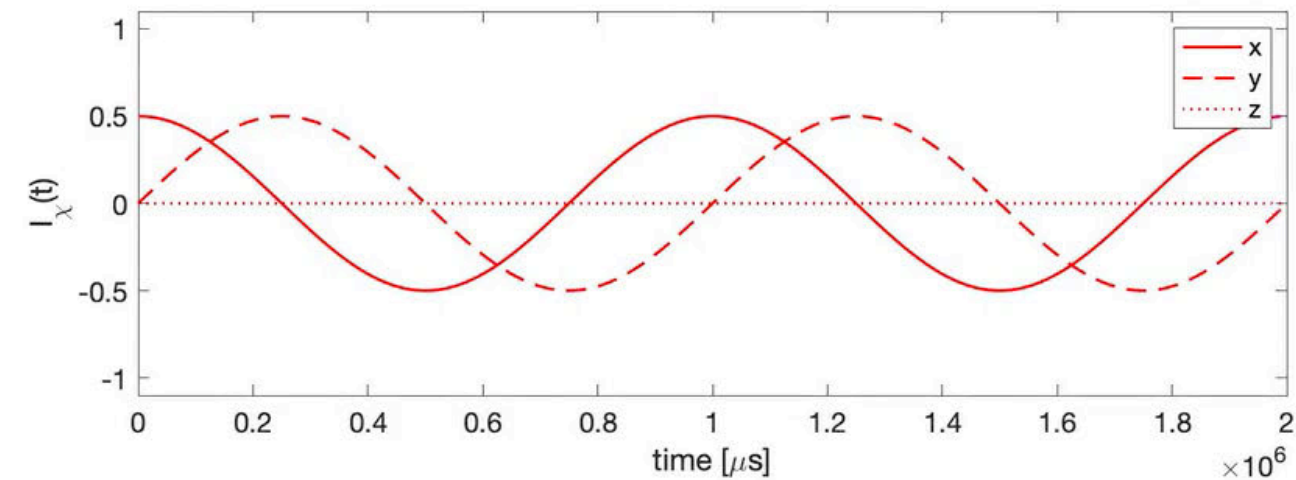
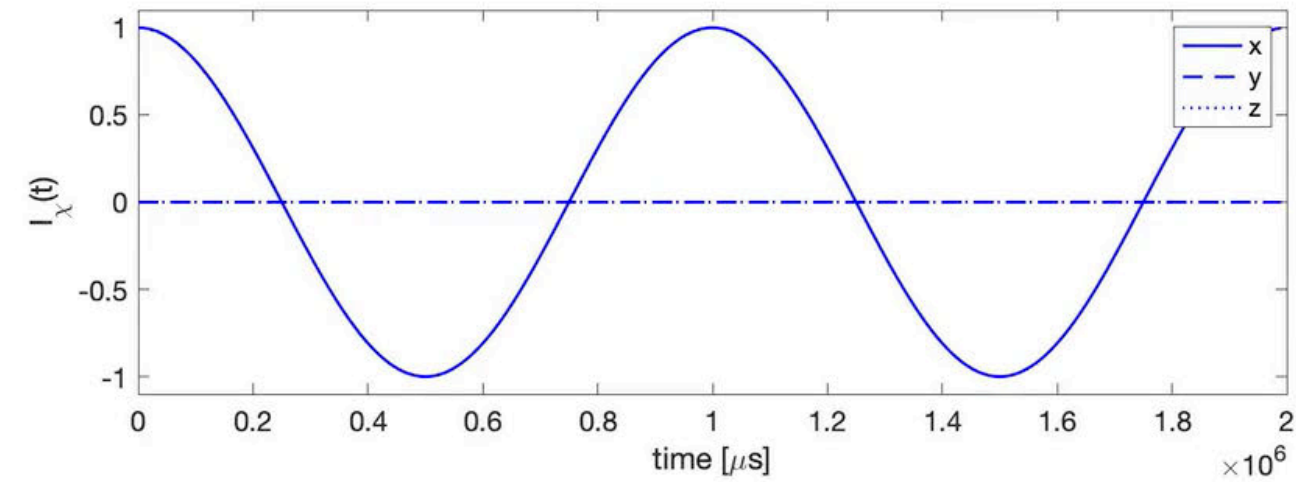
❑ The **linear-polarized field** can be split into two circular-polarized fields, one rotating **clockwise**, the other **counterclockwise**.

RF in Laboratory Frame

$$\hat{\mathcal{H}}(t)$$



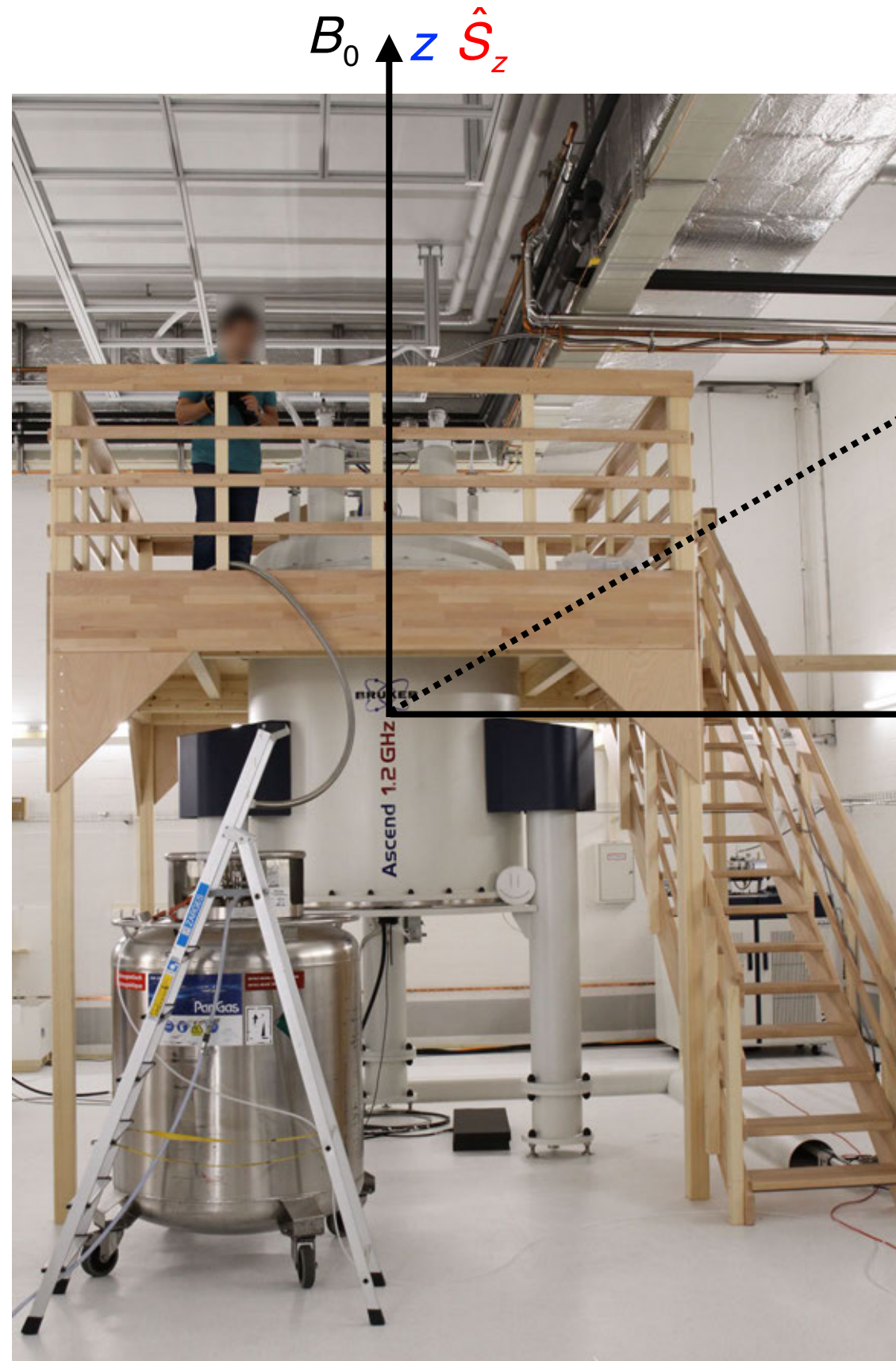
- ❑ Reference is the laboratory frame.
- ❑ Laboratory frame is static.



The Rotating Frame

$$\hat{\mathcal{H}}(t)$$

- ❑ In the laboratory frame of reference, the Cartesian axes are well defined.
- ❑ The B_0 field direction determines the direction of the z axis.
- ❑ The B_1 field direction determines the direction of the x axis.
- ❑ The y axis points into the remaining orthogonal direction.
- ❑ All measurements are done in the laboratory frame of reference.



$$y \hat{S}_y = \hat{\tilde{S}}_y \cos(\omega_0 t) + \hat{\tilde{S}}_x \sin(\omega_0 t)$$

$$x \hat{S}_x = \hat{\tilde{S}}_x \cos(\omega_0 t) - \hat{\tilde{S}}_y \sin(\omega_0 t)$$

The Rotating-Frame Hamiltonian

$$\hat{\mathcal{H}}(t)$$

□ Rotating-frame transformation:
$$\hat{\tilde{\mathcal{H}}}(t) = e^{-i\hat{\mathcal{H}}_0 t} \hat{\mathcal{H}} e^{+i\hat{\mathcal{H}}_0 t} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q A_{\ell,q}^{(i)} e^{-i\hat{\mathcal{H}}_0 t} \hat{T}_{\ell,-q}^{(i)} e^{+i\hat{\mathcal{H}}_0 t}$$

$$= \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q A_{\ell,q}^{(i)} \hat{T}_{\ell,-q}^{(i)}(t)$$

□ The spin-system Hamiltonian becomes time dependent.

□ Example: homonuclear dipolar Hamiltonian: $\ell = 2, q = -2 \dots 2, (i) = (1,2)$

$$\hat{\tilde{\mathcal{H}}}(t) = \sum_{q=-\ell}^{\ell} (-1)^q A_{2,q}^{(1,2)} \hat{T}_{2,-q}^{(1,2)}(t) \left\{ \begin{array}{ll} \hat{T}_{2,0}^{(1,2)}(t) = \frac{1}{\sqrt{6}} (3I_{1z}I_{2z} - \hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) & A_{2,0}^{(1,2)} = \sqrt{\frac{3}{8}} \delta_D^{(1,2)} (3\cos^2(\theta) - 1) \\ \hat{T}_{2,\pm 1}^{(1,2)}(t) = \mp (\hat{I}_1^{\pm} \hat{I}_{2z} + \hat{I}_{1z} \hat{I}_2^{\pm}) e^{\pm i\omega_0 t} & A_{2,\pm 1}^{(1,2)} = \pm \frac{3}{4} \delta_D^{(1,2)} e^{\mp i\gamma} \sin(2\beta) \\ \hat{T}_{2,\pm 2}^{(1,2)}(t) = \frac{1}{2} (\hat{I}_1^{\pm} \hat{I}_2^{\pm}) e^{\pm i2\omega_0 t} & A_{2,\pm 2}^{(1,2)} = \frac{3}{4} \delta_D^{(1,2)} e^{\mp i2\gamma} \sin^2(\beta) \end{array} \right.$$

□ In a first-order approximation, we neglect all time-dependent terms and approximate the rotating-frame Hamiltonian by the time-independent component (secular approximation):

$$\hat{\tilde{\mathcal{H}}} \approx \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)} \hat{T}_{\ell,0}^{(i)}$$

□ This is the spin-system Hamiltonian that we typically start from in NMR theory!

The Rotating-Frame Hamiltonian

$$\hat{\mathcal{H}}(t)$$

□ Rotating-frame transformation: $\hat{\tilde{\mathcal{H}}}(t) = e^{-i\hat{\mathcal{H}}_0 t} \hat{\mathcal{H}} e^{+i\hat{\mathcal{H}}_0 t} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q A_{\ell,q}^{(i)} e^{-i\hat{\mathcal{H}}_0 t} \hat{T}_{\ell,-q}^{(i)} e^{+i\hat{\mathcal{H}}_0 t}$

$$= \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q A_{\ell,q}^{(i)} \hat{\tilde{T}}_{\ell,-q}^{(i)}(t)$$

□ The spin-system Hamiltonian becomes time dependent.

□ Example: homonuclear dipolar Hamiltonian: $\ell = 2, q = -2 \dots 2, (i) = (1,2)$

$$\hat{\tilde{\mathcal{H}}}(t) = \sum_{q=-\ell}^{\ell} (-1)^q A_{2,q}^{(1,2)} \hat{\tilde{T}}_{2,-q}^{(1,2)}(t) \left\{ \begin{array}{ll} \hat{\tilde{T}}_{2,0}^{(1,2)}(t) = \frac{1}{\sqrt{6}} (3I_{1z}I_{2z} - \hat{\vec{I}}_1 \cdot \hat{\vec{I}}_2) & A_{2,0}^{(1,2)} = \sqrt{\frac{3}{8}} \delta_D^{(1,2)} (3\cos^2(\theta) - 1) \\ \hat{\tilde{T}}_{2,\pm 1}^{(1,2)}(t) = \mp (\hat{I}_1^{\pm} \hat{I}_{2z} + \hat{I}_{1z} \hat{I}_2^{\pm}) e^{\pm i\omega_0 t} & A_{2,\pm 1}^{(1,2)} = \pm \frac{3}{4} \delta_D^{(1,2)} e^{\pm i\gamma} \sin(2\beta) \\ \hat{\tilde{T}}_{2,\pm 2}^{(1,2)}(t) = \frac{1}{2} (\hat{I}_1^{\pm} \hat{I}_2^{\pm}) e^{\pm i2\omega_0 t} & A_{2,\pm 2}^{(1,2)} = \frac{3}{4} \delta_D^{(1,2)} e^{\pm i2\gamma} \sin^2(\beta) \end{array} \right.$$

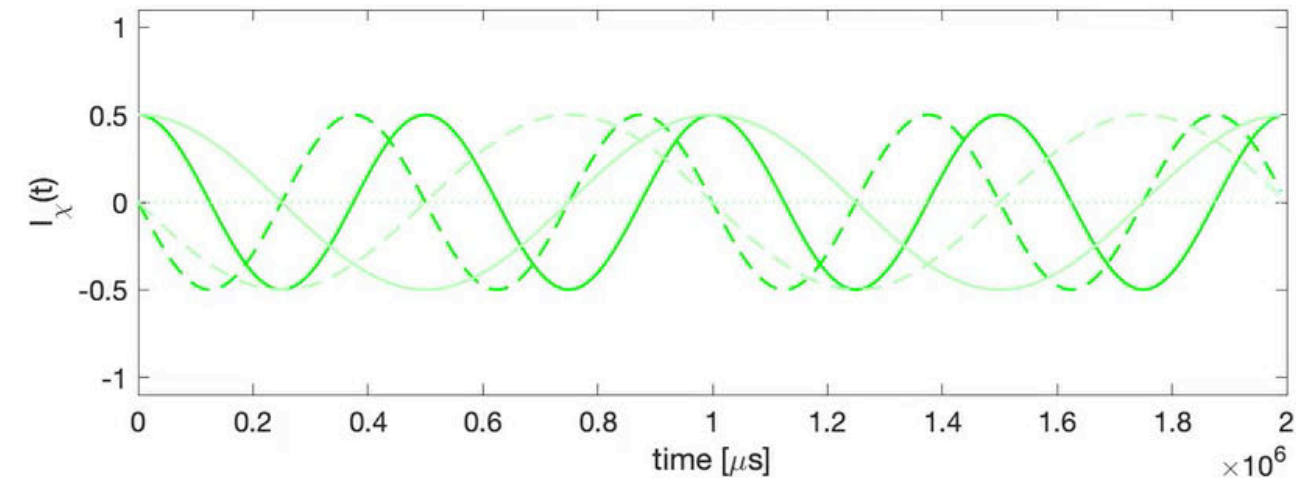
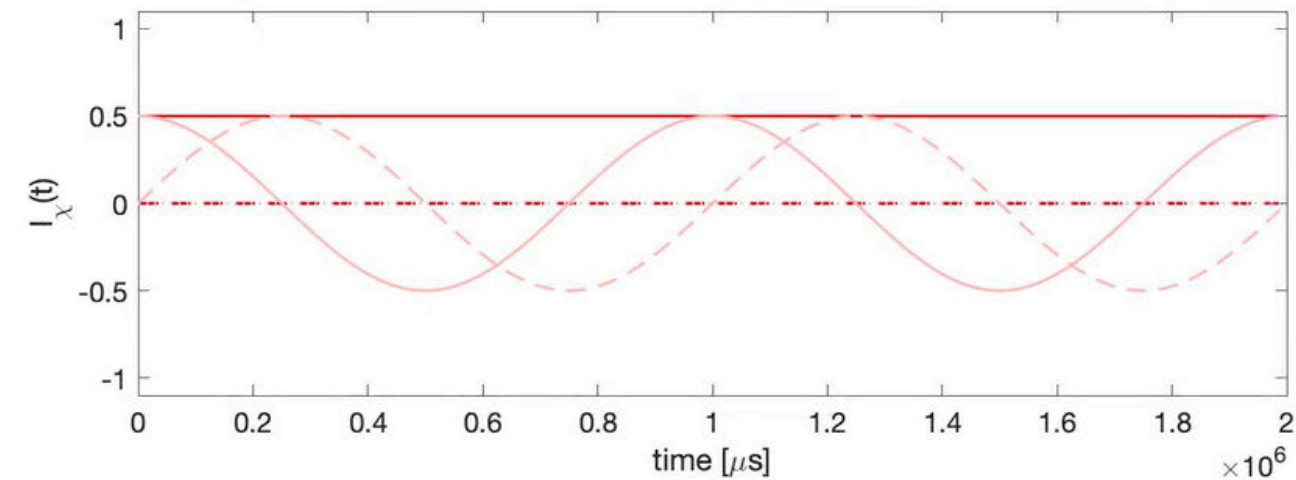
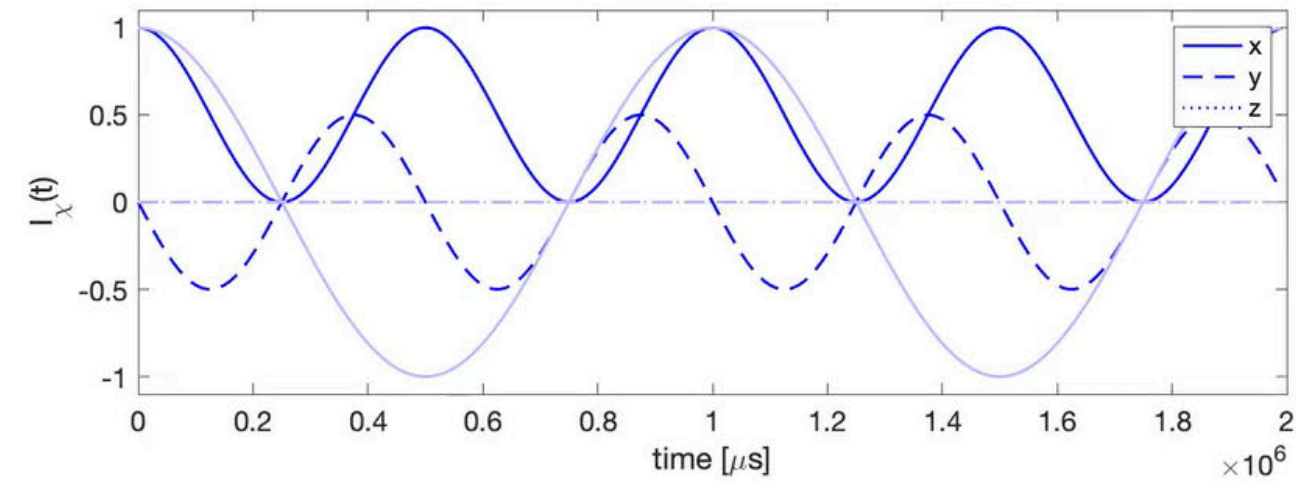
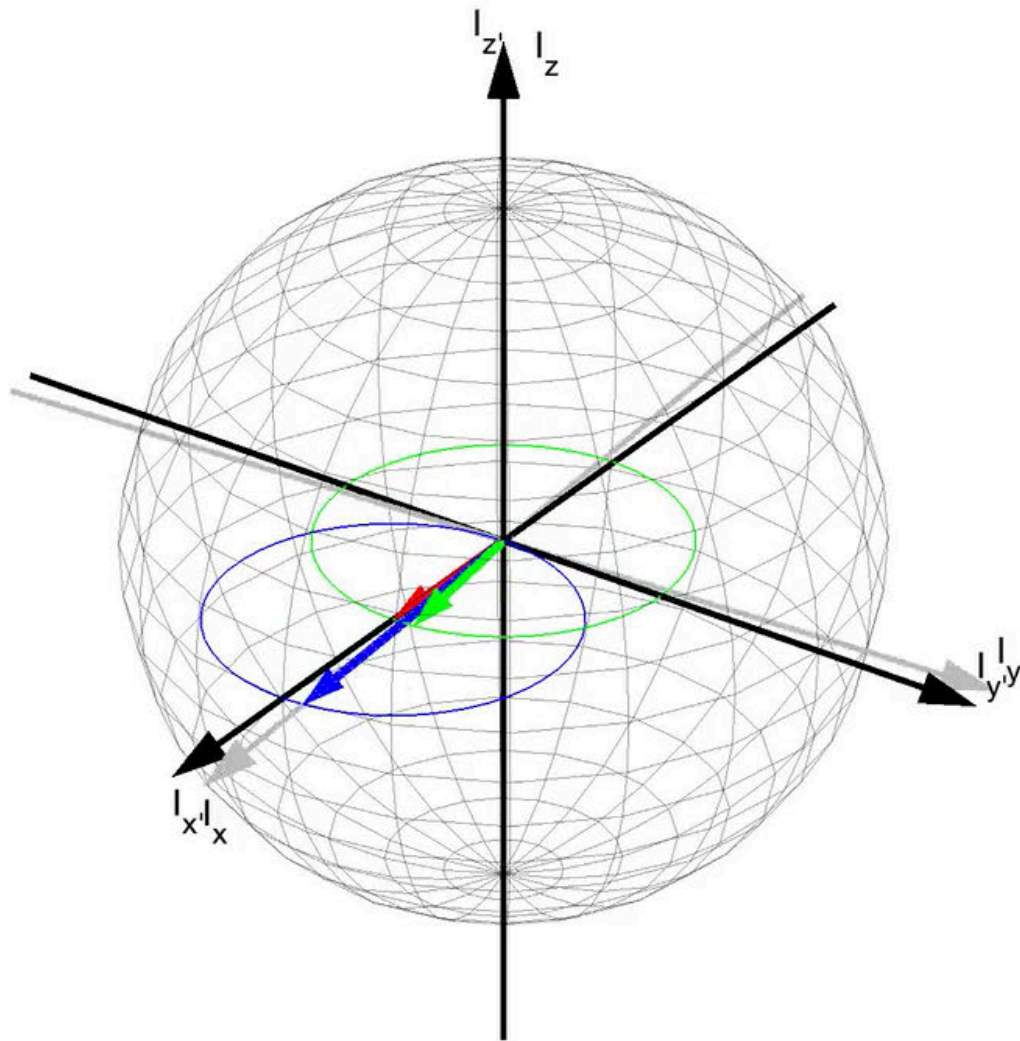
□ In a first-order approximation, we neglect all time-dependent terms and approximate the rotating-frame Hamiltonian by the time-independent component (secular approximation):

$$\hat{\tilde{\mathcal{H}}} \approx \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)} \hat{\tilde{T}}_{\ell,0}^{(i)}$$

□ This is the spin-system Hamiltonian that we typically start from in NMR theory!

RF Hamiltonian in the Rotating Frame

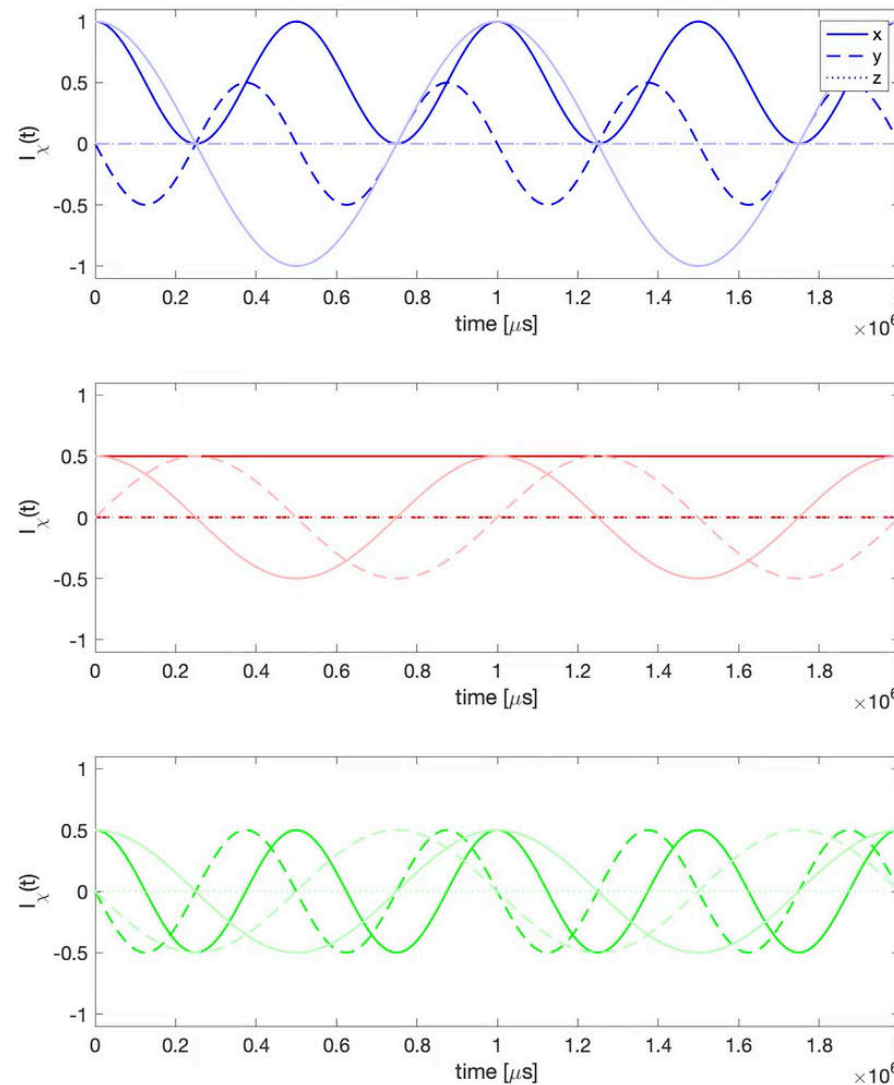
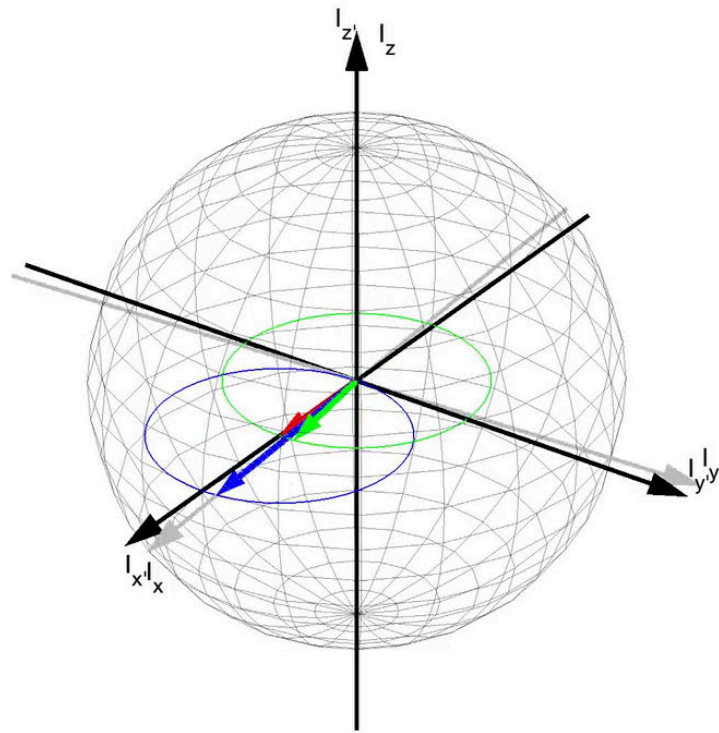
$$\hat{\mathcal{H}}(t)$$



- ☐ Reference is the rotating frame.
- ☐ Laboratory frame is now rotating.

RF Hamiltonian in the Rotating Frame

$$\hat{\mathcal{H}}(t)$$



☐ Reference is the rotating frame.

☐ Laboratory frame is now rotating.

$$\hat{\mathcal{H}}_{\text{rf}}(t) = e^{-i\hat{\mathcal{H}}_0 t} \hat{\mathcal{H}}_{\text{rf}}(t) e^{+i\hat{\mathcal{H}}_0 t} = -2\gamma B_1 \cos(\omega_{\text{rf}} t + \phi(t)) e^{-i\hat{\mathcal{H}}_0 t} \hat{I}_x e^{+i\hat{\mathcal{H}}_0 t}$$

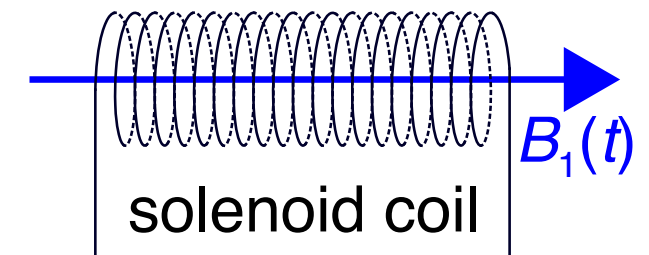
$$= -\gamma B_1 \left(e^{i(\omega_{\text{rf}} t + \phi(t))} + e^{-i(\omega_{\text{rf}} t + \phi(t))} \right) \frac{1}{2} (\hat{I}^+ e^{+i\omega_0 t} + \hat{I}^- e^{-i\omega_0 t})$$

$$= -\gamma B_1 \left(\cos(\phi(t)) \hat{I}_x + \sin(\phi(t)) \hat{I}_y \right) - \gamma B_1 \left(\cos(2\omega_{\text{rf}} + \phi(t)) \hat{I}_x + \sin(2\omega_{\text{rf}} + \phi(t)) \hat{I}_y \right)$$

- The spin-system Hamiltonian in the *laboratory frame* is static and time independent except for the radio-frequency part.

$$\hat{\mathcal{H}} = \sum_i \sum_{\ell=0}^2 \sum_{q=-\ell}^{\ell} (-1)^q A_{\ell,q}^{(i)} \hat{T}_{\ell,-q}^{(i)}$$

$$\begin{aligned} \hat{\mathcal{H}}_{\text{rf}}(t) &= -2\gamma B_1 \cos(\omega_{\text{rf}} t) \hat{I}_x \\ &= -\gamma B_1 (e^{i\omega_{\text{rf}} t} + e^{-i\omega_{\text{rf}} t}) \hat{I}_x \end{aligned}$$



- This is the relevant Hamiltonian for all the physics we do.

- We go into a *rotating frame* with the Zeeman Hamiltonian to:

- get rid of the large Zeeman interaction and terms that do not commute with it.
- make the rf-field Hamiltonian time independent.

$$\hat{\tilde{\mathcal{H}}} \approx \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)} \hat{\tilde{T}}_{\ell,0}^{(i)}$$

$$\hat{\tilde{\mathcal{H}}}_{\text{rf}} = -\gamma B_1 (\cos(\phi) \hat{\tilde{I}}_x + \sin(\phi) \hat{\tilde{I}}_y)$$

- In NMR we almost always start from this truncated *rotating-frame* Hamiltonian.

- This does not work when the interactions are not much smaller than the Zeeman interaction (quadrupolar interaction, low static magnetic fields, hyperfine interaction).

- Relaxation needs to be calculated in the laboratory frame using the full Hamiltonian.

- There are two main reasons to go into the rotating frame:
 - The rf-field Hamiltonian has a time-independent component for linear polarized rf which makes calculations simple.
 - The Zeeman Hamiltonian is eliminated. This makes calculating the effects of smaller contributions like chemical shift and J coupling more obvious.
- All interactions are truncated by the Zeeman Hamiltonian and only parts that commute with the Zeeman Hamiltonian are retained. This truncation introduces the anisotropic nature (orientation dependence) of the spin interactions by breaking the symmetry of space.

□ Spin-Field Interactions:

- RF Hamiltonian:
$$\hat{\mathcal{H}}_{\text{rf}}^{(k,B)} = -\gamma B_1 (\hat{I}_{kx} \cos \phi + \hat{I}_{ky} \sin \phi)$$
- CS Hamiltonian:
$$\hat{\mathcal{H}}_{\text{CS}}^{(k,B)} = -\gamma B_0 \sigma_{zz} \hat{I}_{kz}$$

□ Spin-Spin Interactions:

- Dipolar-coupling Hamiltonian:
$$\hat{\mathcal{H}}_D^{(k,n)} = -\frac{\mu_0}{4\pi} \frac{\gamma_k \gamma_n \hbar}{r_{kn}^3} \frac{3 \cos^2 \theta - 1}{2} \left(2\hat{I}_{kz} \hat{I}_{nz} - (\hat{I}_{kx} \hat{I}_{nx} + \hat{I}_{ky} \hat{I}_{ny}) \right)$$
- J-coupling Hamiltonian:
$$\hat{\mathcal{H}}_J^{(k,n)} = 2\pi J_{iso}^{(k,n)} \hat{\vec{I}}_k \cdot \hat{\vec{I}}_n$$
- Quadrupolar-coupling Hamiltonian:
$$\hat{\mathcal{H}}_Q^{(k)} = \frac{\delta_Q^{(k)}}{2} \left(\frac{3 \cos^2 \beta - 1}{2} - \frac{\eta_Q^{(k)}}{2} \sin^2 \beta \cos(2\alpha) \right) \left(3\hat{I}_{kz}^2 - I_k(I_k + 1) \right)$$

The Rotating-Frame Hamiltonian

$$\hat{\mathcal{H}}(t)$$

- We start most of our calculations from a time-independent high-field truncated rotating-frame Hamiltonian:

$$\hat{\mathcal{H}} \approx \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)} \hat{T}_{\ell,0}^{(i)}$$

$$\hat{\mathcal{H}}_{\text{rf}} = -\gamma B_1 \left(\cos(\phi) \hat{I}_x + \sin(\phi) \hat{I}_y \right)$$

- So, why do we need to talk about time-dependent Hamiltonians?

The Rotating-Frame Hamiltonian

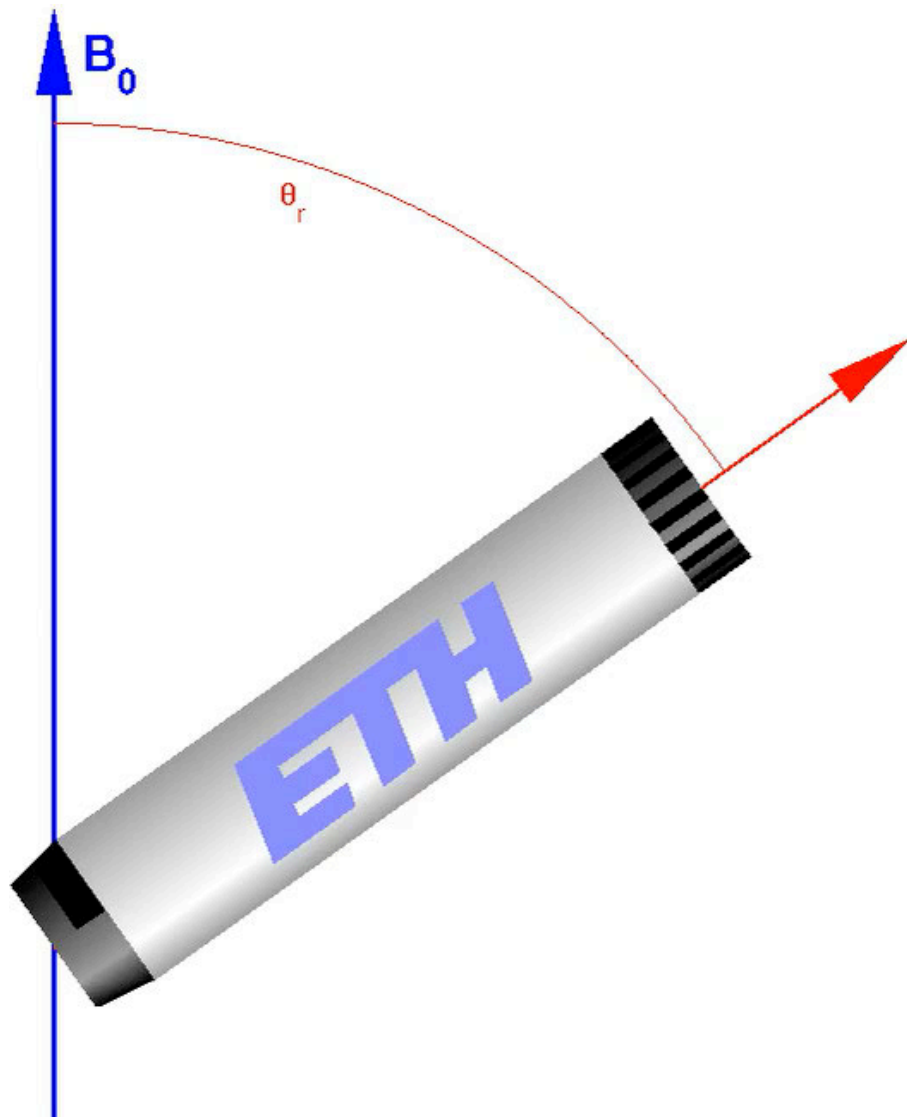
$$\hat{\mathcal{H}}(t)$$

- We start most of our calculations from a time-independent high-field truncated rotating-frame Hamiltonian:

$$\hat{\mathcal{H}} \approx \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)} \hat{T}_{\ell,0}^{(i)}$$

$$\hat{\mathcal{H}}_{\text{rf}} = -\gamma B_1 \left(\cos(\phi) \hat{I}_x + \sin(\phi) \hat{I}_y \right)$$

- So, why do we need to talk about time-dependent Hamiltonians?



The Rotating-Frame Hamiltonian

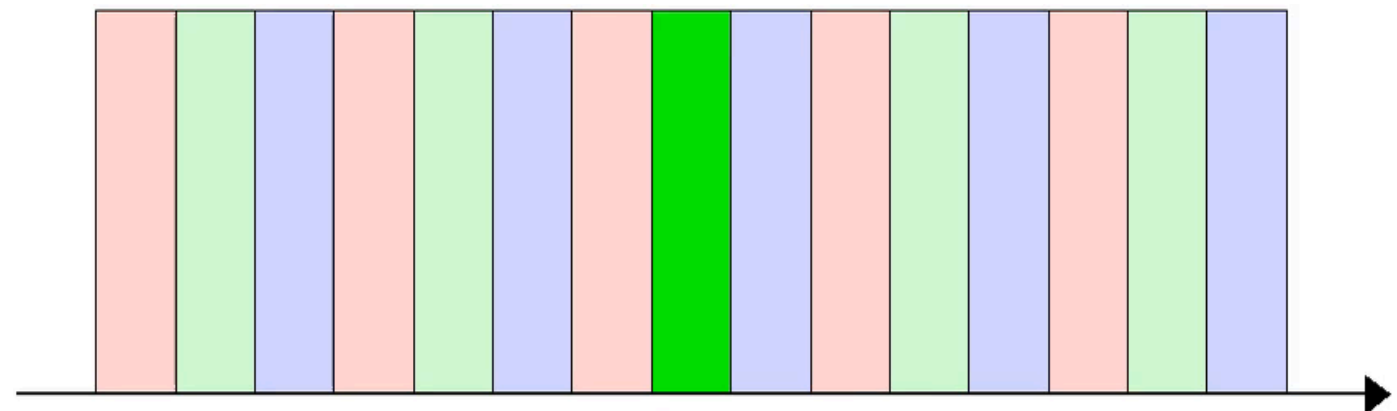
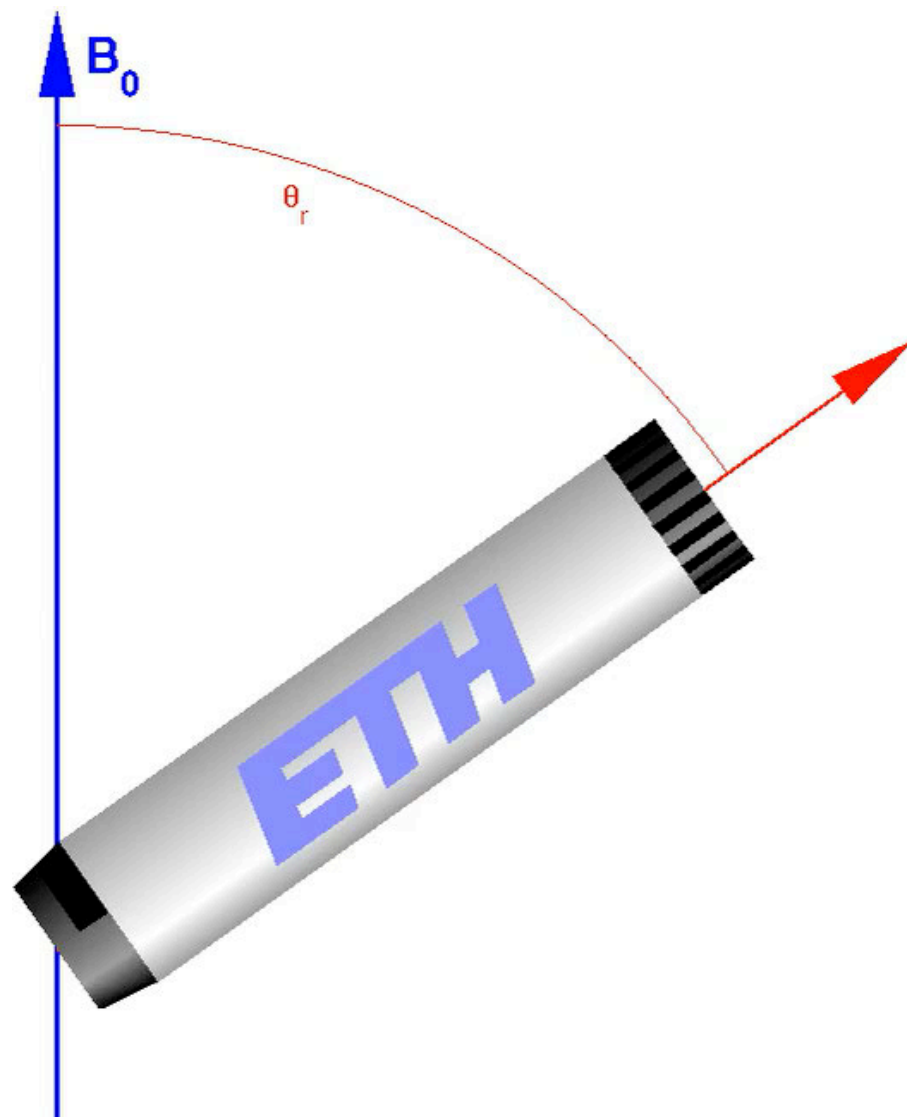
$$\hat{\mathcal{H}}(t)$$

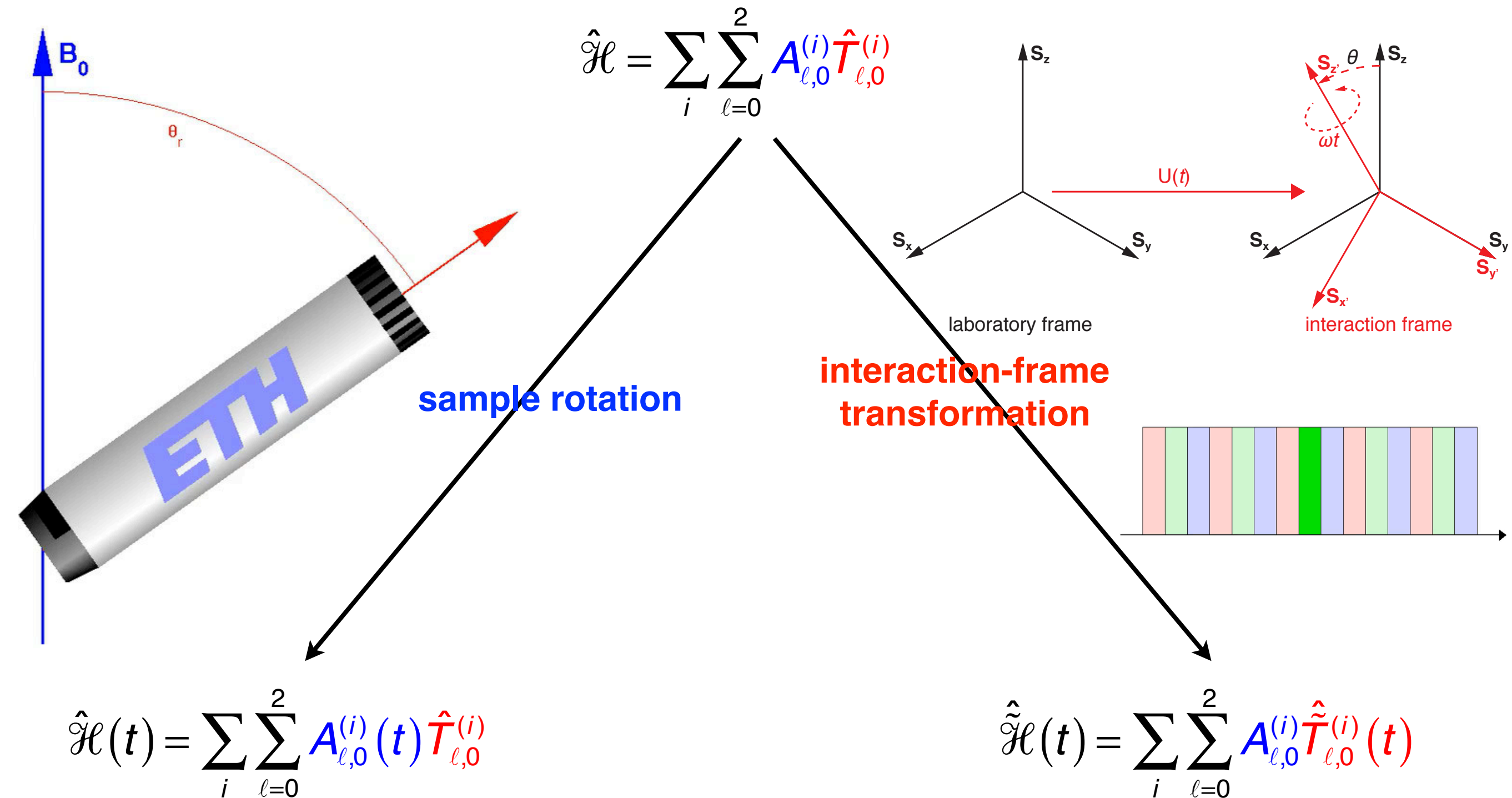
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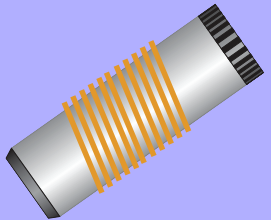
- So, why do we need to talk about time-dependent Hamiltonians?



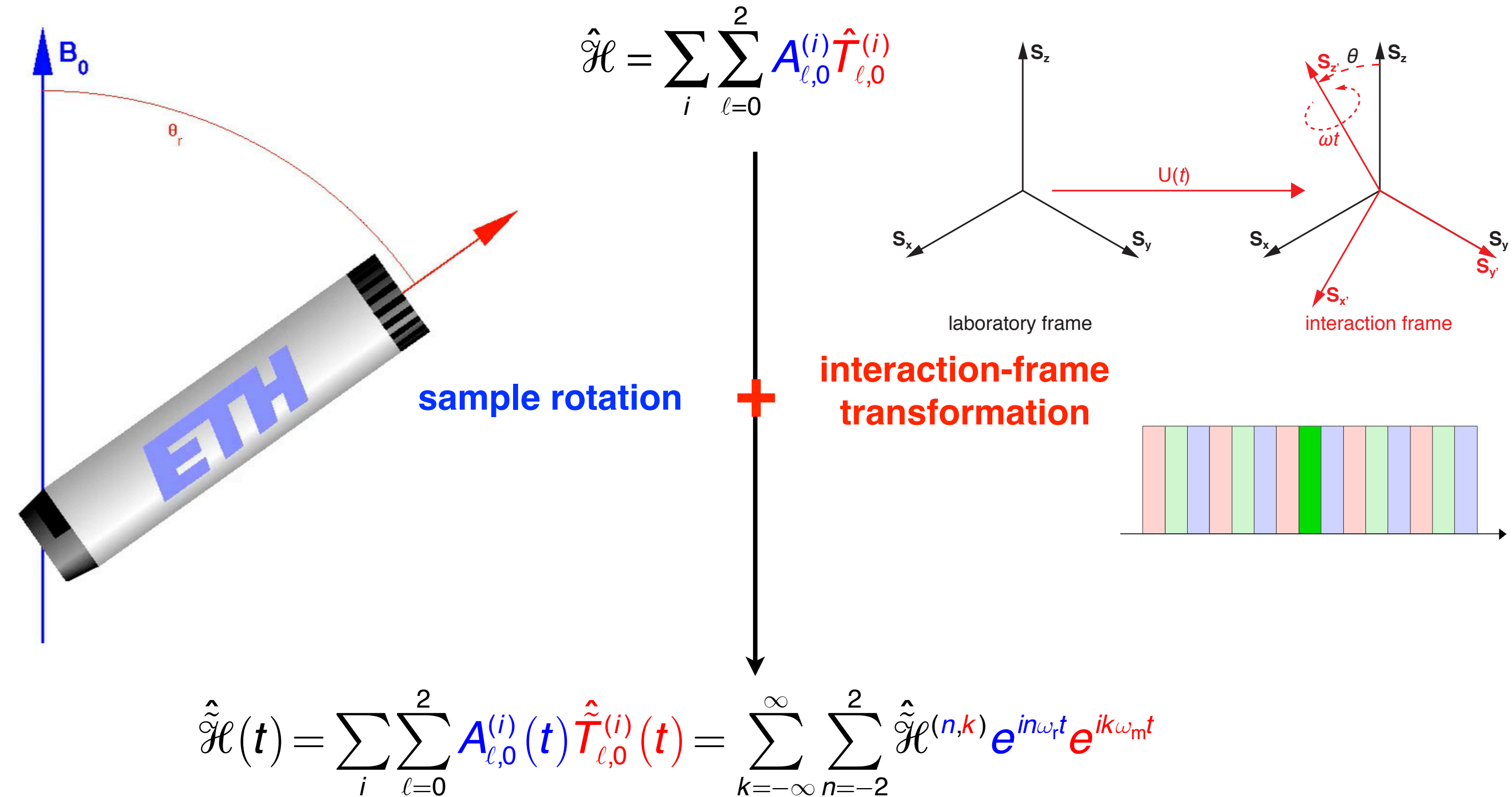


I

Origin of Time-Dependent Hamiltonians

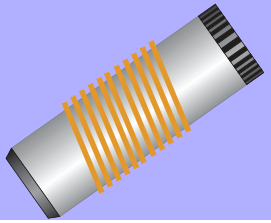


❑ The spin-system Hamiltonian in the rotating frame is static if the molecule is static.

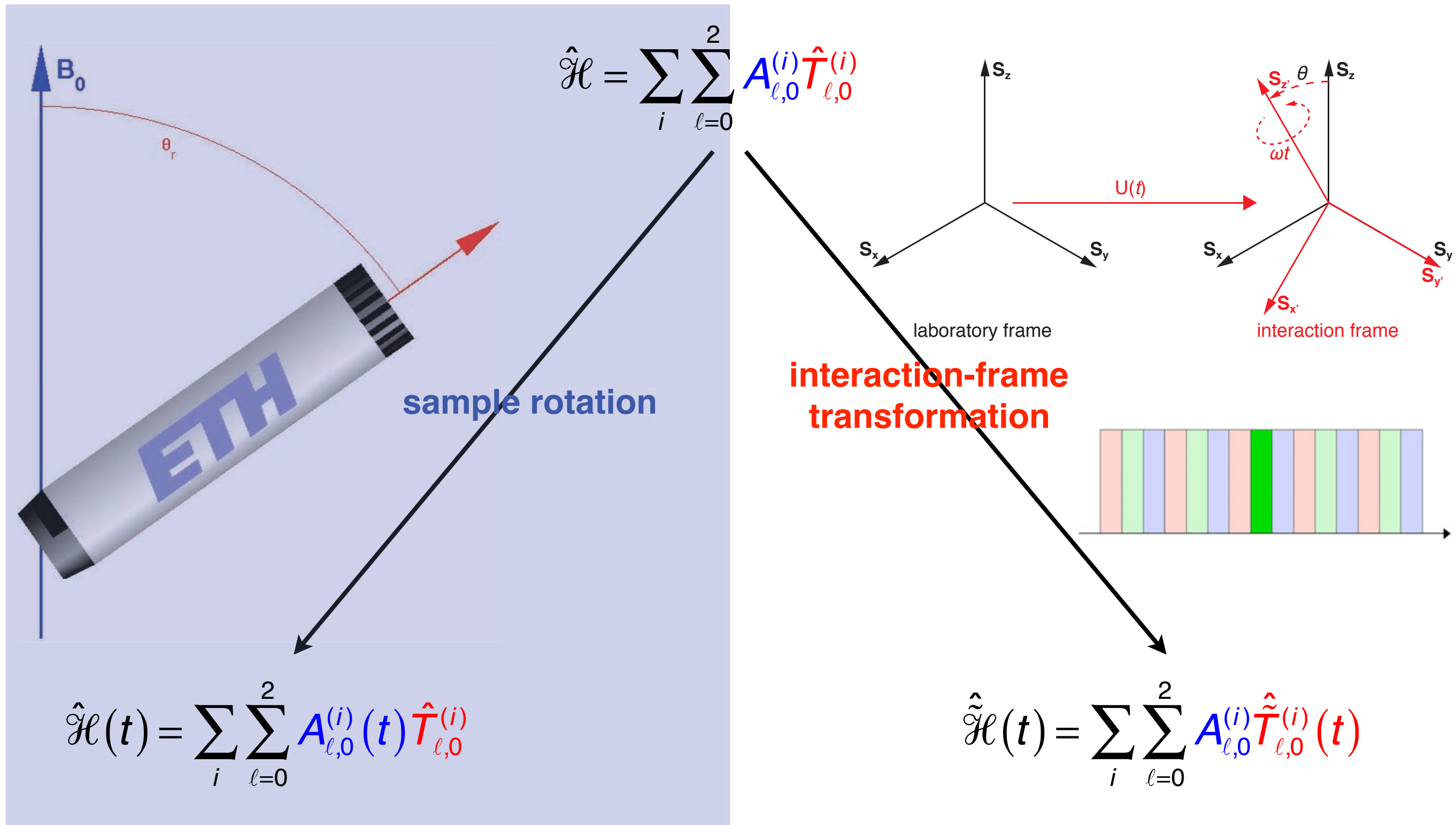


❑ Hamiltonian in solid-state NMR has often multiple time dependencies!

Time-Dependent Hamiltonians: Sample Rotation

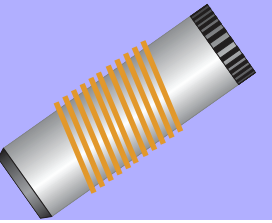


□ The spin-system Hamiltonian in the rotating frame is static if the molecule is static.

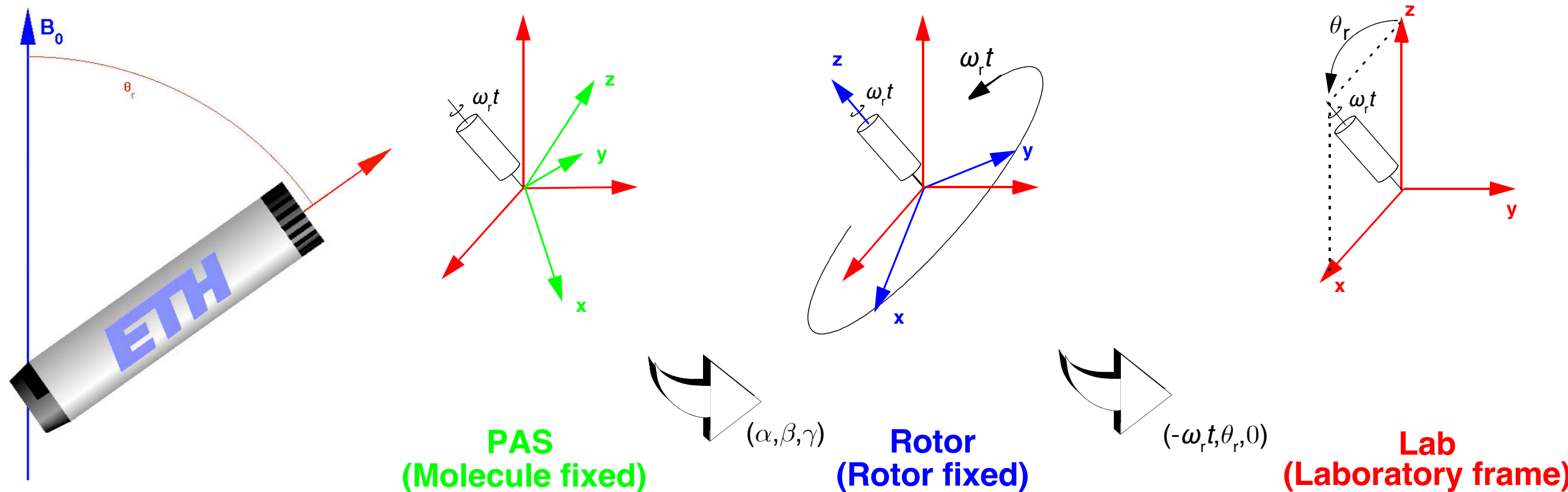


□ Sample rotation modulates the **spatial part** of the Hamiltonian.

Sample Rotation



Transformation of the spatial-tensor parts from the PAS to the laboratory frame:

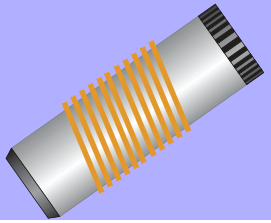


Spatial components of the Hamiltonian become time dependent:

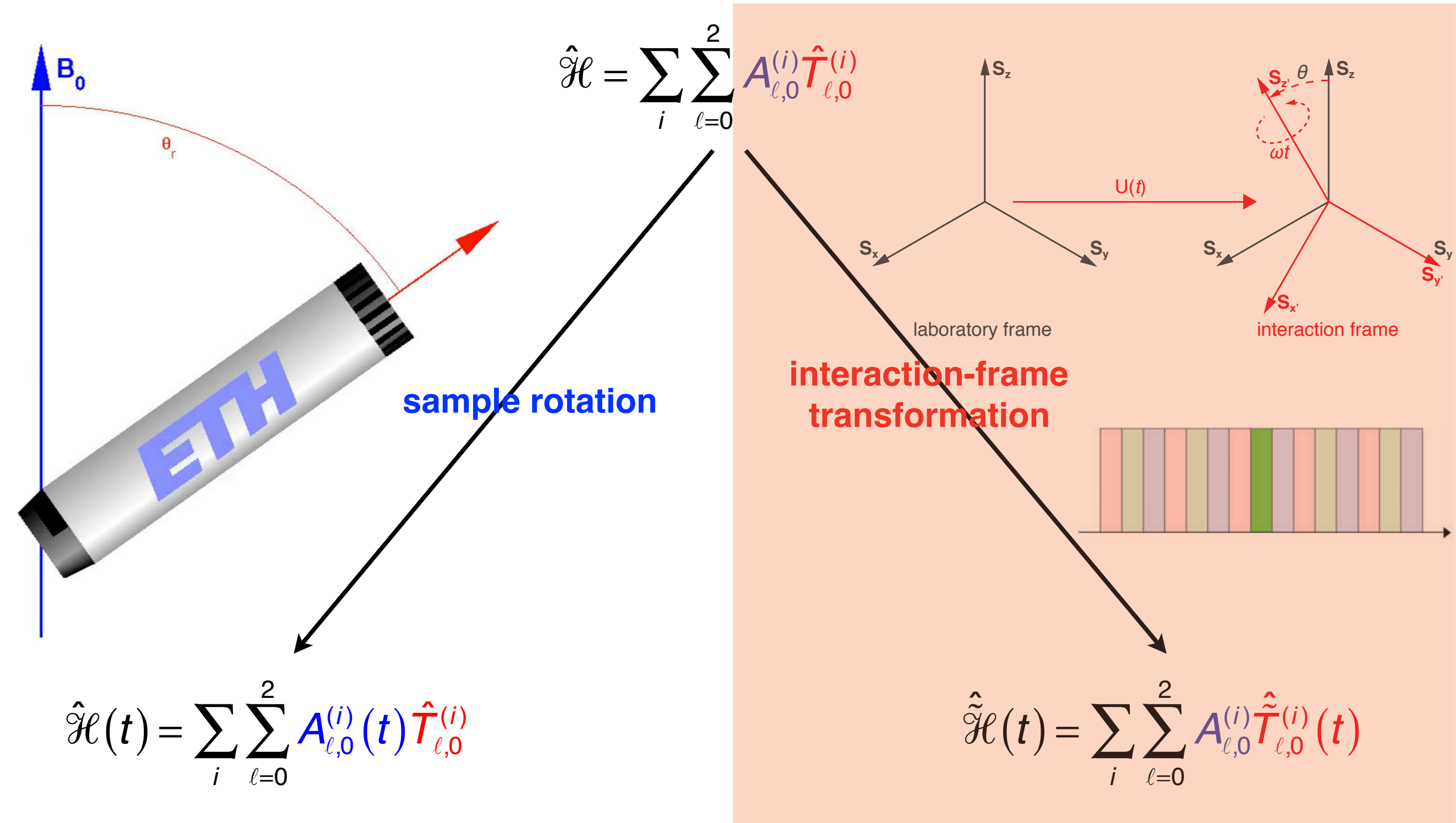
$$\begin{aligned}
 A_{\ell, m''}^{(\text{lab})}(t) &= \sum_{m'=-\ell}^{\ell} \mathcal{D}_{m', m''}^{\ell}(-\omega_r t, -\theta_r, 0) \sum_{m=-\ell}^{\ell} \mathcal{D}_{m, m'}^{\ell}(\alpha, \beta, \gamma) \rho_{\ell, m}^{(\text{PAS})} \\
 &= \sum_{m'=-\ell}^{\ell} \mathcal{D}_{m', m''}^{\ell}(-\omega_r t, -\theta_r, 0) A_{\ell, m'}^{(\text{rot})} = \sum_{m'=-\ell}^{\ell} e^{im' \omega_r t} d_{m', m''}^{\ell}(-\theta_r) A_{\ell, m'}^{(\text{rot})}
 \end{aligned}$$

Spatial components of the Hamiltonian can be expressed in a Fourier series with ω_r as the basic frequency.

Time-Dependent Hamiltonians: Interaction Frame

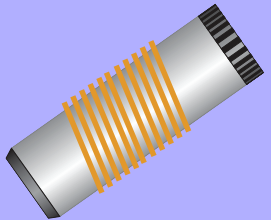


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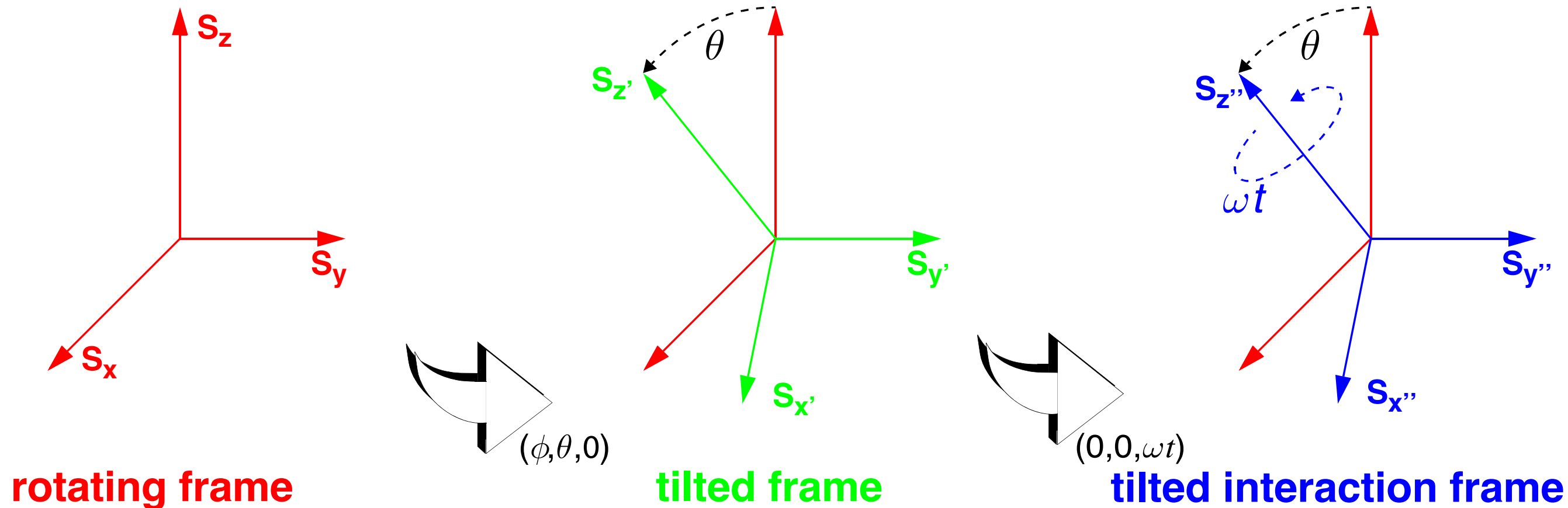


□ Interaction-frame transformations modulate the **spin part** of the Hamiltonian.

Interaction-Frame Transformation



Transformation of the spin-tensor parts from the rotating frame to the interaction frame:

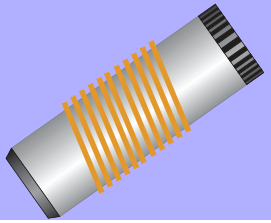


Spin part of the Hamiltonian become time dependent:

$$\hat{\hat{T}}_{\ell,q'}^{(i)}(t) = \sum_{q=-\ell}^{\ell} \mathcal{D}_{q,q'}^{\ell}(\phi, \theta, \omega t) \hat{T}_{\ell,q}^{(i)} = e^{-iq'\omega t} \sum_{q=-\ell}^{\ell} d_{q,q'}^{\ell}(\theta) e^{-iq\phi} \hat{T}_{\ell,q}^{(i)}$$

Spin components of the Hamiltonian can be expressed in a Fourier series with ω as the basic frequency.

Origin of Time-Dependent Hamiltonians



❑ The spin-system Hamiltonian in the rotating frame is static if the molecule is static.

sample rotation

$$\hat{\mathcal{H}} = \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)} \hat{T}_{\ell,0}^{(i)}$$

$$\hat{\tilde{\mathcal{H}}}(t) = \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)}(t) \hat{\tilde{T}}_{\ell,0}^{(i)}(t) = \sum_{k=-\infty}^{\infty} \sum_{n=-2}^2 \hat{\tilde{\mathcal{H}}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_m t}$$

laboratory frame interaction frame

interaction-frame transformation

❑ Hamiltonians in solid-state NMR have often multiple time dependencies!

❑ Rotating-frame Hamiltonians in MAS solid-state NMR are usually periodic in time.

❑ MAS:

$$\hat{\mathcal{H}}(t) = \mathbf{A}_{\ell,0}^{(i)}(t) \hat{\mathbf{T}}_{\ell,0}^{(i)} = \left(\sum_{m'=-\ell}^{\ell} e^{im'\omega_r t} d_{m',0}^{\ell}(-\theta_r) \mathbf{A}_{\ell,m'}^{(\text{rot})} \right) \hat{\mathbf{T}}_{\ell,0}^{(i)}$$

❑ Interaction-frame transformation:

$$\hat{\hat{\mathcal{H}}}(t) = \mathbf{A}_{\ell,0}^{(i)} \hat{\hat{\mathbf{T}}}_{\ell,0}^{(i)}(t) = \mathbf{A}_{\ell,0}^{(i)} e^{-iq'\omega t} \sum_{q=-\ell}^{\ell} d_{q,0}^{\ell}(\theta) e^{-iq\phi} \hat{\mathbf{T}}_{\ell,q}^{(i)}$$

❑ We can write such periodic time-dependent Hamiltonians as a Fourier series:

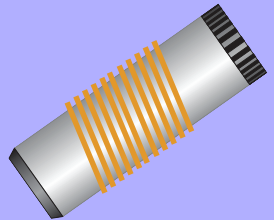
$$\hat{\hat{\mathcal{H}}}(t) = \sum_{n=-\infty}^{\infty} \hat{\hat{\mathcal{H}}}^{(n)} e^{in\omega_m t} \quad \text{with} \quad \hat{\hat{\mathcal{H}}}^{(n)} = \left(\hat{\hat{\mathcal{H}}}^{(-n)} \right)^{\dagger}$$

❑ For multiple time dependencies with different frequencies, we can write:

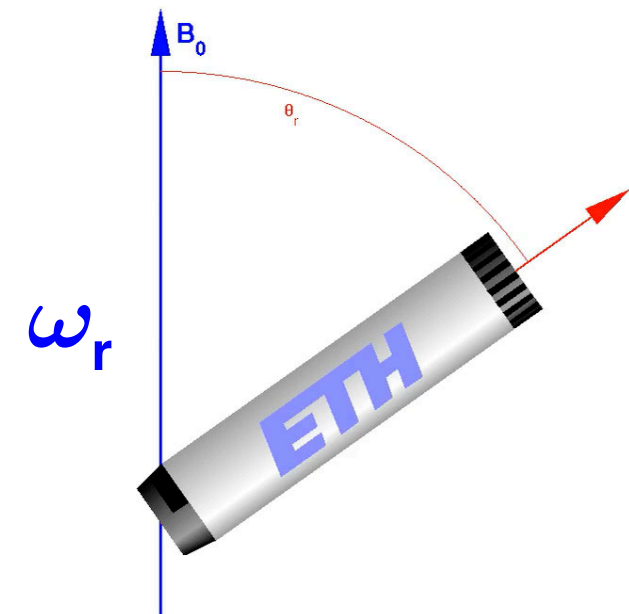
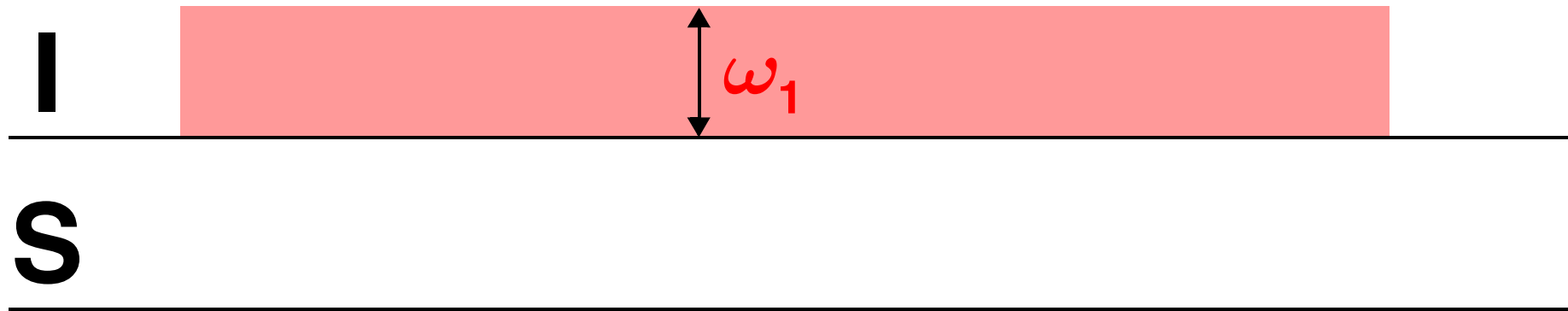
$$\hat{\hat{\mathcal{H}}}(t) = \sum_{n=-\infty}^{\infty} \hat{\hat{\mathcal{H}}}^{(n_1, n_2)} e^{in_1\omega_{m1}t} e^{in_2\omega_{m2}t} \quad \text{with} \quad \hat{\hat{\mathcal{H}}}^{(n_1, n_2)} = \left(\hat{\hat{\mathcal{H}}}^{(-n_1, -n_2)} \right)^{\dagger}$$

❑ Piece-wise constant Hamiltonians (toggling frame) can be expressed as periodic Hamiltonians using Fourier series.

Example: MAS and CW Irradiation



- Heteronuclear coupled I-S two-spin system:
Continuous-wave (cw) irradiation on one spin under MAS.



- Examples for such a situation:

- Heteronuclear CW decoupling (non resonant)
- Rotary-resonance recoupling (R^3) ($n_0 \omega_r, \pm \omega_1 = 0, n_0 = \pm 1, \pm 2$)
- HORROR recoupling ($n_0 \omega_r, \pm k_0 \omega_1 = 0, n_0 = \pm 1, \pm 2, k_0 = \pm 2$)
- Higher-order R^3 experiments ($n_0 \omega_r, \pm \omega_1 = 0, n_0 = \pm 3, \pm 4$)
- DARR or MIRROR recoupling ($n_0 \omega_r, \pm \omega_1 + \ell_0 \Delta\Omega_{\text{iso}} = 0, n_0 = \pm 3, \pm 4, \ell_0 = \pm 1$)

M. Ernst, A. Samoson, B.H. Meier, Decoupling and recoupling using continuous-wave irradiation in magic-angle-spinning solid-state NMR: A unified description using bimodal Floquet theory, J. Chem. Phys. 123 (2005) 064102. doi:10.1063/1.1944291.

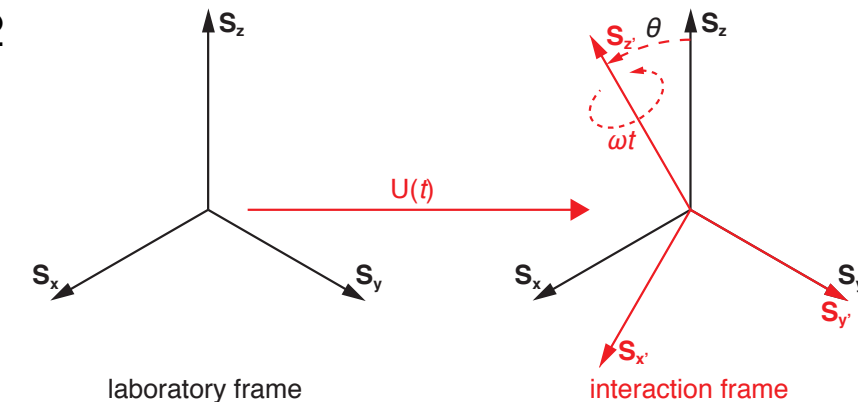
Theoretical Description of CW Irradiation in Rotating Solids $\hat{\mathcal{H}}(t)$

- Spin-system Hamiltonian in the rotating frame is time dependent due to magic-angle spinning (MAS).

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_I(t) + \hat{\mathcal{H}}_{IS}(t) + \hat{\mathcal{H}}_S(t) + \hat{\mathcal{H}}_{II}(t) + \hat{\mathcal{H}}_{SS}(t) = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t}$$

interaction-frame transformation:

$$\hat{U}(t) = \hat{T} \exp \left(-i \int_0^t \hat{\mathcal{H}}_{rf}(t_1) dt_1 \right) e^{i\pi/2 \hat{F}_y} = e^{-i\omega_1 \hat{F}_z t} e^{i\pi/2 \hat{F}_y}$$



$$\hat{\tilde{\mathcal{H}}}(t) = \hat{\tilde{\mathcal{H}}}_I(t) + \hat{\tilde{\mathcal{H}}}_{IS}(t) + \hat{\tilde{\mathcal{H}}}_S(t) + \hat{\tilde{\mathcal{H}}}_{II}(t) + \hat{\tilde{\mathcal{H}}}_{SS}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\tilde{\mathcal{H}}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$$

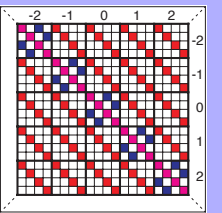
- Interaction-frame transformation with the rf-field introduces a second time-dependence in the Hamiltonian. There are now two frequencies: ω_r and ω_1 .

- Average Hamiltonian theory requires that

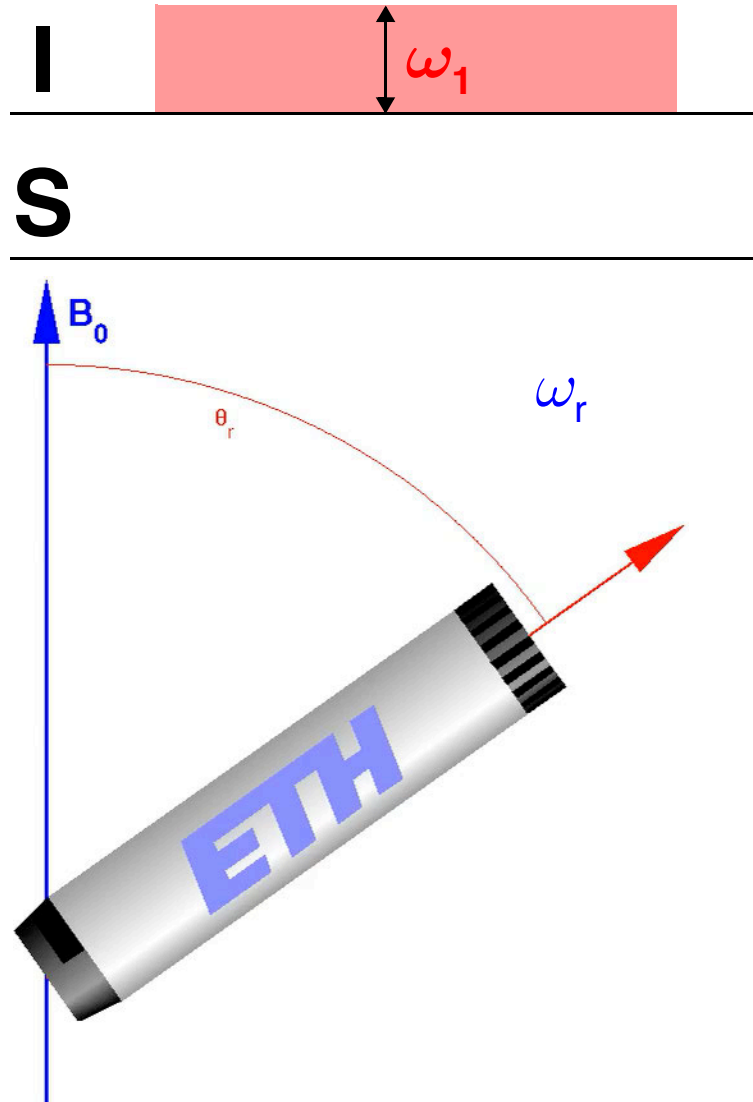
- the two frequencies are commensurate, i.e., $n \omega_r = k \omega_1$ (simultaneous averaging) or
- a separation of time scales, i.e., $\omega_r \ll \omega_1$ or $\omega_r \gg \omega_1$ (sequential averaging).

- Floquet theory allows a unified description for all values of ω_r and ω_1 .

Fourier Coefficients Under CW Irradiation

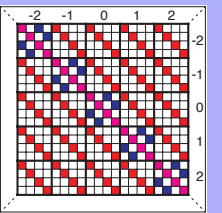


Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_1 t} e^{ik\omega_1 t}$

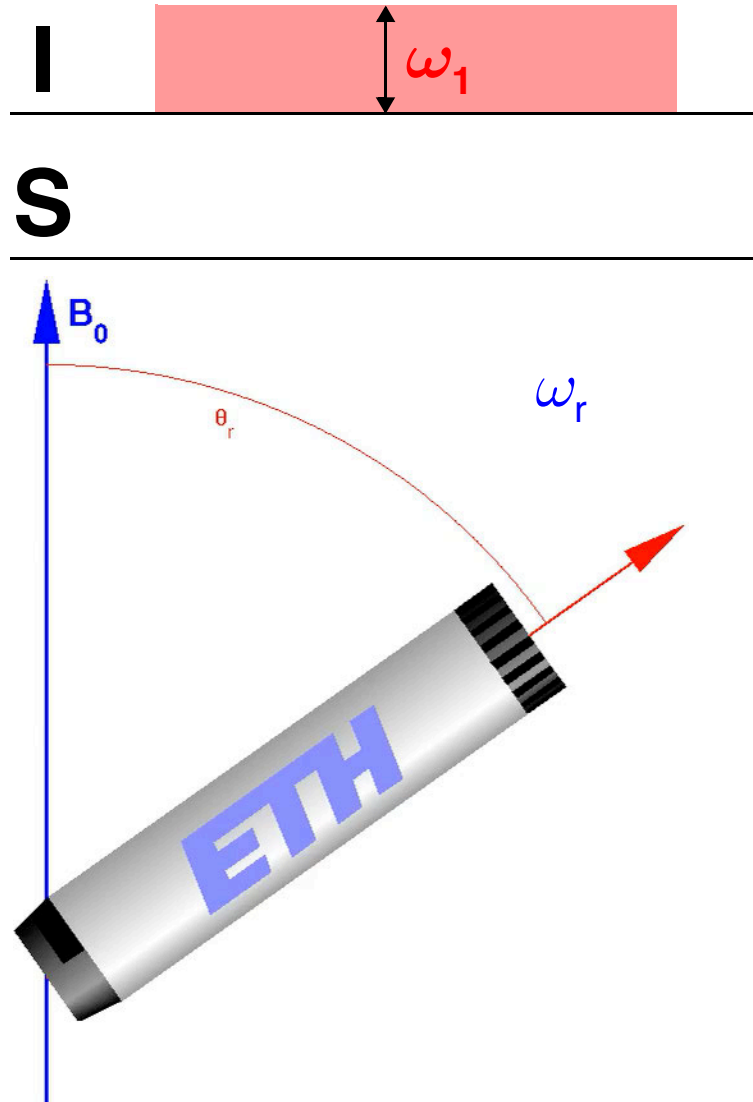


$$\left\{ \begin{array}{l} \hat{\mathcal{H}}^{(0,0)} = \omega_S^{(0)} S_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m) \\ \hat{\mathcal{H}}^{(n,0)} = \omega_S^{(n)} S_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right) \\ \hat{\mathcal{H}}^{(0,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp \\ \hat{\mathcal{H}}^{(n,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp \\ \hat{\mathcal{H}}^{(0,\pm 2)} = 0 \\ \hat{\mathcal{H}}^{(n,\pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp \end{array} \right.$$

Fourier Coefficients Under CW Irradiation



Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$



$$\hat{\mathcal{H}}^{(0,0)} = \omega_S^{(0)} \hat{S}_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m)$$

$$\hat{\mathcal{H}}^{(n,0)} = \omega_S^{(n)} \hat{S}_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right)$$

$$\hat{\mathcal{H}}^{(0,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp$$

$$\hat{\mathcal{H}}^{(n,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp$$

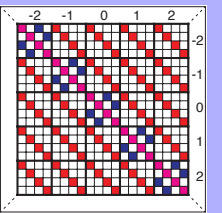
$$\hat{\mathcal{H}}^{(0,\pm 2)} = 0$$

$$\hat{\mathcal{H}}^{(n,\pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp$$

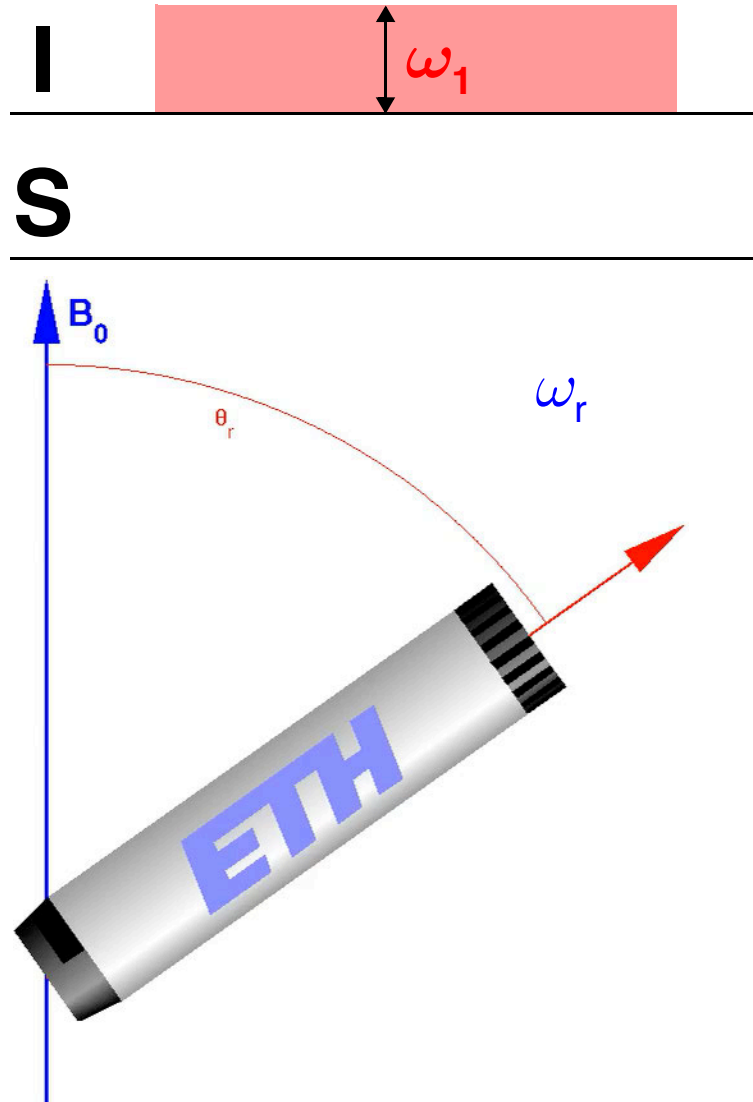
Chemical shift of S spin:

$$\hat{\mathcal{H}}_S(t) = \hat{S}_z \sum_{n=-2}^2 \omega_S^{(n)} e^{in\omega_r t}$$

Fourier Coefficients Under CW Irradiation



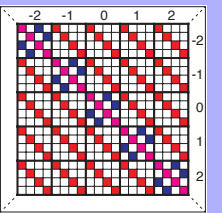
Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$



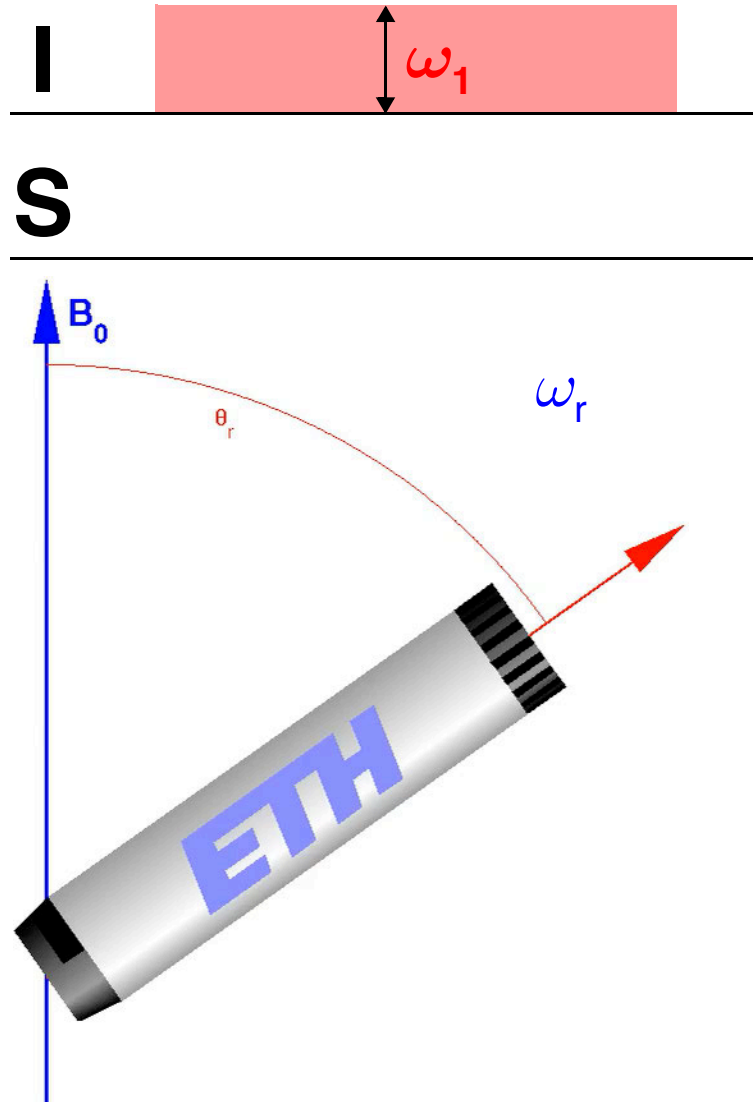
$$\left\{ \begin{aligned} \hat{\mathcal{H}}^{(0,0)} &= \omega_S^{(0)} S_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m) \\ \hat{\mathcal{H}}^{(n,0)} &= \omega_S^{(n)} S_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right) \\ \hat{\mathcal{H}}^{(0,\pm 1)} &= -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp \\ \hat{\mathcal{H}}^{(n,\pm 1)} &= -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp \\ \hat{\mathcal{H}}^{(0,\pm 2)} &= 0 \\ \hat{\mathcal{H}}^{(n,\pm 2)} &= \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp \end{aligned} \right.$$

Chemical shift of I spins: $\hat{\mathcal{H}}_I(t) = \sum_m \hat{I}_{mz} \sum_{n=-2}^2 \omega_m^{(n)} e^{in\omega_r t}$

Fourier Coefficients Under CW Irradiation



Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$



$$\hat{\mathcal{H}}^{(0,0)} = \omega_S^{(0)} S_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m)$$

$$\hat{\mathcal{H}}^{(n,0)} = \omega_S^{(n)} S_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right)$$

$$\hat{\mathcal{H}}^{(0,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp$$

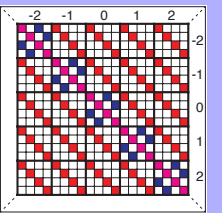
$$\hat{\mathcal{H}}^{(n,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp$$

$$\hat{\mathcal{H}}^{(0,\pm 2)} = 0$$

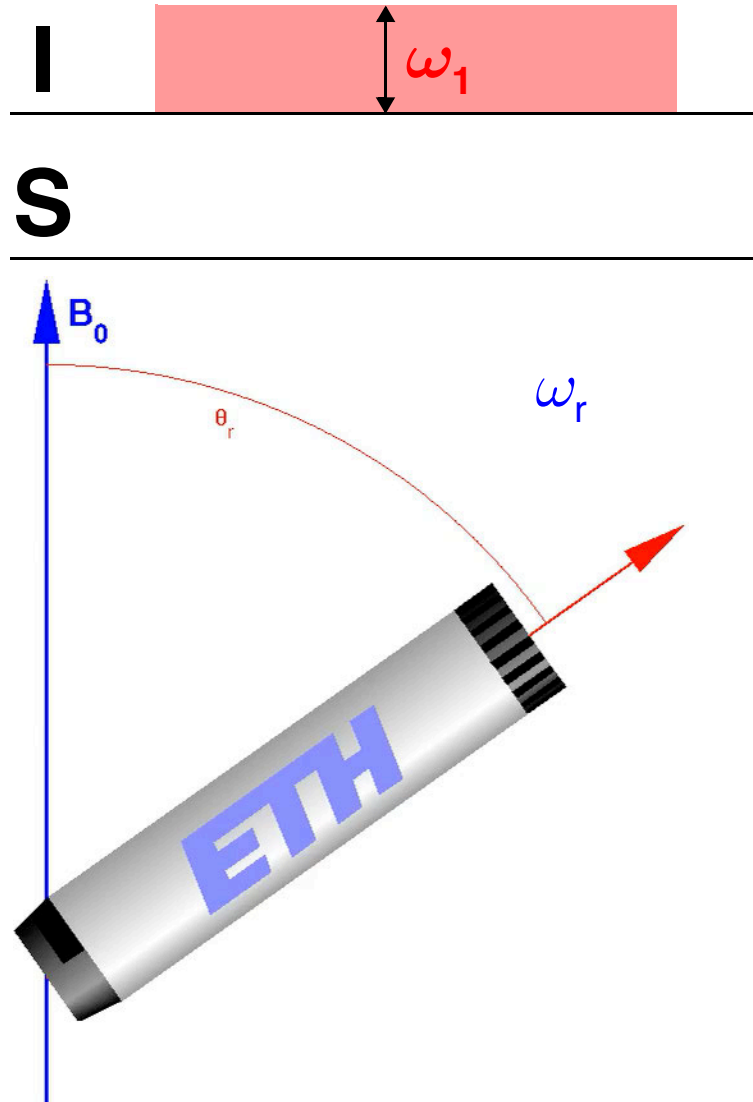
$$\hat{\mathcal{H}}^{(n,\pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp$$

Homonuclear couplings (I-I): $\hat{\mathcal{H}}_{II}(t) = \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m) + \sum_{\ell < m} \left(2\hat{I}_{\ell z} \hat{I}_{m z} - (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right) \sum_{\substack{n=-2 \\ n \neq 0}}^2 \omega_{\ell,m}^{(n)} e^{in\omega_r t}$

Fourier Coefficients Under CW Irradiation



Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$



$$\hat{\mathcal{H}}^{(0,0)} = \omega_S^{(0)} S_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m)$$

$$\hat{\mathcal{H}}^{(n,0)} = \omega_S^{(n)} S_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right)$$

$$\hat{\mathcal{H}}^{(0,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp$$

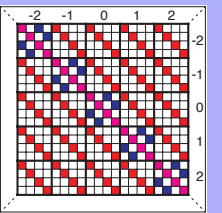
$$\hat{\mathcal{H}}^{(n,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp$$

$$\hat{\mathcal{H}}^{(0,\pm 2)} = 0$$

$$\hat{\mathcal{H}}^{(n,\pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp$$

Heteronuclear couplings (I-S): $\hat{\mathcal{H}}_{IS}(t) = \sum_m 2\hat{S}_z \hat{I}_{mz} \sum_{\substack{n=-2 \\ n \neq 0}}^2 \omega_{S,m}^{(n)} e^{in\omega_r t}$

Treatment of Time-Dependent Hamiltonians



Delhi, 2024

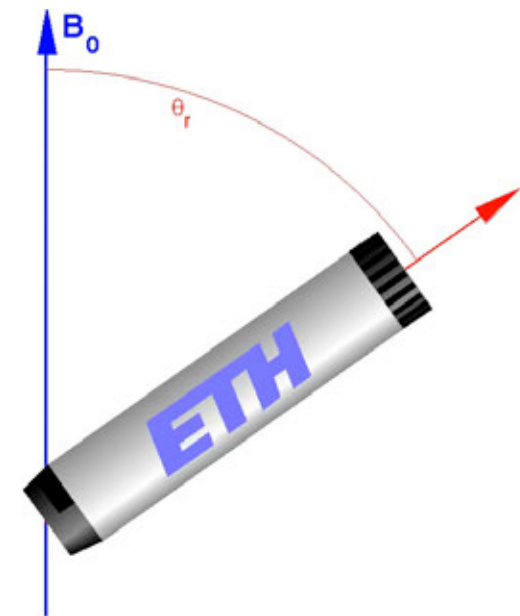
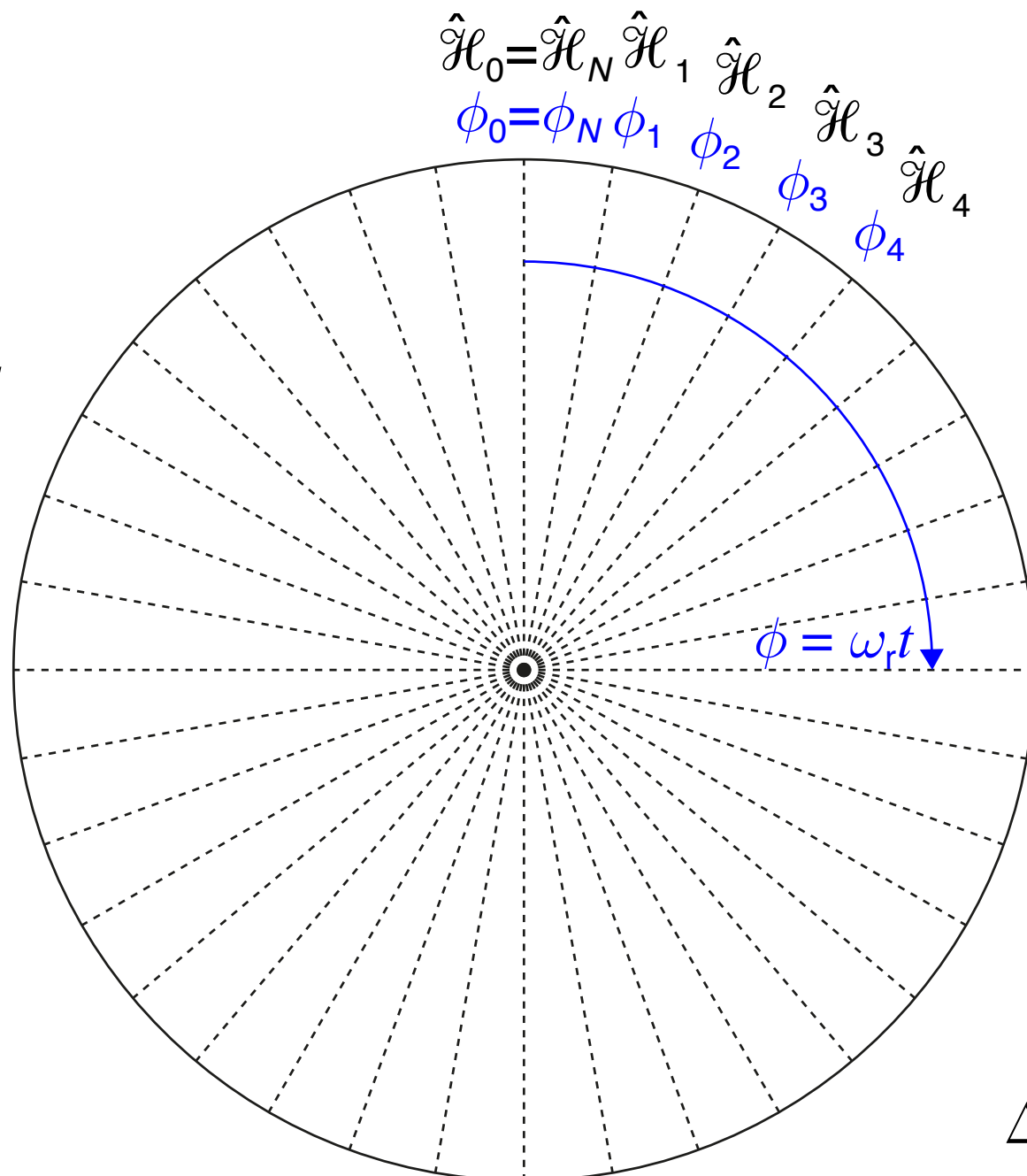
Magic-Angle Spinning: Time Slicing



- We can use time slicing, i.e. we assume that the Hamiltonian can be approximated by a constant value for a short time.

$$\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{-in\omega_r t} = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{-in\phi} = \hat{\mathcal{H}}(\phi)$$

- We divide the rotor period into N equal time periods of length $\Delta t = \tau_r / N = 2\pi / (\omega_r N)$.
- The rotor phase for an interval i is given by $\phi_i = i \omega_r \Delta t = i 2\pi / N$.
- The Hamiltonian during an interval i is given by $\mathcal{H}(\phi_i)$.
- We have now again a piecewise constant Hamiltonian and can solve the Liouville-von Neumann equation.

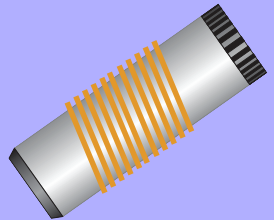


$$\phi_i = i \omega_r \Delta t = i 2\pi / N$$

$$\hat{\mathcal{H}}_i = \hat{\mathcal{H}}(\phi_i)$$

$$\Delta t = \tau_r / N = 2\pi / (\omega_r N)$$

Magic-Angle Spinning: Time Slicing



- We can now calculate the propagator for a full rotor cycle:

$$\hat{U}(\tau_r) = \prod_{i=0}^{N-1} \hat{U}_i = \hat{U}_{N-1} \cdots \hat{U}_i \cdots \hat{U}_4 \hat{U}_3 \hat{U}_2 \hat{U}_1 \hat{U}_0$$

- The time evolution of the density operator at multiples of the rotor period is now simply:

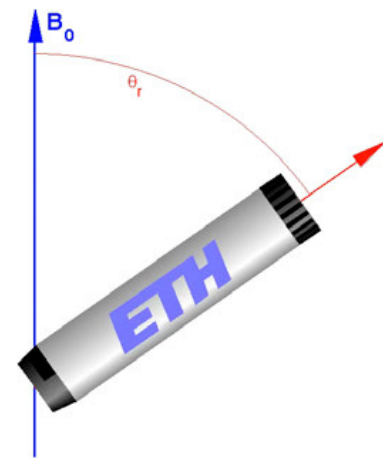
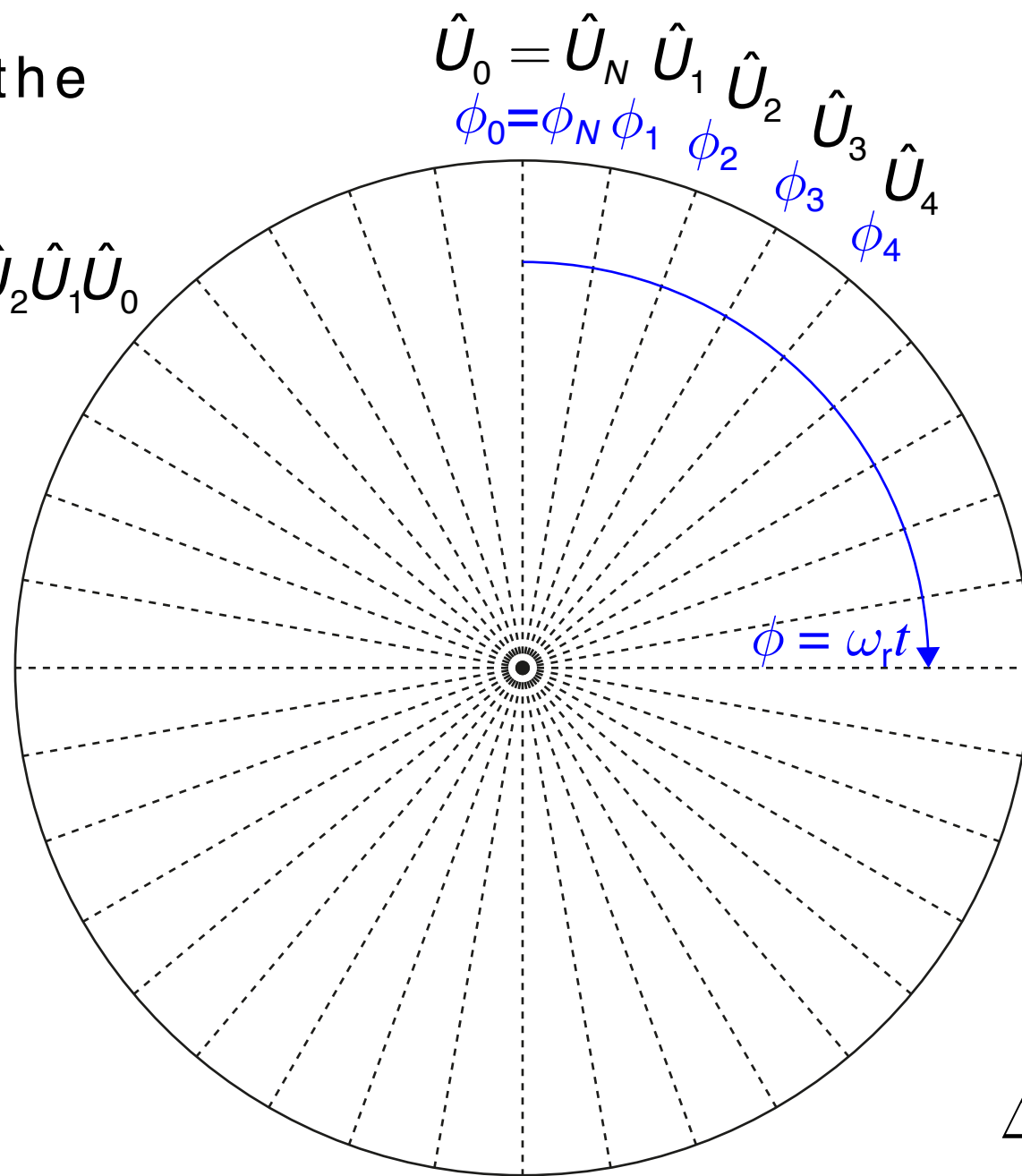
$$\hat{\sigma}(n\tau_r) = \left(\hat{U}(\tau_r) \right)^n \hat{\sigma}(0) \left(\hat{U}^{-1}(\tau_r) \right)^n$$

- This is of course only possible if the Hamiltonian is also cyclic with the MAS frequency, i.e.:

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}(t + n\tau_r)$$

- If we have a *rotor-synchronized pulse sequence* (C7, RFDR, CP, ...) this can always be achieved over one or multiple rotor cycles.

- For *asynchronous sequences* (most decoupling sequences, DREAM, APHHCP, ...) this is not the case and one has to calculate all propagators over the full sequence.

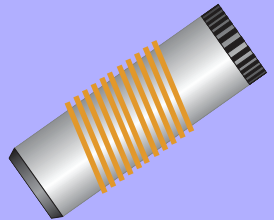


$$\phi_i = i\omega_r \Delta t = i2\pi/(N)$$

$$\hat{U}_i = \hat{U}_i(\phi_i)$$

$$\Delta t = \tau_r/N = 2\pi/(\omega_r N)$$

Magic-Angle Spinning: Time Slicing



- We can now calculate the propagator for a full rotor cycle:

$$\hat{U}(\tau_r) = \prod_{i=0}^{N-1} \hat{U}_i = \hat{U}_{N-1} \cdots \hat{U}_i \cdots \hat{U}_4 \hat{U}_3 \hat{U}_2 \hat{U}_1 \hat{U}_0$$

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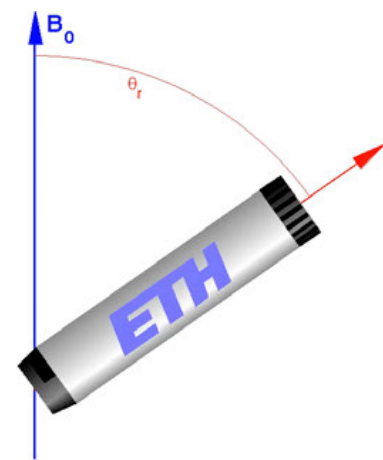
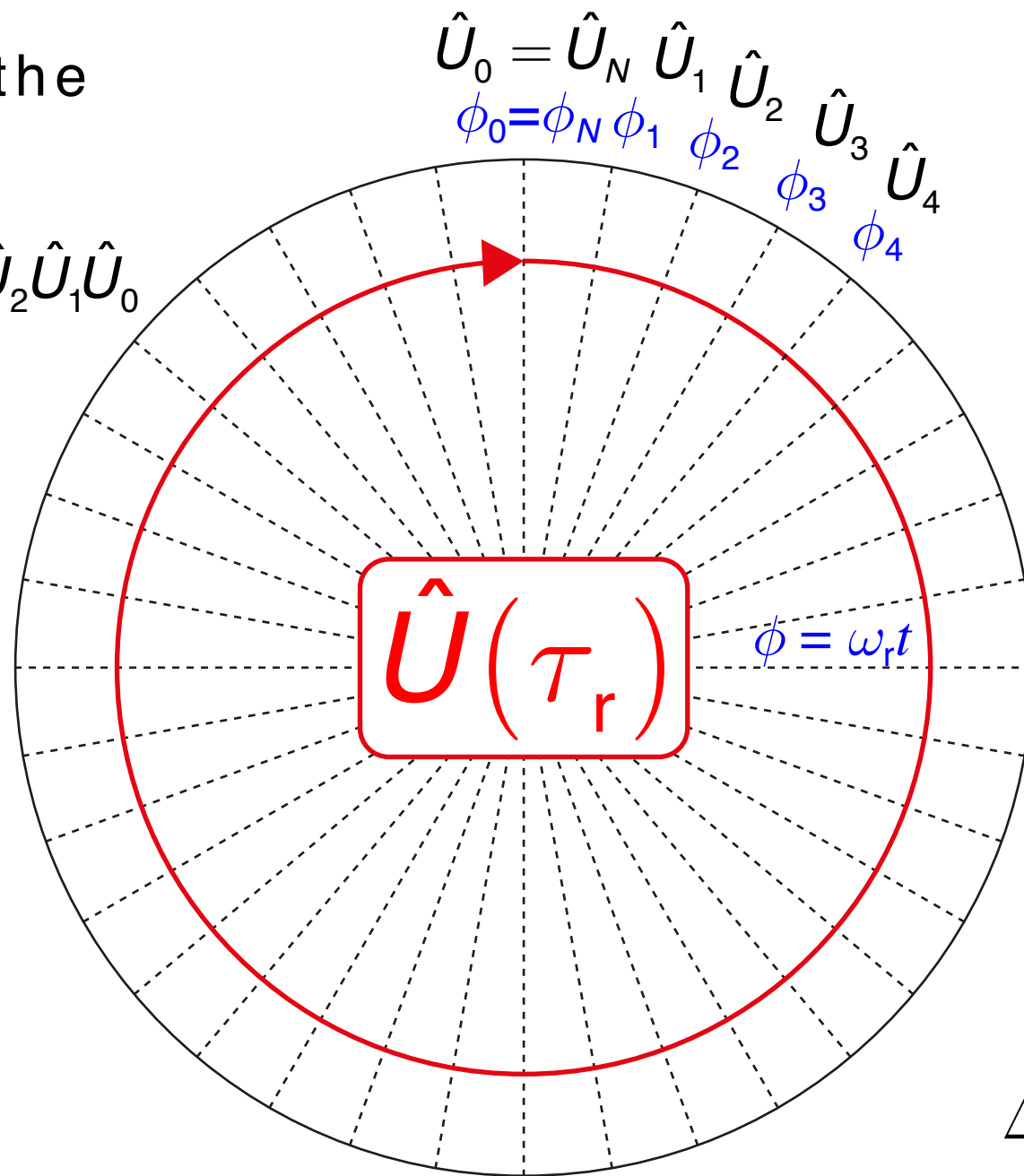
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Magic-Angle Spinning: Time Slicing



❑ Rotor-synchronized sampling limits the spectral width to the value of the spinning frequency.

❑ For higher resolution, we can calculate propagators for fractions of the rotor period:

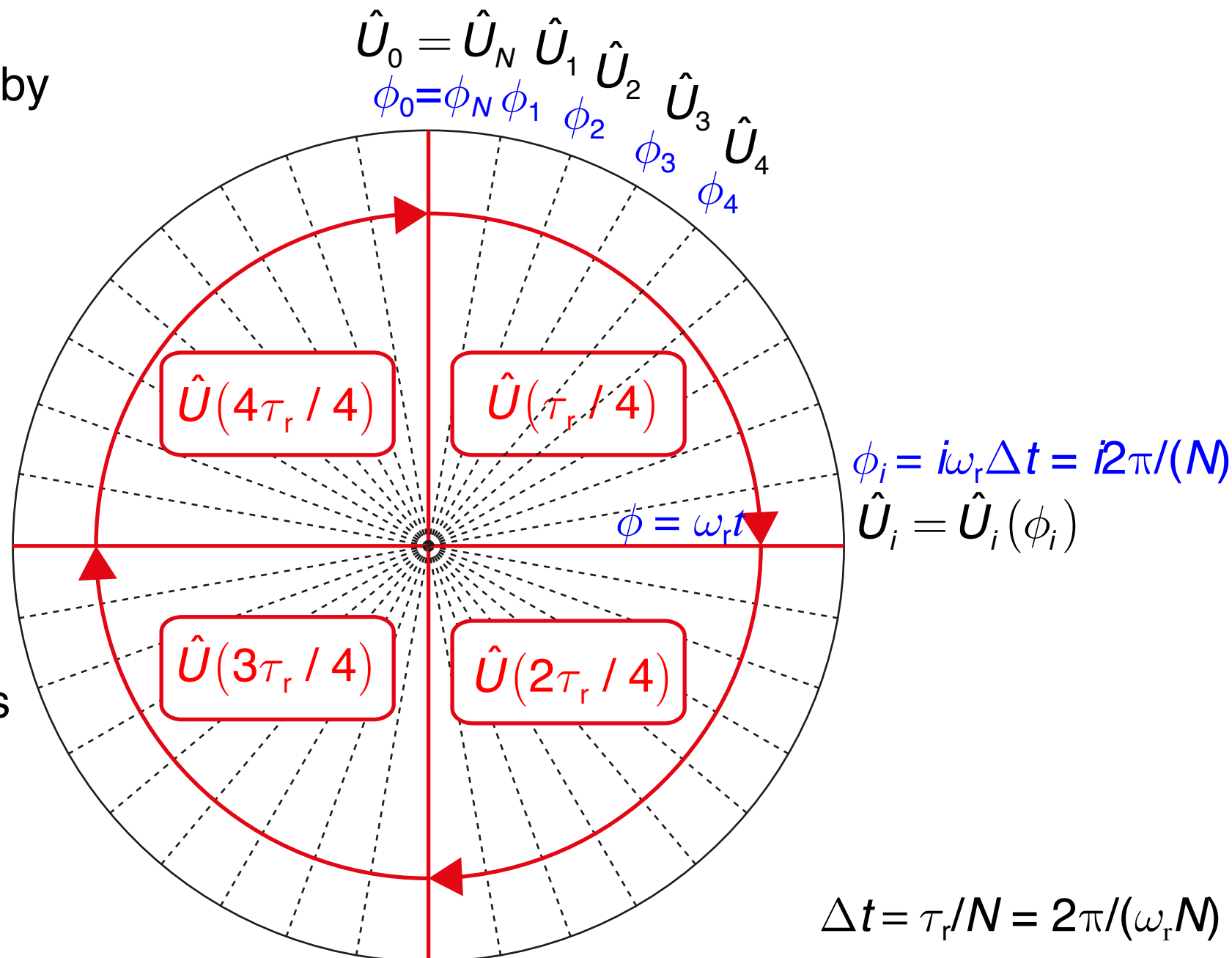
$$\hat{U}(k\tau_r / M)$$

❑ The spectral width is then given by

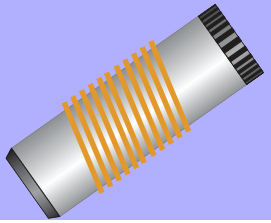
$$SW = M \omega_r.$$

❑ Again this only works for Hamiltonians which are synchronized with the MAS rotation.

❑ We can not only use propagators for fractions of the rotor period but also propagators that cover multiples of a rotor period: $\hat{U}(n\tau_r)$



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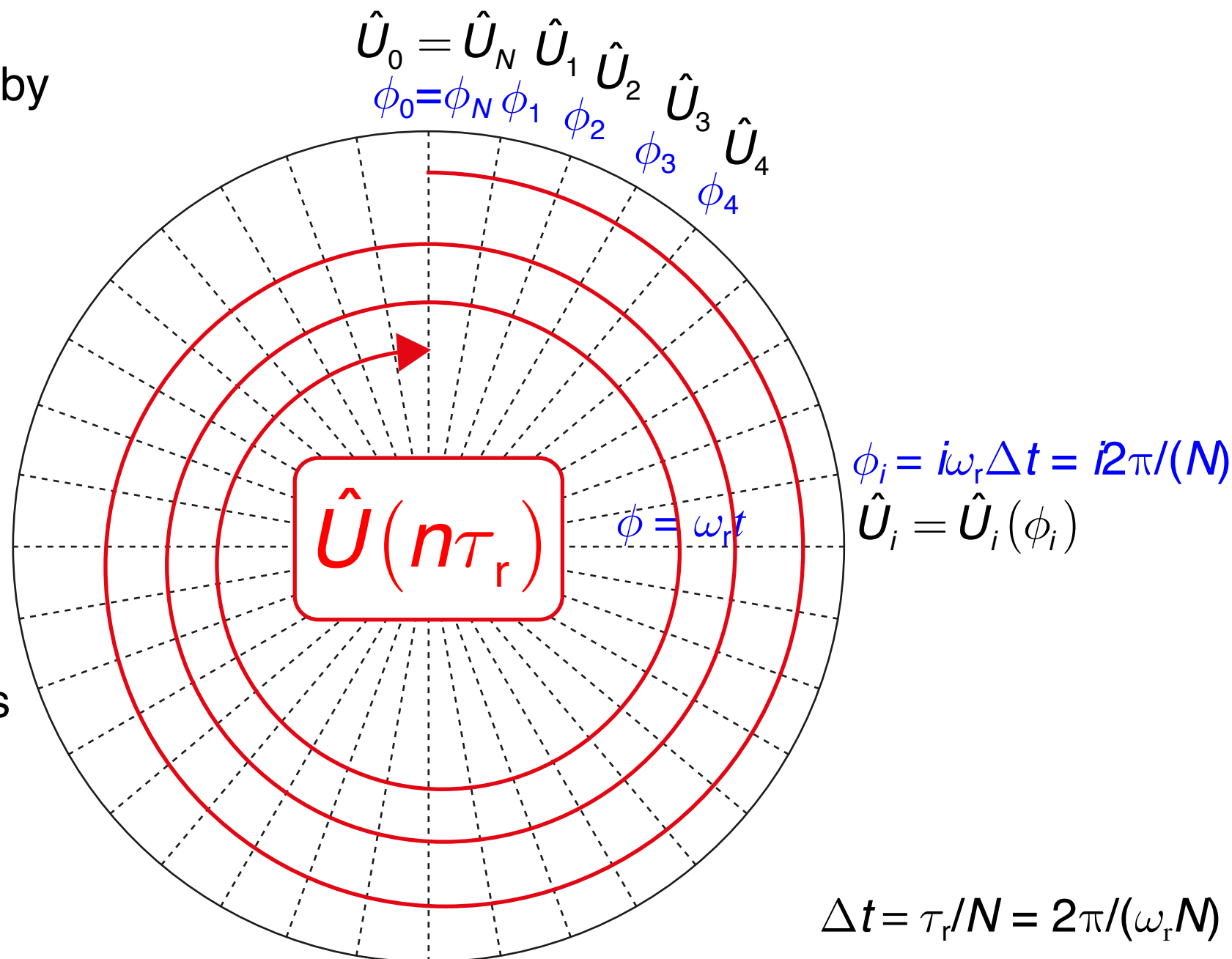
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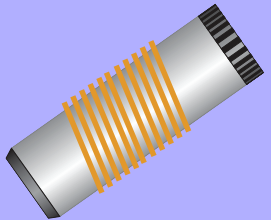
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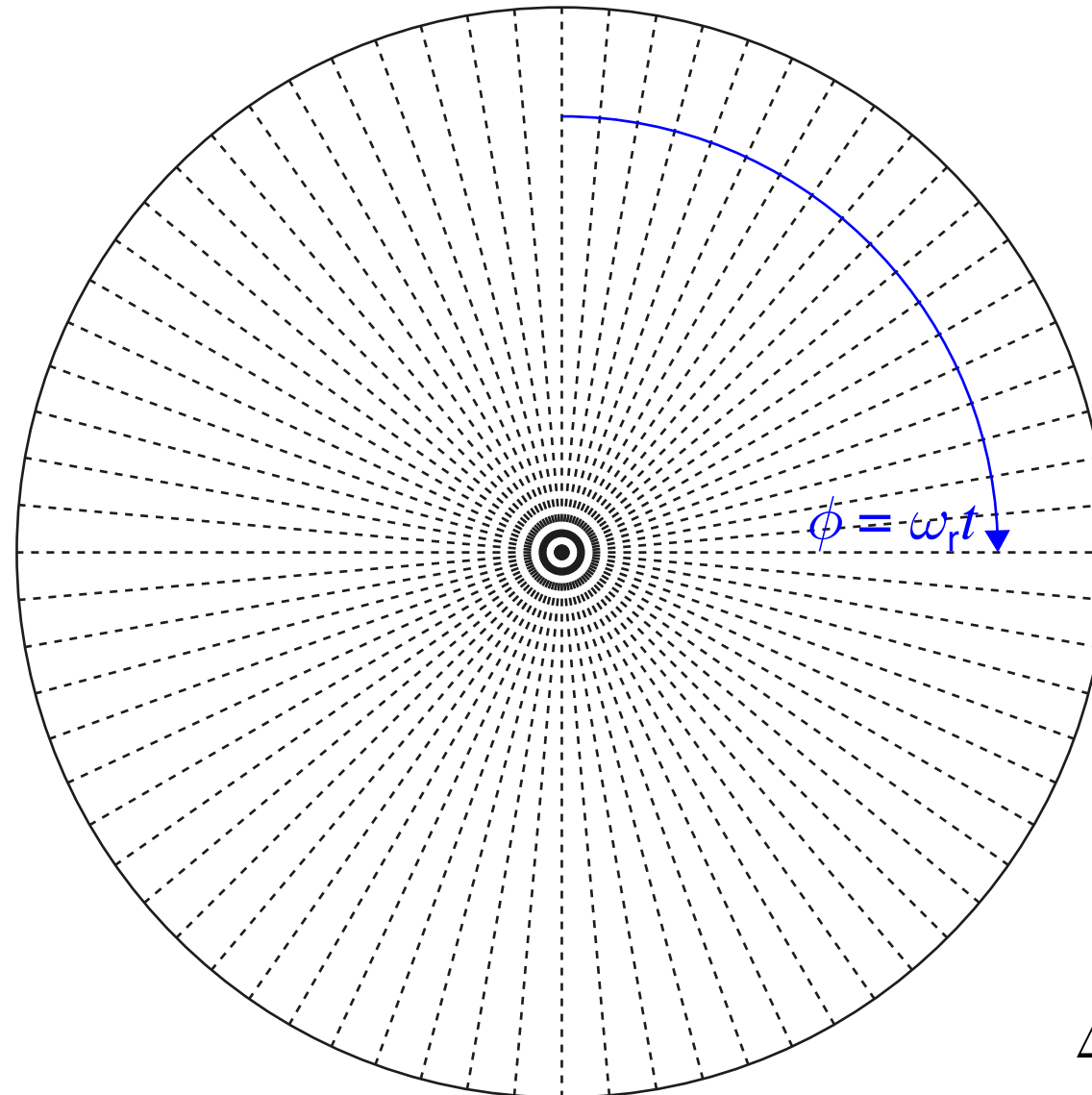


$$\Delta t = \tau_r / N = 2\pi / (\omega_r N)$$

Magic-Angle Spinning: Time Slicing



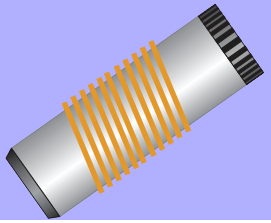
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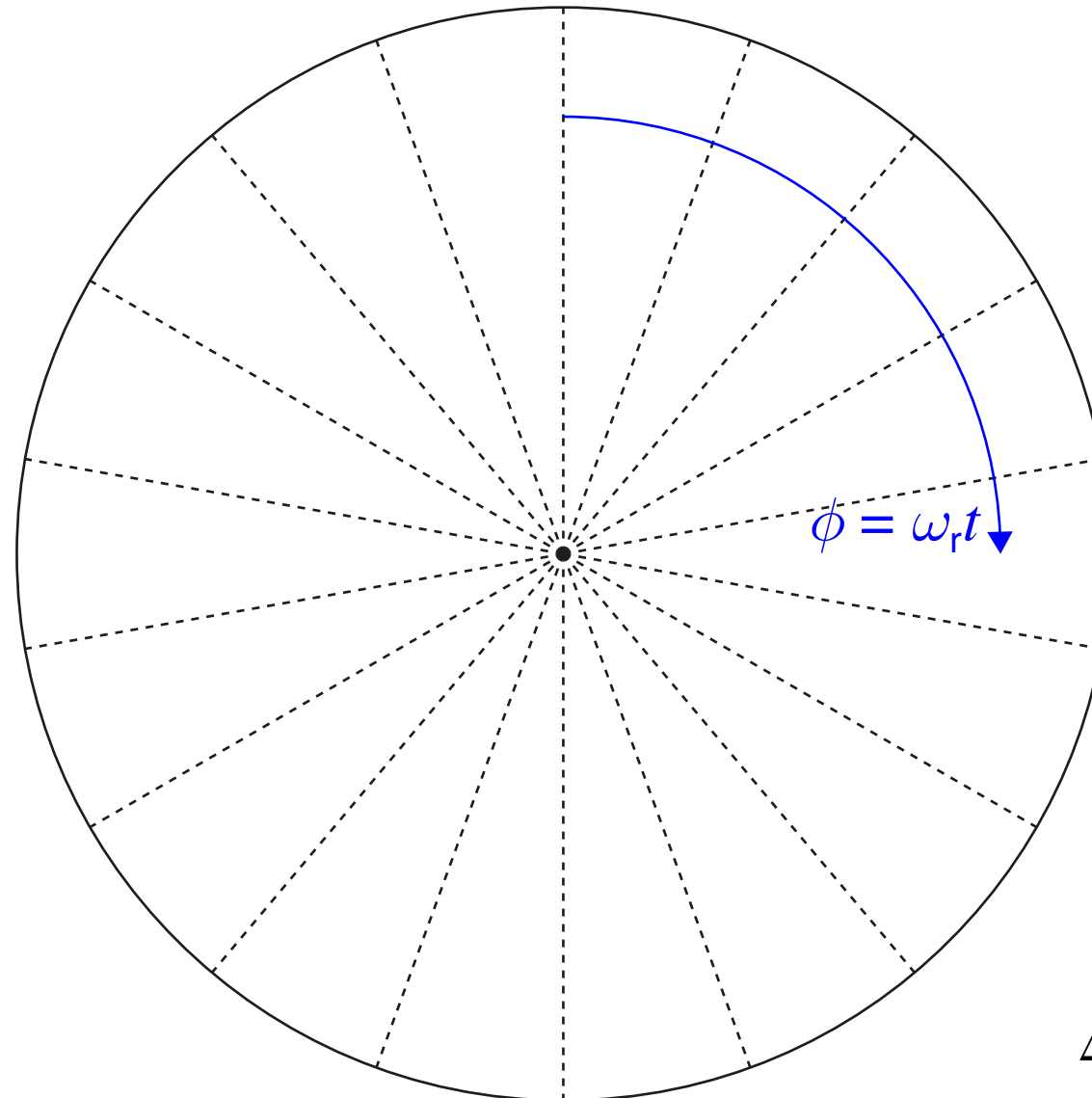
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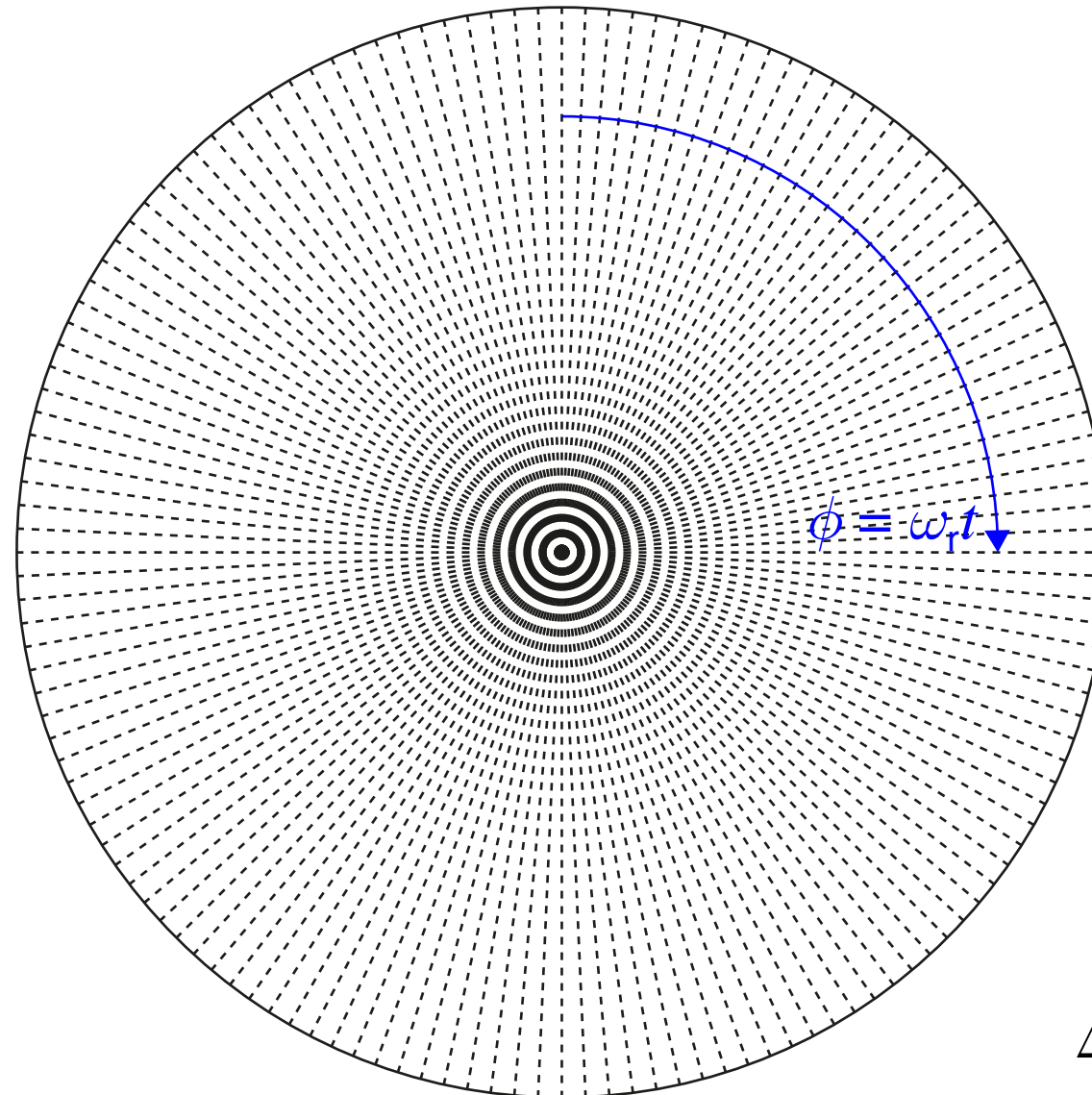
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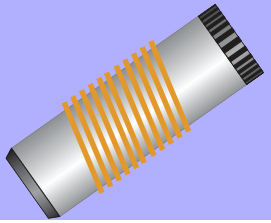
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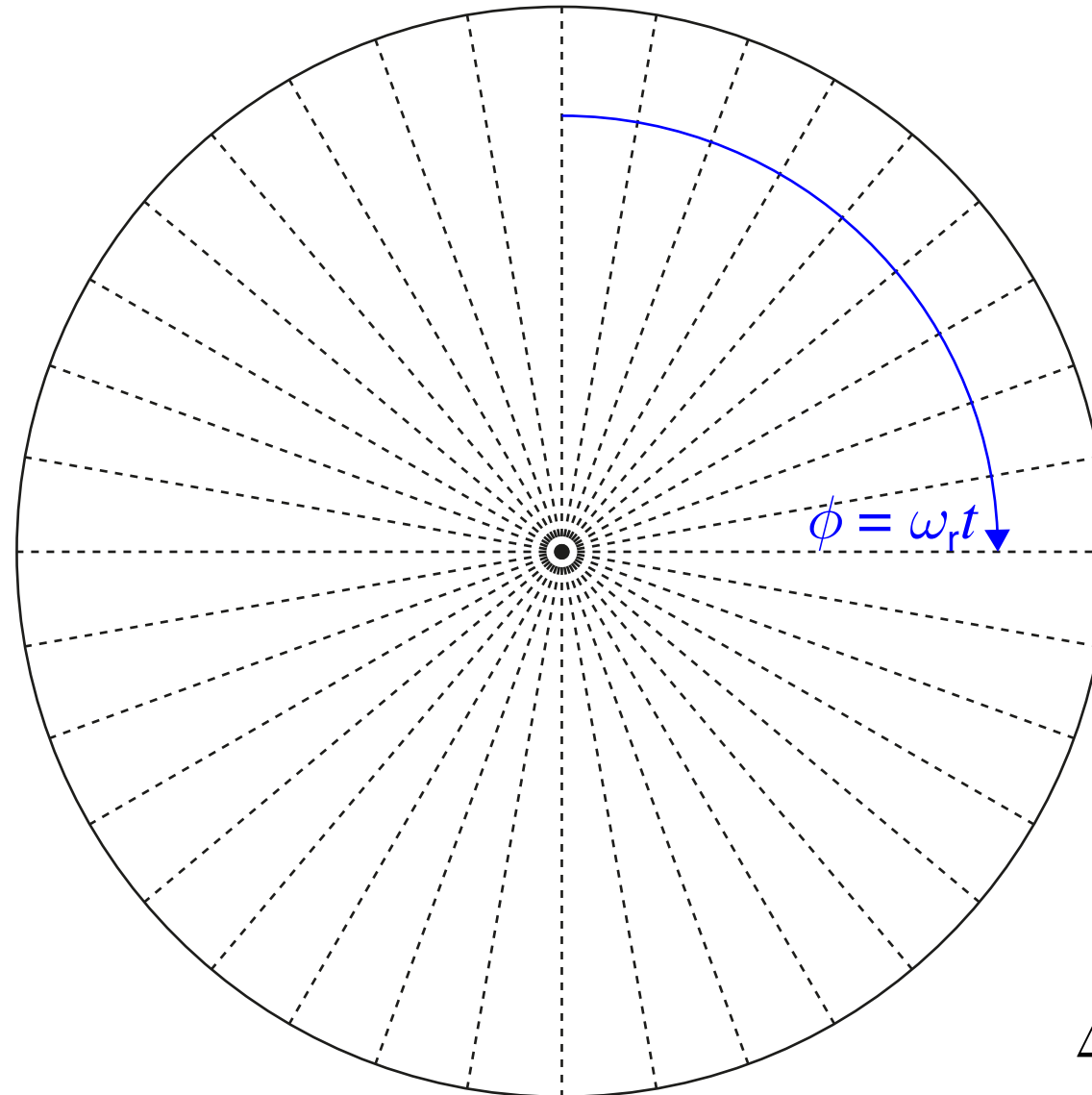
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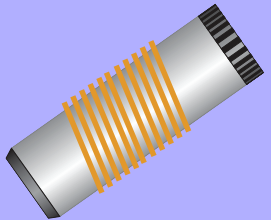
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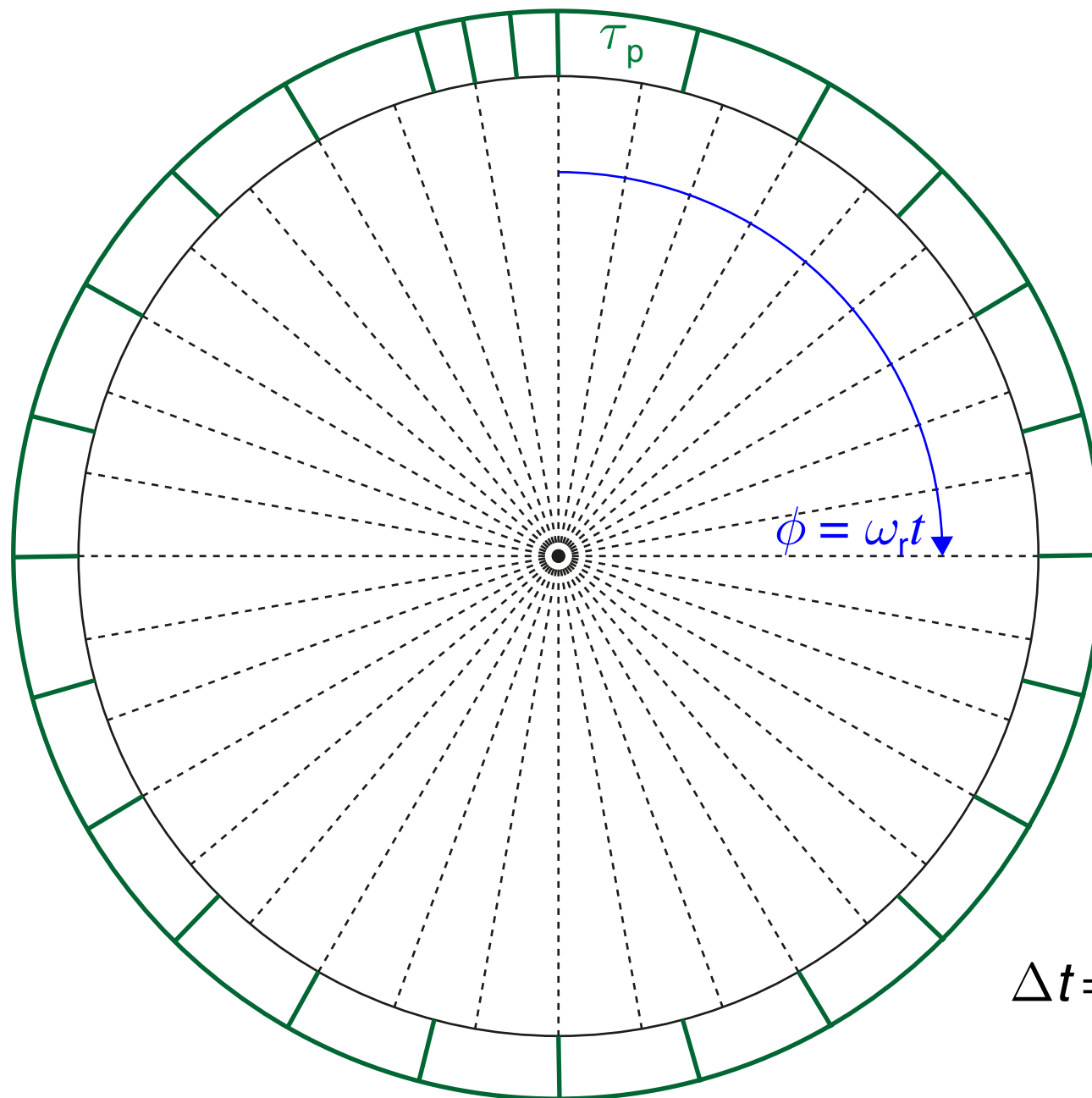
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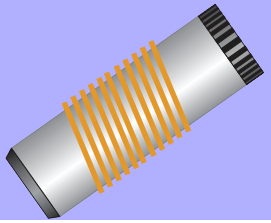
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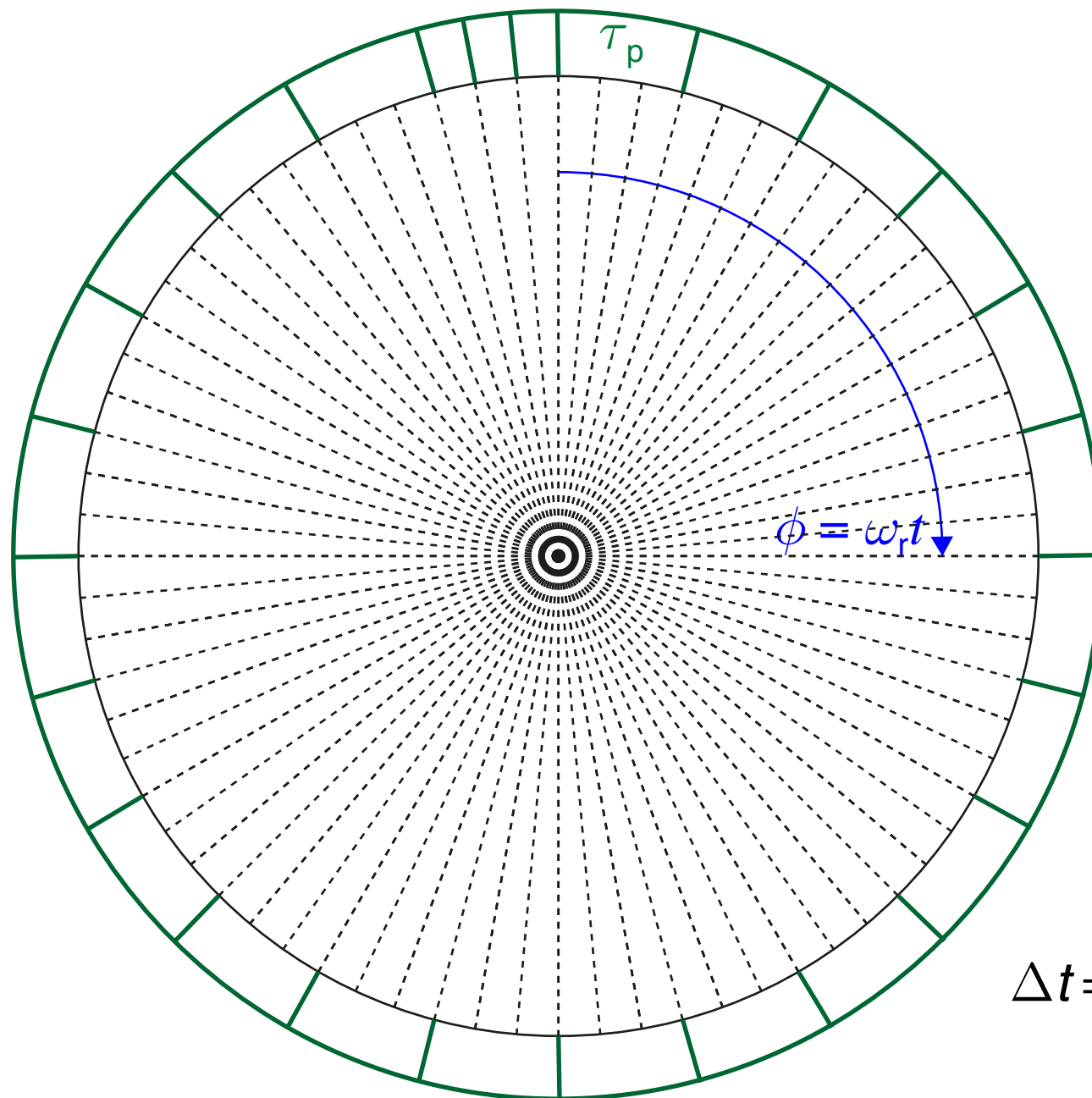
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Methods to Deal with Time-Dependent Hamiltonians $\hat{\mathcal{H}}(t)$

□ Average-Hamiltonian Theory (AHT):



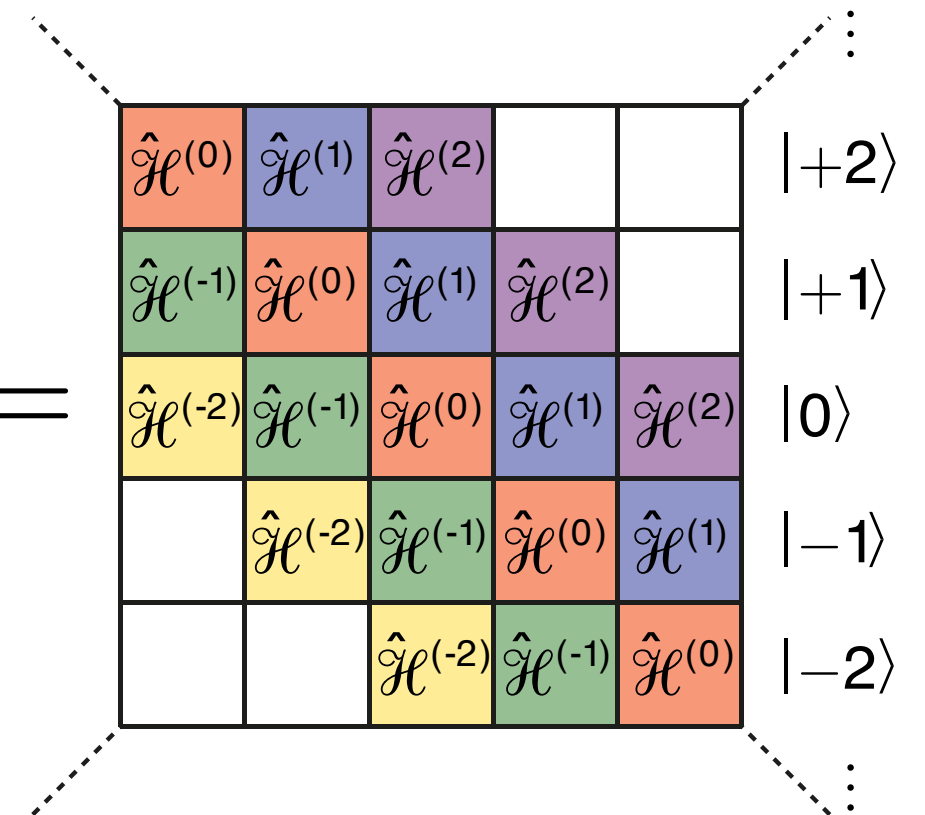
- Replace time-dependent Hamiltonian by a series expansion of a time-independent average Hamiltonian: $\hat{\bar{\mathcal{H}}} = \hat{\bar{\mathcal{H}}}^{(1)} + \hat{\bar{\mathcal{H}}}^{(2)} + \hat{\bar{\mathcal{H}}}^{(3)} + \dots$

□ Floquet Theory:

$$\begin{aligned} \hat{\mathcal{H}}(t) = & \dots + \hat{\mathcal{H}}^{(-2)} e^{-2i\omega_m t} \\ & + \hat{\mathcal{H}}^{(-1)} e^{-i\omega_m t} \\ & + \hat{\mathcal{H}}^{(0)} \\ & + \hat{\mathcal{H}}^{(1)} e^{i\omega_m t} \\ & + \hat{\mathcal{H}}^{(2)} e^{2i\omega_m t} + \dots \end{aligned}$$

Floquet

$$\hat{\mathcal{H}}_F =$$



- Map the finite-dimensional but time-dependent Hilbert-space Hamiltonian onto an infinite dimensional but time independent Floquet Hamiltonian.

AHT: Continuous Time Dependence

$$\hat{\mathcal{H}}(t)$$



- Continuous time dependence: Magnus expansion describes the calculation of different orders of the average Hamiltonian expansion.

$$\hat{\bar{\mathcal{H}}}^{(1)} = \frac{1}{\tau_c} \int_0^{\tau_c} \hat{\mathcal{H}}(t_1) dt_1$$

$$\hat{\bar{\mathcal{H}}}^{(2)} = \frac{-i}{2\tau_c} \int_0^{\tau_c} dt_2 \int_0^{t_2} dt_1 [\hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1)]$$

$$\hat{\bar{\mathcal{H}}}^{(3)} = \frac{-1}{6\tau_c} \int_0^{\tau_c} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \left([\hat{\mathcal{H}}(t_3), [\hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1)]] + [[\hat{\mathcal{H}}(t_3), \hat{\mathcal{H}}(t_2)], \hat{\mathcal{H}}(t_1)] \right)$$

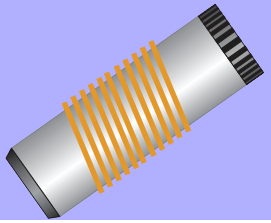
$$\hat{\bar{\mathcal{H}}}^{(4)} = \dots$$

- Magnus Expansion is also important in other fields of physics and there is a large mathematical literature about it.

Review: S. Blanes, F. Casas, J.A. Oteo, and J. Ros “The Magnus Expansion and some of its applications”, Physics Reports 470, 141-238 (2009).

- ❑ A time dependent Hamiltonian is **symmetric** if $\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}(\tau_c - t)$
 - All even orders of $\hat{\mathcal{H}}^{(n)}$ are zero and can be neglected: $\hat{\mathcal{H}}^{(2)} = \hat{\mathcal{H}}^{(4)} = \dots = 0$
 - This feature is often used in liquid-state NMR decoupling sequences to cancel the second-order average Hamiltonian term.
 - In solid-state NMR it is not often used, because the MAS rotation cannot be reversed.
- ❑ A time dependent Hamiltonian is **antisymmetric** if $\hat{\mathcal{H}}(t) = -\hat{\mathcal{H}}(\tau_c - t)$
 - All terms in the average Hamiltonian expansion are zero.
 - Not very useful unless one wants to eliminate the Hamiltonian.
- ❑ A time dependent Hamiltonian under MAS is called **inhomogeneous** if $[\hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1)] = 0$
 - All orders with $n > 1$ are zero since all commutator terms vanish.
 - The exact average Hamiltonian is given by $\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(1)}$.
 - Important in solid-state NMR to discuss the properties of Hamiltonians under MAS.

AHT Example: Magic-Angle Spinning - CSA



❑ MAS modulates the **spatial part** of the Hamiltonian:

$$\hat{\mathcal{H}}(t) = \mathbf{A}_{\ell,0}^{(i)}(t) \hat{\mathbf{T}}_{\ell,0}^{(i)} = \left(\sum_{m'=-\ell}^{\ell} e^{im'\omega_r t} d_{m',0}^{\ell}(-\theta_r) \mathbf{A}_{\ell,m'}^{(\text{rot})} \right) \hat{\mathbf{T}}_{\ell,0}^{(i)} = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t}$$

❑ Chemical-shift Hamiltonian: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t} = \hat{I}_{1z} \sum_{n=-2}^2 \omega_{\text{CS}}^{(n)} e^{in\omega_r t}$

❑ Apply average Hamiltonian expansion:

$$\hat{\mathcal{H}}^{(1)} = \frac{1}{\tau_r} \int_0^{\tau_r} \hat{\mathcal{H}}(t_1) dt_1 = \frac{\omega_r}{2\pi} \int_0^{2\pi/\omega_r} \left(\hat{I}_{1z} \sum_{n=-2}^2 \omega_{\text{CS}}^{(n)} e^{in\omega_r t} \right) dt_1 = \omega_{\text{CS}}^{(0)} \hat{I}_{1z} \quad \text{isotropic chemical shift}$$

$$\begin{aligned} \hat{\mathcal{H}}^{(2)} &= \frac{-i}{2\tau_r} \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 [\hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1)] = \frac{-i}{2\tau_r} \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 \left[\hat{I}_{1z} \sum_{n=-2}^2 \omega_{\text{CS}}^{(n)} e^{in\omega_r t_2}, \hat{I}_{1z} \sum_{n=-2}^2 \omega_{\text{CS}}^{(n)} e^{in\omega_r t_1} \right] \\ &= \frac{-i}{2\tau_r} [\hat{I}_{1z}, \hat{I}_{1z}] \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 \sum_{n=-2}^2 \omega_{\text{CS}}^{(n)} e^{in\omega_r t_2} \sum_{n=-2}^2 \omega_{\text{CS}}^{(n)} e^{in\omega_r t_1} = 0 \quad \text{Hamiltonian is inhomogeneous} \end{aligned}$$

❑ All higher orders of the average Hamiltonian expansion are zero because $[\hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1)] = 0$

❑ Spectrum consists of a single (infinitely) sharp line at the isotropic chemical-shift frequency.

❑ No spinning side bands can be observed because of stroboscopic detection with ω_r .

AHT Example: MAS - Dipolar Coupling



□ MAS modulates the **spatial part** of the Hamiltonian:

$$\hat{\mathcal{H}}(t) = \mathbf{A}_{\ell,0}^{(i)}(t) \hat{\mathbf{T}}_{\ell,0}^{(i)} = \left(\sum_{m'=-\ell}^{\ell} e^{im'\omega_r t} d_{m',0}^{\ell}(-\theta_r) \mathbf{A}_{\ell,m'}^{(\text{rot})} \right) \hat{\mathbf{T}}_{\ell,0}^{(i)} = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t}$$

□ Dipolar-coupling Hamiltonian: $\hat{\mathcal{H}}_D(t) = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t} = \left(3\hat{I}_{1z}\hat{I}_{2z} - \vec{I}_1 \cdot \vec{I}_2 \right) \sum_{n=-2}^2 \omega_D^{(n)} e^{in\omega_r t}$

□ Apply average Hamiltonian expansion:

$$\hat{\mathcal{H}}^{(1)} = \frac{1}{\tau_r} \int_0^{\tau_r} \hat{\mathcal{H}}_D(t_1) dt_1 = \frac{\omega_r}{2\pi} \int_0^{2\pi/\omega_r} \left(\left(3\hat{I}_{1z}\hat{I}_{2z} - \vec{I}_1 \cdot \vec{I}_2 \right) \sum_{n=-2}^2 \omega_D^{(n)} e^{in\omega_r t} \right) dt_1 = 0 \quad \text{no isotropic component}$$

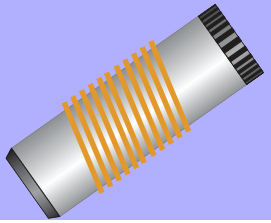
$$\begin{aligned} \hat{\mathcal{H}}^{(2)} &= \frac{-i}{2\tau_r} \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 [\hat{\mathcal{H}}_D(t_2), \hat{\mathcal{H}}_D(t_1)] \\ &= \frac{-i}{2\tau_r} \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 \left[\left(3\hat{I}_{1z}\hat{I}_{2z} - \vec{I}_1 \cdot \vec{I}_2 \right) \sum_{n=-2}^2 \omega_D^{(n)} e^{in\omega_r t_2}, \left(3\hat{I}_{1z}\hat{I}_{2z} - \vec{I}_1 \cdot \vec{I}_2 \right) \sum_{n=-2}^2 \omega_D^{(n)} e^{in\omega_r t_1} \right] \\ &= \frac{-i}{2\tau_r} \left[3\hat{I}_{1z}\hat{I}_{2z} - \vec{I}_1 \cdot \vec{I}_2, 3\hat{I}_{1z}\hat{I}_{2z} - \vec{I}_1 \cdot \vec{I}_2 \right] \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 \sum_{n=-2}^2 \omega_D^{(n)} e^{in\omega_r t_2} \sum_{n=-2}^2 \omega_D^{(n)} e^{in\omega_r t_1} = 0 \end{aligned}$$

Hamiltonian is
inhomogeneous

□ All higher orders of the average Hamiltonian expansion are zero because $[\hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1)] = 0$

□ The total average Hamiltonian under MAS is zero.

AHT Example: MAS - CSA and Dipolar Coupling



❑ MAS modulates the **spatial part** of the Hamiltonian:

$$\hat{\mathcal{H}}(t) = \mathbf{A}_{\ell,0}^{(i)}(t) \hat{\mathbf{T}}_{\ell,0}^{(i)} = \left(\sum_{m'=-\ell}^{\ell} e^{im'\omega_r t} d_{m',0}^{\ell}(-\theta_r) \mathbf{A}_{\ell,m'}^{(\text{rot})} \right) \hat{\mathbf{T}}_{\ell,0}^{(i)} = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t}$$

❑ CS and D Hamiltonian: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t} = \left(3\hat{I}_{1z}\hat{I}_{2z} - \vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2 \right) \sum_{n=-2}^2 \omega_D^{(n)} e^{in\omega_r t} + \hat{I}_{1z} \sum_{n=-2}^2 \omega_{\text{CS}}^{(n)} e^{in\omega_r t}$

❑ Apply average Hamiltonian expansion:

$$\hat{\mathcal{H}}^{(1)} = \frac{1}{\tau_r} \int_0^{\tau_r} \left(\hat{\mathcal{H}}_D(t_1) + \hat{\mathcal{H}}_{\text{CS}}(t_1) \right) dt_1 = \omega_{\text{CS}}^{(0)} \hat{I}_{1z} \quad \text{only isotropic chemical shift}$$

$$\begin{aligned} \hat{\mathcal{H}}^{(2)} &= \frac{-i}{2\tau_r} \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 \left[\hat{\mathcal{H}}_D(t_2) + \hat{\mathcal{H}}_{\text{CS}}(t_2), \hat{\mathcal{H}}_D(t_1) + \hat{\mathcal{H}}_{\text{CS}}(t_1) \right] = \frac{-i}{2\tau_r} \left[3\hat{I}_{1z}\hat{I}_{2z} - \vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2, \hat{I}_{1z} \right] \\ &\times \left\{ \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 \sum_{n=-2}^2 \omega_D^{(n)} e^{in\omega_r t_2} \sum_{m=-2}^2 \omega_{\text{CS}}^{(m)} e^{im\omega_r t_1} - \int_0^{\tau_r} dt_2 \int_0^{t_2} dt_1 \sum_{n=-2}^2 \omega_{\text{CS}}^{(n)} e^{in\omega_r t_2} \sum_{m=-2}^2 \omega_D^{(m)} e^{im\omega_r t_1} \right\} \neq 0 \end{aligned}$$

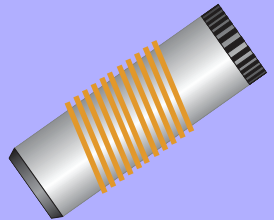
Hamiltonian is **homogeneous**

❑ All higher orders of the average Hamiltonian are in general non zero: $[\hat{\mathcal{H}}_D(t_2), \hat{\mathcal{H}}_{\text{CS}}(t_1)] \neq 0$

❑ Spectrum consists of a broad line due to higher-order average Hamiltonian contributions.

❑ No spinning side bands can be observed because of stroboscopic detection with ω_r .

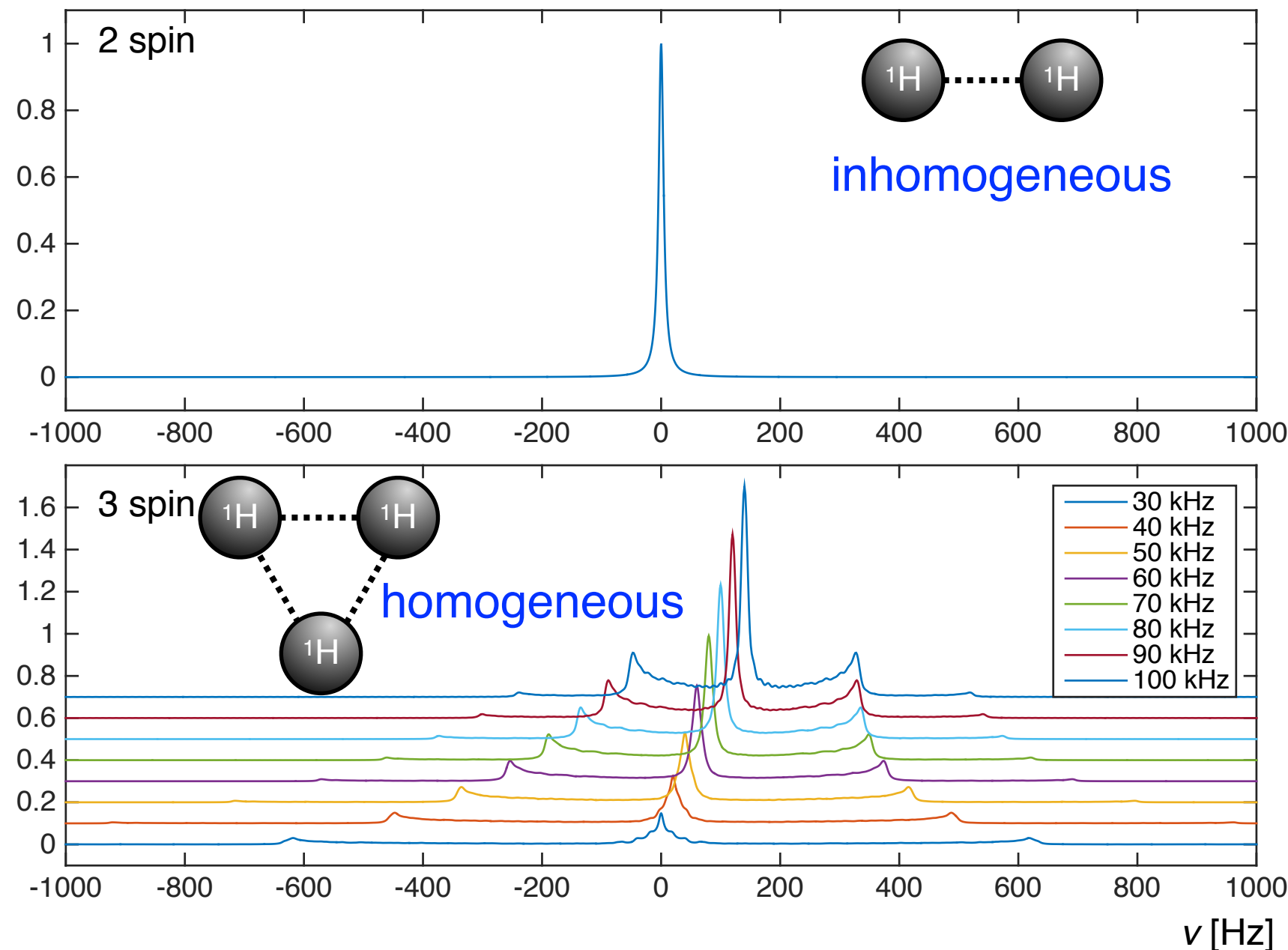
Homogeneous and Inhomogeneous Hamiltonians



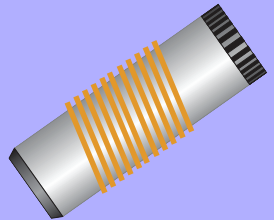
- Under MAS a Hamiltonian is called **inhomogeneous** if the Hamiltonian commutes with itself at all times: $[\hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1)] = 0$
- Under MAS a Hamiltonian is called **homogeneous** if the Hamiltonian does not commute with itself at all times: $[\hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1)] \neq 0$

- Inhomogeneous** Hamiltonians (e.g., a single interactions, multiple chemical shifts, multiple heteronuclear couplings) give rise to spectra with infinitely sharp lines.

- Homogeneous** Hamiltonians (e.g., one homonuclear dipolar coupling and one other interaction) give rise to spectra with broad lines due to higher-order AHT terms.



AHT and Multiple Time Dependencies



□ We have often multiple (incommensurate) basic frequencies:

- Heteronuclear decoupling under MAS (CW, TPPM, XiX, ...)
- Homonuclear decoupling under MAS: Lee-Goldburg irradiation
- Decoupling during recoupling sequences under MAS
- Double rotation for quadrupolar nuclei

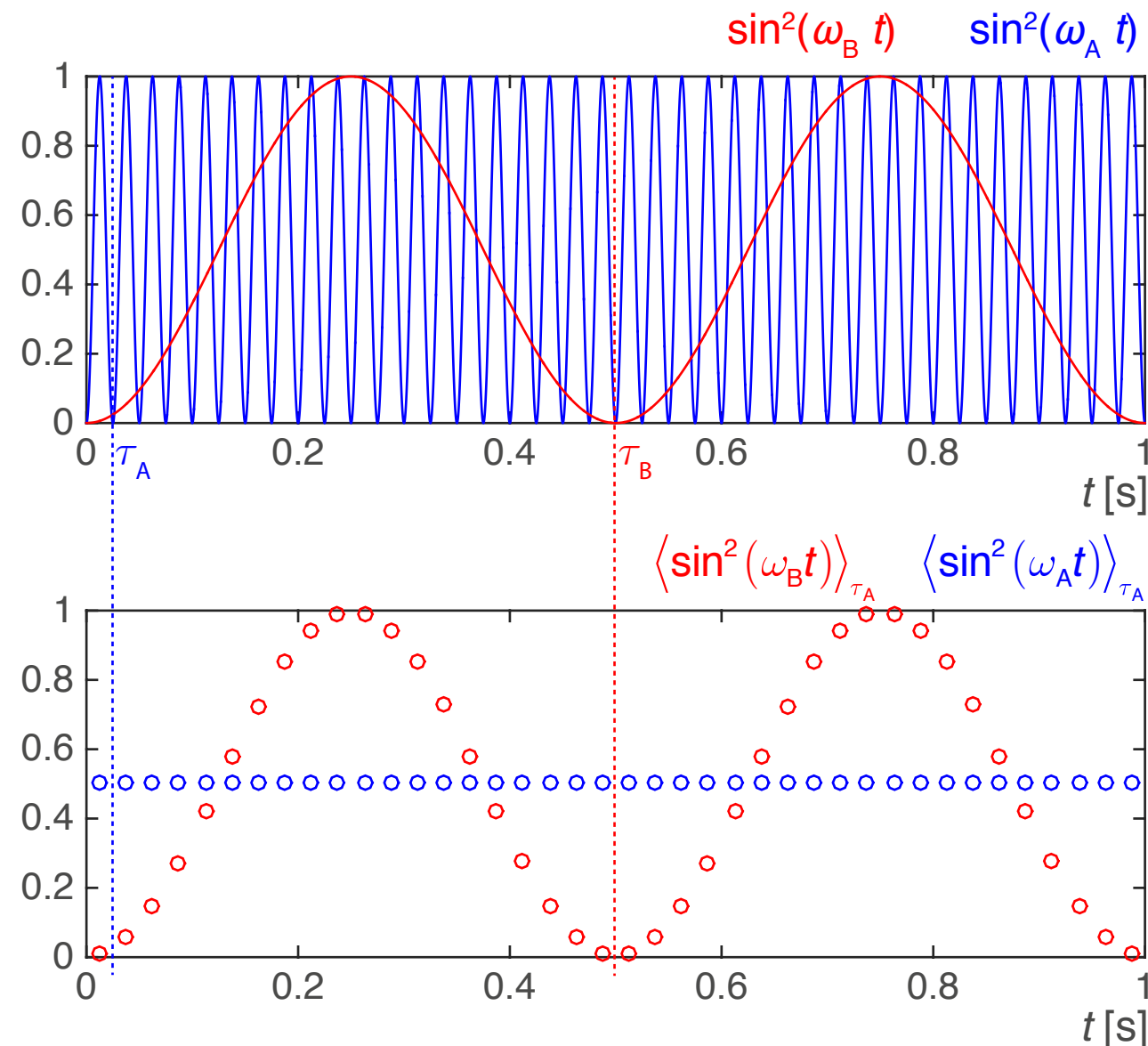
□ Use time-scale separation:

assume $\omega_A \gg \omega_B$ and $\tau_A \ll \tau_B$:

- Averaging over the short cycle time τ_A will not affect the slow oscillation significantly.
- We can then average over the long cycle time τ_B in a second step.

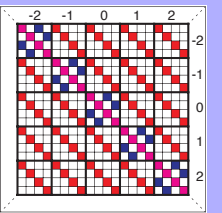
□ Use synchronization conditions: $n_A \omega_A = n_B \omega_B$

- Use cycle time $\tau_c = 2\pi/(n_A \omega_A)$ that averages both frequencies.



- ❑ Not applicable to Hamiltonians with multiple basic frequencies. No single cycle time can be defined if the two frequencies are incommensurate:
 - MAS and rf irradiation must be synchronized or time-scale separated.
 - Multiple rf irradiations must be synchronized or time-scale separated.
- ❑ Only stroboscopic observation is allowed after a full cycle time. Nyquist frequency equals the basic frequency while side bands appear at integer multiples of the basic frequency.
 - Sidebands in MAS spectra cannot be described and are folded back onto the center band.
 - Sidebands in rf-irradiation schemes are neglected and folded back onto the center band.
- ❑ Convergence of the series expansion of the Hamiltonian can be a problem. Usually the basic frequency has to be larger than the transition frequencies in the Hamiltonian.
 - This is one of the reasons why we use interaction-frame transformations to eliminate large terms in the Hamiltonian.
 - The convergence of the AHT series (Magnus expansion) is not yet fully understood.

Floquet Theory



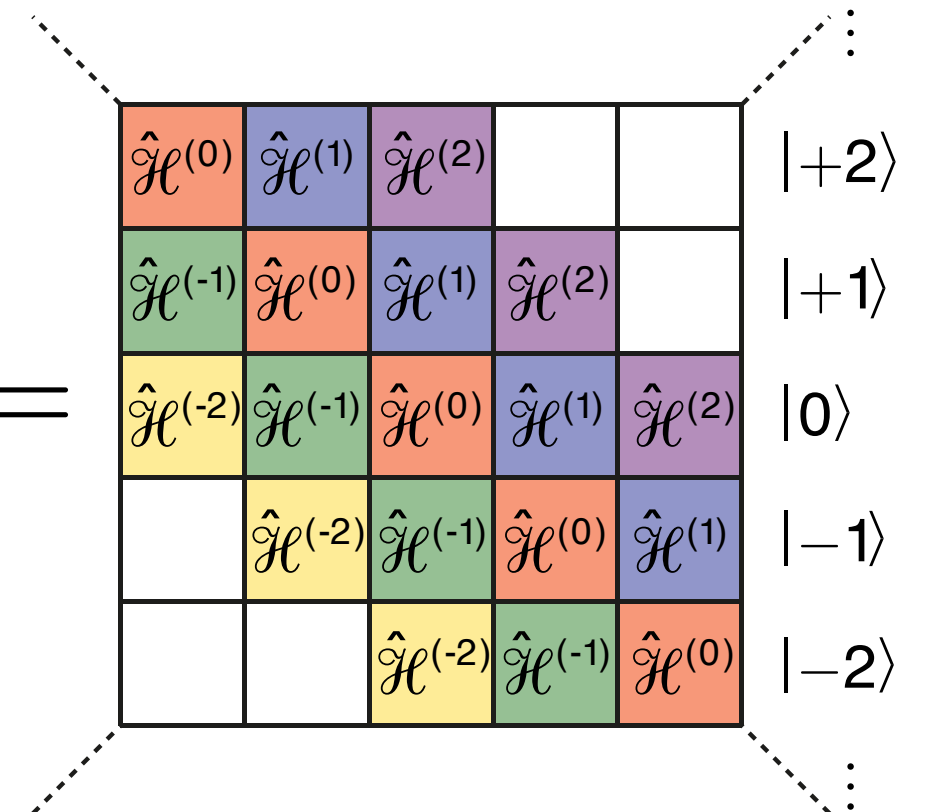
- Floquet theory maps the *time-dependent finite-dimensional* Hilbert (or Liouville) space onto an *time-independent infinite-dimensional* Floquet space.

$$\hat{\mathcal{H}}(t) = \dots$$

$$\begin{aligned}
 &+ \hat{\mathcal{H}}^{(-2)} e^{-2i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(-1)} e^{-i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(0)} \\
 &+ \hat{\mathcal{H}}^{(1)} e^{i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(2)} e^{2i\omega_m t} \\
 &+ \dots
 \end{aligned}$$

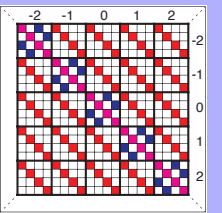
$$\xleftrightarrow{T_{\omega,t}}$$

$$\hat{\mathcal{H}}_F =$$

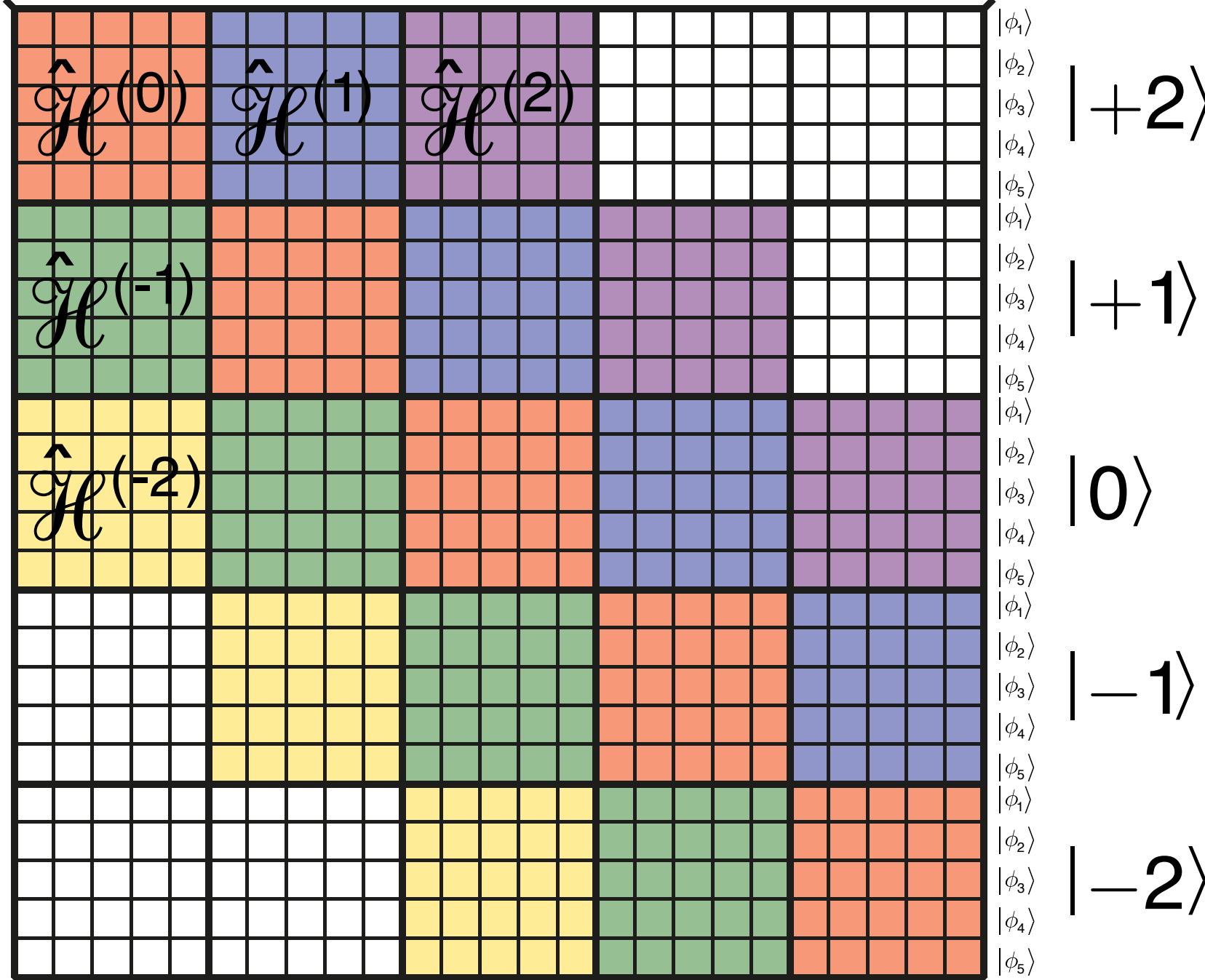


- $T_{\omega,t}$ is a homomorphism: mapping (projection) from Floquet space to Hilbert space is unique but mapping from Hilbert space to Floquet space is not.
- Floquet description needs an additional Fourier space to describe the “quantization” of the motional process.
- Floquet theory is an exact method and does not imply any assumptions or approximations.

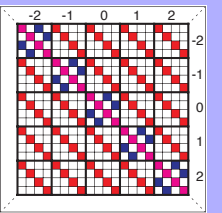
The Floquet Space



- Floquet theory tells us how to build the matrix representation of the Floquet operators from the time-dependent Fourier coefficients.
- This can be formally written as a direct product of the spin-Hilbert space with the basis $\{|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_N\rangle\}$ and a Fourier space with the basis $\{|-\infty\rangle, \dots, |-1\rangle, |0\rangle, |1\rangle, \dots, |\infty\rangle\}$ that describes the time-dependent process.
- Can we define operators on this space?



Operator-Based Floquet Theory



$$\hat{\mathcal{H}}(t) = \dots$$

$$\begin{aligned}
 &+ \hat{\mathcal{H}}^{(-2)} e^{-2i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(-1)} e^{-i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(0)} \\
 &+ \hat{\mathcal{H}}^{(1)} e^{i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(2)} e^{2i\omega_m t} \\
 &+ \dots
 \end{aligned}$$

Construction of
Floquet Hamiltonian

$$\hat{\mathcal{H}}_F =$$

$\hat{\mathcal{H}}^{(0)}$	$\hat{\mathcal{H}}^{(1)}$	$\hat{\mathcal{H}}^{(2)}$			$ +2\rangle$
$\hat{\mathcal{H}}^{(-1)}$	$\hat{\mathcal{H}}^{(0)}$	$\hat{\mathcal{H}}^{(1)}$	$\hat{\mathcal{H}}^{(2)}$		$ +1\rangle$
$\hat{\mathcal{H}}^{(-2)}$	$\hat{\mathcal{H}}^{(-1)}$	$\hat{\mathcal{H}}^{(0)}$	$\hat{\mathcal{H}}^{(1)}$	$\hat{\mathcal{H}}^{(2)}$	$ 0\rangle$
	$\hat{\mathcal{H}}^{(-2)}$	$\hat{\mathcal{H}}^{(-1)}$	$\hat{\mathcal{H}}^{(0)}$	$\hat{\mathcal{H}}^{(1)}$	$ -1\rangle$
		$\hat{\mathcal{H}}^{(-2)}$	$\hat{\mathcal{H}}^{(-1)}$	$\hat{\mathcal{H}}^{(0)}$	$ -2\rangle$

Block diagonalization
using van Vleck method

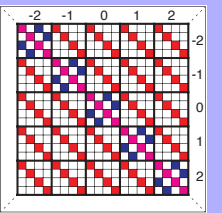
$$\hat{\Lambda}_F =$$

$\hat{\mathcal{H}}$					$ +2\rangle$
	$\hat{\mathcal{H}}$				$ +1\rangle$
		$\hat{\mathcal{H}}$			$ 0\rangle$
			$\hat{\mathcal{H}}$		$ -1\rangle$
				$\hat{\mathcal{H}}$	$ -2\rangle$

Projection back
into Hilbert space

$$\begin{aligned}
 \hat{\mathcal{H}} &= \hat{\mathcal{H}}^{(1)} + \\
 &\hat{\mathcal{H}}^{(2)} + \\
 &\hat{\mathcal{H}}^{(3)} + \dots
 \end{aligned}$$

Operator-Based Floquet Theory



$$\hat{\mathcal{H}}(t) = \dots$$

$$\begin{aligned}
 &+ \hat{\mathcal{H}}^{(-2)} e^{-2i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(-1)} e^{-i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(0)} \\
 &+ \hat{\mathcal{H}}^{(1)} e^{i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(2)} e^{2i\omega_m t} \\
 &+ \dots
 \end{aligned}$$

Effective Hamiltonians

$$\begin{aligned}
 \hat{\mathcal{H}} = & \hat{\mathcal{H}}^{(1)} + \\
 & \hat{\mathcal{H}}^{(2)} + \\
 & \hat{\mathcal{H}}^{(3)} + \dots
 \end{aligned}$$

Construction of
Floquet Hamiltonian

$$\hat{\mathcal{H}}_F =$$

$\hat{\mathcal{H}}^{(0)}$	$\hat{\mathcal{H}}^{(1)}$	$\hat{\mathcal{H}}^{(2)}$			$ +2\rangle$
$\hat{\mathcal{H}}^{(-1)}$	$\hat{\mathcal{H}}^{(0)}$	$\hat{\mathcal{H}}^{(1)}$	$\hat{\mathcal{H}}^{(2)}$		$ +1\rangle$
$\hat{\mathcal{H}}^{(-2)}$	$\hat{\mathcal{H}}^{(-1)}$	$\hat{\mathcal{H}}^{(0)}$	$\hat{\mathcal{H}}^{(1)}$	$\hat{\mathcal{H}}^{(2)}$	$ 0\rangle$
	$\hat{\mathcal{H}}^{(-2)}$	$\hat{\mathcal{H}}^{(-1)}$	$\hat{\mathcal{H}}^{(0)}$	$\hat{\mathcal{H}}^{(1)}$	$ -1\rangle$
		$\hat{\mathcal{H}}^{(-2)}$	$\hat{\mathcal{H}}^{(-1)}$	$\hat{\mathcal{H}}^{(0)}$	$ -2\rangle$

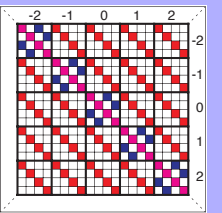
Block diagonalization
using van Vleck method

$$\hat{\Lambda}_F =$$

$\hat{\mathcal{H}}$					$ +2\rangle$
	$\hat{\mathcal{H}}$				$ +1\rangle$
		$\hat{\mathcal{H}}$			$ 0\rangle$
			$\hat{\mathcal{H}}$		$ -1\rangle$
				$\hat{\mathcal{H}}$	$ -2\rangle$

Projection back
into Hilbert space

Operator-Based Floquet Theory



$$\hat{\mathcal{H}}(t) = \dots$$

$$\begin{aligned}
 &+ \hat{\mathcal{H}}^{(-2)} e^{-2i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(-1)} e^{-i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(0)} \\
 &+ \hat{\mathcal{H}}^{(1)} e^{i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(2)} e^{2i\omega_m t} \\
 &+ \dots
 \end{aligned}$$

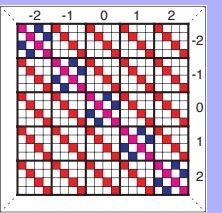
- Calculation is independent of the detailed structure of the spin-Hilbert space blocks.
- We can do the perturbation treatment once and calculate the effective Hamiltonians for arbitrary problems.
- We only need to know the Fourier series of the Hamiltonian.

Effective Hamiltonians



$$\begin{aligned}
 \hat{\mathcal{H}} = &\hat{\mathcal{H}}^{(1)} + \\
 &\hat{\mathcal{H}}^{(2)} + \\
 &\hat{\mathcal{H}}^{(3)} + \dots
 \end{aligned}$$

Operator-Based Floquet Theory



$$\hat{\mathcal{H}}(t) = \dots$$

$$\begin{aligned}
 &+ \hat{\mathcal{H}}^{(-2)} e^{-2i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(-1)} e^{-i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(0)} \\
 &+ \hat{\mathcal{H}}^{(1)} e^{i\omega_m t} \\
 &+ \hat{\mathcal{H}}^{(2)} e^{2i\omega_m t} \\
 &+ \dots
 \end{aligned}$$

Effective Hamiltonians



$$\begin{aligned}
 \hat{\mathcal{H}} &= \hat{\mathcal{H}}^{(1)} + \\
 &\hat{\mathcal{H}}^{(2)} + \\
 &\hat{\mathcal{H}}^{(3)} + \dots
 \end{aligned}$$

- Calculation is independent of the detailed structure of the spin-Hilbert space blocks.
- We can do the perturbation treatment once and calculate the effective Hamiltonians for arbitrary problems.
- We only need to know the Fourier series of the Hamiltonian.

$$\hat{\mathcal{H}}(t) = \sum_{n=-\infty}^{\infty} \hat{\mathcal{H}}^{(n)} e^{in\omega_m t}$$

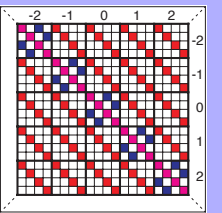
$$\hat{\mathcal{H}}(t) = \sum_{n=-\infty}^{\infty} \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_m t}$$

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(1)} + \hat{\mathcal{H}}^{(2)} + \dots = \hat{\mathcal{H}}^{(0)} - \frac{1}{2} \sum_{n \neq 0} \frac{[\hat{\mathcal{H}}^{(n)}, \hat{\mathcal{H}}^{(-n)}]}{n\omega_m} + \dots$$

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(1)} + \hat{\mathcal{H}}^{(2)} + \dots = \sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} - \frac{1}{2} \sum_{n_0, k_0} \sum_{\nu, \kappa} \frac{[\hat{\mathcal{H}}^{(n_0 - \nu, k_0 - \kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)}]}{\nu\omega_r + \kappa\omega_m} + \dots$$

$$n_0\omega_r + k_0\omega_m = 0 \quad \nu\omega_r + \kappa\omega_m \neq 0$$

Effective Hamiltonians from Floquet Theory



□ We can calculate effective Hamiltonians for Hamiltonians with multiple time dependencies in a way very similar to AHT.

□ Appearance of *resonance conditions* for more than one frequency:

single frequency:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} - \frac{1}{2} \sum_{n \neq 0} \frac{[\hat{\mathcal{H}}^{(-n)}, \hat{\mathcal{H}}^{(n)}]}{n\omega_m} + \dots$$

two frequencies:

$$\hat{\mathcal{H}} = \sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} - \frac{1}{2} \sum_{n_0, k_0} \sum_{\nu, \kappa} \frac{[\hat{\mathcal{H}}^{(n_0 - \nu, k_0 - \kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)}]}{\nu\omega_r + \kappa\omega_m} + \dots$$

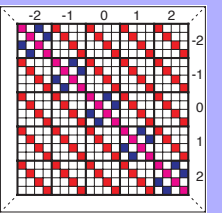
resonance conditions $n_0\omega_r + k_0\omega_m = 0$

□ With multiple frequencies we have *resonant* and *non-resonant* contributions to the effective Hamiltonian in different orders:

$$\bar{\mathcal{H}} \approx \underbrace{\hat{\mathcal{H}}^{(0,0)} + \hat{\mathcal{H}}_{(2)}^{(0,0)} + \dots}_{\text{non-resonant: } n_0 = k_0 = 0} + \underbrace{\sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} + \sum_{n_0, k_0} \hat{\mathcal{H}}_{(2)}^{(n_0, k_0)} + \dots}_{\text{resonant: } n_0\omega_r + k_0\omega_m = 0}$$

$$\hat{\mathcal{H}}_{(2)}^{(n_0, k_0)} = -\frac{1}{2} \sum_{\nu, \kappa} \frac{[\hat{\mathcal{H}}^{(n_0 - \nu, k_0 - \kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)}]}{\nu\omega_r + \kappa\omega_m}$$

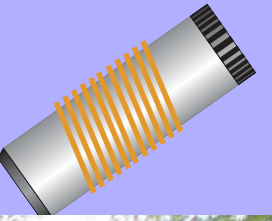
□ At these resonance conditions, certain Fourier coefficients of the time-dependent interaction-frame Hamiltonian are time independent.



(Dis-)Advantages of Operator-Based Floquet Theory

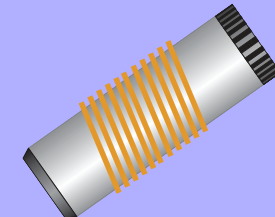
- ❑ Can easily be expanded to multiple incommensurate frequencies.
- ❑ Expressions are independent of the detailed structure of the spin-Hilbert-space Hamiltonian.
- ❑ Leads to an effective Hamiltonian that can be written as an analytical operator expression.
- ❑ Can be used to treat systems with many spins as long as the commutators can be calculated.
- ❑ Projection back into Hilbert space eliminates the side bands at integer multiples of the Fourier frequencies. What is the cycle time in multi-mode Floquet theory?
- ❑ Resonance conditions that involve simultaneous transitions in Fourier space and spin space can not be treated.

Building Blocks in Solid-State NMR

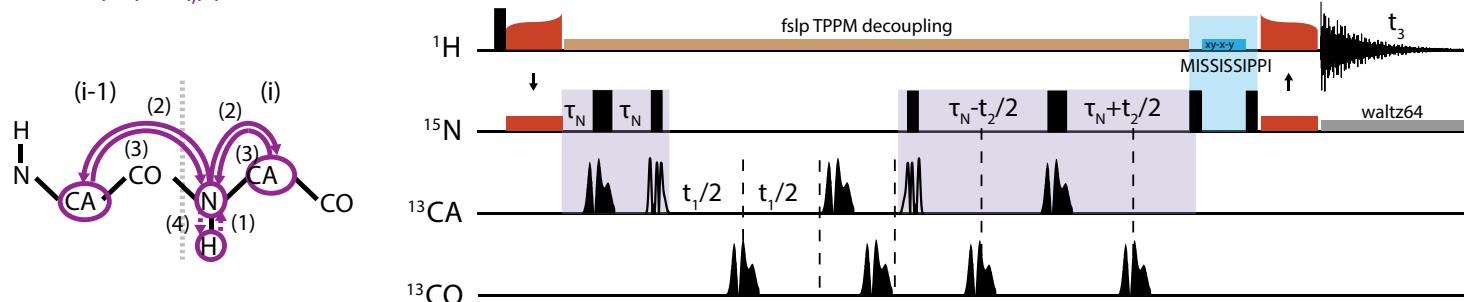


Undavalli, 2022

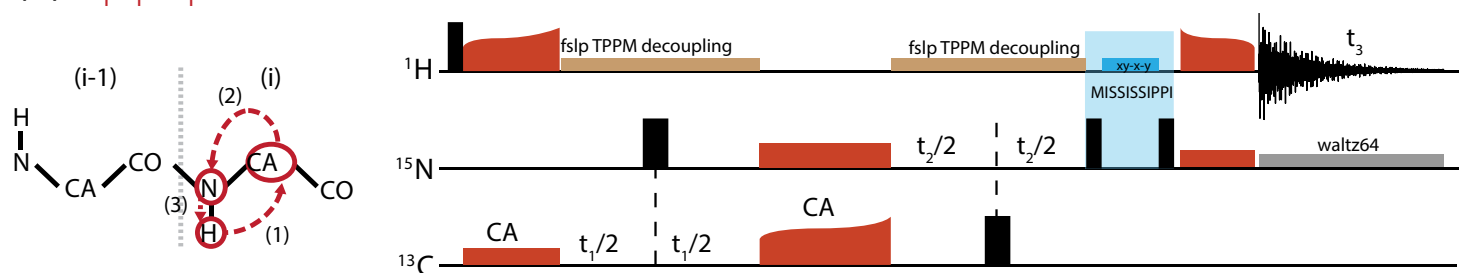
Important Building Blocks in MAS NMR



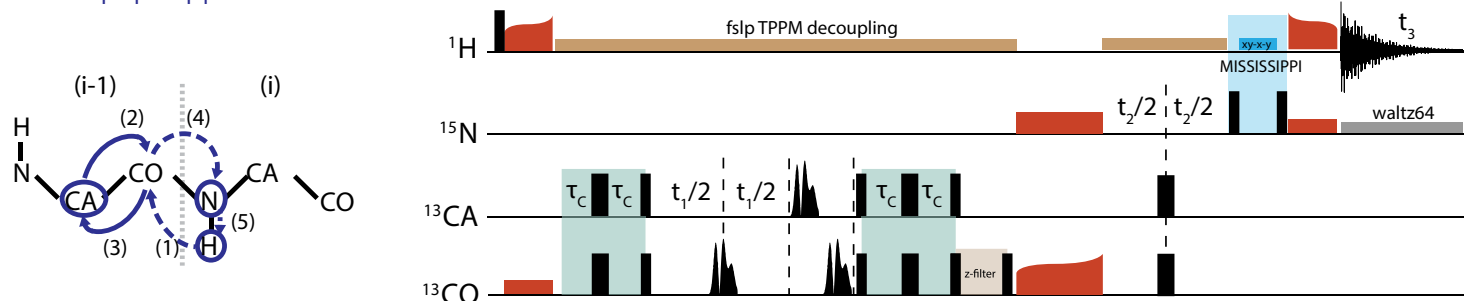
(a) $H_i N_i C\alpha_{i,i-1}$ correlation: (HN)CANH



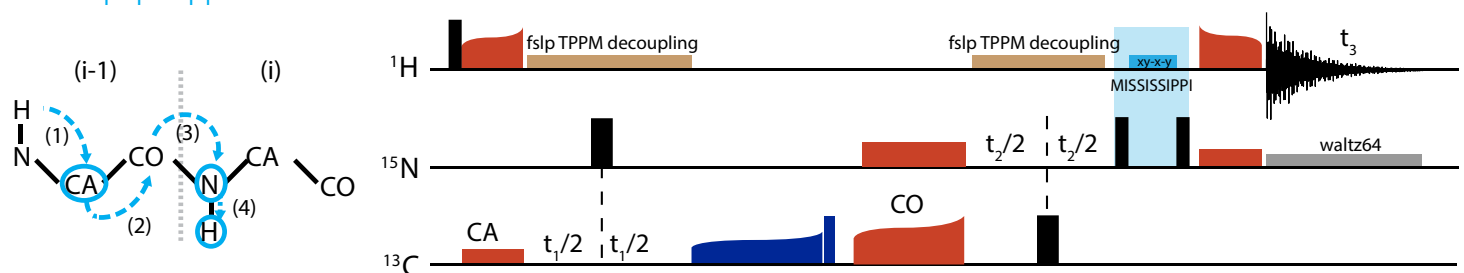
(b) $H_i N_i C\alpha_i$ correlation: (H)CANH



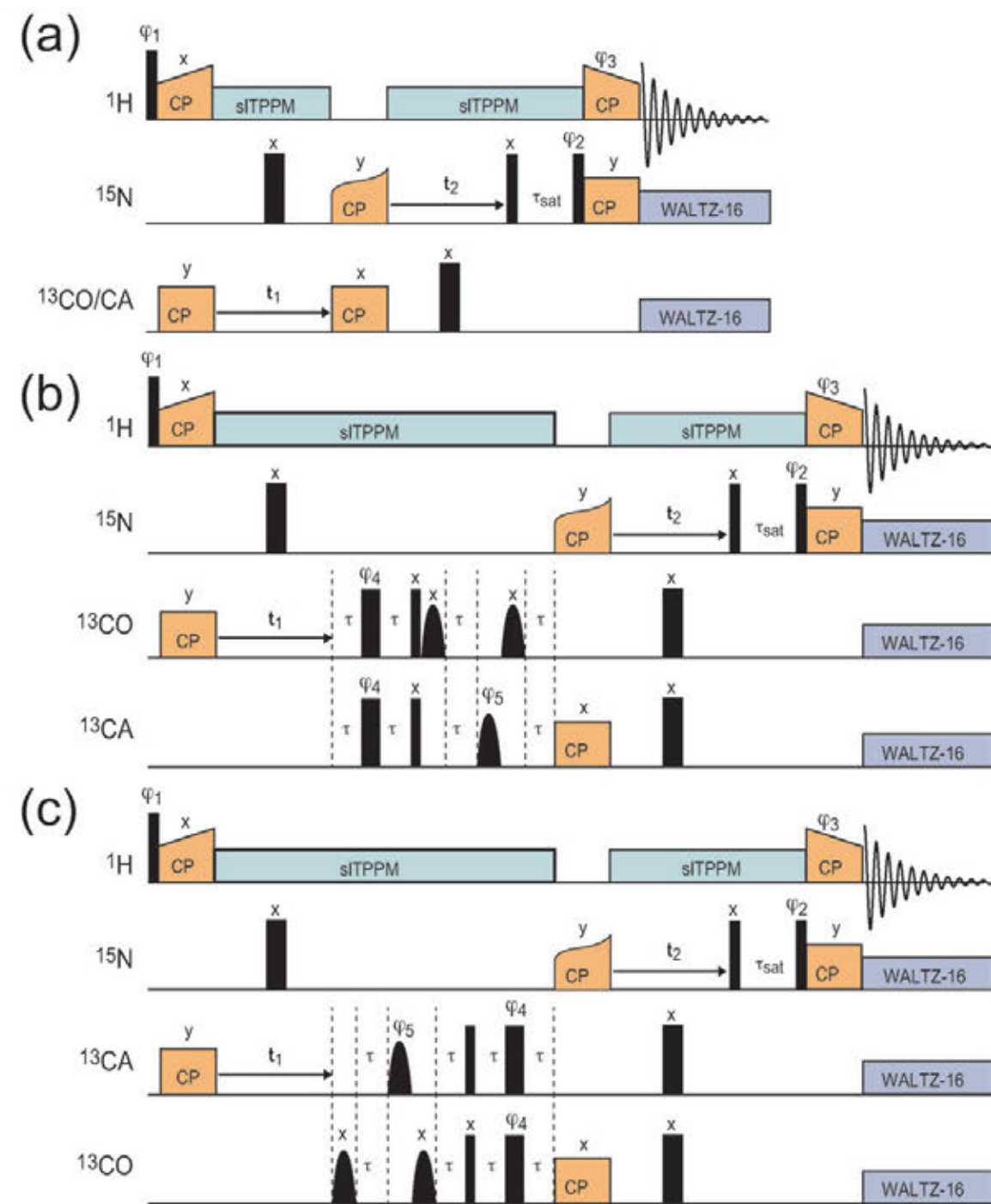
(c) $H_i N_i C\alpha_{i-1}$ correlation: (HCO)CA(CO)NH



(d) $H_i N_i C\alpha_i$ correlation: (H)CA(CO)NH



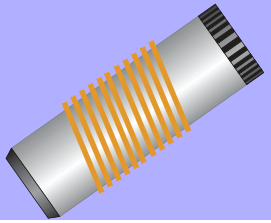
S. Penzel, ... , B.H. Meier, J. Biomol. NMR. 63 (2015) 165–186.
<https://doi.org/10.1007/s10858-015-9975-y>.



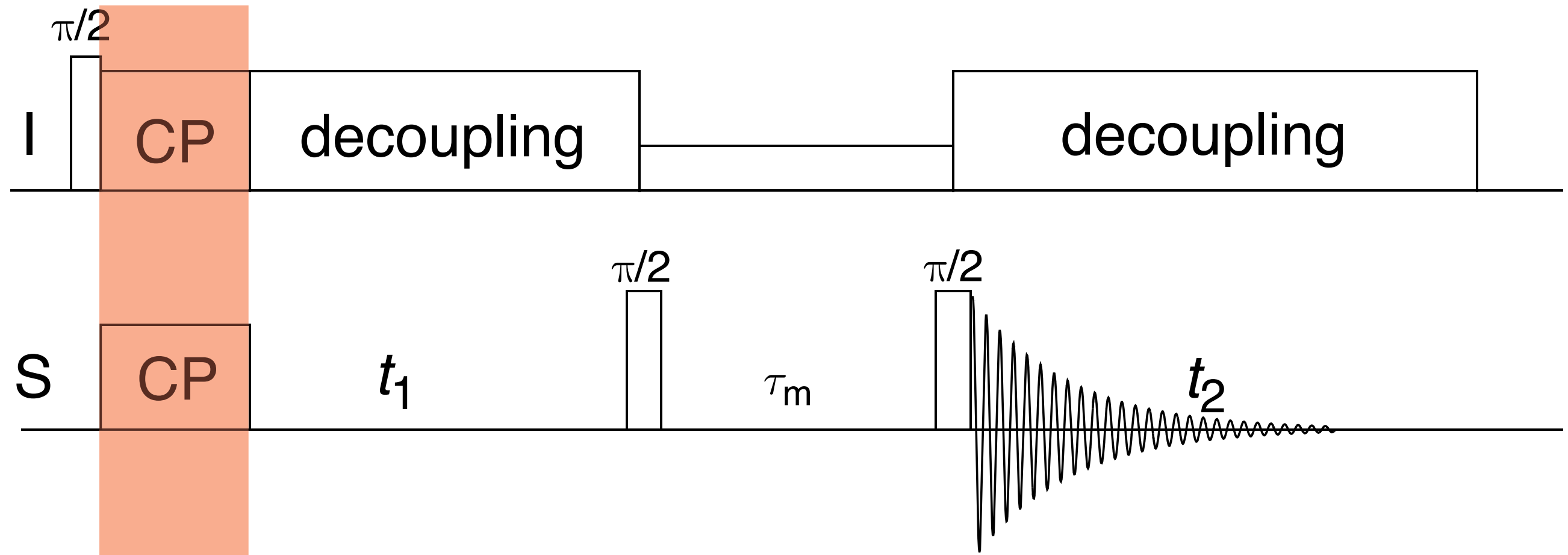
A. Marchetti, ..., G. Pintacuda, Angew. Chem. Int. Ed. Engl. 51 (2012) 10756–10759. <https://doi.org/10.1002/anie.201203124>.

Cross Polarization

Hartmann-Hahn Cross Polarization



❑ Proton-Driven Spin Diffusion under MAS (PDSD)/DARR

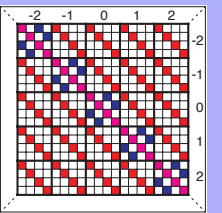


❑ The time-dependent Hamiltonian with the exception of the radio-frequency part is the same during all times of the experiment:

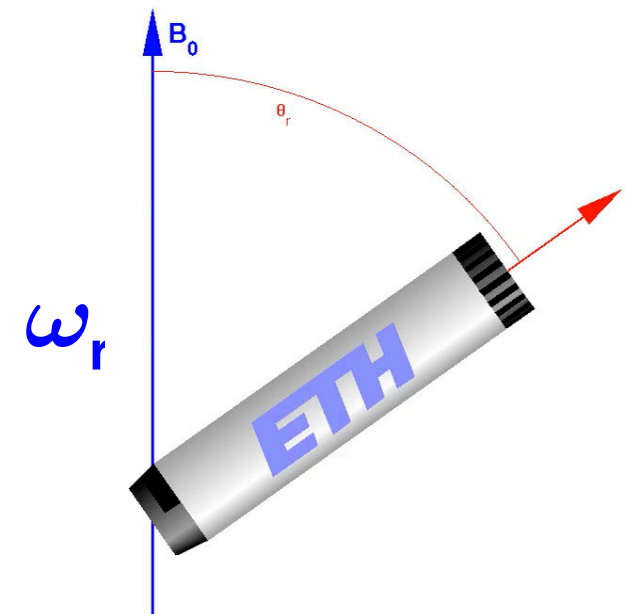
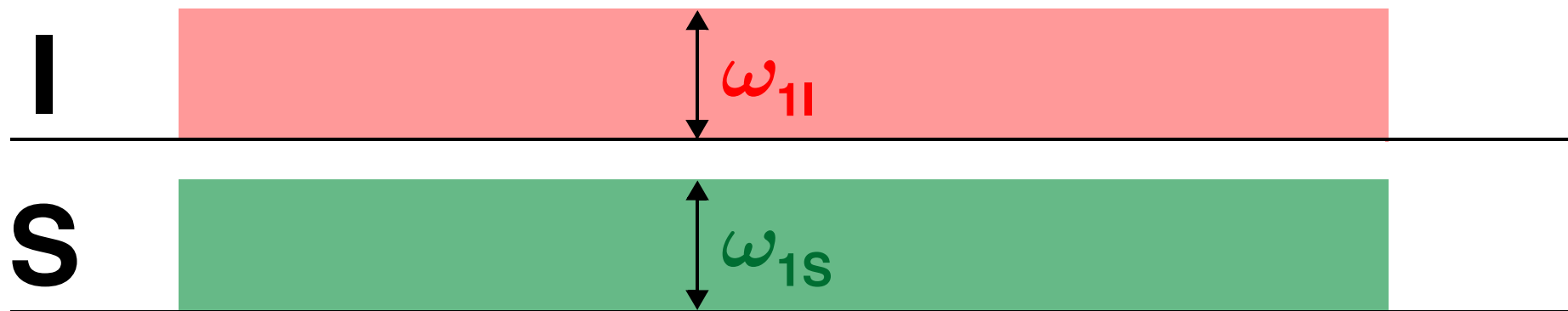
$$\hat{\mathcal{H}}(t) = \sum_i \sum_{\ell=0}^2 \mathbf{A}_{\ell,0}^{(i)}(t) \hat{\mathbf{T}}_{\ell,0}^{(i)} + \hat{\mathcal{H}}_{\text{rf}}(t) = \hat{\mathcal{H}}_{\text{D}}(t) + \hat{\mathcal{H}}_{\text{CS}}(t) + \hat{\mathcal{H}}_{\text{J}}(t) + \hat{\mathcal{H}}_{\text{rf}}(t)$$

❑ Effective Hamiltonian during Hartmann-Hahn cross polarization: heteronuclear zero-quantum Hamiltonian: $\hat{\mathcal{H}} \approx \omega_{\text{IS}}^{(\text{eff})} (\hat{I}^+ \hat{S}^- + \hat{I}^- \hat{S}^+)$

Example: MAS and Double CW Irradiation



- Heteronuclear coupled I-S two-spin system:
Continuous-wave (cw) irradiation on both spins under MAS.



- Examples for such a situation:

- Hartmann-Hahn cross polarization (high-power and low-power CP).
- HORROR or rotary-resonance recoupling (R^3) with simultaneous heteronuclear decoupling.
- Proton-assisted recoupling (PAR) polarization transfer.

Theoretical Description of Double CW Irradiation and MAS $\hat{\mathcal{H}}(t)$

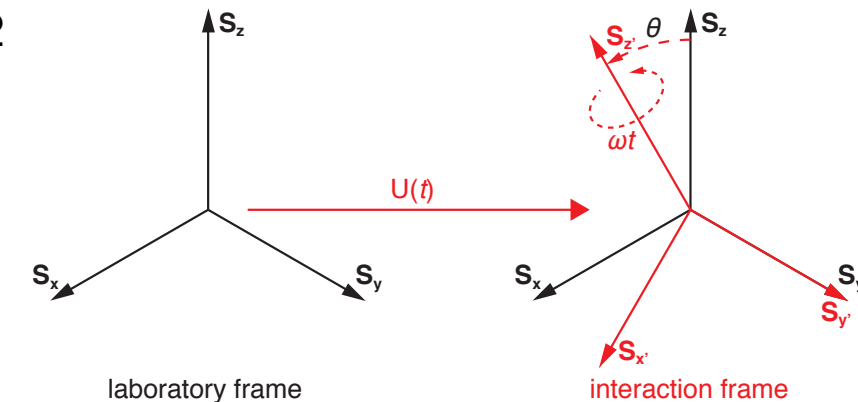
- Spin-system Hamiltonian in the rotating frame is time dependent due to magic-angle spinning (MAS).

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_I(t) + \hat{\mathcal{H}}_{IS}(t) + \hat{\mathcal{H}}_S(t) + \hat{\mathcal{H}}_{II}(t) + \hat{\mathcal{H}}_{SS}(t) = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t}$$

$$\hat{U}_I(t) = \hat{T} \exp \left(-i \int_0^t \hat{\mathcal{H}}_{rf}(t_1) dt_1 \right) e^{i\pi/2 \hat{F}_y} = e^{-i\omega_1 \hat{F}_z t} e^{i\pi/2 \hat{F}_y}$$

$$\hat{U}_S(t) = \hat{T} \exp \left(-i \int_0^t \hat{\mathcal{H}}_{rf}(t_1) dt_1 \right) e^{i\pi/2 \hat{F}_y} = e^{-i\omega_1 \hat{F}_z t} e^{i\pi/2 \hat{F}_y}$$

$$\hat{\tilde{\mathcal{H}}}(t) = \hat{\tilde{\mathcal{H}}}_I(t) + \hat{\tilde{\mathcal{H}}}_{IS}(t) + \hat{\tilde{\mathcal{H}}}_S(t) + \hat{\tilde{\mathcal{H}}}_{II}(t) + \hat{\tilde{\mathcal{H}}}_{SS}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\tilde{\mathcal{H}}}^{(n,k,l)} e^{in\omega_r t} e^{ik\omega_1 t} e^{il\omega_1 s t}$$



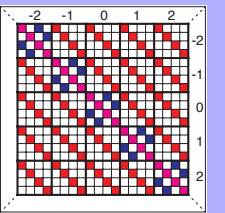
- Interaction-frame transformation with the two rf fields introduces a two more time-dependencies in the Hamiltonian. There are now three frequencies: ω_r and ω_1 and $\omega_1 s$.

- Average Hamiltonian theory requires that

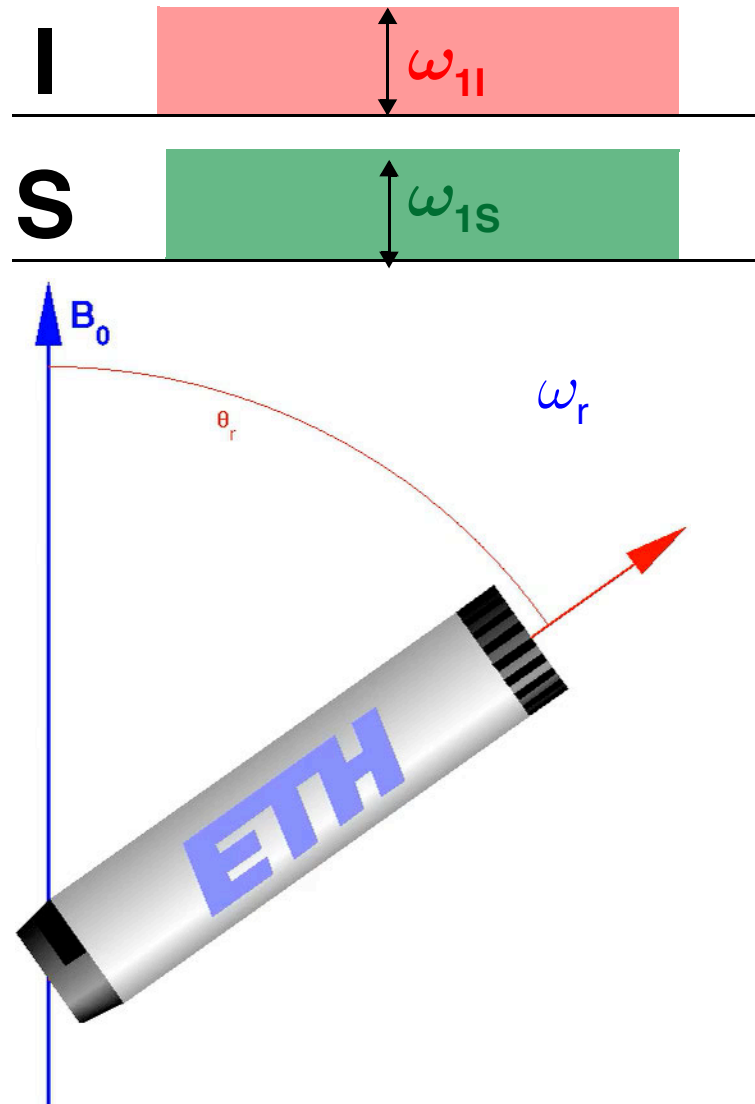
- the three frequencies are commensurate, i.e., $n \omega_r + k \omega_1 + l \omega_1 s = 0$ or
- a separation of time scales, i.e., $\omega_r \ll \omega_1 \ll \omega_1 s$ or $\omega_r \gg \omega_1 \gg \omega_1 s$ (sequential averaging).

- Floquet theory allows a unified description for all values of ω_r and ω_1 and $\omega_1 s$.

Fourier Coefficients Under CW Irradiation



Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k,\ell)} e^{in\omega_r t} e^{ik\omega_{1I} t} e^{ik\omega_{1S} t}$



$$\hat{\mathcal{H}}^{(0,0,0)} = \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_{\ell} \cdot \hat{I}_m) + \sum_{p < q} \omega_{p,q}^{(0)} (\hat{S}_p \cdot \hat{S}_q)$$

$$\begin{aligned} \hat{\mathcal{H}}^{(n,0,0)} = & - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{mz} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{mx} + \hat{I}_{\ell y} \hat{I}_{my}) \right) \\ & - \sum_{p < q} \omega_{p,q}^{(n)} \left(\hat{S}_{pz} \hat{S}_{qz} - \frac{1}{2} (\hat{S}_{px} \hat{S}_{qx} + \hat{S}_{py} \hat{S}_{qy}) \right) \end{aligned}$$

$$\hat{\mathcal{H}}^{(n,\pm 1,0)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^{\mp}$$

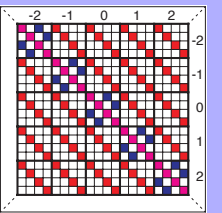
$$\hat{\mathcal{H}}^{(n,0,\pm 1)} = -\frac{1}{2} \sum_p \omega_p^{(n)} \hat{S}_p^{\mp}$$

$$\hat{\mathcal{H}}^{(n,\pm 1,\pm 1)} = -\frac{1}{2} \sum_{m,p} \omega_{m,p}^{(n)} \hat{I}_m^{\mp} \hat{S}_p^{\mp}$$

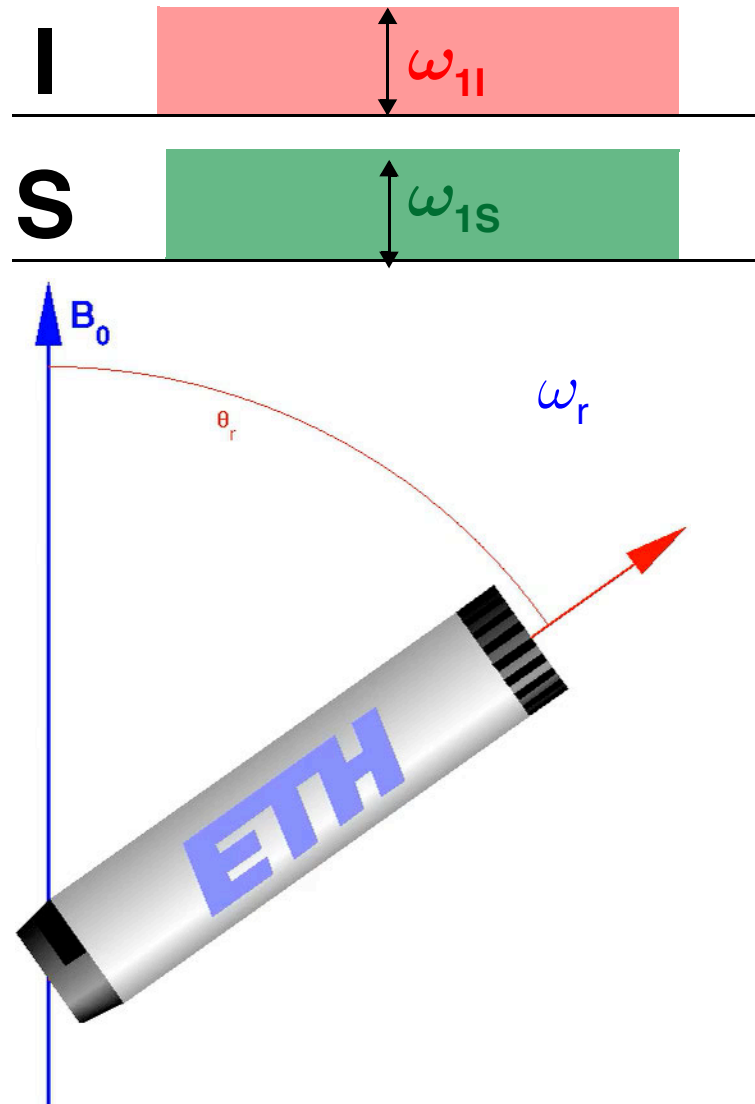
$$\hat{\mathcal{H}}^{(n,\pm 2,0)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_{\ell}^{\mp} \hat{I}_m^{\mp}$$

$$\hat{\mathcal{H}}^{(n,0,\pm 2)} = \frac{3}{4} \sum_{p < q} \omega_{p,q}^{(n)} \hat{S}_p^{\mp} \hat{S}_q^{\mp}$$

Fourier Coefficients Under CW Irradiation



Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k,\ell)} e^{in\omega_r t} e^{ik\omega_1 t} e^{i\ell\omega_1 s}$



$$\hat{\mathcal{H}}^{(0,0,0)} = \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_{\ell} \cdot \hat{I}_m) + \sum_{p < q} \omega_{p,q}^{(0)} (\hat{S}_p \cdot \hat{S}_q)$$

$$\begin{aligned} \hat{\mathcal{H}}^{(n,0,0)} = & - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right) \\ & - \sum_{p < q} \omega_{p,q}^{(n)} \left(\hat{S}_{p z} \hat{S}_{q z} - \frac{1}{2} (\hat{S}_{p x} \hat{S}_{q x} + \hat{S}_{p y} \hat{S}_{q y}) \right) \end{aligned}$$

$$\hat{\mathcal{H}}^{(n,\pm 1,0)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^{\mp}$$

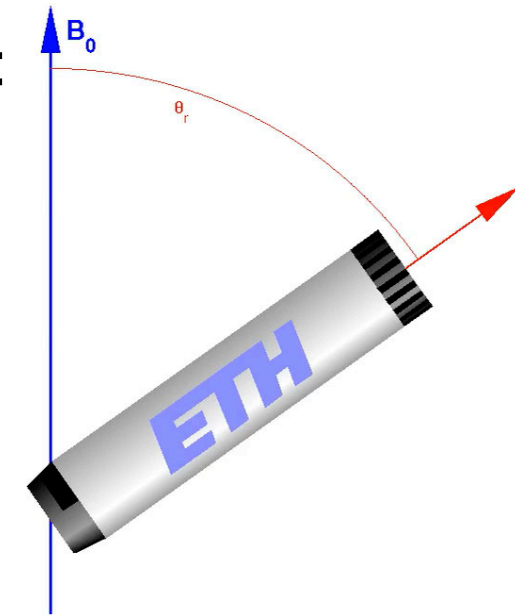
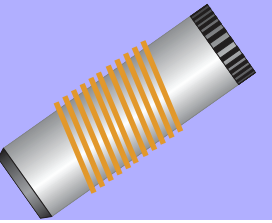
$$\hat{\mathcal{H}}^{(n,0,\pm 1)} = -\frac{1}{2} \sum_p \omega_p^{(n)} \hat{S}_p^{\mp}$$

$$\hat{\mathcal{H}}^{(n,\pm 1,\pm 1)} = -\frac{1}{2} \sum_{m,p} \omega_{m,p}^{(n)} \hat{I}_m^{\mp} \hat{S}_p^{\mp}$$

$$\hat{\mathcal{H}}^{(n,\pm 2,0)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_{\ell}^{\mp} \hat{I}_m^{\mp}$$

$$\hat{\mathcal{H}}^{(n,0,\pm 2)} = \frac{3}{4} \sum_{p < q} \omega_{p,q}^{(n)} \hat{S}_p^{\mp} \hat{S}_q^{\mp}$$

High-Power Cross Polarization



- ❑ The resonance condition at the Hartmann-Hahn conditions under MAS is:

$$n_0\omega_r + k_0\omega_{1I} + l_0\omega_{1S} = 0 \Rightarrow (n_0, k_0, l_0) = (\pm 1, \pm 1, \pm 1), (\pm 2, \pm 1, \pm 1)$$

- ❑ Zero-quantum polarization transfer: $n_0\omega_r = \omega_{1I} - \omega_{1S}$

- ❑ Hamiltonian at $n = n_0$ ($n_0 = 1, 2$) zero-quantum HHCP condition:

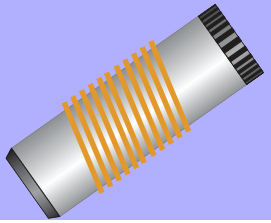
$$\hat{\mathcal{H}}^{(1)} = \sum_{n_0, k_0, l_0} \hat{\mathcal{H}}^{(n_0, k_0, l_0)} = \hat{\mathcal{H}}^{(-n_0, 1, -1)} + \hat{\mathcal{H}}^{(n_0, -1, 1)} = -\frac{1}{2} \sum_{m,p} \left(\omega_{m,p}^{(-n_0)} \hat{I}_m^+ \hat{S}_p^- + \omega_{m,p}^{(n_0)} \hat{I}_m^- \hat{S}_p^+ \right)$$

- ❑ Double-quantum polarization transfer: $n_0\omega_r = \omega_{1I} + \omega_{1S}$

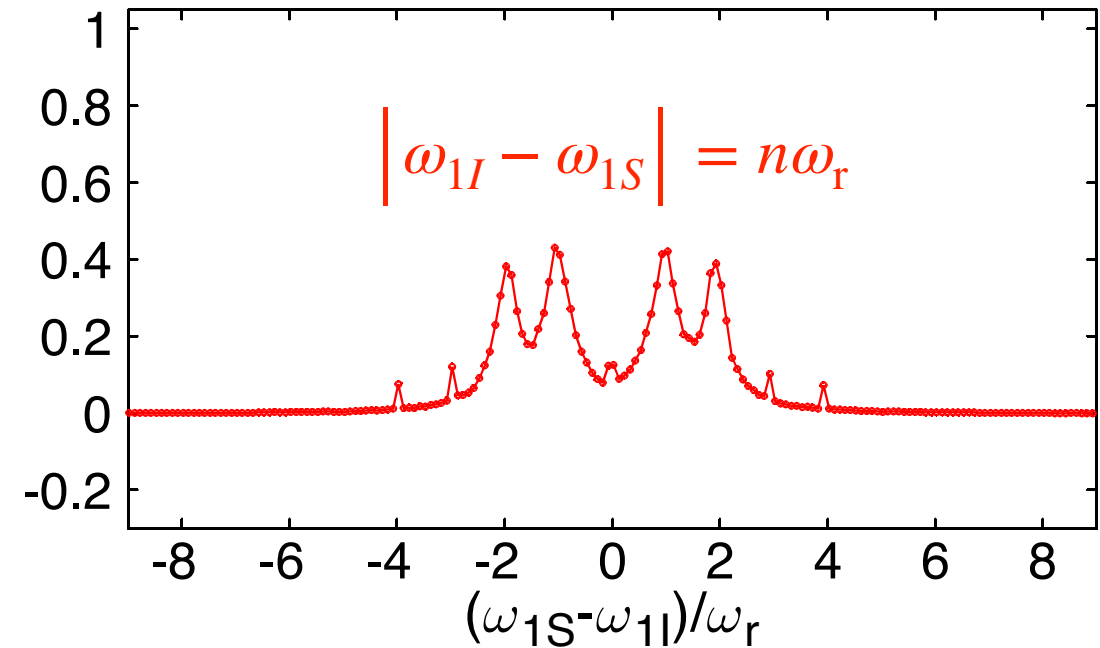
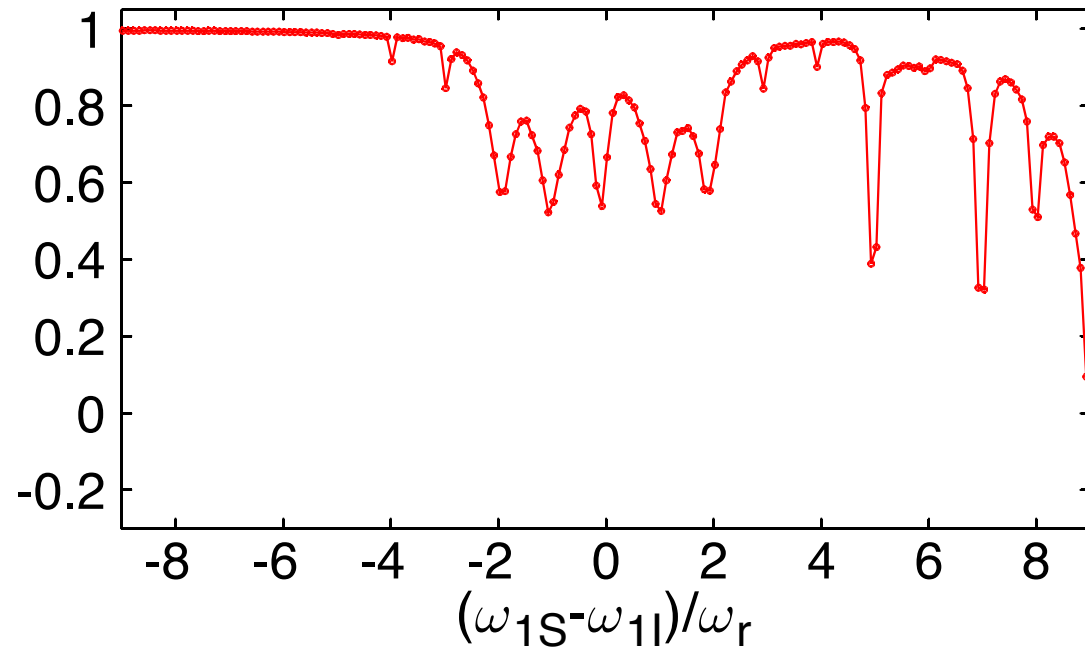
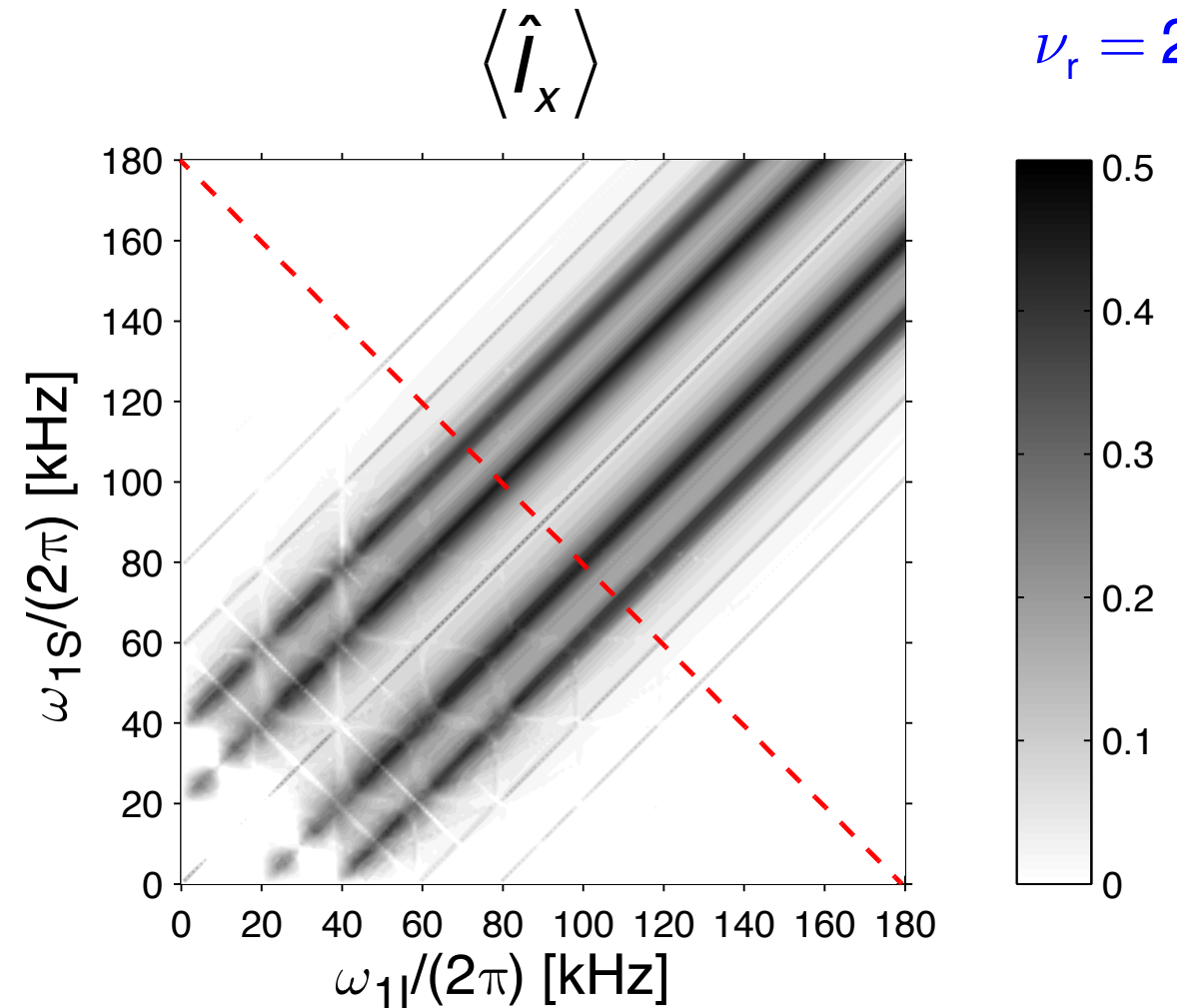
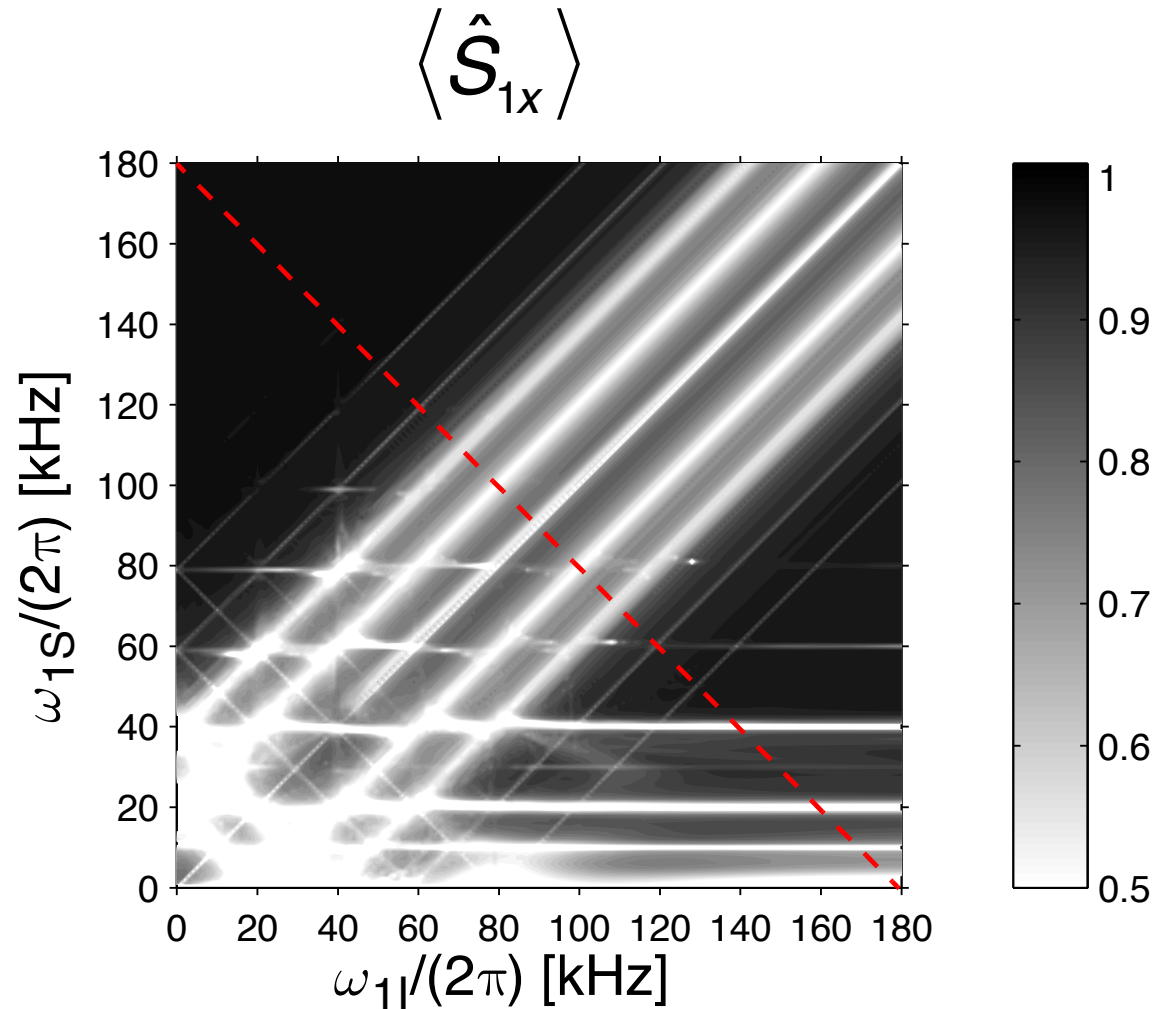
- ❑ Hamiltonian at $n = n_0$ ($n_0 = 1, 2$) double-quantum HHCP condition:

$$\hat{\mathcal{H}}^{(1)} = \sum_{n_0, k_0, l_0} \hat{\mathcal{H}}^{(n_0, k_0, l_0)} = \hat{\mathcal{H}}^{(-n_0, 1, 1)} + \hat{\mathcal{H}}^{(n_0, -1, -1)} = -\frac{1}{2} \sum_{m,p} \left(\omega_{m,p}^{(-n_0)} \hat{I}_m^+ \hat{S}_p^+ + \omega_{m,p}^{(n_0)} \hat{I}_m^- \hat{S}_p^- \right)$$

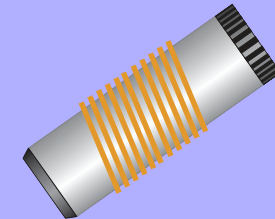
Simulation of Cross Polarization



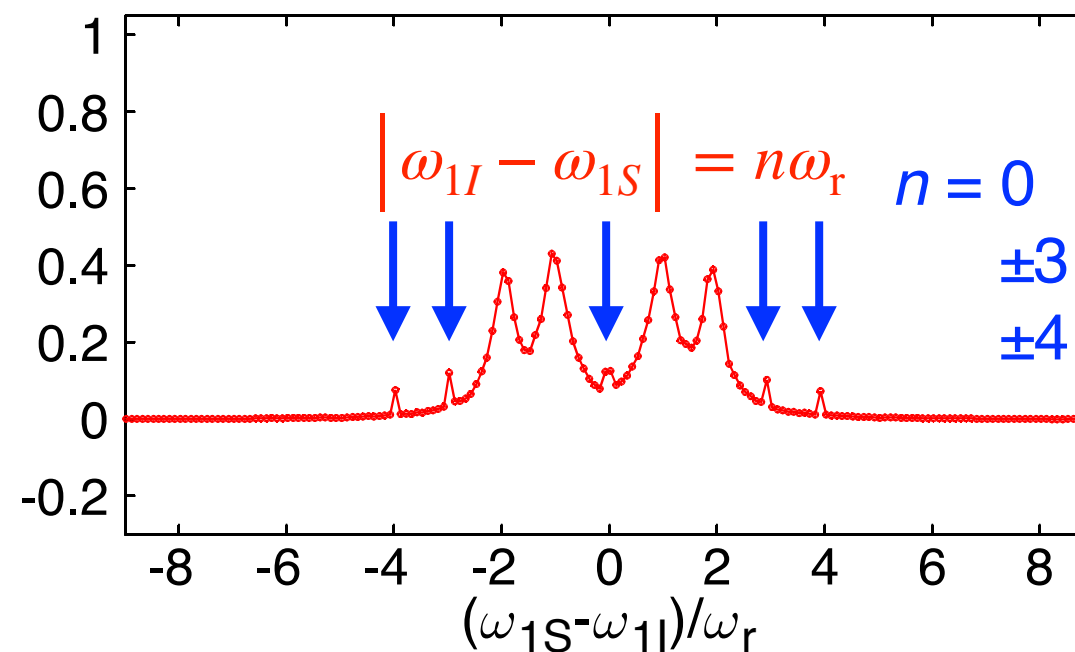
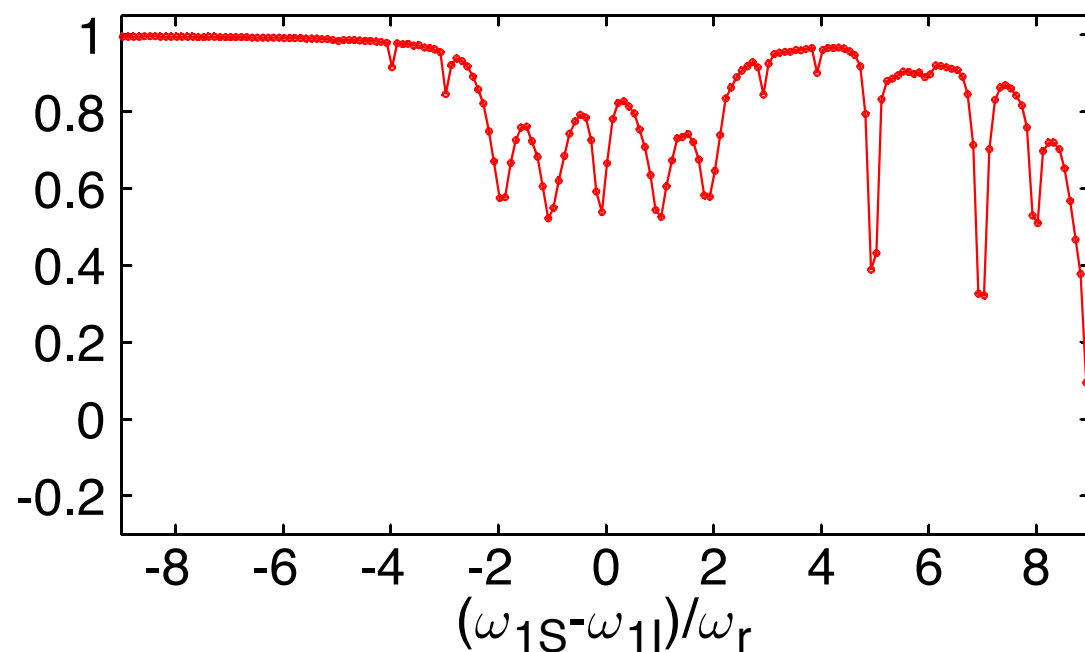
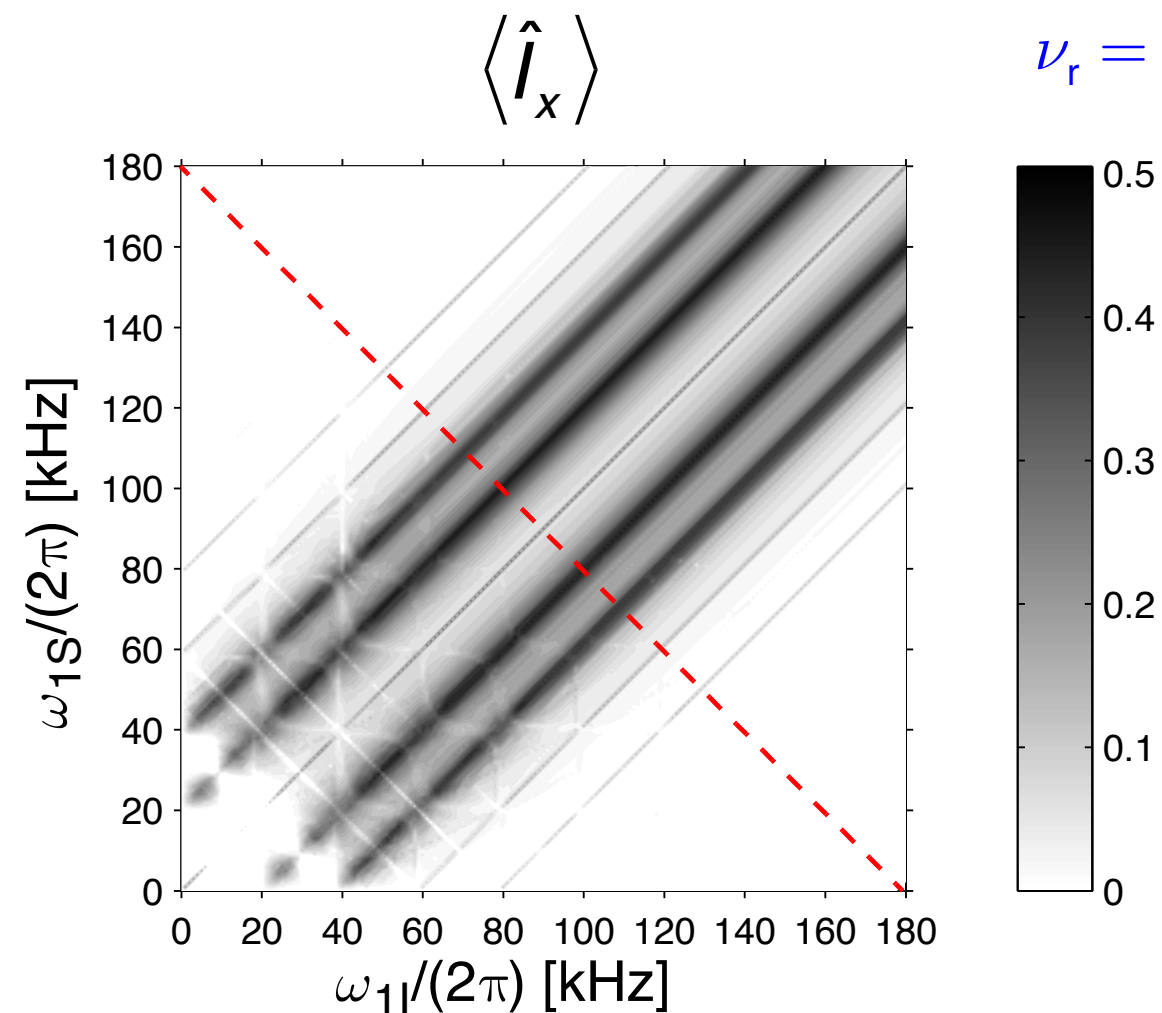
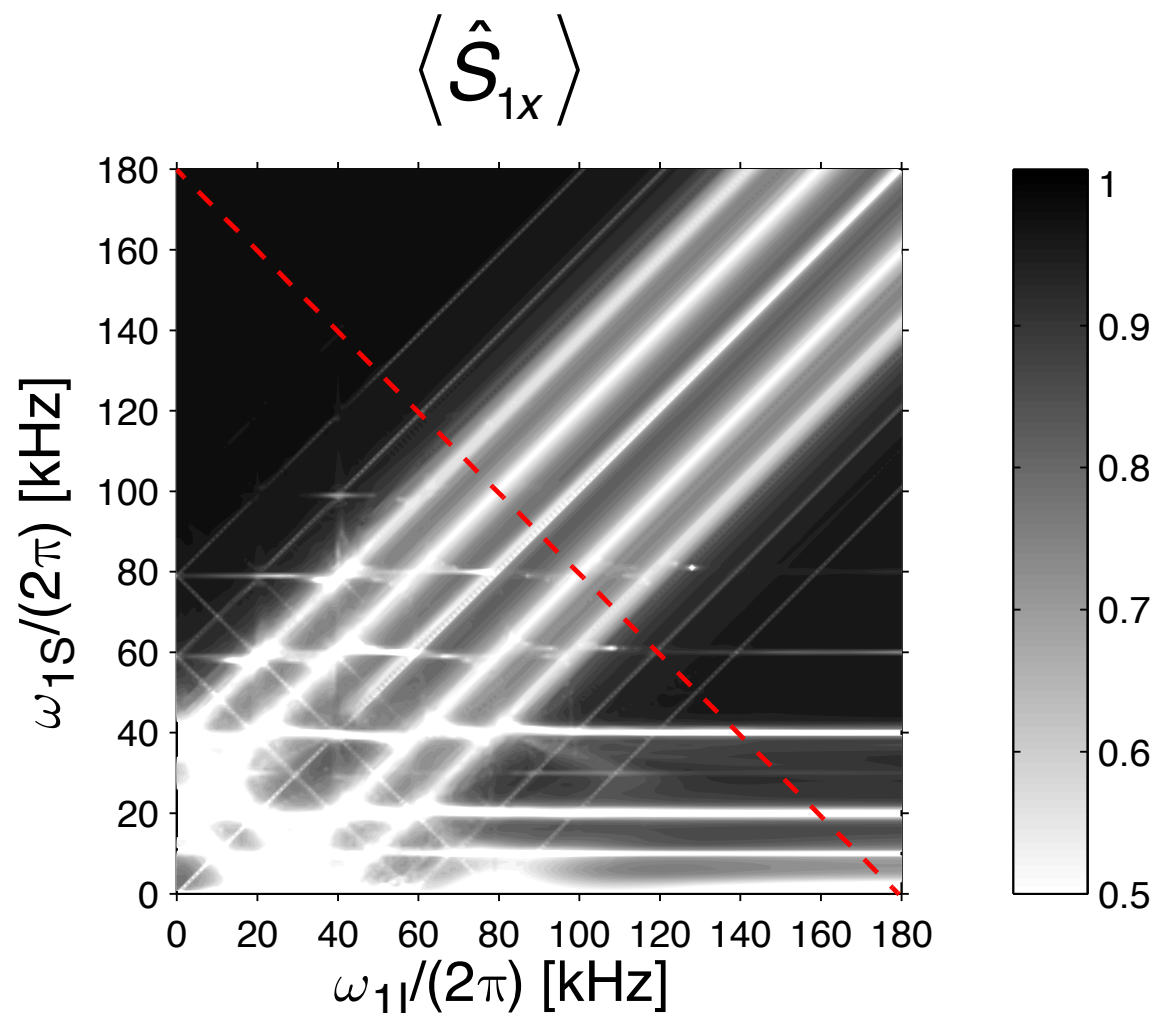
$\nu_r = 20 \text{ kHz}$



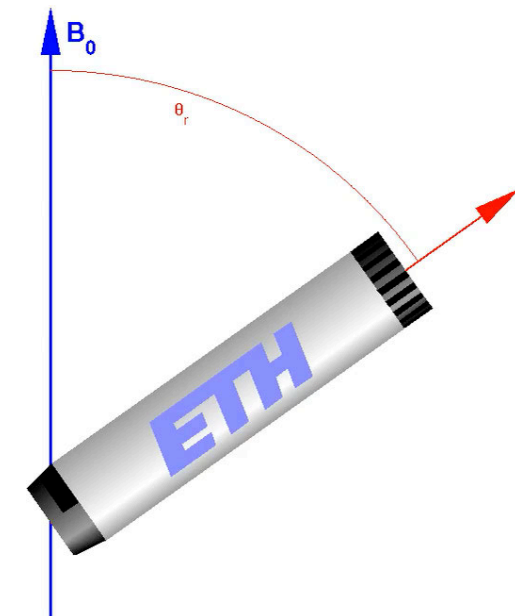
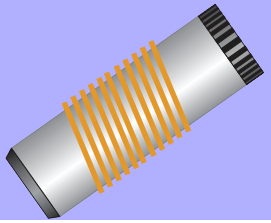
Simulation of Cross Polarization



$\nu_r = 20$ kHz



Low-Power CP at $n = 0$ Hartmann-Hahn Condition



At very high MAS frequencies, high-power ZQ cross polarization is difficult because it requires very high rf fields.

Low-power CP at the $n = 0$ Hartmann-Hahn condition:

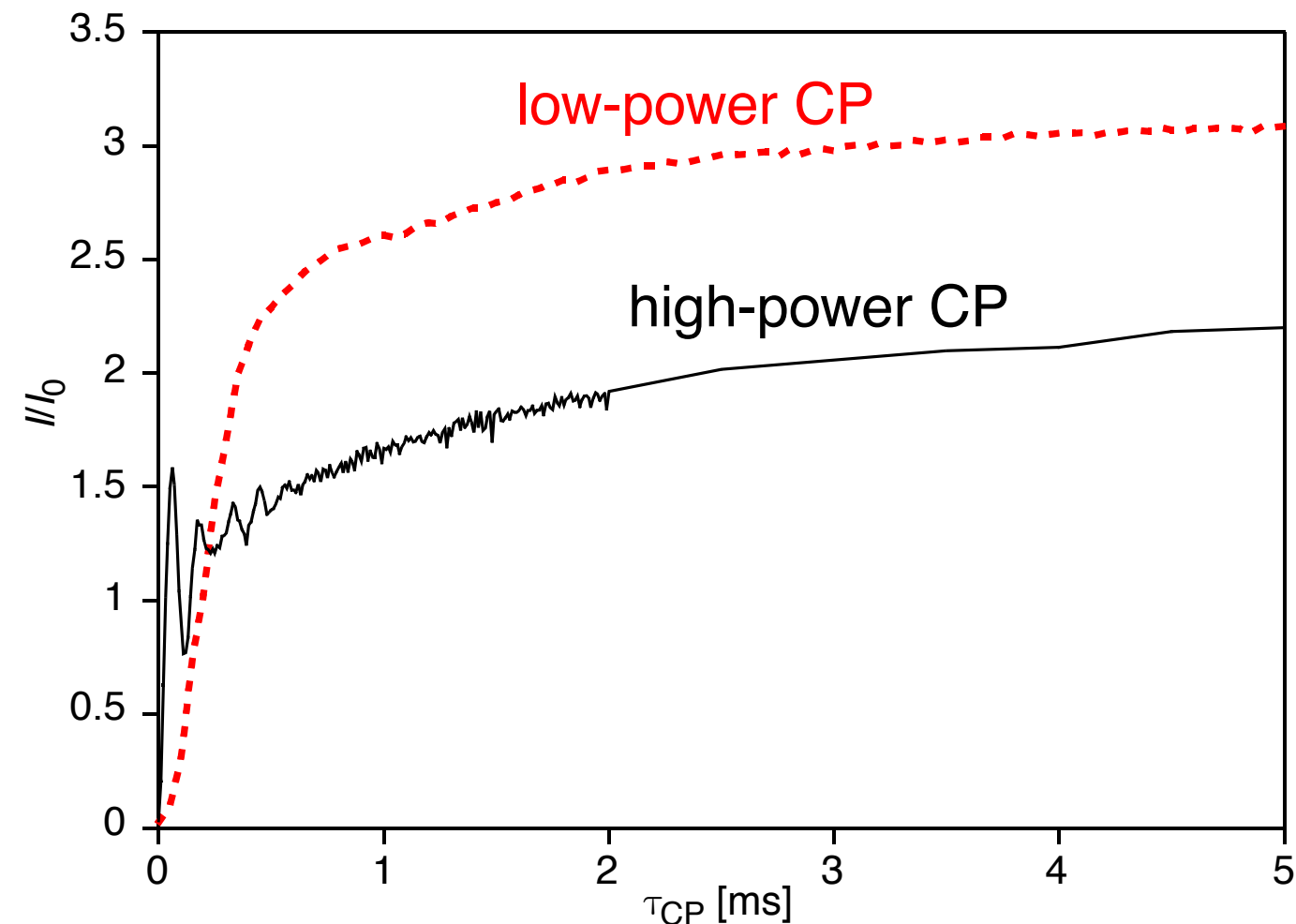
$$0\omega_r + k_0\omega_{1I} + l_0\omega_{1S} = 0 \Rightarrow (0, k_0, l_0) = (0, \pm 1, \pm 1)$$

First-order Hamiltonian at $n = 0$ zero-quantum HHCP condition:

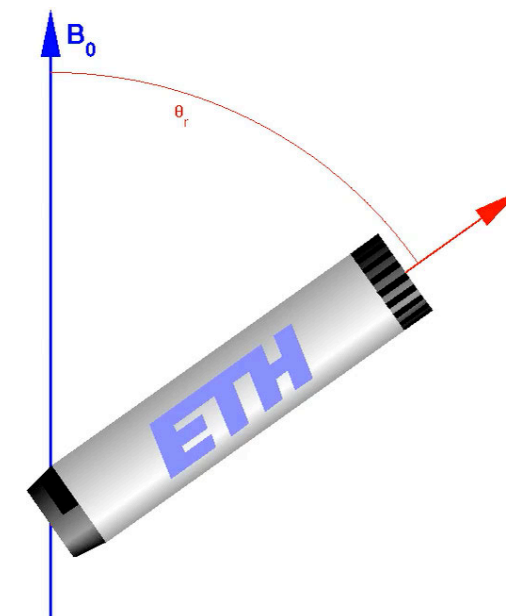
$$\hat{\mathcal{H}}^{(1)} = \sum_{n_0, k_0, l_0} \hat{\mathcal{H}}^{(0, k_0, l_0)} = \hat{\mathcal{H}}^{(0, 1, -1)} + \hat{\mathcal{H}}^{(0, -1, 1)} = -\frac{1}{2} \sum_{m, p} \omega_{m, p}^{(0)} (\hat{I}_m^+ \hat{S}_p^- + \hat{I}_m^- \hat{S}_p^+) = -\frac{1}{2} \sum_{m, p} \pi J_{m, p} (\hat{I}_m^+ \hat{S}_p^- + \hat{I}_m^- \hat{S}_p^+)$$

Polarization transfer is too fast for a J -coupling mediated polarization transfer.

Other higher-order terms have to be considered for a full explanation.



Low-Power CP at $n = 0$ Hartmann-Hahn Condition



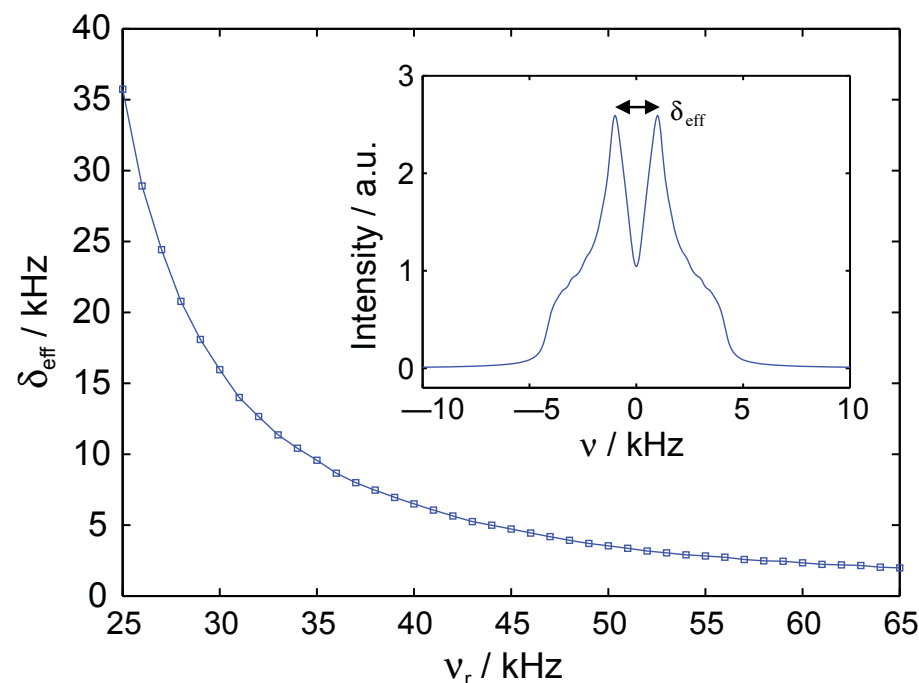
At very high MAS frequencies, high-power ZQ cross polarization is difficult because it requires very high rf fields.

Low-power CP at the $n = 0$ Hartmann-Hahn condition:

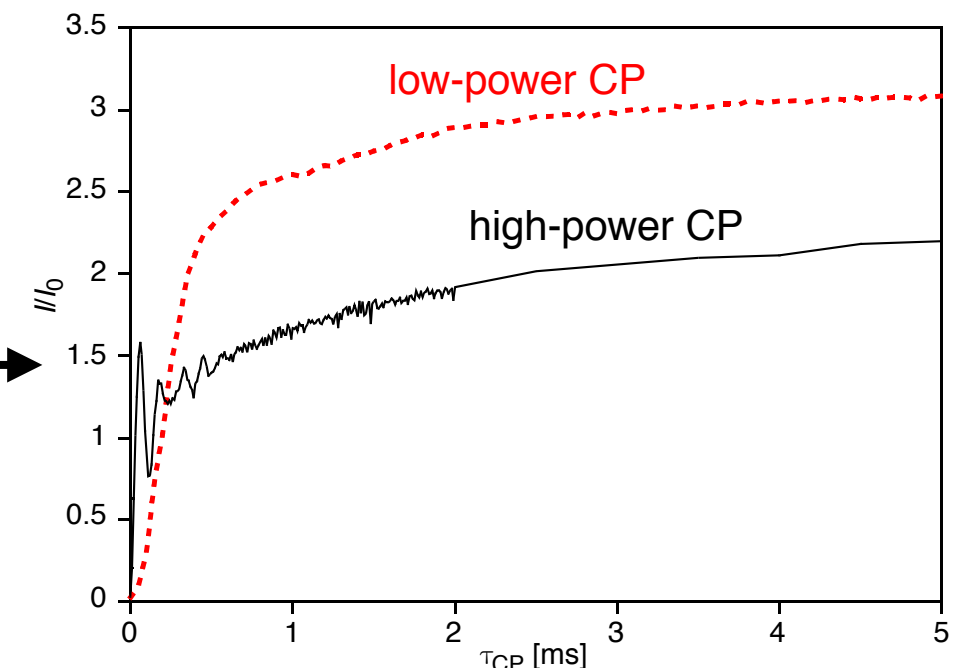
$$0\omega_r + \kappa_0\omega_{1f} + \ell_0\omega_{1s} = 0 \Rightarrow (0, \kappa_0, \ell_0) = (0, \pm 1, \pm 1)$$

Second-order Hamiltonian at $n = 0$ zero-quantum HHCP condition:

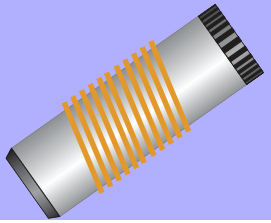
$$\begin{aligned} \hat{\mathcal{H}}^{(2)} &= \sum_{n_0, k_0, \ell_0} \hat{\mathcal{H}}_{(2)}^{(0, k_0, \ell_0)} = \hat{\mathcal{H}}_{(2)}^{(0, 1, -1)} + \hat{\mathcal{H}}_{(2)}^{(0, -1, 1)} = -\frac{1}{2} \sum_{\nu, \kappa, \lambda} \frac{[\hat{\mathcal{H}}^{(0-\nu, 1-\kappa, -1-\lambda)}, \hat{\mathcal{H}}^{(\nu, \kappa, \lambda)}]}{\nu\omega_r + \kappa\omega_{1f} + \lambda\omega_{1s}} - \frac{1}{2} \sum_{\nu, \kappa, \lambda} \frac{[\hat{\mathcal{H}}^{(0-\nu, -1-\kappa, 1-\lambda)}, \hat{\mathcal{H}}^{(\nu, \kappa, \lambda)}]}{\nu\omega_r + \kappa\omega_{1f} + \lambda\omega_{1s}} \\ &= -\frac{1}{2} \sum_{m, n, p} \omega_{m, n, p} (\hat{I}_m^+ \hat{S}_p^- \hat{I}_{nz} + \hat{I}_m^- \hat{S}_p^+ \hat{I}_{nz}) \end{aligned}$$



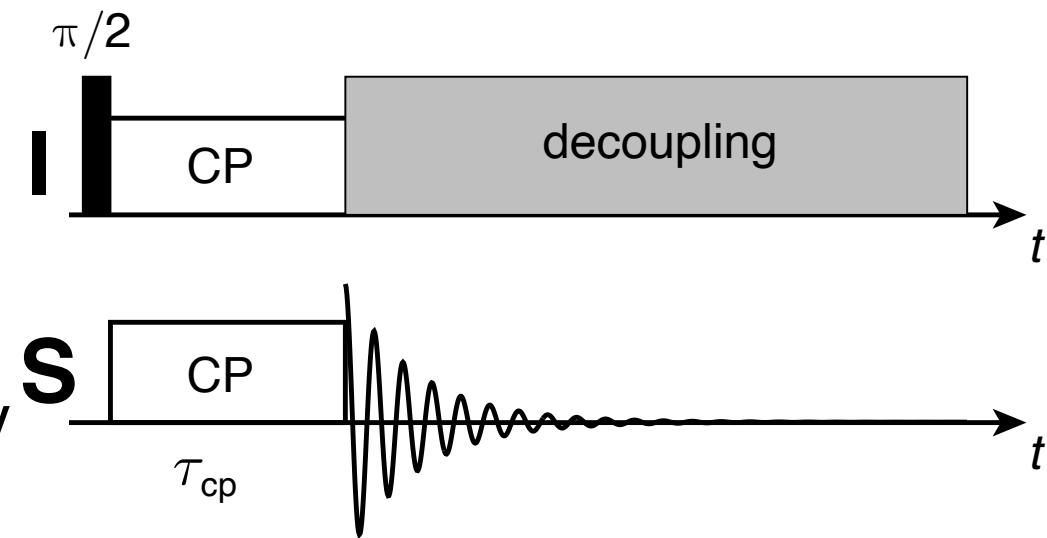
good agreement
between theory
and experiment



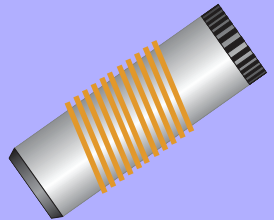
Practical Aspects of Cross Polarization



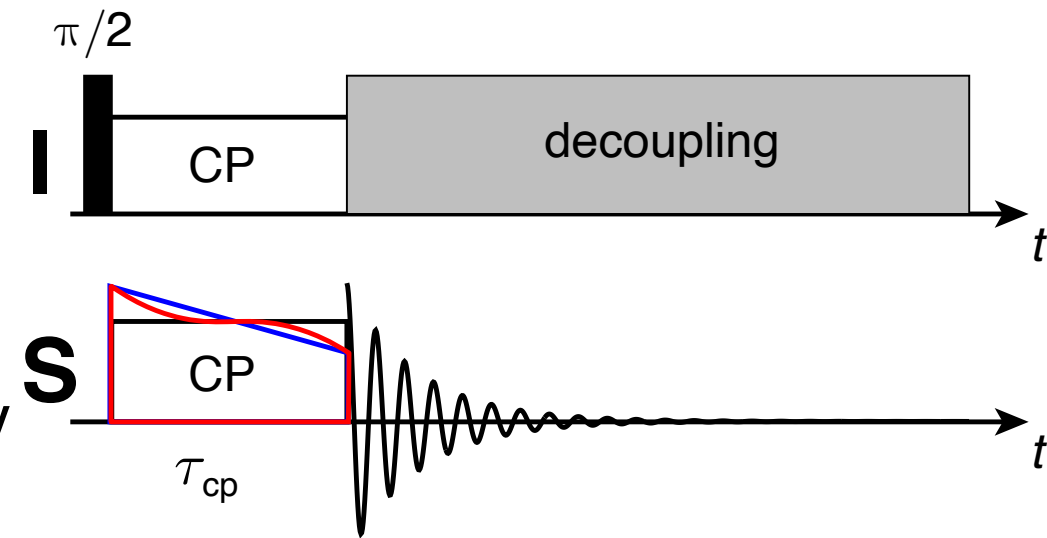
- ❑ Select a spinning frequency that does not match a chemical-shift difference.
- ❑ Experimentally optimize the two rf-field amplitudes such that the polarization transfer is maximized.
 - Avoid rf-field amplitudes $\omega_1 \approx n\omega_r$ to avoid fast decay of magnetization due to homonuclear recoupling.
- ❑ Experimentally optimize the length of the cross-polarization time τ_{cp} .
- ❑ Polarization transfer on the $n = 1$ condition is faster than on the $n = 2$ condition.



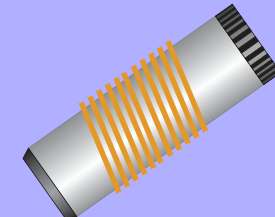
Practical Aspects of Cross Polarization



- ❑ Select a spinning frequency that does not match a chemical-shift difference.
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 - Avoid rf-field amplitudes $\omega_1 \approx n\omega_r$ to avoid fast decay of magnetization due to homonuclear recoupling.
- ❑ Experimentally optimize the length of the cross-polarization time τ_{cp} .
- ❑ Polarization transfer on the $n = 1$ condition is faster than on the $n = 2$ condition.
- ❑ Implement a **linear ramp** or even better a **tangential sweep** of the amplitude to compensate for rf-field inhomogeneity over the rotor and to get higher (adiabatic) transfer efficiency.
- ❑ The shape of the sweep needs to be optimized. For hints how to do this, see:
M. Ernst, B.H. Meier, Adiabatic Polarization-Transfer Methods in MAS Spectroscopy, John Wiley & Sons, Ltd, 2010. <https://doi.org/10.1002/9780470034590.emrstm0004.pub2>.
- ❑ Typical gain in sensitivity are a factor of 2-10 depending on the ratio of the Larmor frequencies.
- ❑ Additional gain in sensitivity stems from the faster possible repetition rate due to faster relaxation of proton spins.
- ❑ At fast MAS the DQ Hartmann Hahn condition $|\omega_{1I} + \omega_{1S}| = n\omega_r$ is more advantageous and should be used.

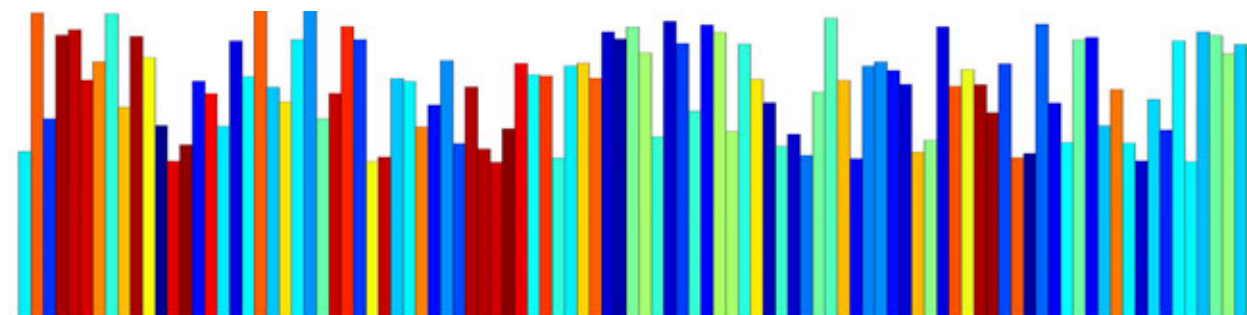


Numerical Pulse Sequence Optimization



Radio-frequency irradiation:

$$\hat{\mathcal{H}}_{\text{rf}}(t) = \omega_1(t)(\hat{F}_x \cos(\phi(t)) + \hat{F}_y \sin(\phi(t)))$$



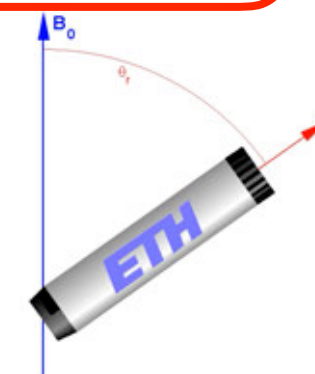
$$\sigma(0) = \hat{S}_{1z}$$



$$\sigma(T) = \hat{S}_{2z}$$

Spin-system Hamiltonian:

$$\hat{\mathcal{H}}(t) = \omega_{S_1} \hat{S}_{1z} + \omega_{S_2} \hat{S}_{2z} + \omega_{12}(t)(2\hat{S}_{1z}\hat{S}_{2z} - (\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y}))$$



Parameter ranges:

$$\omega_{S_1}/(2\pi) \in [-10, 10] \text{ kHz}$$

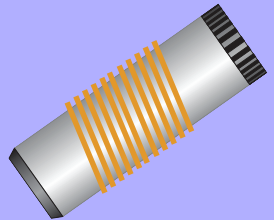
$$\omega_{S_2}/(2\pi) \in [-10, 10] \text{ kHz}$$

$$\delta_{12}/(2\pi) \in [2, 10] \text{ kHz}$$

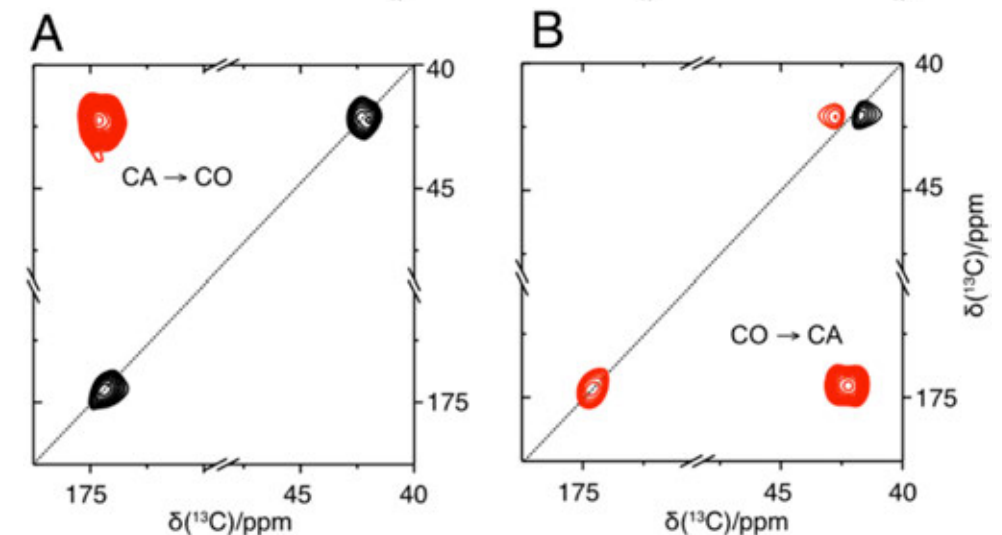
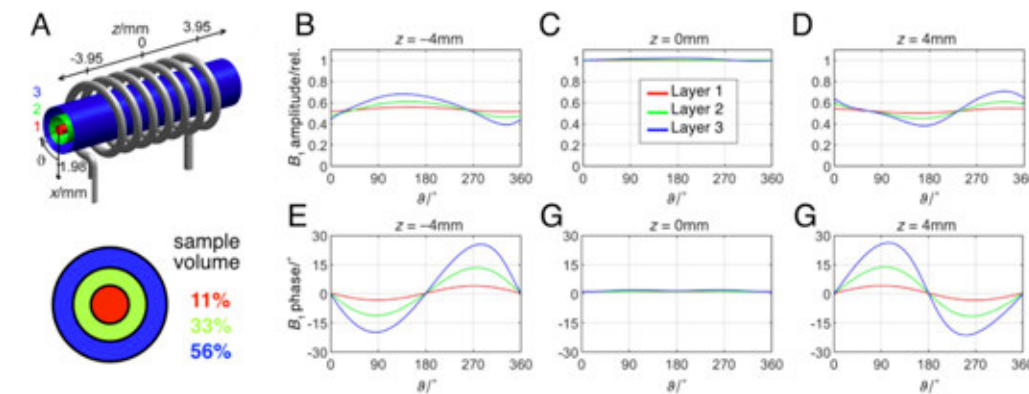
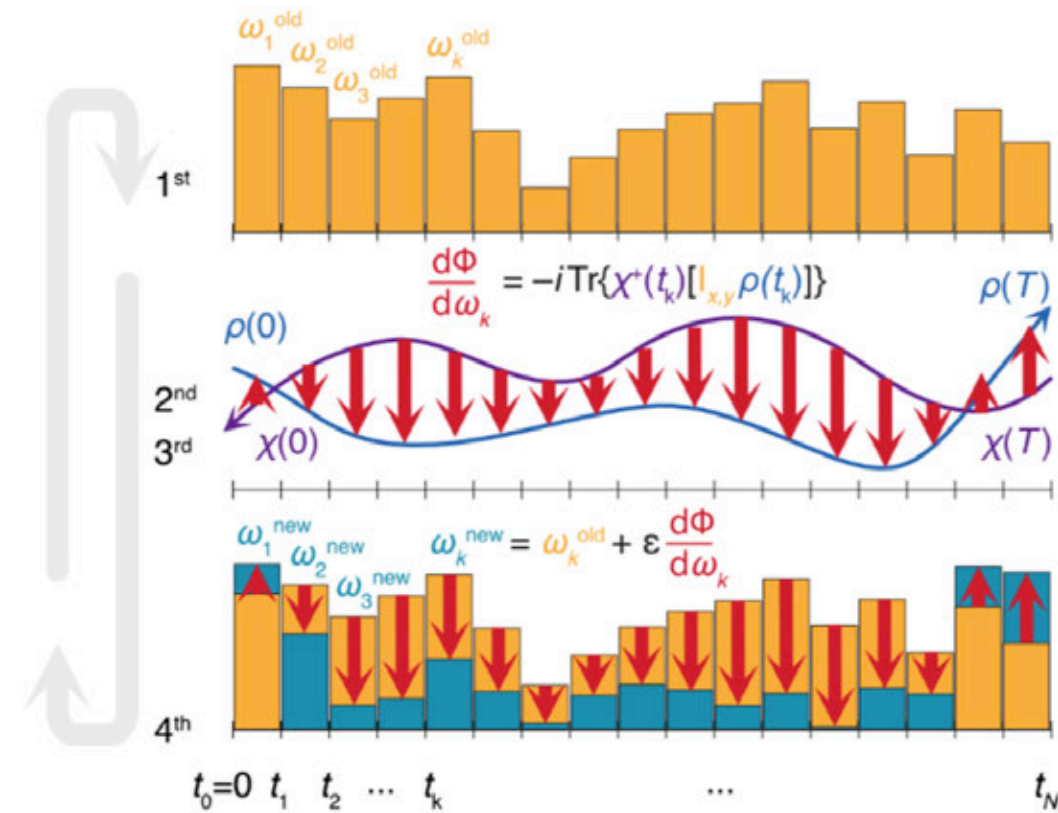
$$\omega_1/(2\pi) \in [0, 50] \text{ kHz}$$

- ☐ Full quantum-mechanical simulation required.
- ☐ Numerical pulse-sequence optimization in Simpson, Spinach or any other program of your choice.

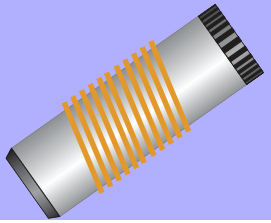
Computer Optimization of Pulse Sequences



- ❑ This is often done using optimal control theory where we do a state-to-state optimization.
- ❑ Initial and final state are propagated forward and backward to give the most efficient transfer by modifying the amplitude and phases of pulses.
- ❑ In solid-state NMR, this has mostly been implemented for heteronuclear polarization transfer as an alternative to the cross polarization experiment.
- ❑ Sequences can be designed to compensate typical rf-field inhomogeneity better than standard CP sequences.
- ❑ There are also some homonuclear sequences but they are more complex to optimize. One can also implement directed transfer which would not be so simple with effective Hamiltonians.



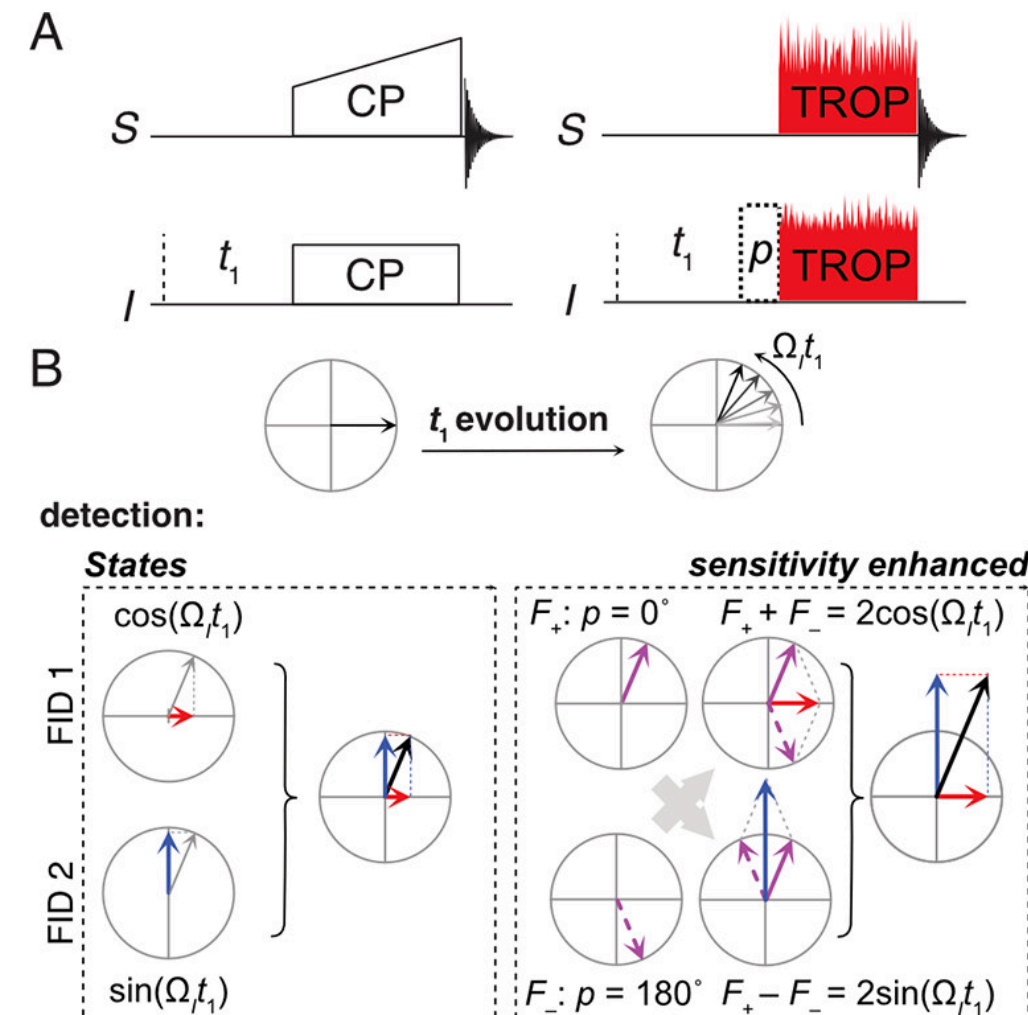
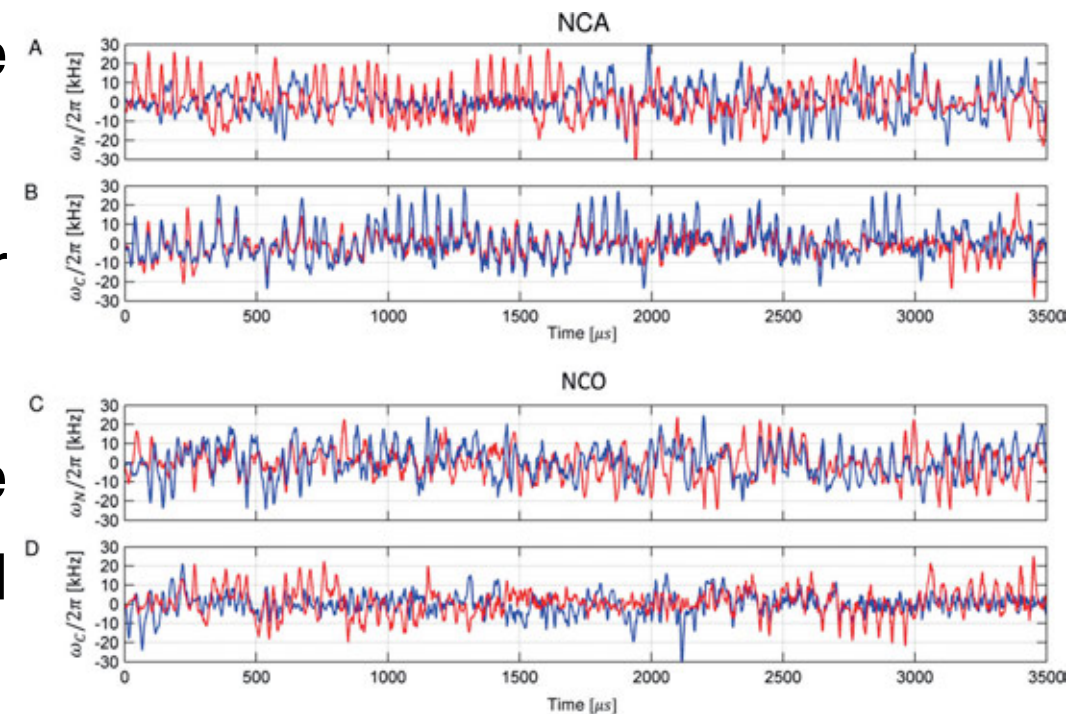
Computer Optimization of Pulse Sequences



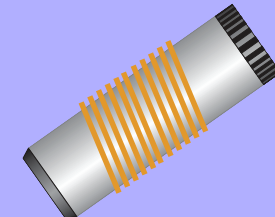
- Optimal control pulse sequences often look like “noise”.
- Early implementations showed a quite erratic behavior and would work some places and not in other places.
- Newer sequences seem to be more stable due to the inclusion of MAS modulations of the rf-field inhomogeneity.
- If one uses mixing of transverse components, one can gain an additional factor of $\sqrt{2}$ for each indirect dimension. In higher-dimensional experiments this can be an important factor!
- One has to make sure that the sine and cosine modulated signal are not mixed up (echo/anti-echo processing) which can be achieved by an additional 180° pulse before the transfer.

J. Blahut, Z. Tošner, ..., Solid State Nucl. Magn. Reson. 135 (2025) 101984. <https://doi.org/10.1016/j.ssnmr.2024.101984>.

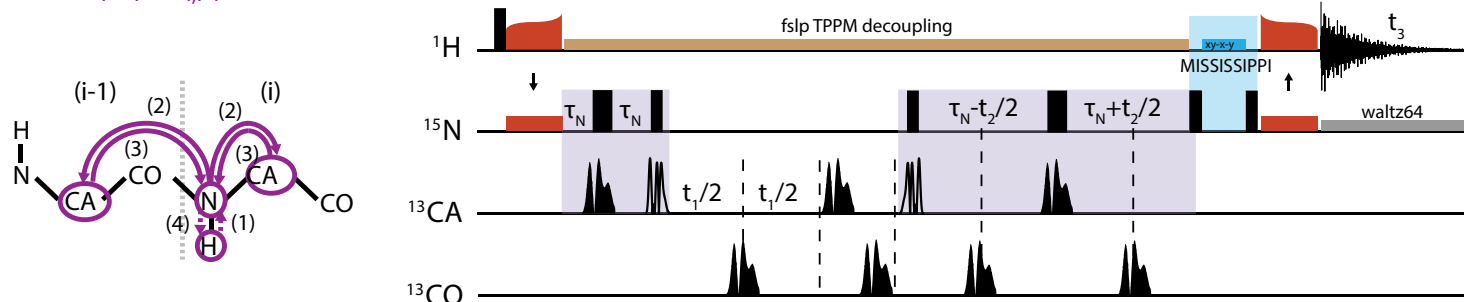
Alexander Klein, ..., Rasmus Linser, High-dimensional solid-state NMR facilitated by transverse-mixing optimal control, <https://doi.org/10.21203/rs.3.rs-8003957/v1>



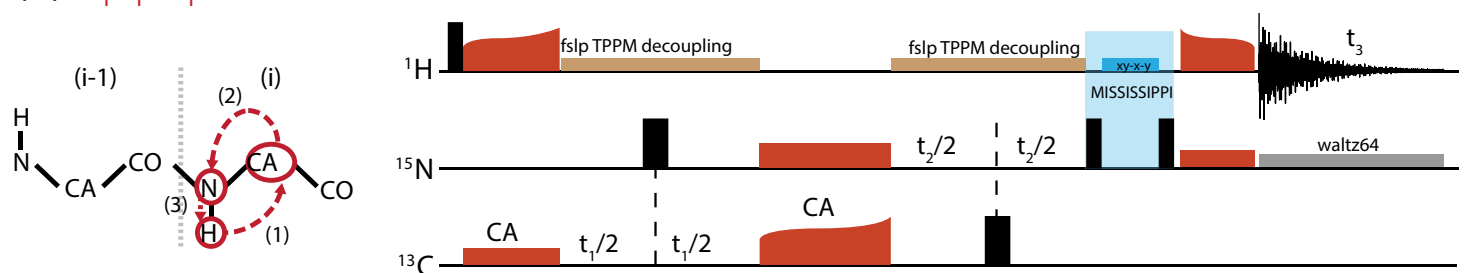
Important Building Blocks in MAS NMR



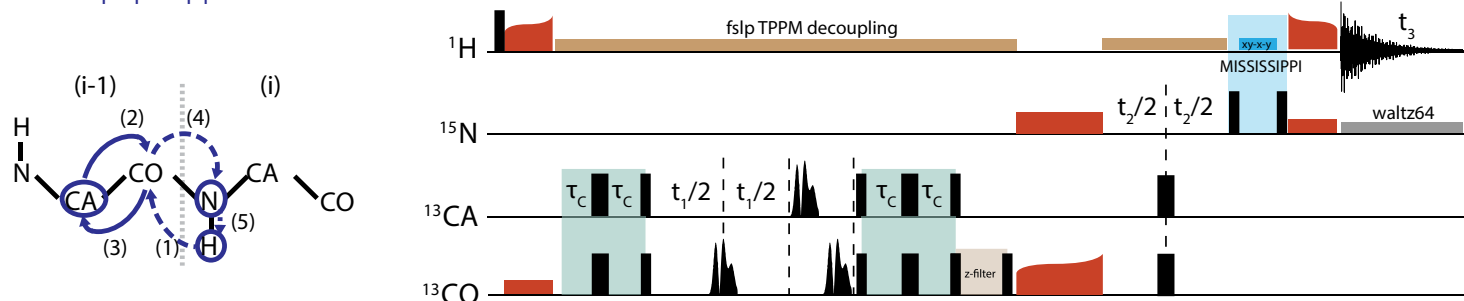
(a) $H_i N_i C\alpha_{i,i-1}$ correlation: (HN)CANH



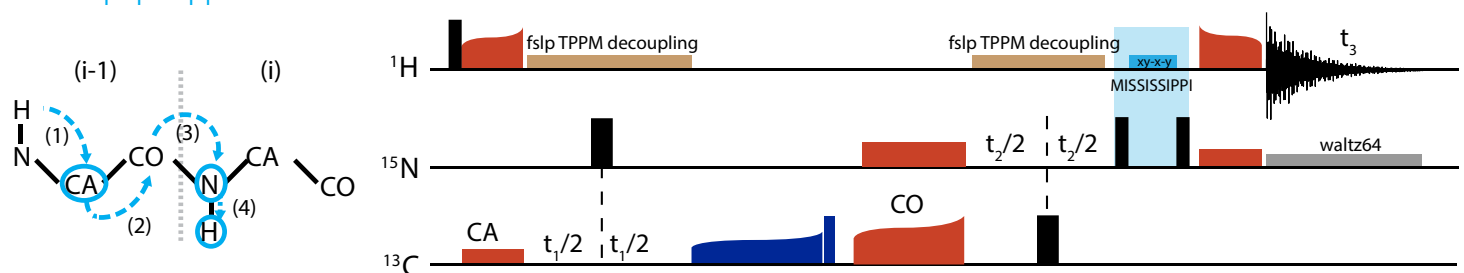
(b) $H_i N_i C\alpha_i$ correlation: (H)CANH



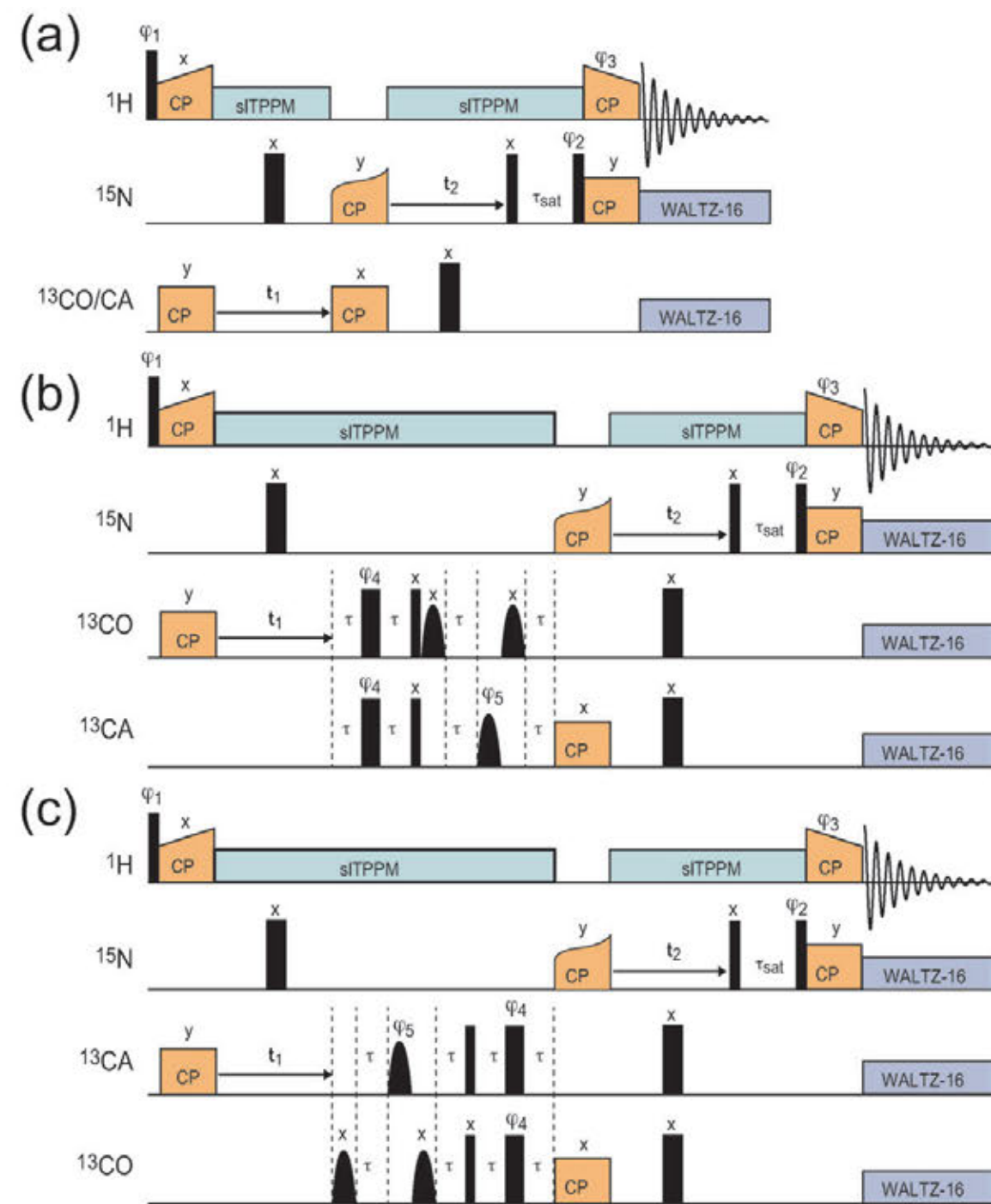
(c) $H_i N_i C\alpha_{i-1}$ correlation: (HCO)CA(CO)NH



(d) $H_i N_i C\alpha_i$ correlation: (H)CA(CO)NH



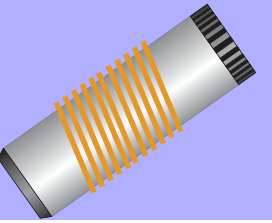
S. Penzel, ... , B.H. Meier, J. Biomol. NMR. 63 (2015) 165–186.
<https://doi.org/10.1007/s10858-015-9975-y>.



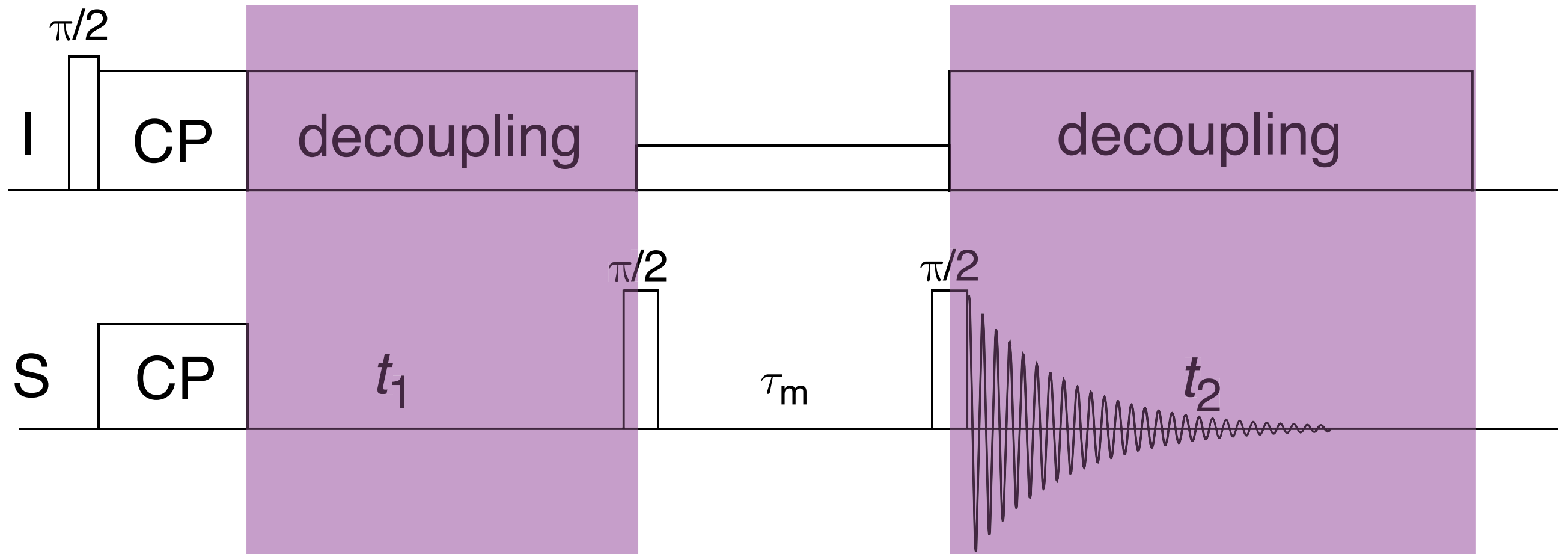
A. Marchetti, ..., G. Pintacuda, Angew. Chem. Int. Ed. Engl. 51 (2012) 10756–10759. <https://doi.org/10.1002/anie.201203124>.

Heteronuclear Decoupling

Heteronuclear Decoupling



Proton-Driven Spin Diffusion under MAS (PDSD)/DARR



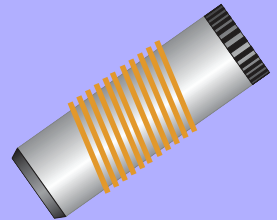
The time-dependent Hamiltonian with the exception of the radio-frequency part is the same during all times of the experiment:

$$\hat{\mathcal{H}}(t) = \sum_i \sum_{\ell=0}^2 \mathbf{A}_{\ell,0}^{(i)}(t) \hat{\mathbf{T}}_{\ell,0}^{(i)} + \hat{\mathcal{H}}_{\text{rf}}(t) = \hat{\mathcal{H}}_{\text{D}}(t) + \hat{\mathcal{H}}_{\text{CS}}(t) + \hat{\mathcal{H}}_{\text{J}}(t) + \hat{\mathcal{H}}_{\text{rf}}(t)$$

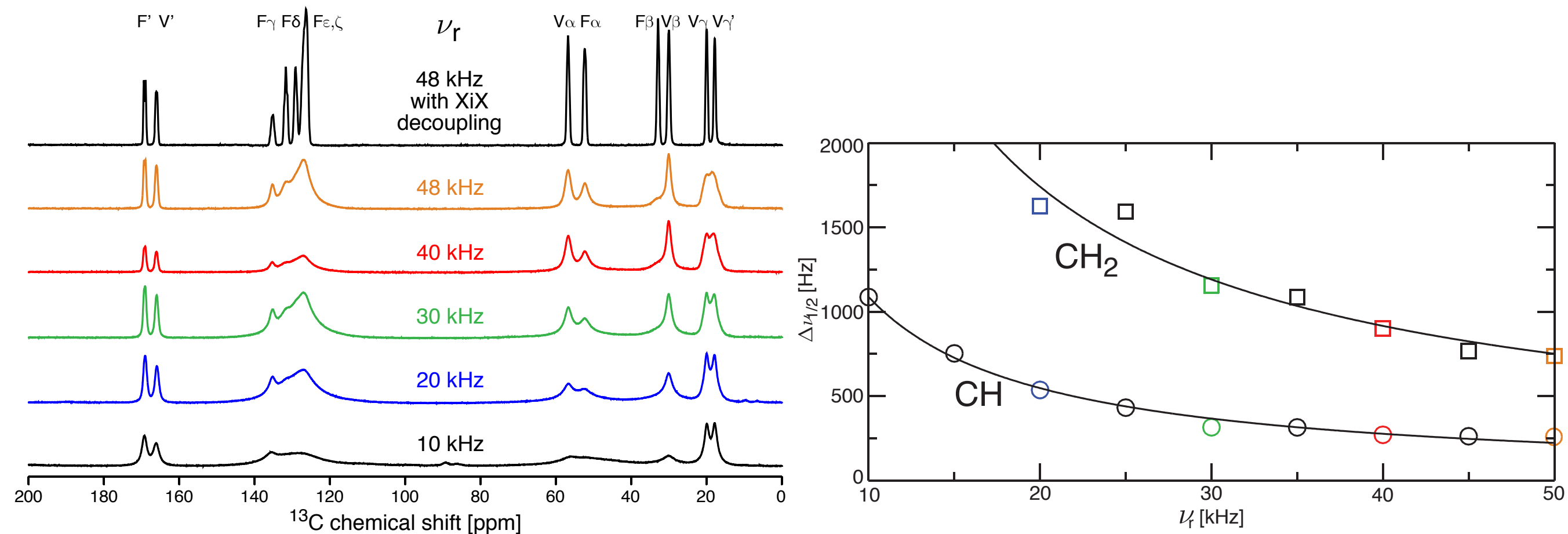
Effective Hamiltonian during free evolution (t_1 and t_2): S-spin isotropic chemical-shift

Hamiltonian: $\hat{\mathcal{H}} \approx \omega_{\text{S}}^{(\text{iso})} \hat{\mathbf{S}}_z$

Do We Need Decoupling Under Fast MAS?



❑ MAS will average in first-order all the second-rank spatial tensors but ...



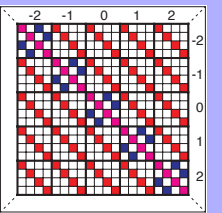
❑ Higher-orders will lead to a residual line width due to cross terms between heteronuclear and homonuclear dipolar couplings: $\Delta\omega_{1/2} \propto 1/\omega_r$

❑ Faster MAS (~ 250 kHz) will lead to a liquid-like NMR spectrum.

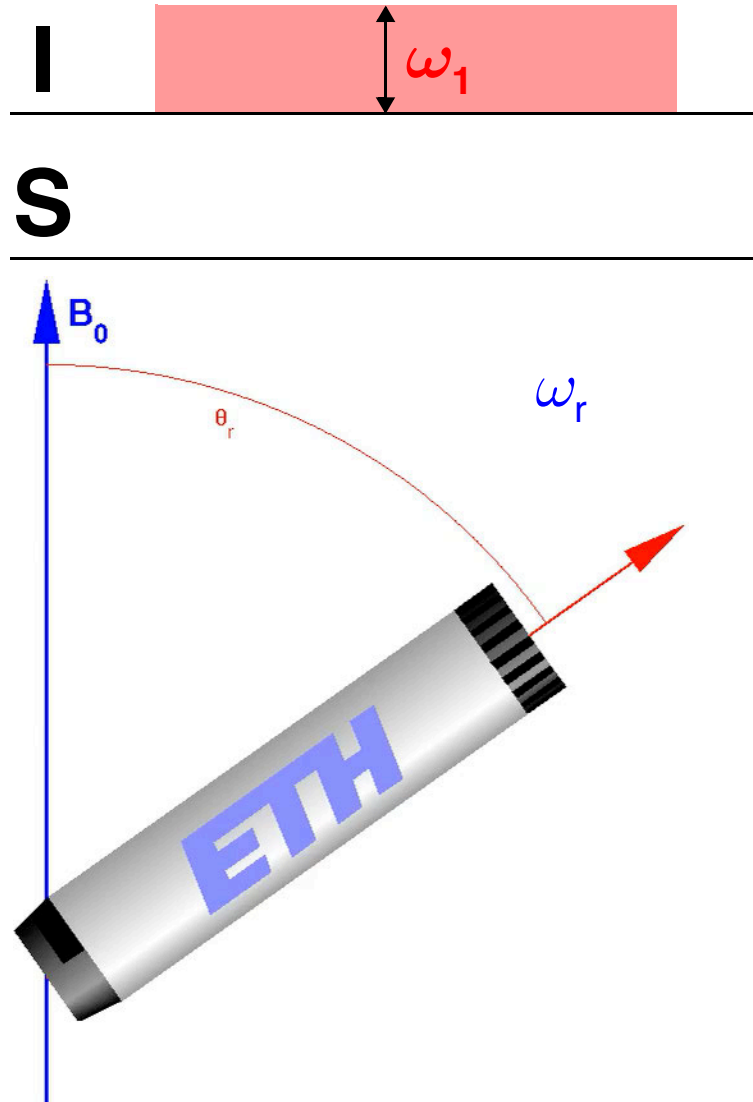
❑ Isotropic J couplings are not averaged.

❑ I-spin spin diffusion will lead to a line broadening of the J multiplet lines.

Heteronuclear Decoupling



Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$



$$\hat{\mathcal{H}}^{(0,0)} = \omega_S^{(0)} S_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m)$$

$$\hat{\mathcal{H}}^{(n,0)} = \omega_S^{(n)} S_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right)$$

$$\hat{\mathcal{H}}^{(0,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp$$

$$\hat{\mathcal{H}}^{(n,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp$$

$$\hat{\mathcal{H}}^{(0,\pm 2)} = 0$$

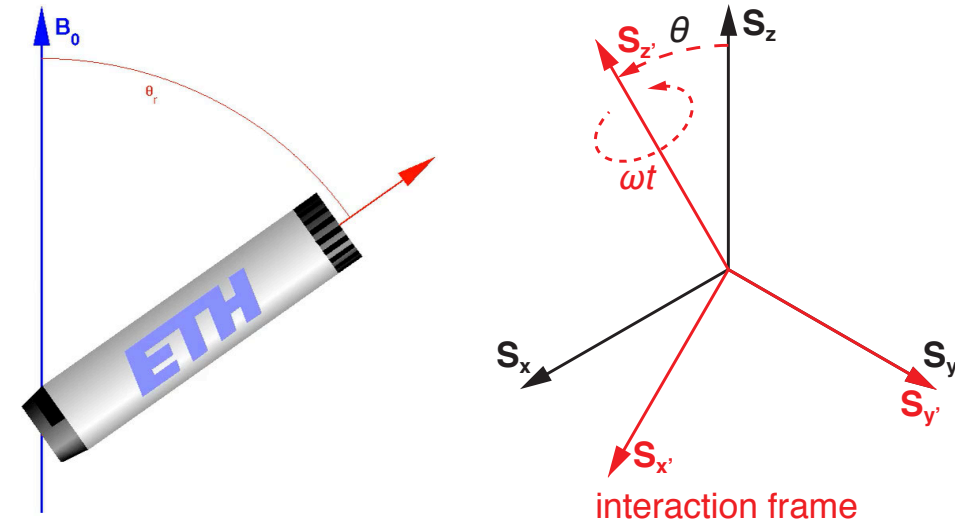
$$\hat{\mathcal{H}}^{(n,\pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp$$

- Time-dependent interaction-frame Hamiltonian under decoupling in rotating solids has (at least) two modulation frequencies:

$$\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-\infty}^{\infty} \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_m t}$$

Floquet Theory

$$\hat{\mathcal{H}} = \sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} - \frac{1}{2} \sum_{n_0, k_0} \sum_{\nu, \kappa} \frac{\left[\hat{\mathcal{H}}^{(n_0-\nu, k_0-\kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)} \right]}{\nu\omega_r + \kappa\omega_m} + \dots$$



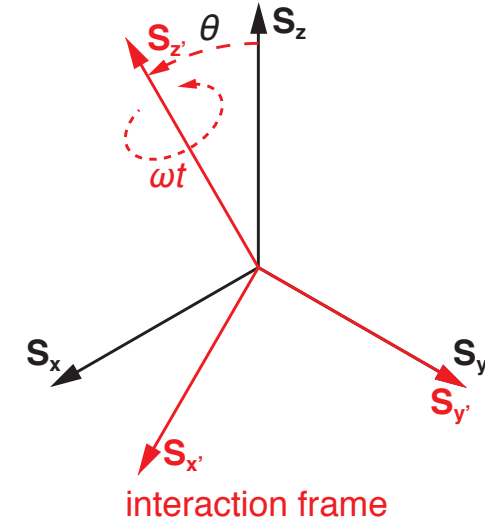
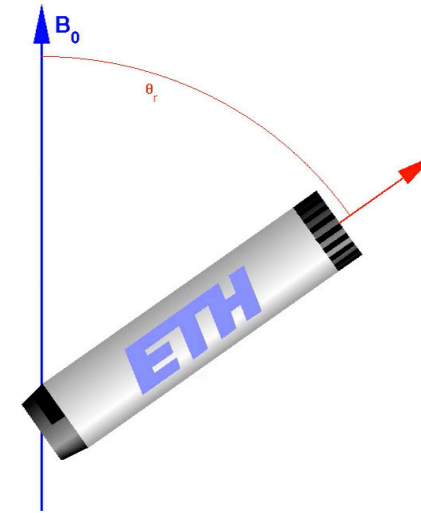
- Factors determining the observed line width:
 - Residual coupling* is given by the **non-resonant** ($\hat{\mathcal{H}}_{(2)}^{(0,0)}$) second-order commutator term because the interaction-frame Hamiltonian is not “symmetric” due to the MAS rotation.
 - Resonance conditions** ($\hat{\mathcal{H}}^{(n_0, k_0)}$ or $\hat{\mathcal{H}}_{(2)}^{(n_0, k_0)}$) between the two modulation frequencies can lead to large terms which can be beneficial or detrimental to the decoupling process.
 - I-spin spin diffusion* (resulting from **resonant** or **non-resonant** terms) leads to an additional averaging of the residual couplings.
- Only the interaction between these three effects will explain the decoupling behavior in rotating solids.

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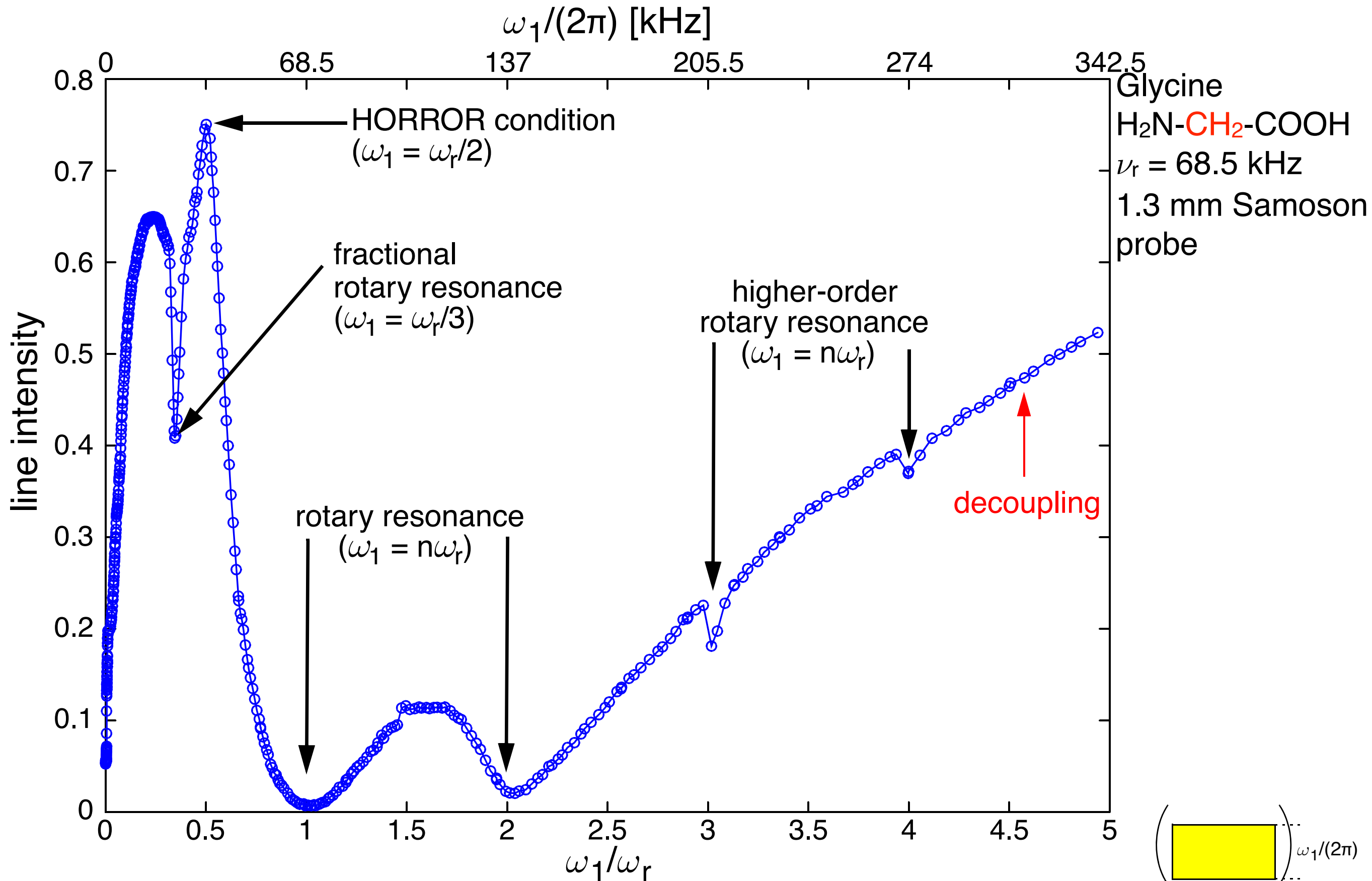
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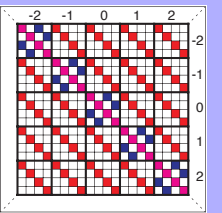


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CW Decoupling in Rotating Solids



Outside Resonance Conditions: Decoupling



Outside the resonance conditions, the non-resonant contributions are important:

$$\bar{\mathcal{H}} = \hat{\mathcal{H}}^{(1)} + \hat{\mathcal{H}}^{(2)} + \dots = \hat{\mathcal{H}}^{(0,0)} + \hat{\mathcal{H}}_{(2)}^{(0,0)} + \dots = \hat{\mathcal{H}}^{(n_0, k_0)} - \frac{1}{2} \sum_{\nu, \kappa} \frac{\left[\hat{\mathcal{H}}^{(-\nu, -\kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)} \right]}{\nu\omega_r + \kappa\omega_m} + \dots$$

In first order we have the isotropic chemical shift of the S spin and the J couplings of the I spins:

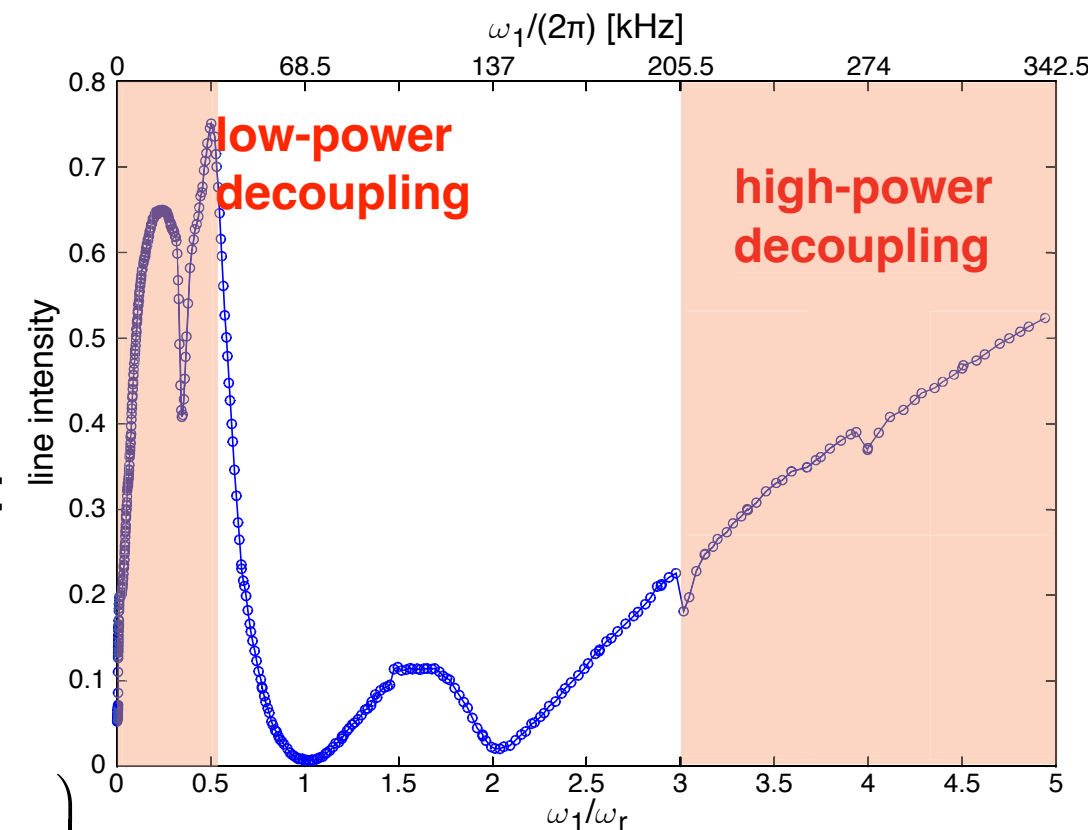
$$\hat{\mathcal{H}}^{(1)} = \omega_S^{(0)} \mathbf{S}_z + \sum_{\ell < m} \omega_{\ell, m}^{(0)} \left(\hat{\mathbf{I}}_{\ell} \cdot \hat{\mathbf{I}}_m \right)$$

The second-order non-resonant effective Hamiltonian:

$$\begin{aligned} \hat{\mathcal{H}}^{(2)} &= -\frac{1}{2} \sum_{\nu, \kappa} \frac{\left[\hat{\mathcal{H}}^{(-\nu, -\kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)} \right]}{\nu\omega_r + \kappa\omega_m} \\ &= +\frac{1}{4} \sum_{\nu, \kappa} \left(\frac{\omega_I^{(\nu)} \omega_{IS}^{(-\nu)} + \omega_{IS}^{(\nu)} \omega_I^{(-\nu)}}{\nu\omega_r + \kappa\omega_1} 2\mathbf{S}_z \mathbf{I}_z + \frac{\omega_I^{(\nu)} \omega_I^{(-\nu)} + \omega_{IS}^{(\nu)} \omega_{IS}^{(-\nu)}}{\nu\omega_r + \kappa\omega_1} \mathbf{I}_z \right) \end{aligned}$$

In second order we have cross terms between the heteronuclear dipolar coupling and the I-spin CSA tensor.

There are no homonuclear/heteronuclear dipolar-coupling cross terms.

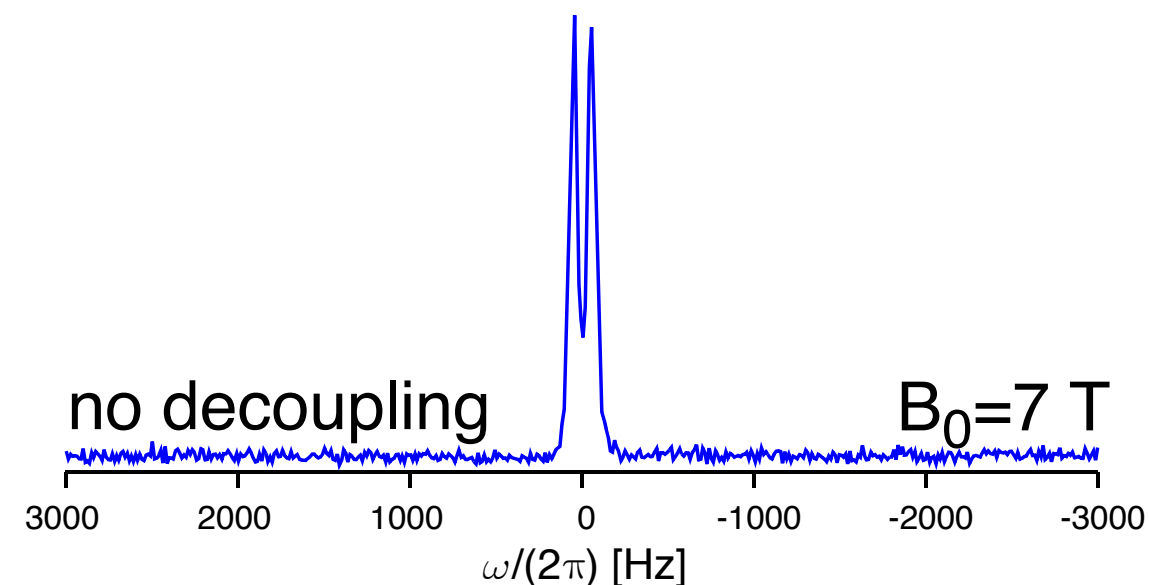
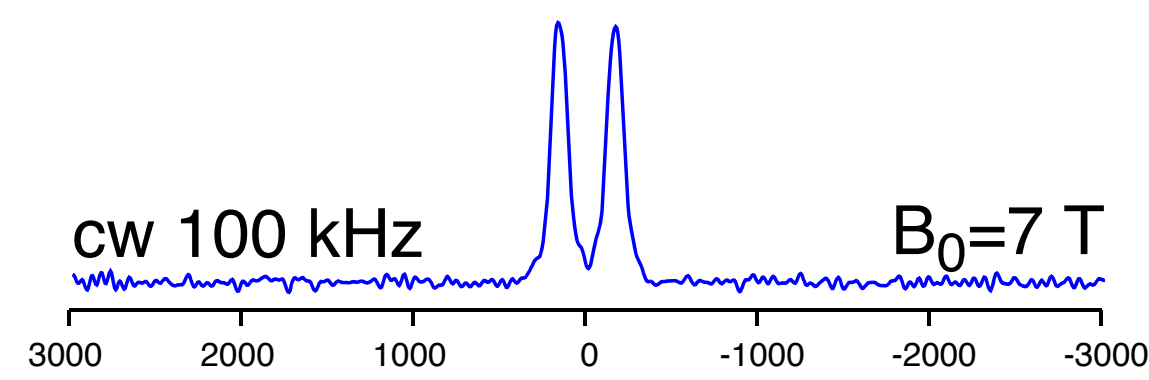
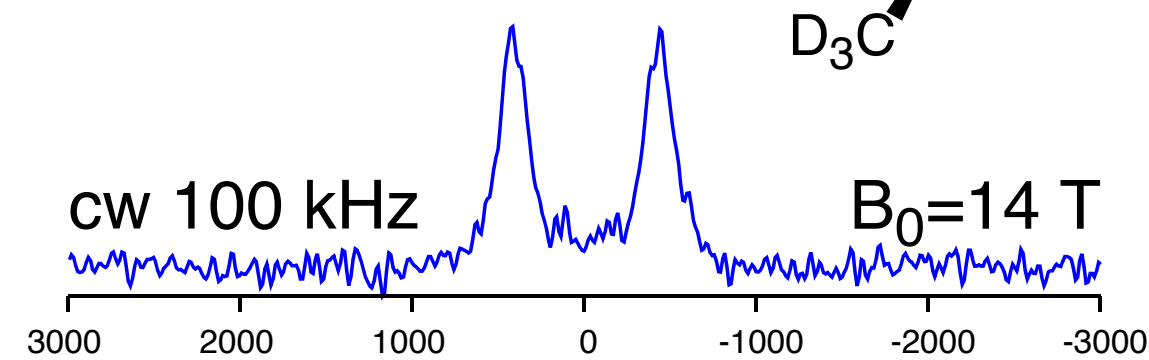
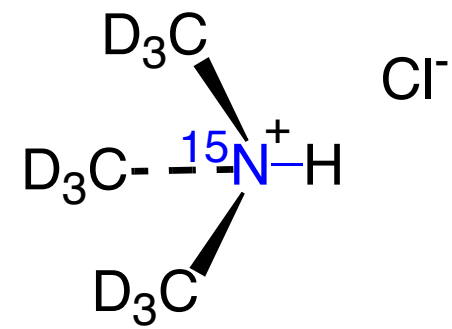
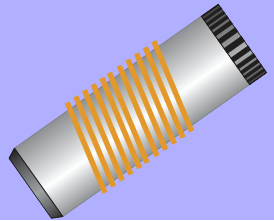


$$\hat{\mathcal{H}}^{(0,0)} = \omega_S^{(0)} \mathbf{S}_z + \sum_{\ell < m} \omega_{\ell, m}^{(0)} \left(\hat{\mathbf{I}}_{\ell} \cdot \hat{\mathbf{I}}_m \right)$$

$$\hat{\mathcal{H}}^{(n, \pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{\mathbf{I}}_m^{\mp} - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{\mathbf{S}}_z \hat{\mathbf{I}}_m^{\mp}$$

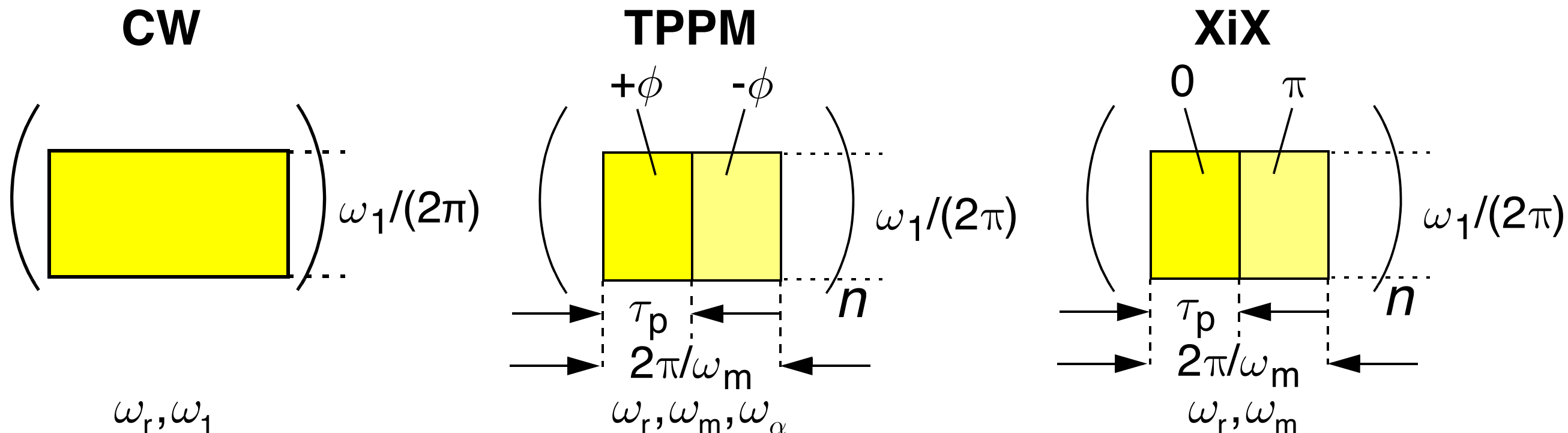
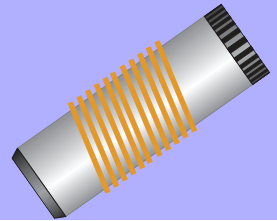
$$\hat{\mathcal{H}}^{(n, \pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell, m}^{(n)} \hat{\mathbf{I}}_{\ell}^{\mp} \hat{\mathbf{I}}_m^{\mp}$$

Continuous-Wave Decoupling in Rotating Solids



- ❑ Continuous-wave decoupling is a terrible decoupling sequence with a large residual coupling.
- ❑ Residual coupling increases with increasing B_0 field strength (CSA term!).
- ❑ Rotary-resonance conditions have to be avoided:
 - High-power decoupling: $\omega_1 > 3\omega_r$.
 - Low-power decoupling: $\omega_1 < \omega_r/2$ for high MAS frequencies.
- ❑ I-spin spin diffusion averages the residual coupling:
 - Observable line width increases with increasing spinning frequency: spin diffusion is slowed down.
 - Low-power decoupling at the HORROR condition leads to a narrower line width.
- ❑ High-power decoupling: $\Delta\omega_1$ decreases with ω_1 .
- ❑ Low-power decoupling: $\Delta\omega_1$ decreases with ω_r .

Asynchronous Decoupling Sequences



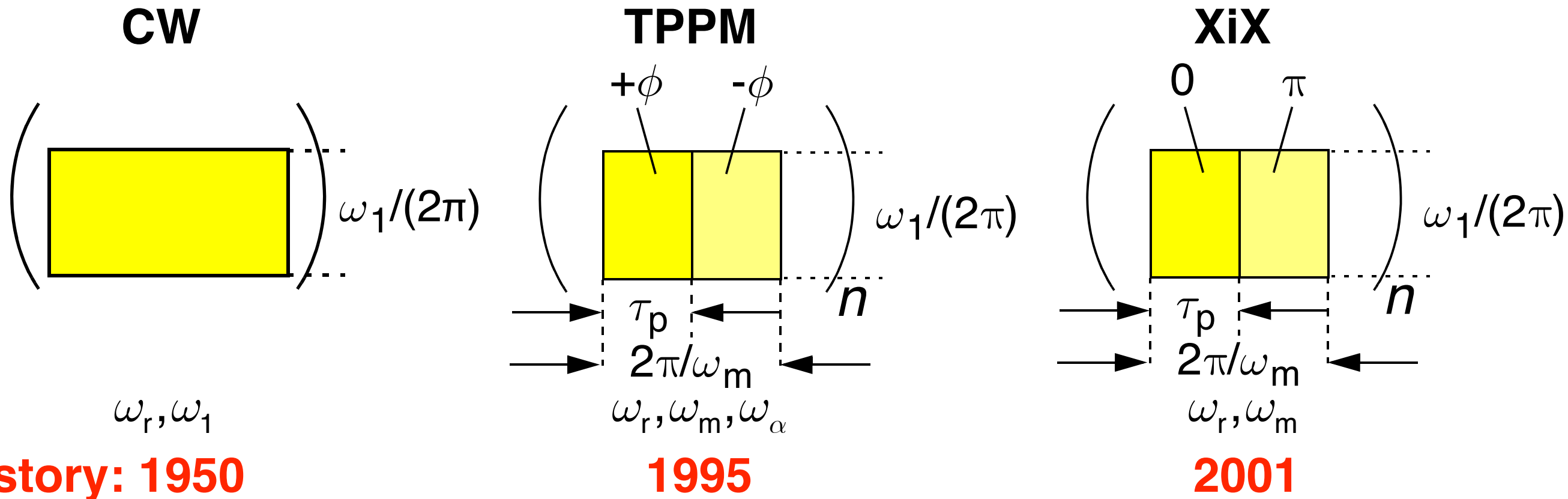
❑ All sequences have at least two frequencies in the interaction frame.

❑ There are many modifications of the TPPM sequence:

- frequency-modulated and phase-modulated (FMPPM) TPPM
- small phase angle rapid cycling (SPARC) small phase incremental alternation (SPINAL)
- CPM m-n; amplitude-modulated TPPM (AM-TPPM); GT-n
- continuous modulation (CM) TPPM
- swept-frequency TPPM ($\text{SW}_f\text{-TPPM}$)

TPPM: A. E. Bennett, et al., J. Chem. Phys. **103** (1995) 6951. **XiX:** A. Detken, et al., Chem. Phys. Lett. **356** (2002) 298.

Asynchronous Decoupling Sequences



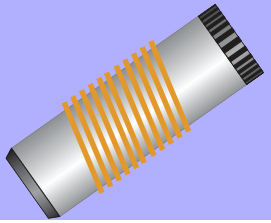
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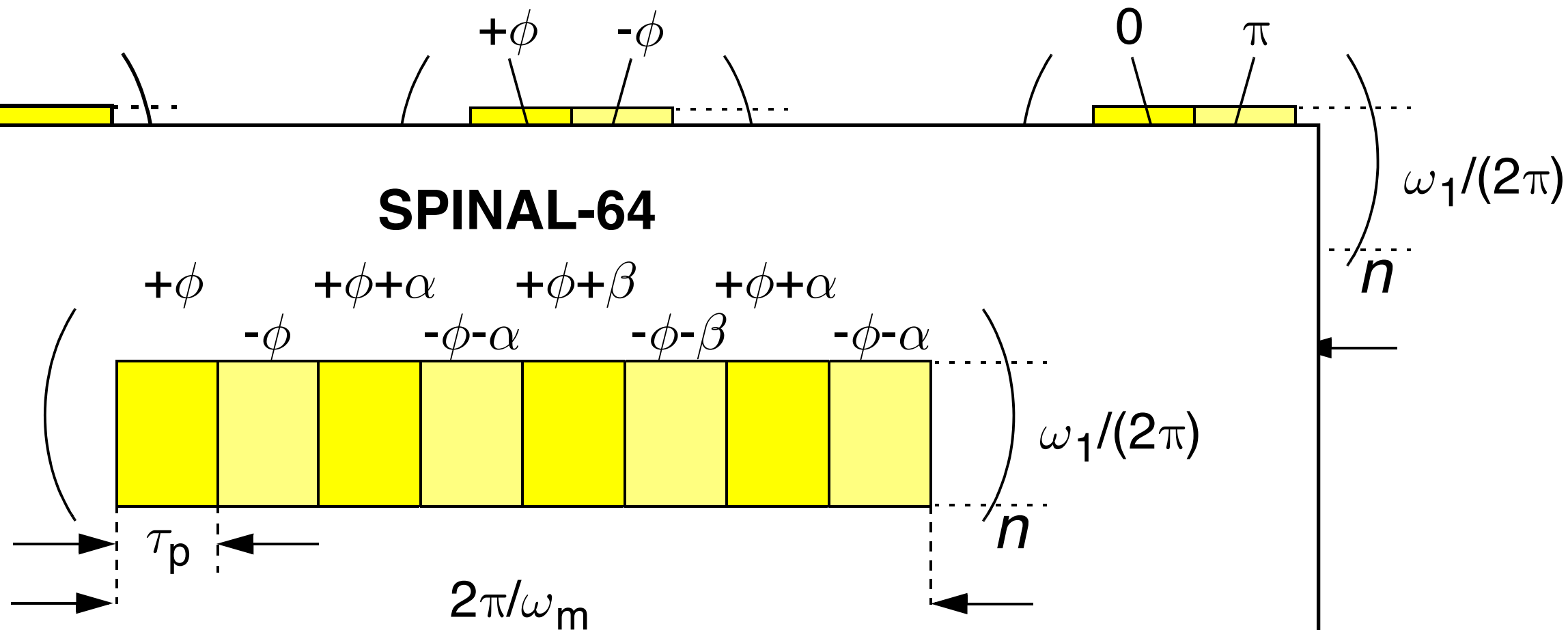


CW

TPPM

XiX

SPINAL-64



Hist

☐ All

☐ Th

- fr ☐ SPINAL-64: $\phi=10^\circ$, $\alpha=5^\circ$, $\beta=2\alpha$, super cycle $Q\bar{Q}\bar{Q}Q\bar{Q}Q\bar{Q}Q\bar{Q}$

- S ☐ Phase angles and pulse lengths have to be optimized.

- C

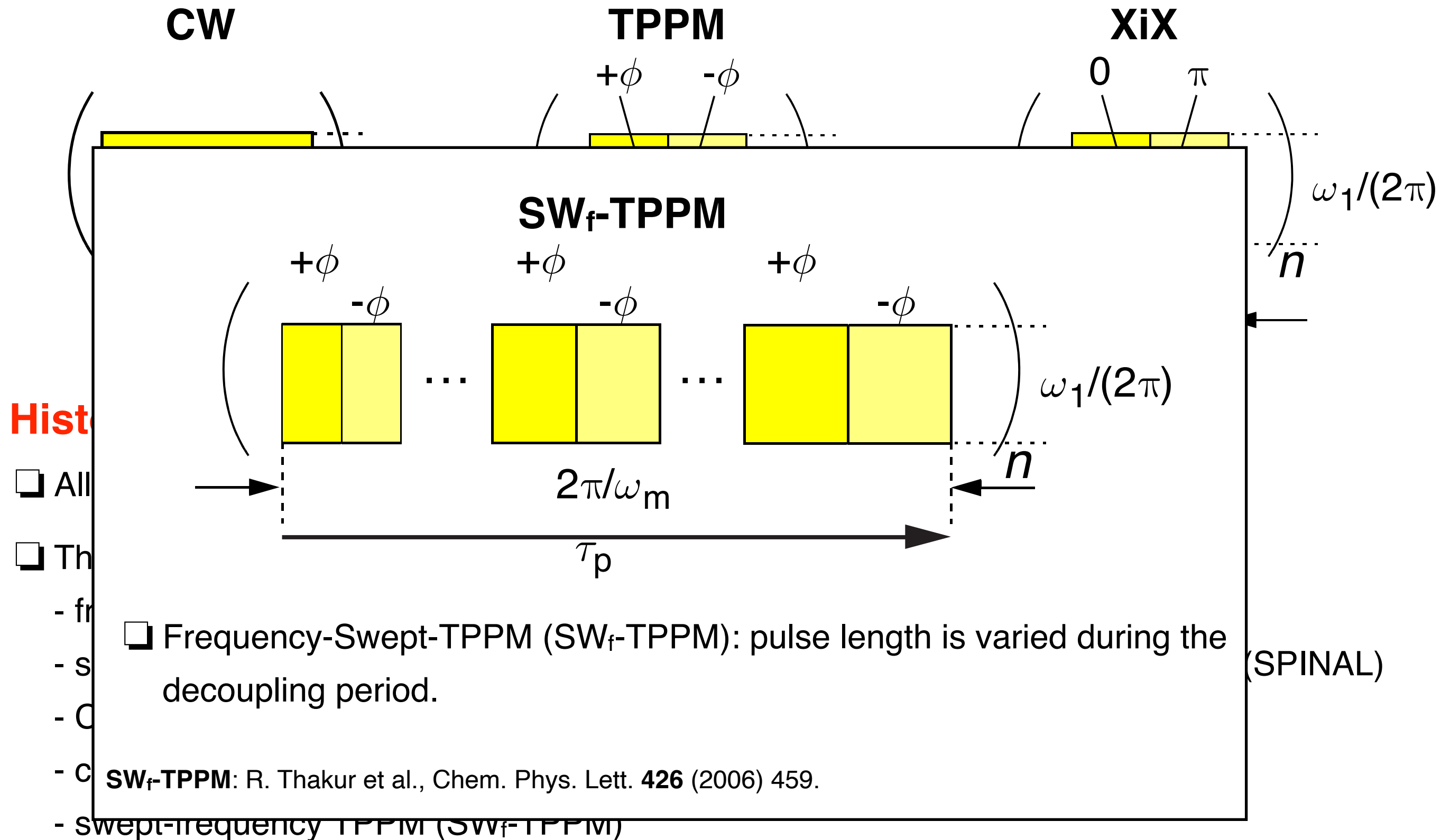
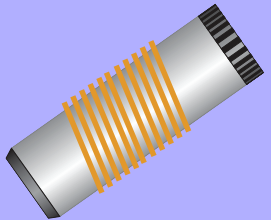
- C **SPINAL-64**: B. A. Fung, et al., J. Magn. Reson. **142** (2000) 97. G. Comellas et al., J. Magn. Reson. **209** (2011) 131.

- Swept-frequency TPPM (Svff-TPPM)

(SPINAL)

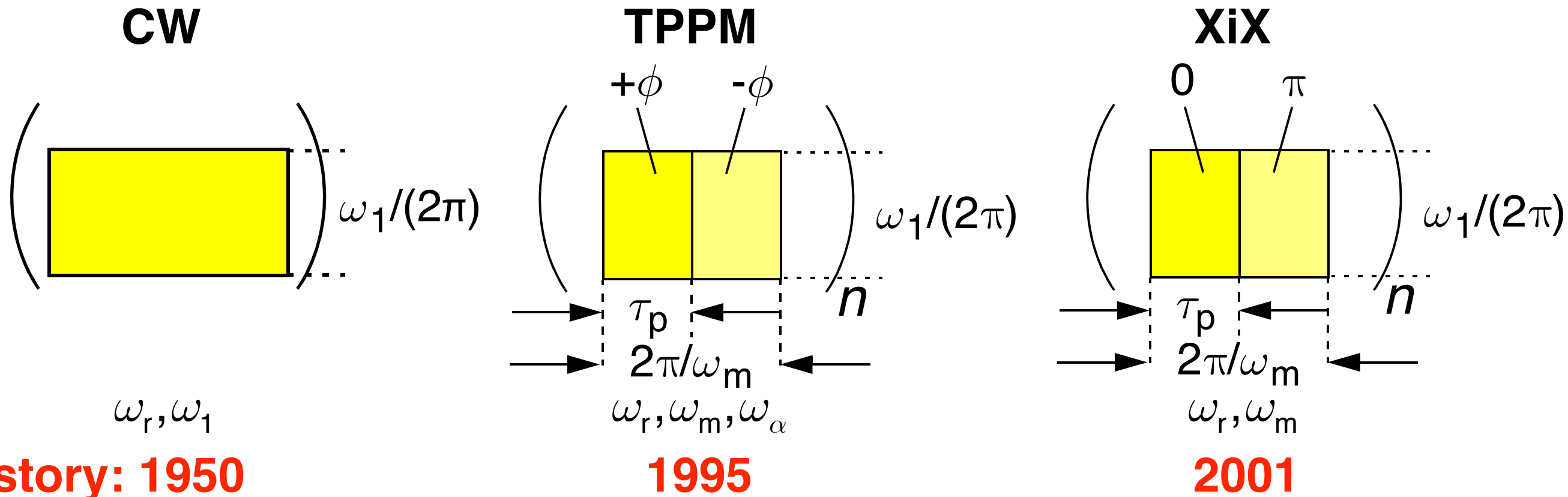
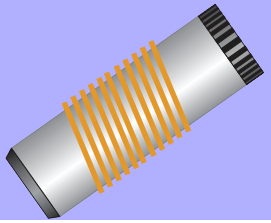
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XiX Decoupling in Rotating Solids



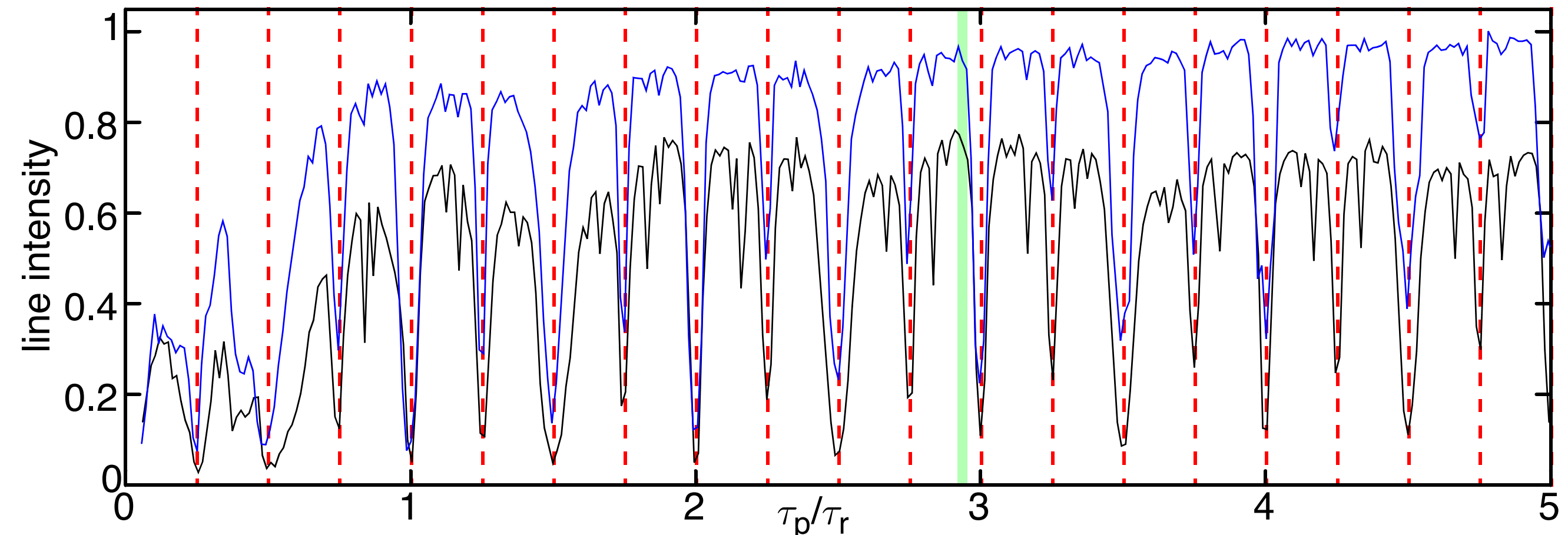
- Residual coupling is given by a non-resonant second-order cross term between the I-spin homonuclear and the heteronuclear dipolar coupling:

$$\hat{\mathcal{H}}_{(2)}^{(0,0)} = -\frac{3}{8} \sum_{\nu, \kappa} \sum_{\ell \neq m} \frac{\omega_{\ell m}^{(\nu)} \omega_{\ell s}^{(-\nu)} + \omega_{\ell s}^{(\nu)} \omega_{\ell m}^{(-\nu)}}{\nu \omega_r + \kappa \omega_m} \left(a_x^{(\kappa)} b_x^{(\kappa)} + a_y^{(\kappa)} b_y^{(\kappa)} \right) 4S_z I_{\ell z} I_{mz}$$

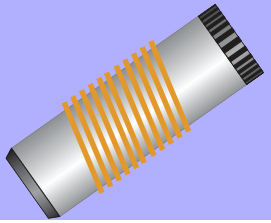
- First-order resonance conditions at $n_0 = \pm 1, \pm 2$: $\tau_p/\tau_r = -k_0/2$ and $\tau_p/\tau_r = -k_0/4$.

- Very strong and rf-field and spinning frequency independent.
- Heteronuclear dipolar coupling is directly recoupled. Strength is determined by $a^{(k)}$.

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(n_0, k_0)} + \hat{\mathcal{H}}^{(-n_0, -k_0)} = 2 \sum_{\ell} \text{Re} \left(\omega_{\ell s}^{(n_0)} \right) \left(a_x^{(k_0)} 2S_z I_{\ell x} + a_y^{(k_0)} 2S_z I_{\ell y} \right)$$



XiX Decoupling in Rotating Solids



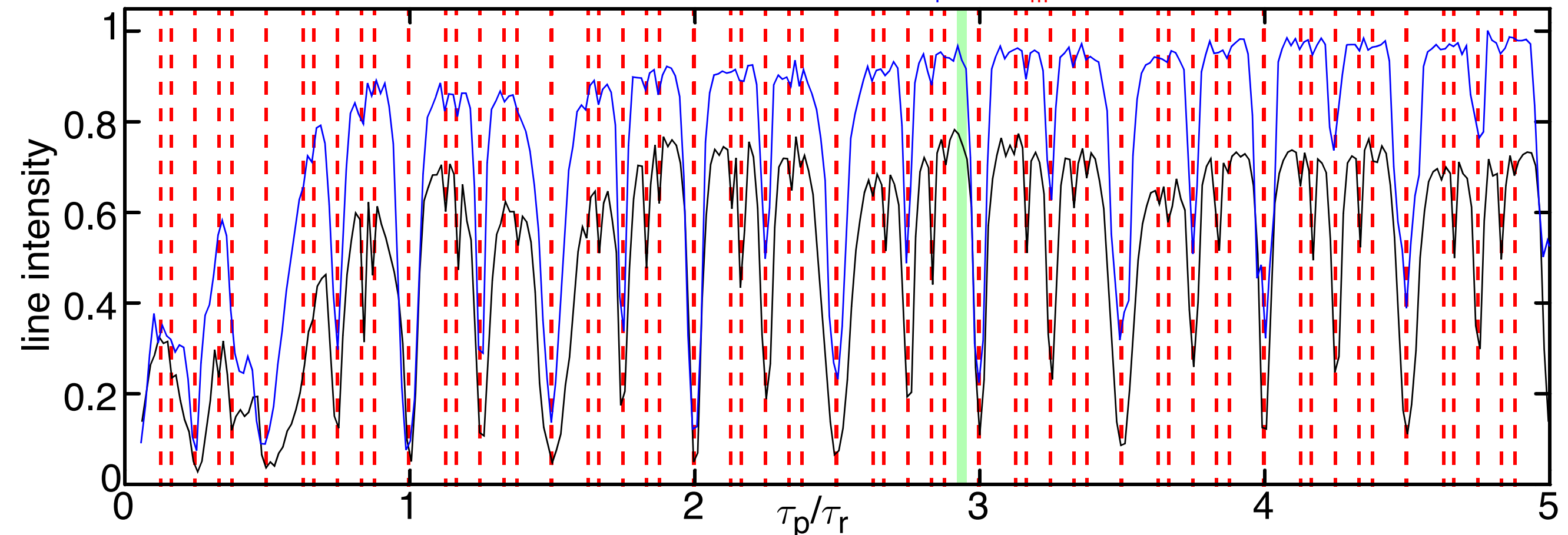
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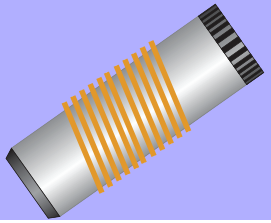
- Second-order resonance conditions at $n_0 = \pm 3, \pm 4$: $\tau_p/\tau_r = -k_0/6$ and $\tau_p/\tau_r = -k_0/8$.

- Decreases with increasing rf-field amplitude and increasing MAS frequency.
- Cross term between I-spin CSA and heteronuclear dipolar coupling..

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{(2)}^{(n_0, k_0)} + \hat{\mathcal{H}}_{(2)}^{(-n_0, -k_0)} = 2 \sum_{\ell} \text{Im} \left(\omega_{\ell s}^{(+2)} \omega_{\ell}^{(+2)} \right) \sum_{\kappa} \frac{\left(a_x^{(k_0 - \kappa)} a_y^{(\kappa)} - a_x^{(\kappa)} a_y^{(k_0 - \kappa)} \right)}{\nu\omega_r + \kappa\omega_m} 2S_z I_{\ell z}$$



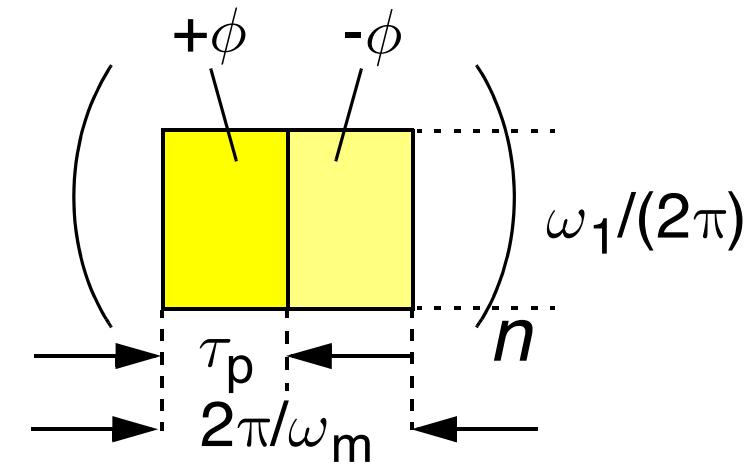
TPPM Decoupling in Rotating Solids



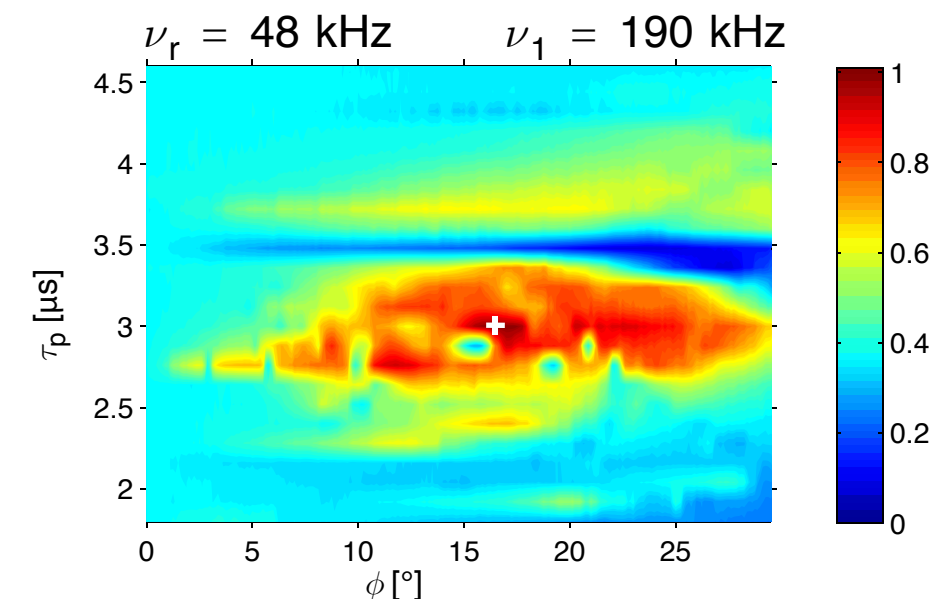
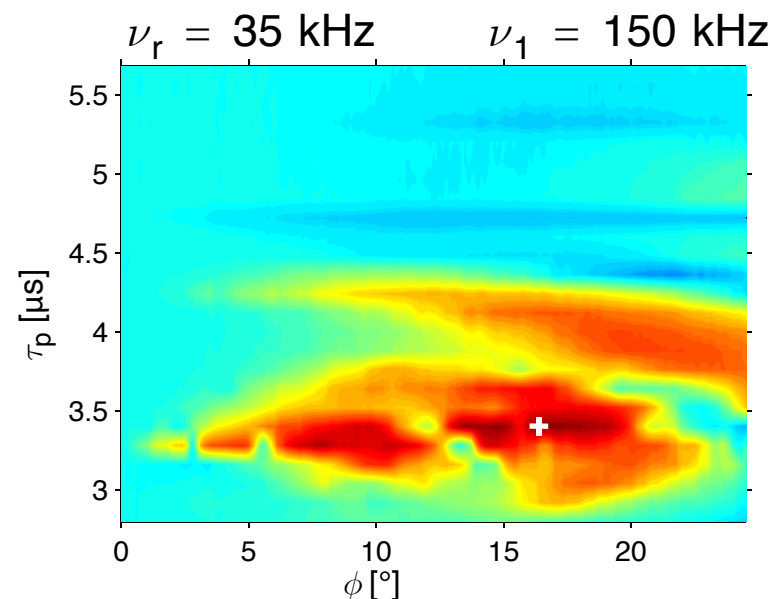
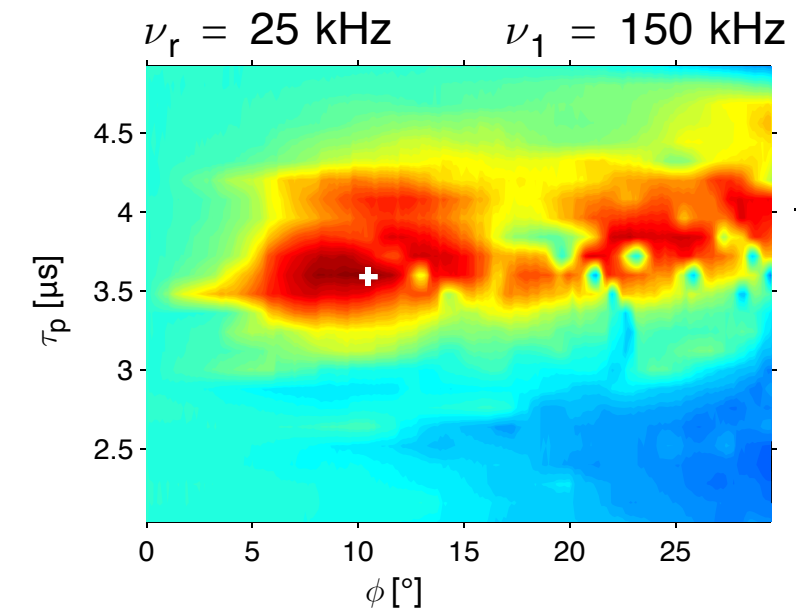
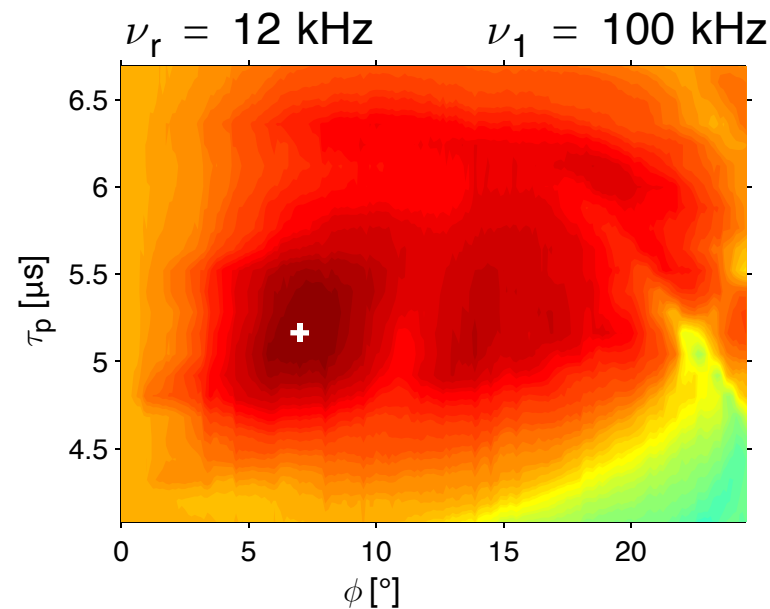
TPPM decoupling consists of two pulses with a phase shift of 2ϕ .

Flip-angle of the pulses is roughly a 180° pulse.

Phase angle and flip angle (pulse length) have to be optimized.



$\frac{\nu_1}{\text{kHz}}$	$\frac{\nu_r}{\text{kHz}}$	$\frac{\tau_p^{(\max)}}{\mu\text{s}}$	$\frac{\phi^{(\max)}}{^\circ}$	$\frac{\tau_p^{(\max)}}{\tau_\pi}$	$\frac{I^{(\max)}}{I(\text{cw})}$
100	12	5.2	7	1.03	1.4
150	25	3.6	10.5	1.08	2.4
150	35	3.4	16.4	1.02	2.6
190	48	3	16.5	1.14	2.6

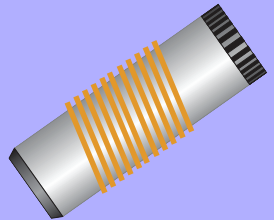


Optimum phase angle changes significantly with experimental parameters.

Optimum pulse length is always close to a 180° pulse.

A. E. Bennett, et al., J. Chem. Phys. **103** (1995) 6951.

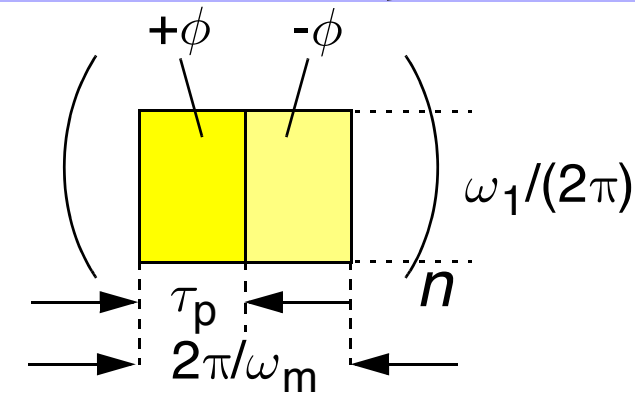
Theory of TPPM Decoupling Under MAS



There is no analytical solution for the interaction-frame transformation under TPPM.

Interaction-frame transformation has more than one frequency because the basic TPPM element has an effective nutation frequency:

$$\hat{S}_x \rightarrow \hat{S}_x a_{xx}(t) + \hat{S}_y a_{xy}(t) + \hat{S}_z a_{xz}(t) = \sum_{k=-\infty}^{\infty} \sum_{l=-2}^2 \left(\hat{S}_x a_{xx}^{(k,l)} + \hat{S}_{xy} a_{xy}^{(k,l)} + \hat{S}_z a_{xz}^{(k,l)} \right) e^{ik\omega_m t} e^{il\omega_{\text{eff}} t}$$

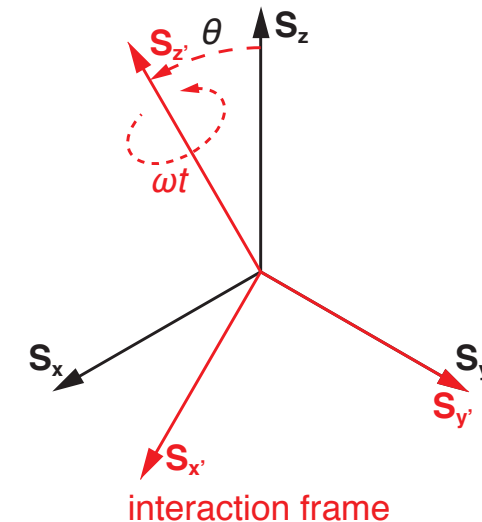
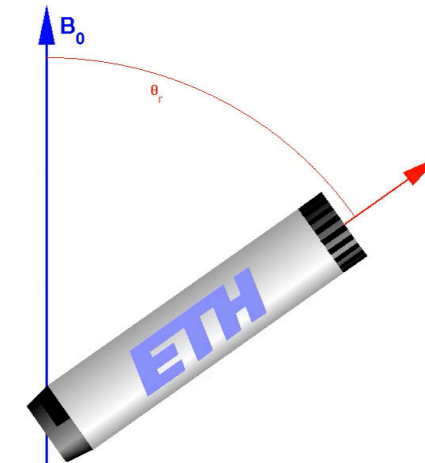


Interaction-frame Hamiltonian has now three frequencies: ω_r , ω_m , ω_{α}

$$\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-\infty}^{\infty} \sum_{l=-2}^2 \hat{\mathcal{H}}^{(n,k,l)} e^{in\omega_r t} e^{ik\omega_m t} e^{il\omega_{\text{eff}} t}$$

Floquet Theory

$$\hat{\mathcal{H}} = \sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0, l_0)} - \frac{1}{2} \sum_{n_0, k_0} \sum_{\nu, \kappa} \frac{\left[\hat{\mathcal{H}}^{(n_0-\nu, k_0-\kappa, l_0-\lambda)}, \hat{\mathcal{H}}^{(\nu, \kappa, \lambda)} \right]}{\nu\omega_r + \kappa\omega_m + \lambda\omega_{\text{eff}}} + \dots$$



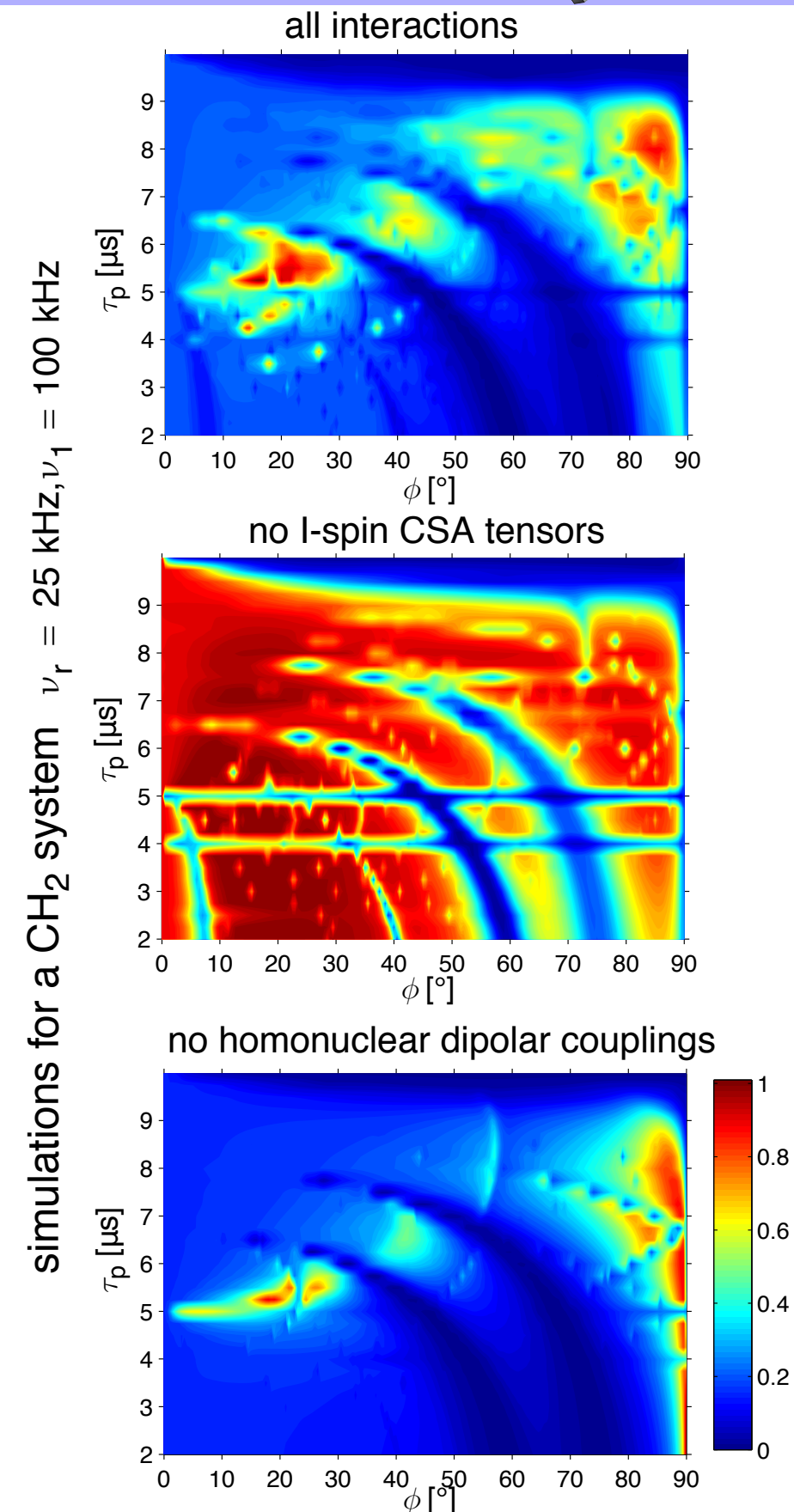
Triple-mode Floquet theory is required to describe TPPM decoupling properly.

There are additional and more complex resonance conditions possible.

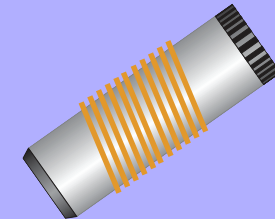
TPPM Decoupling in Rotating Solids



- TPPM decoupling is a sequence that has small **residual couplings** that originate from cross term between I-spin CSA and heteronuclear dipolar-coupling tensors. Cross terms between the heteronuclear and the homonuclear dipolar couplings are only important for $\phi = 90^\circ$ (XiX!).
- Some **resonance conditions** reintroduce the heteronuclear dipolar coupling ($n_0\omega_r = \omega_m$, $n_0\omega_r = \omega_{\epsilon\phi\phi}$) and have to be avoided. Others reintroduce the homonuclear dipolar couplings of the I spins ($n_0\omega_r = \pm(\omega_m - \omega_{\epsilon\phi\phi})$) and are beneficial for the decoupling process by increasing the I-spin spin diffusion process.
- I-spin spin diffusion** is present everywhere but is emphasized on the homonuclear resonance conditions.
- Numerical simulations with different contributions to the Hamiltonian support this picture.



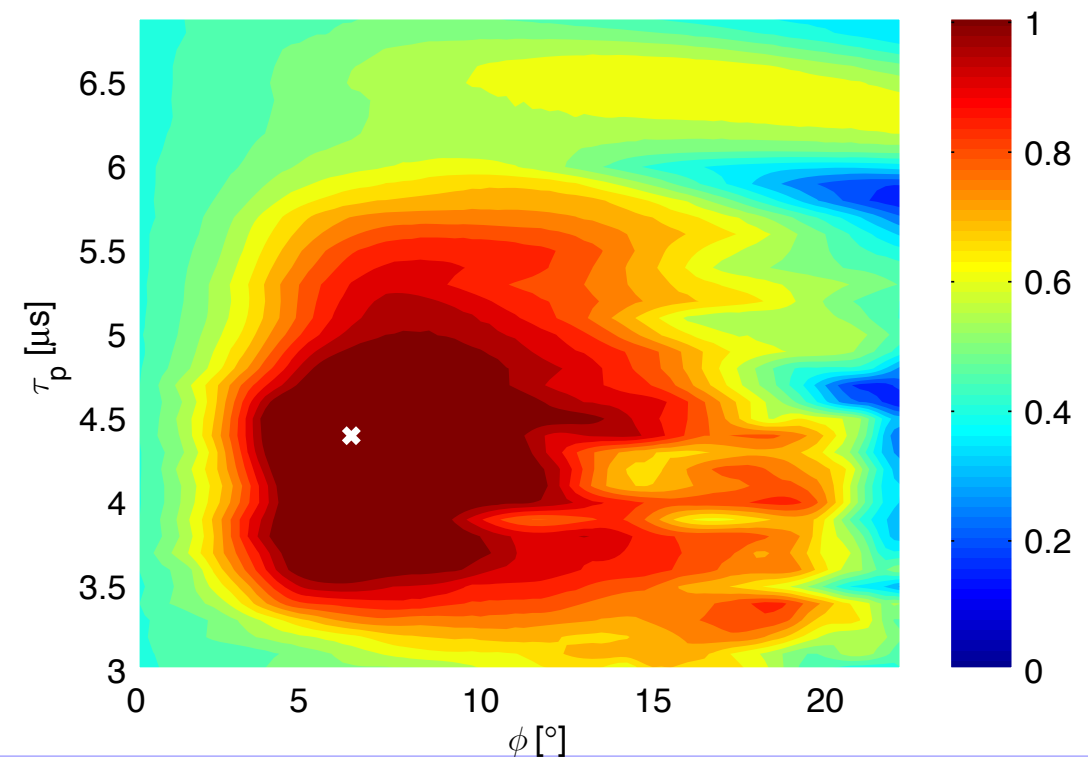
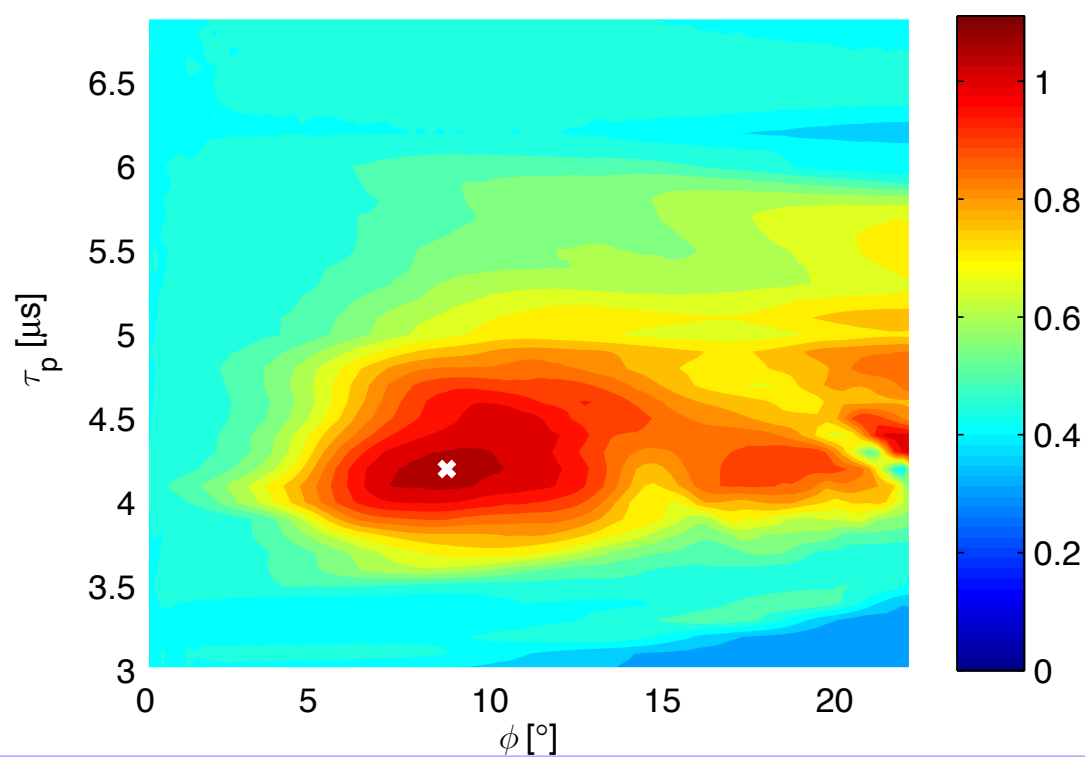
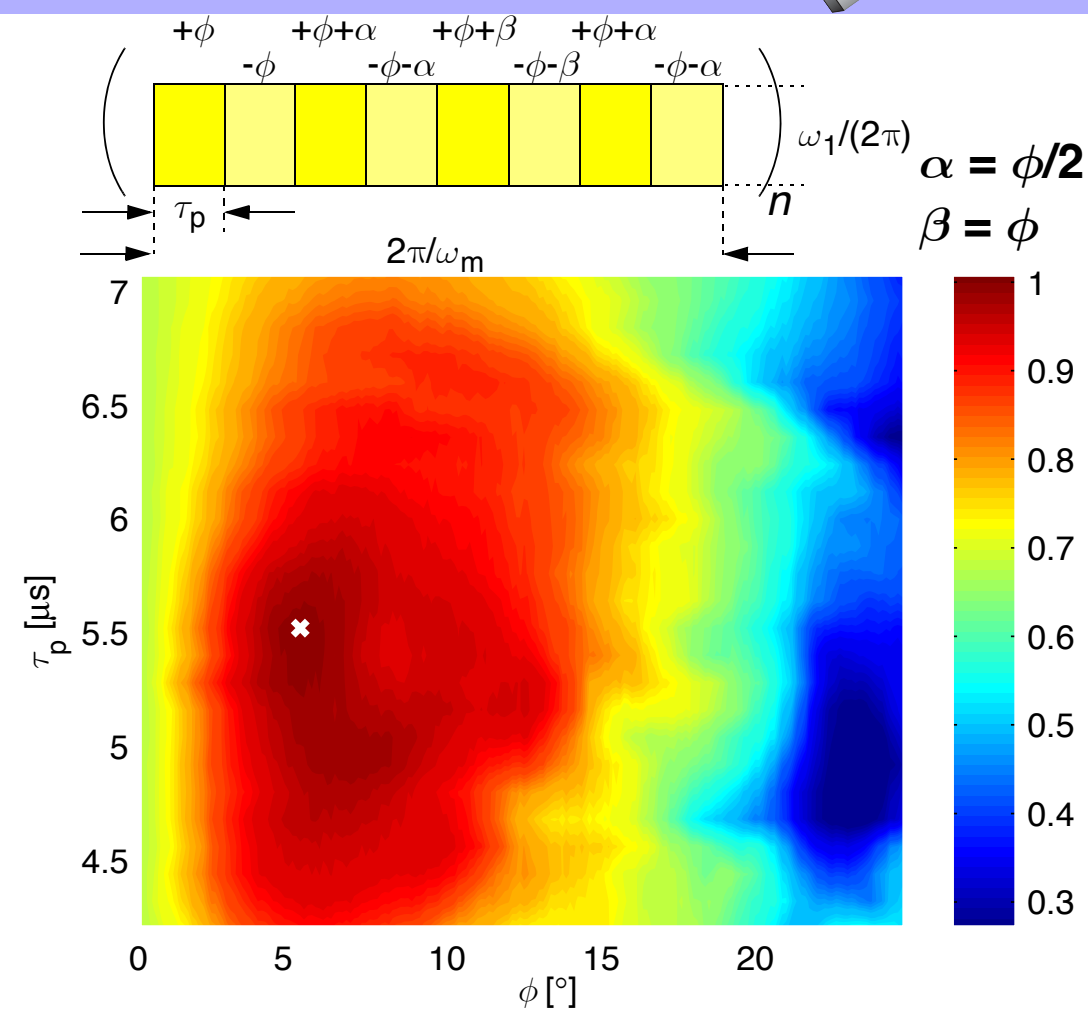
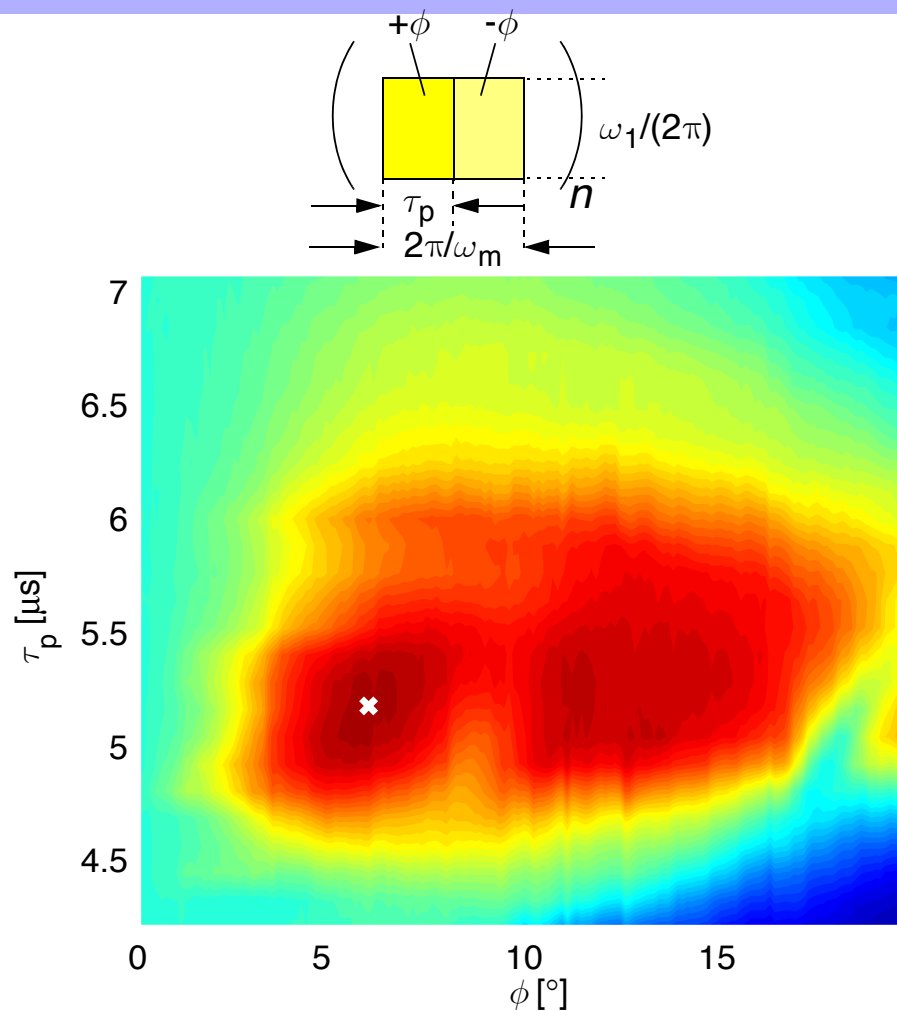
TPPM Versus SPINAL-64 for “slower” MAS



□ About 10% differences in intensities and significantly broader optimum.

$\nu_r = 10 \text{ kHz}$, $\nu_1 = 100 \text{ kHz}$
 $B_0 = 11.7 \text{ T}$

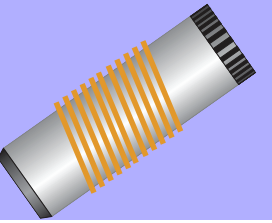
$\nu_r = 19 \text{ kHz}$, $\nu_1 = 120 \text{ kHz}$
 $B_0 = 20 \text{ T}$



$$\alpha = \phi/2$$

$$\beta = \phi$$

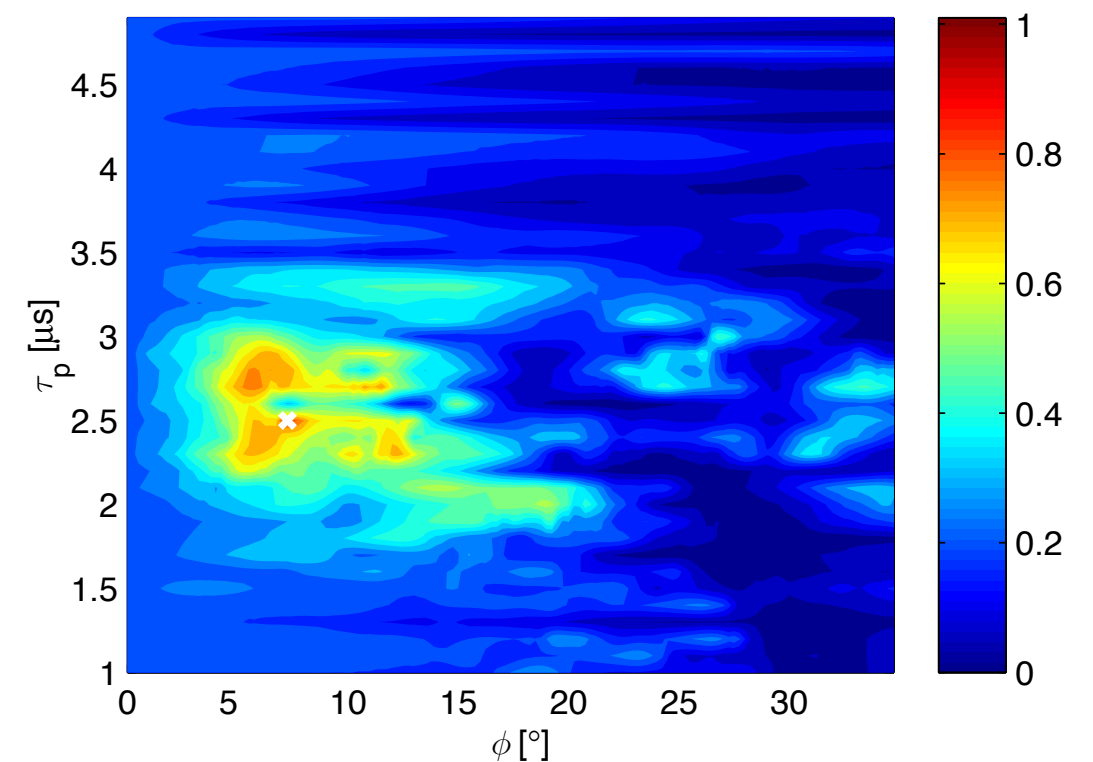
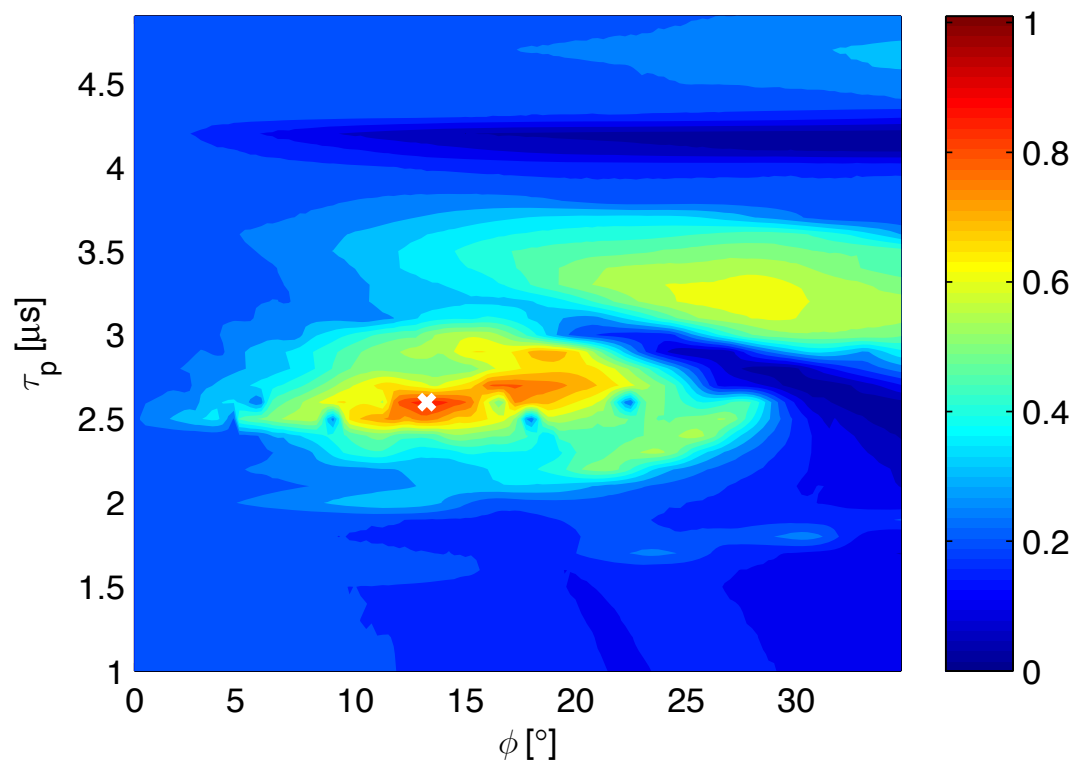
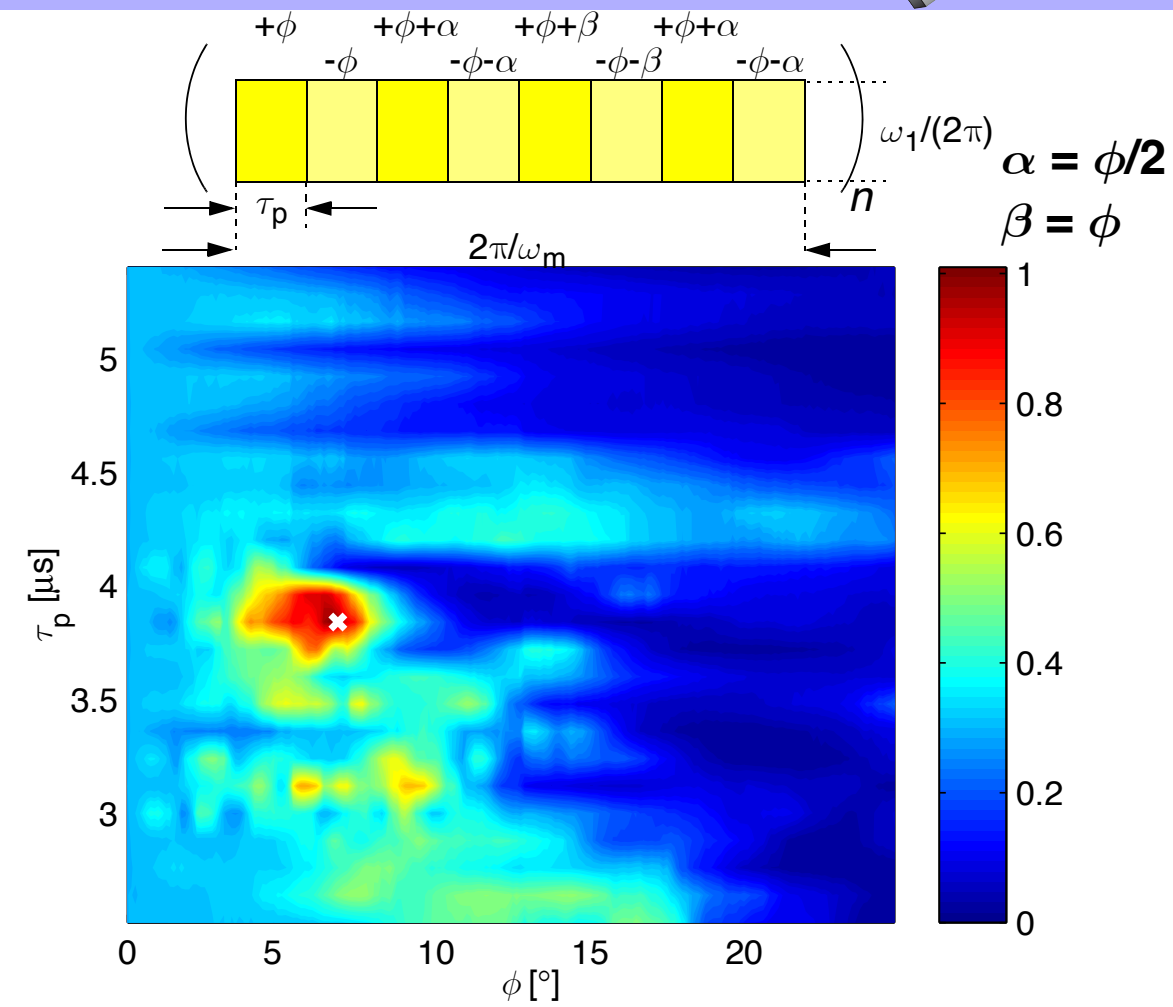
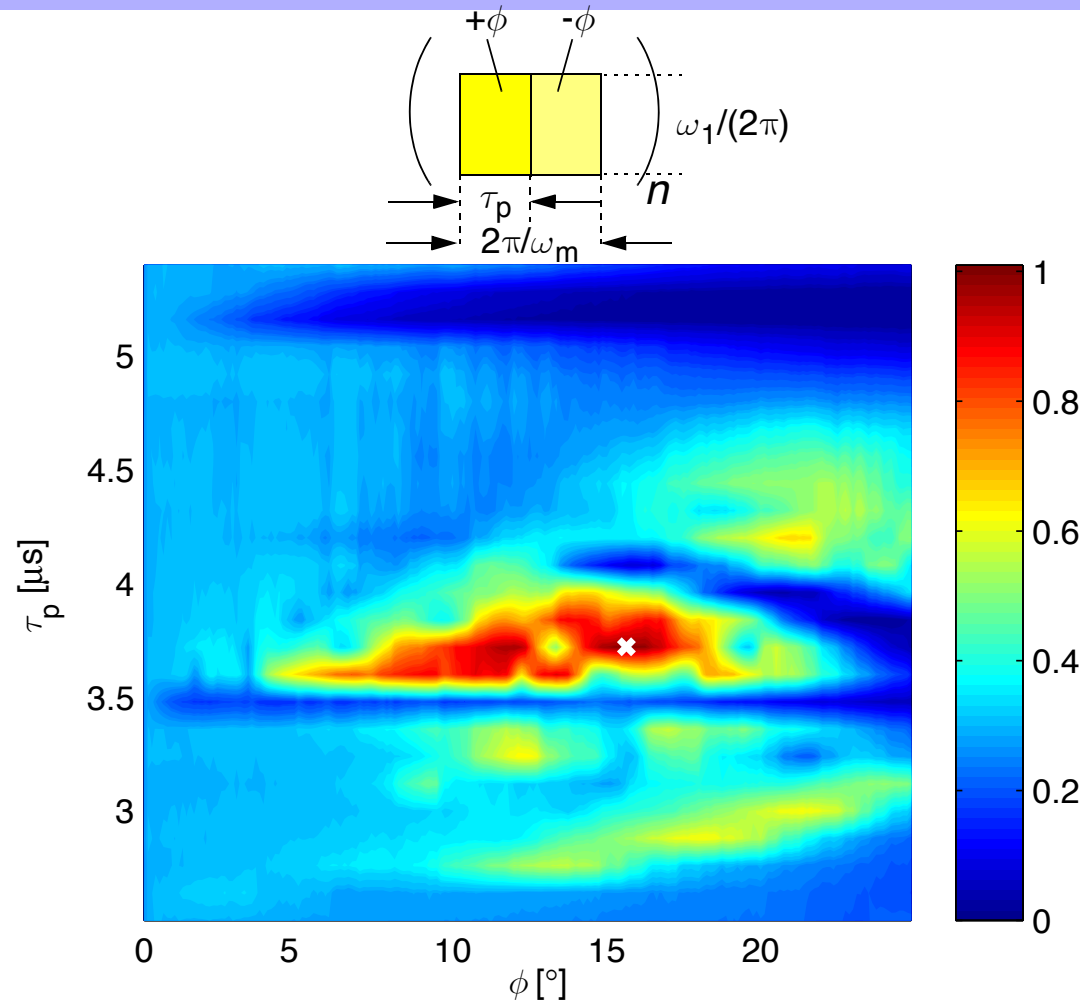
TPPM Versus SPINAL-64 for Fast MAS



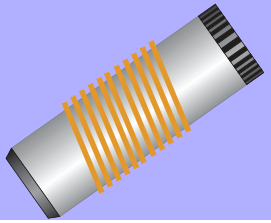
❑ No significant differences in intensities or in the ease of optimization.

$\nu_r = 48 \text{ kHz}$, $\nu_1 = 150 \text{ kHz}$
 $B_0 = 11.7 \text{ T}$

$\nu_r = 68 \text{ kHz}$, $\nu_1 = 190 \text{ kHz}$
 $B_0 = 20 \text{ T}$

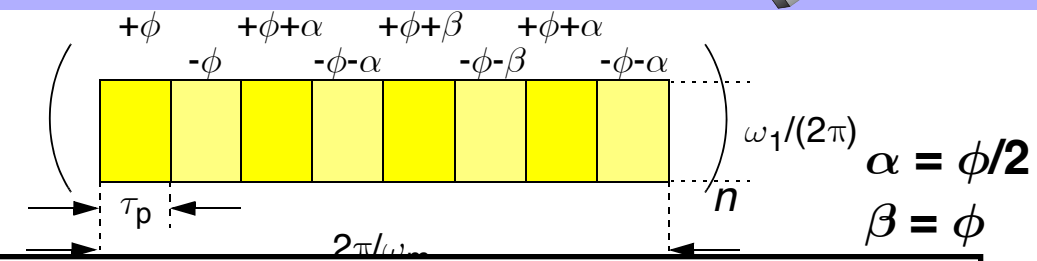
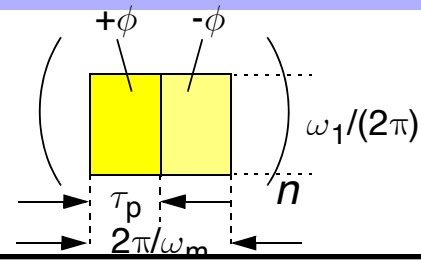


TPPM Versus SPINAL-64 for Fast MAS

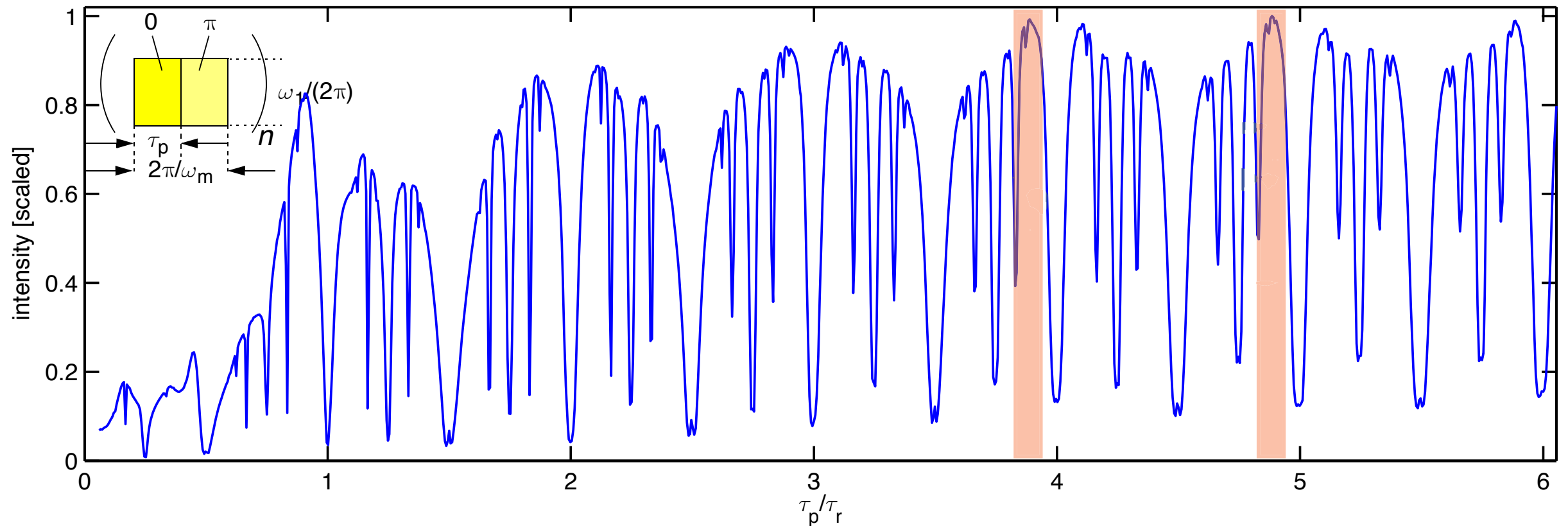


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$\mathbf{Z}$



$\nu_r = 68 \text{ kHz}, \nu_1 = 190 \text{ kHz}, B_0 = 20 \text{ T}$

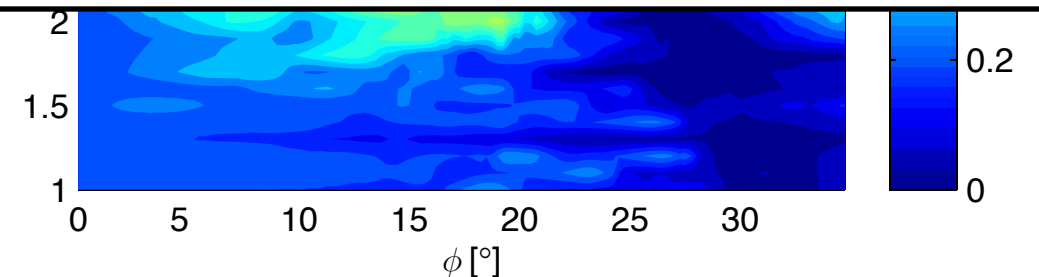
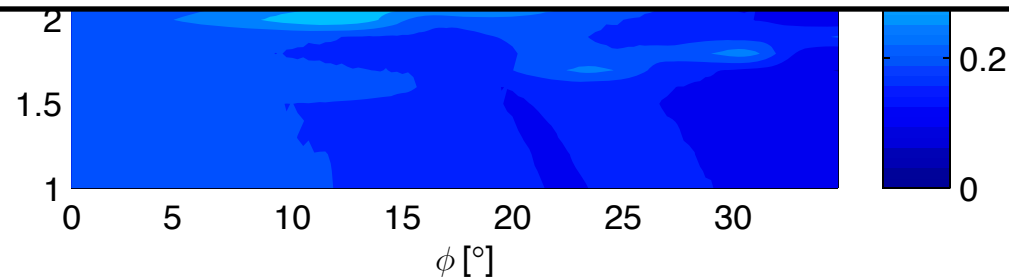


❑ XiX gives about 10-15% higher line intensities but at $\tau_p/\tau_r = 3.88$ and 4.88 .

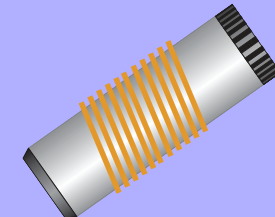
❑ No sig

optimi

$\nu_r = 68 \text{ kHz}$
 $B_0 = 20 \text{ T}$



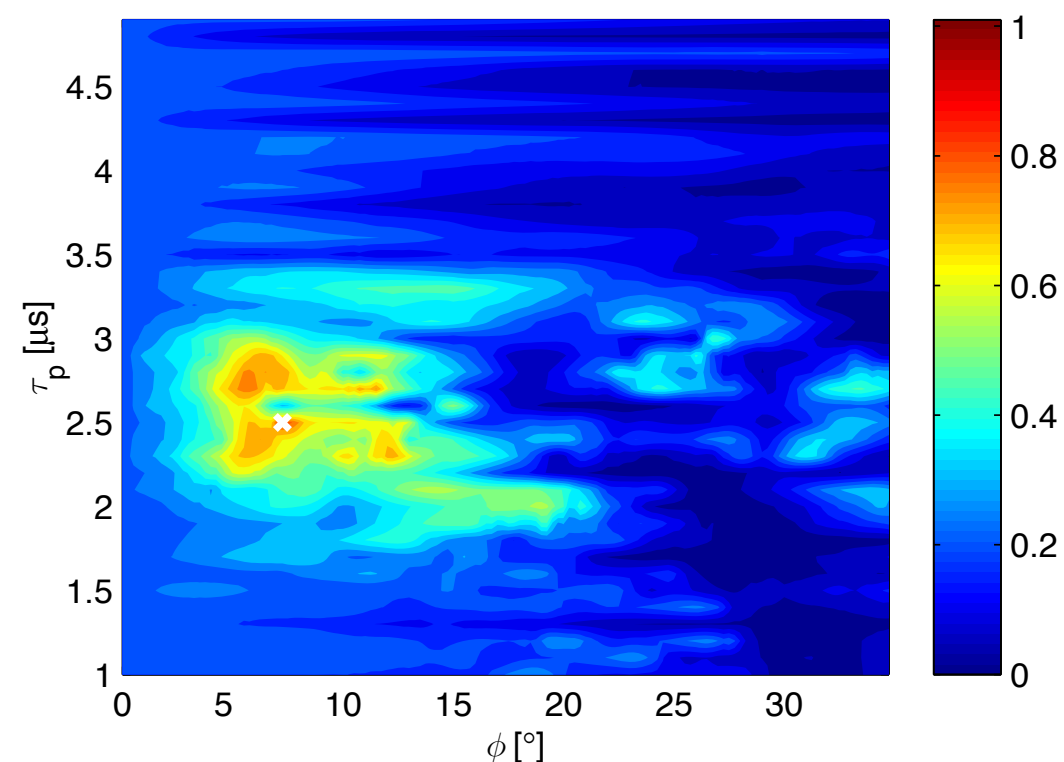
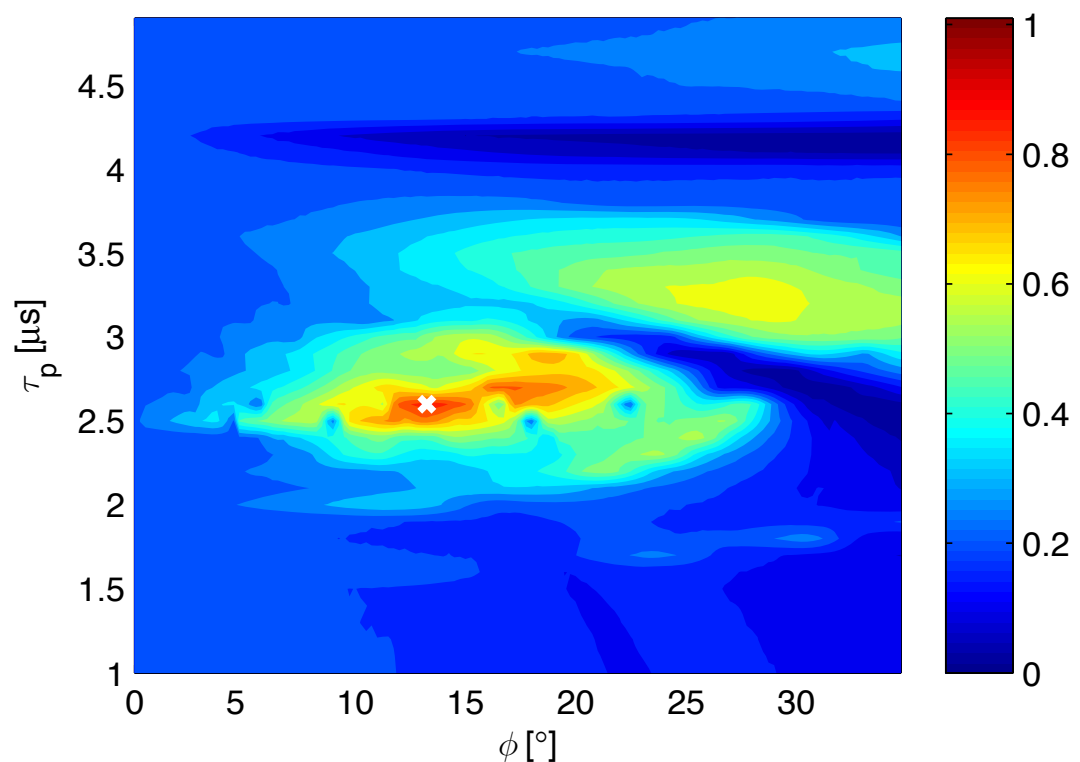
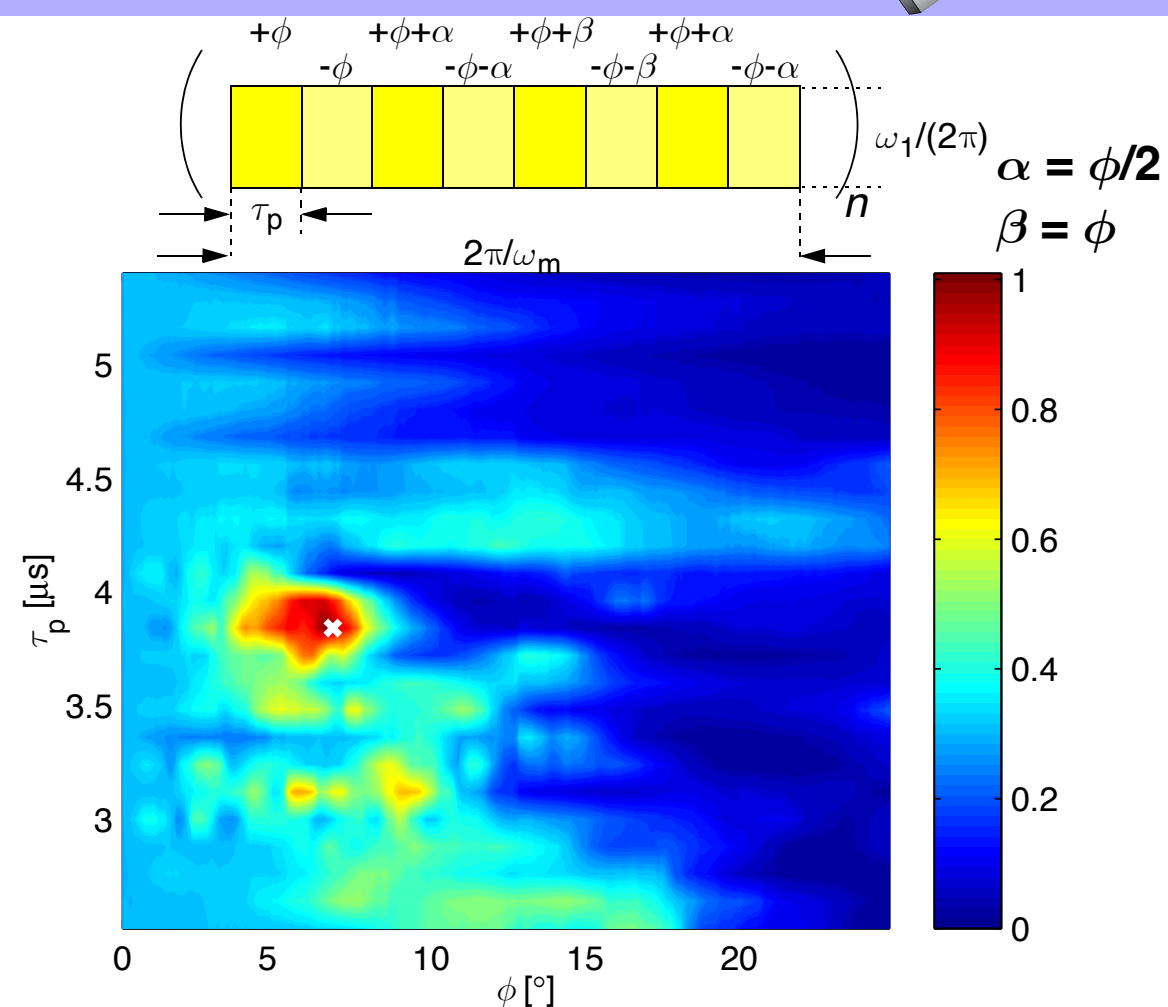
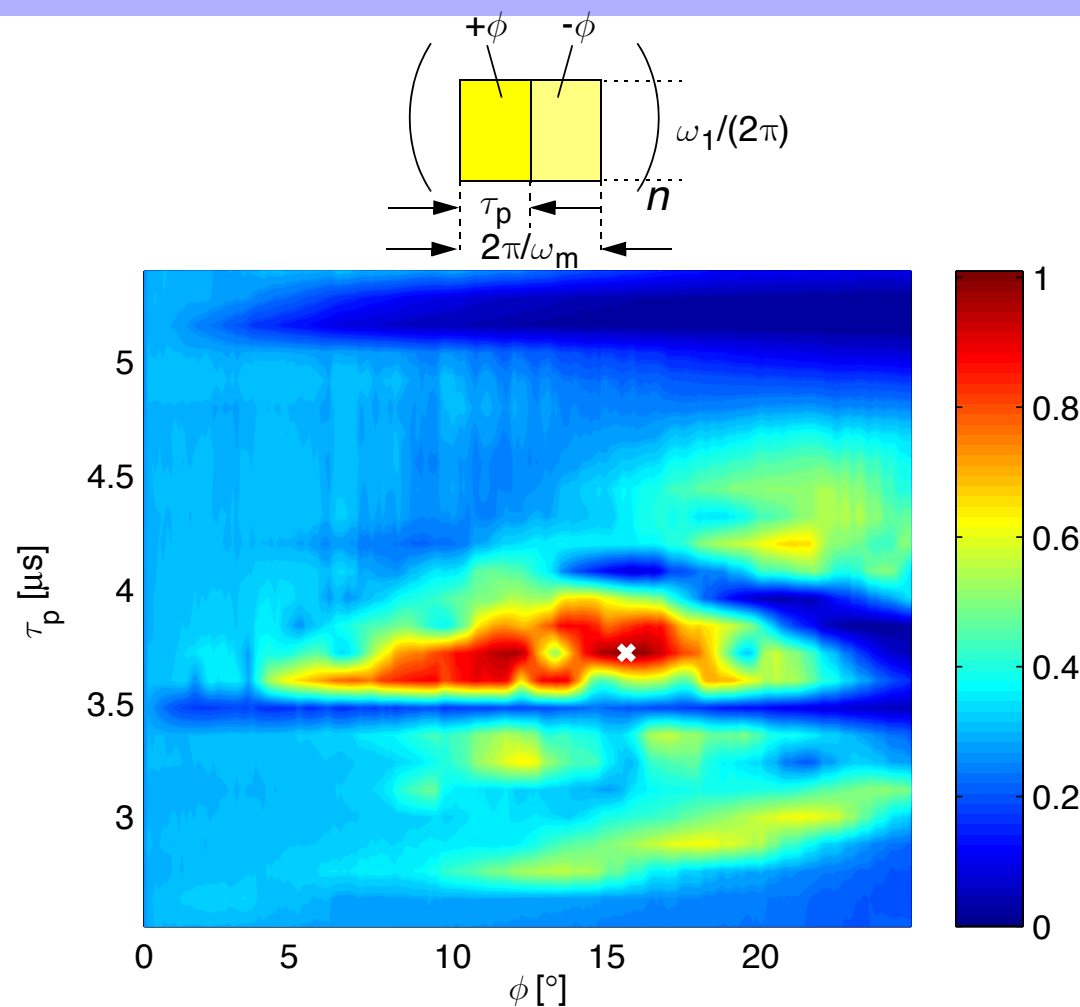
TPPM Versus SPINAL-64 for Fast MAS



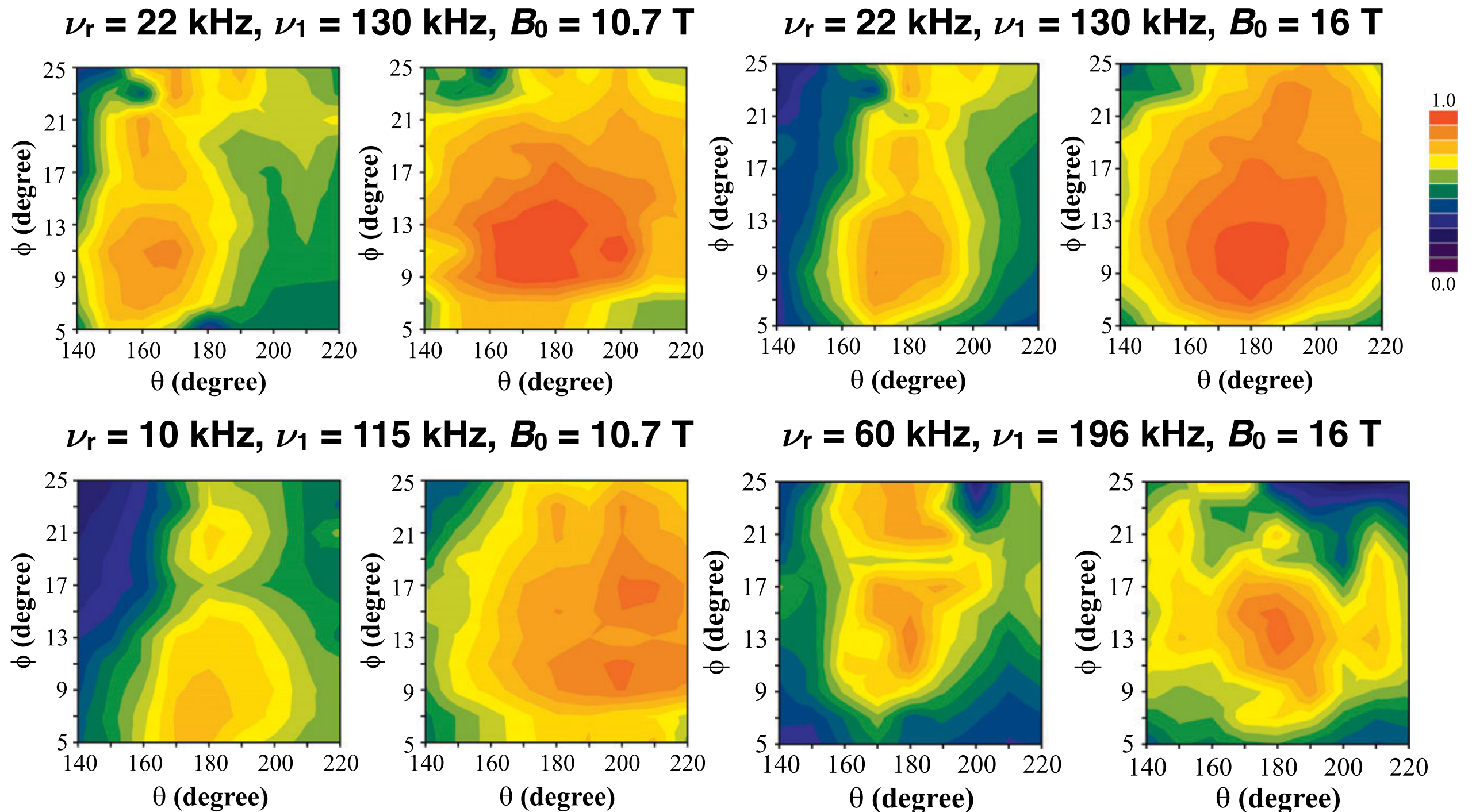
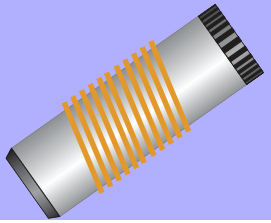
❑ No significant differences in intensities or in the ease of optimization.

$\nu_r = 48 \text{ kHz}$, $\nu_1 = 150 \text{ kHz}$
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$\nu_r = 68 \text{ kHz}$, $\nu_1 = 190 \text{ kHz}$
 $B_0 = 20 \text{ T}$



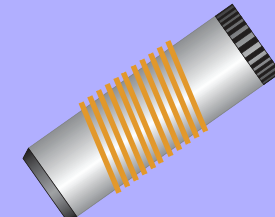
TPPM Versus SW_f-TPPM



V.S. Mithu, S. Pratihari, S. Paul, P.K. Madhu, "Efficiency of heteronuclear dipolar decoupling schemes in solid-state NMR: Investigation of effective transverse relaxation times", Journal of Magnetic Resonance. 220 (2012) 8–17.

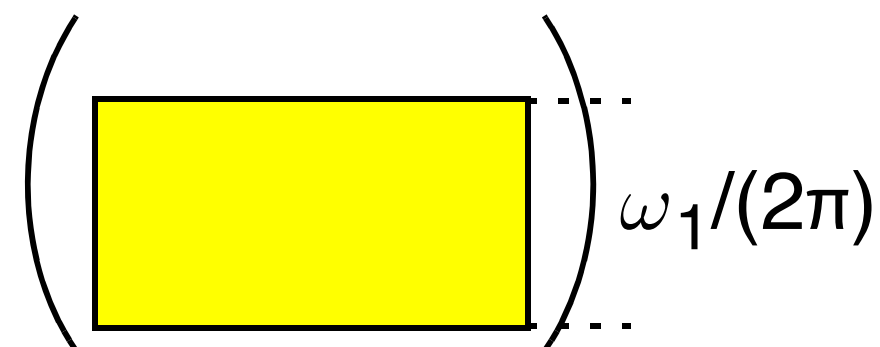
SW_f-TPPM broadens the area of good decoupling and makes optimization simpler.

Low-Power Decoupling



□ In cw decoupling we have two possible regimes:

- high-power decoupling with $\omega_1 > 3\omega_r$.
- low-power decoupling with $\omega_1 < 0.5\omega_r$.



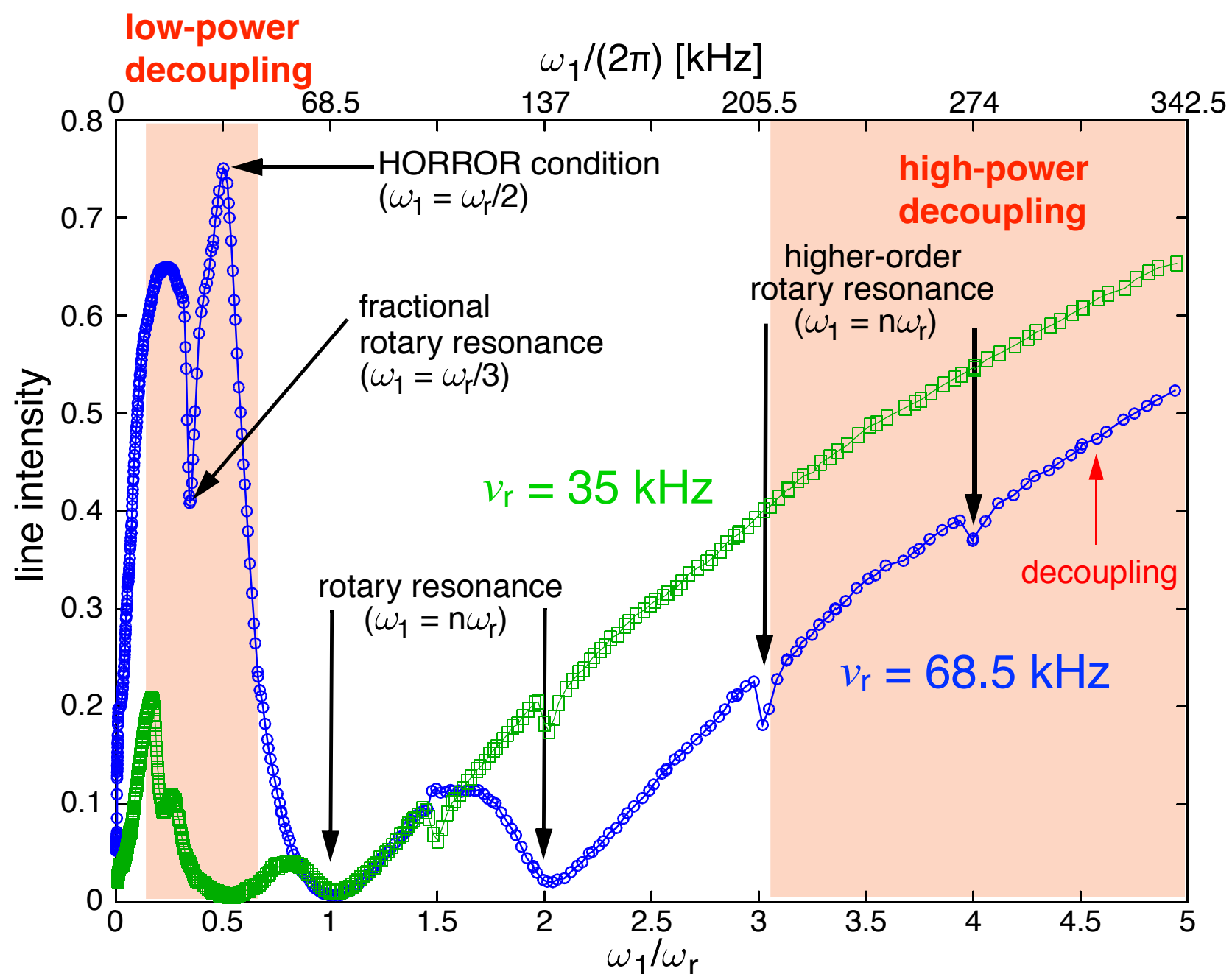
□ Decoupling with rf-field amplitudes in between is inefficient.

□ At fast MAS ($\nu_r > 50$ kHz), high-power decoupling becomes difficult.

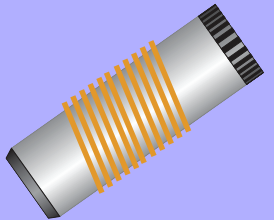
□ Can we improve over low-power cw decoupling?

□ At what spinning frequencies does low-power decoupling become comparable/better than high-power decoupling?

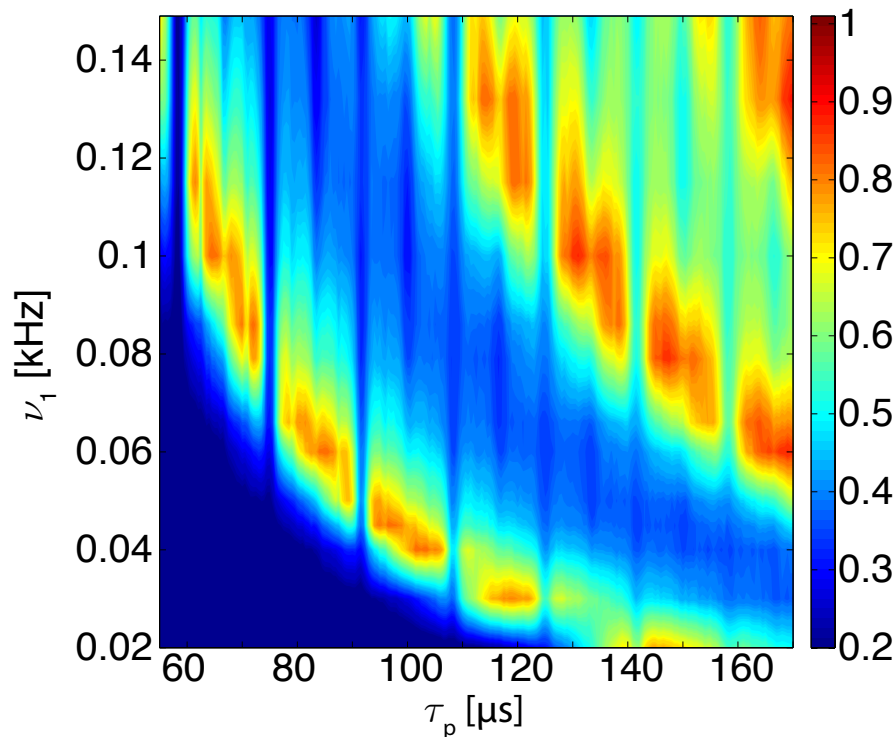
□ What is the best sequence for low-power decoupling?



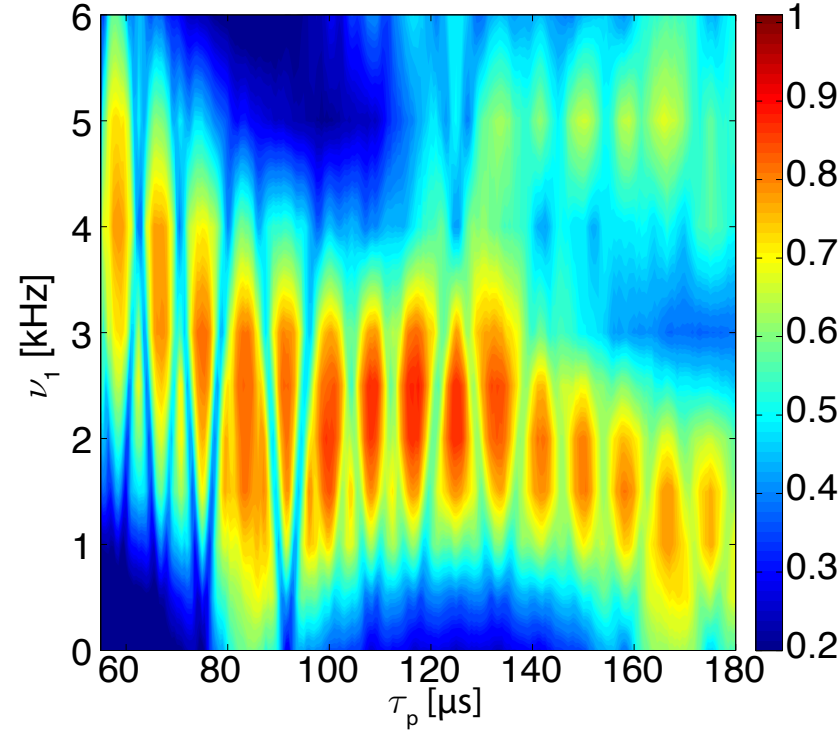
Low-Power Decoupling: Comparison



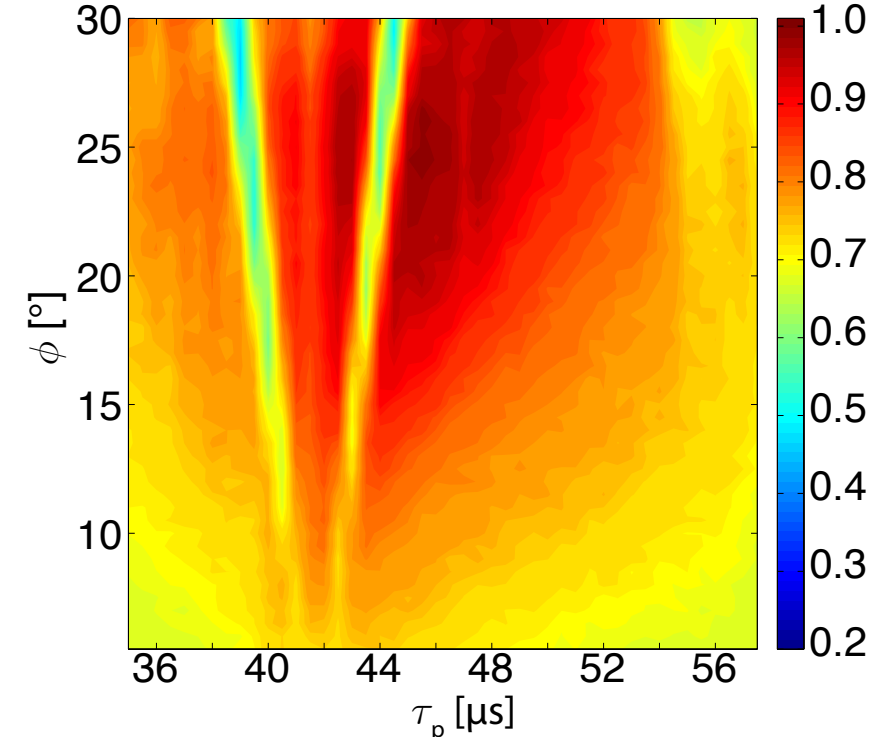
XiX



XiX^{CW}



TPPM

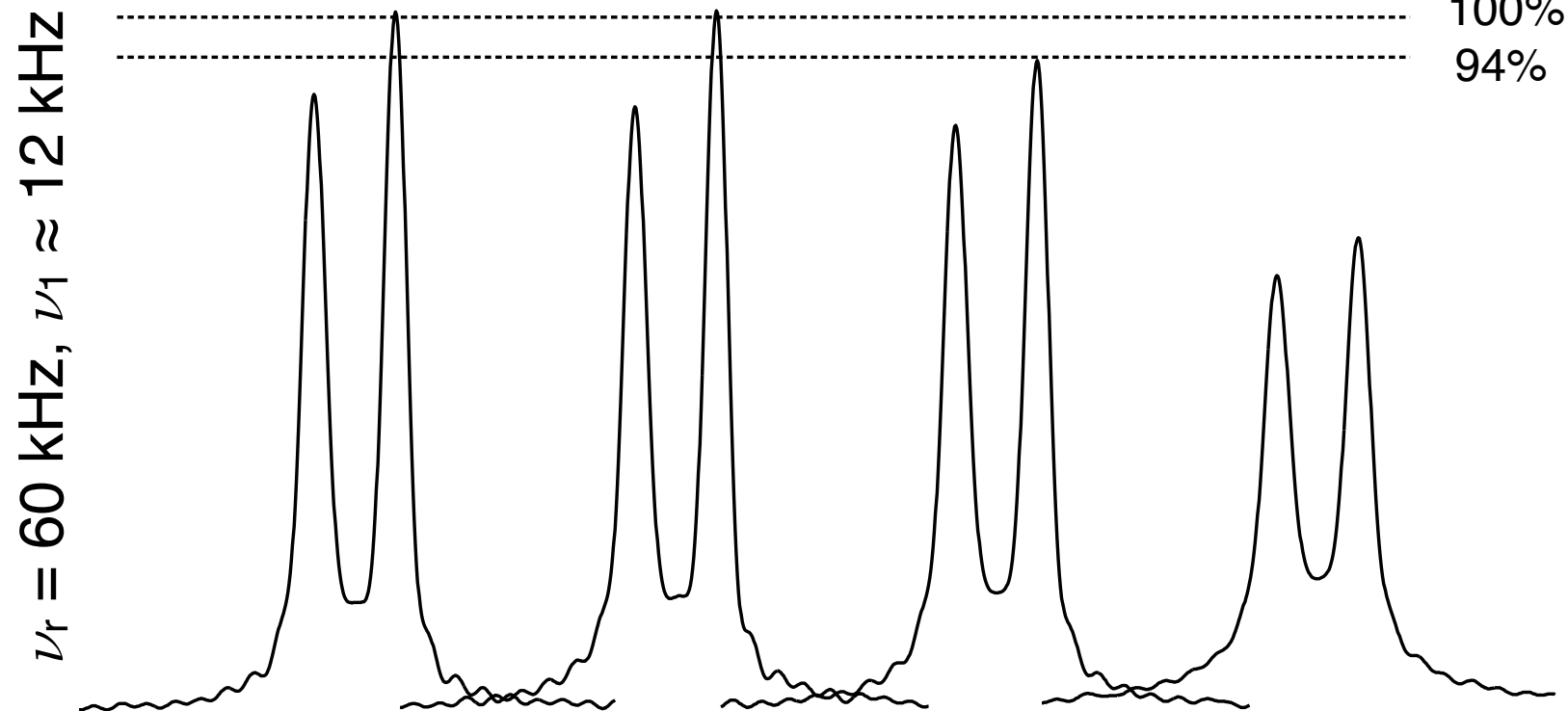


XiX^{CW}

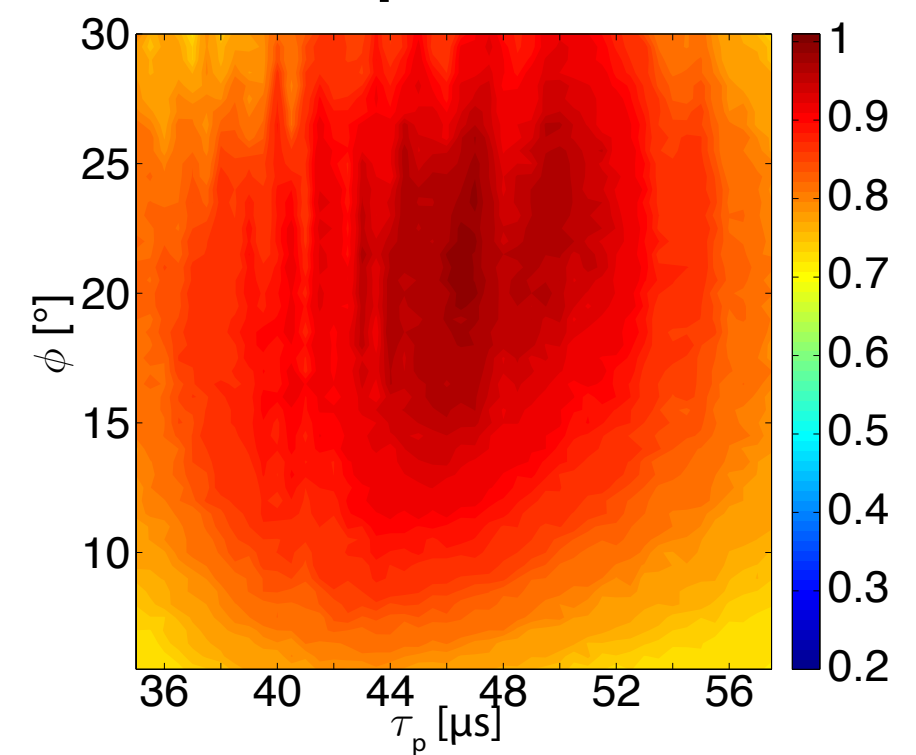
TPPM

SW_f-TPPM

XiX

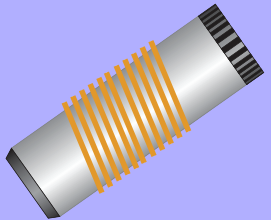


SW_f-TPPM

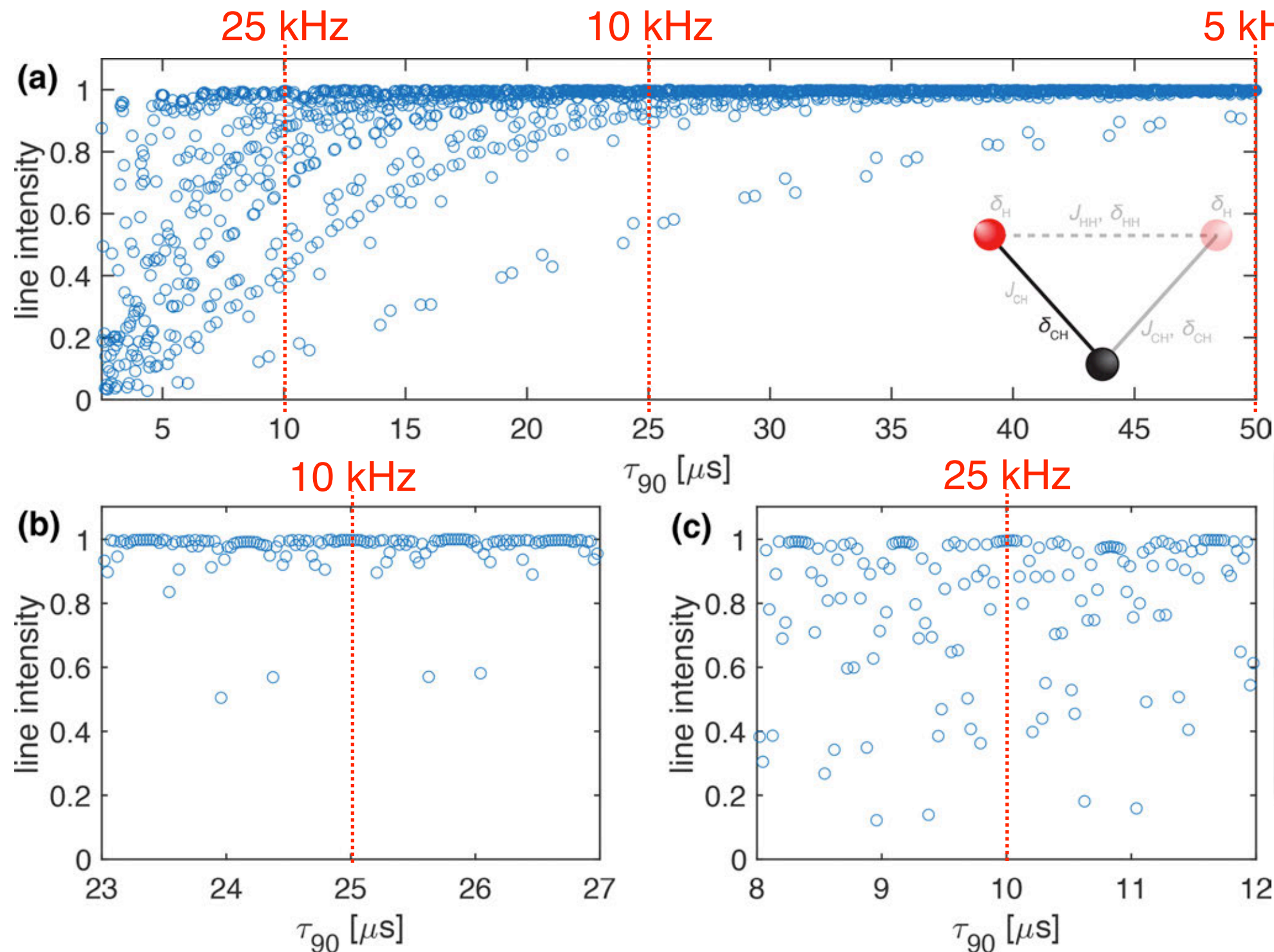


TPPM and XiX^{CW} give about the same line width and line height.

Low-Power WALTZ-64 Decoupling



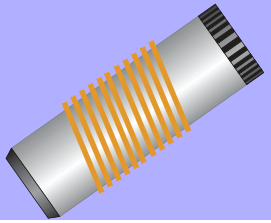
- Low-power WALTZ decoupling is mostly avoiding resonance conditions!
- Line intensity (**simulation**) at 100 kHz MAS as a function of the pulse length τ_{90} .



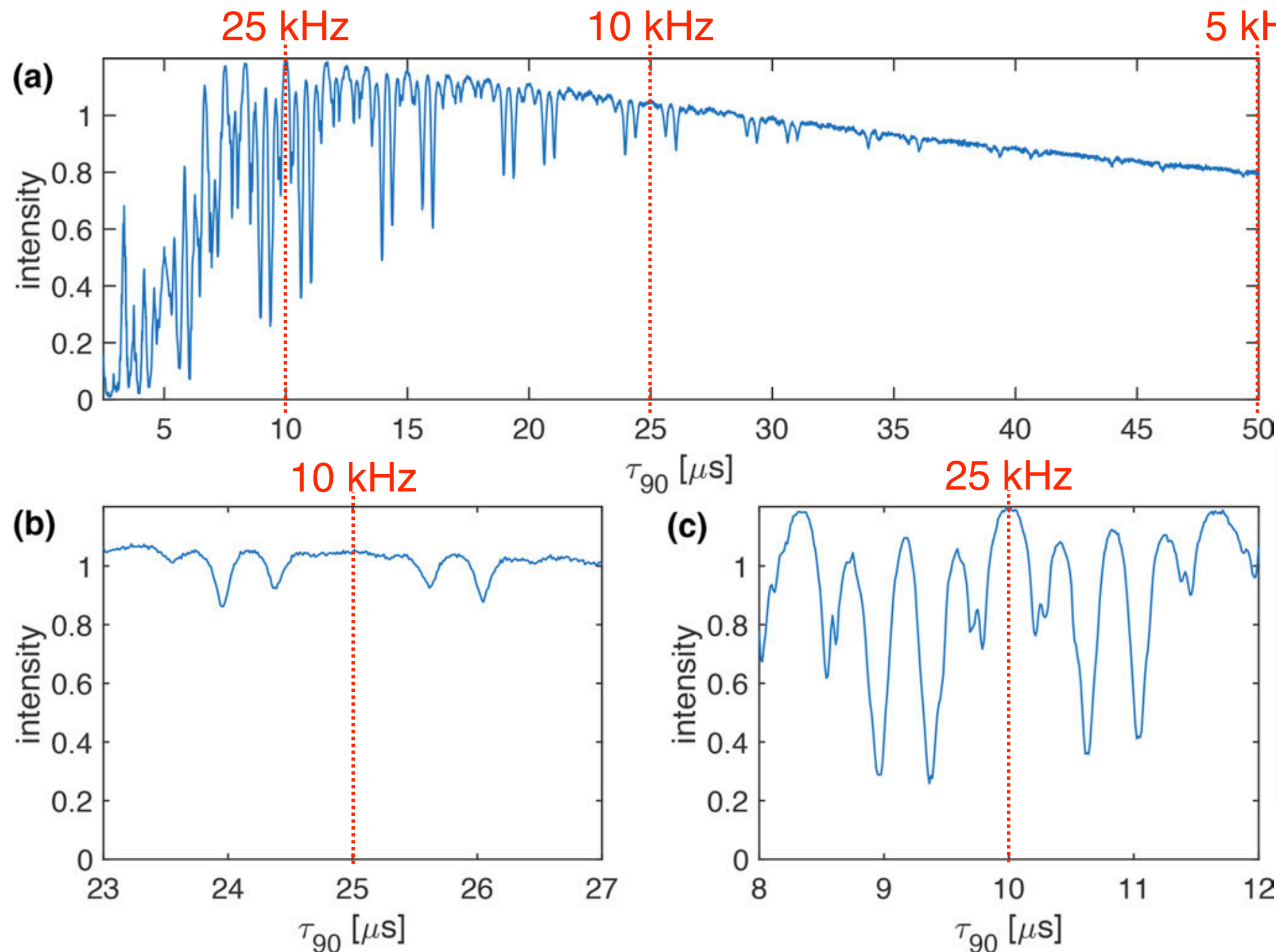
$$\nu_1 = 1/(4 * \tau_{90})$$

There are narrow ranges of pulse lengths where we have no resonance conditions.

Low-Power WALTZ-64 Decoupling



- Low-power WALTZ decoupling is mostly avoiding resonance conditions!
- Line intensity (**experiments**) at 100 kHz MAS as a function of the pulse length τ_{90} .



$\nu_1 = 1/(4 * \tau_{90})$

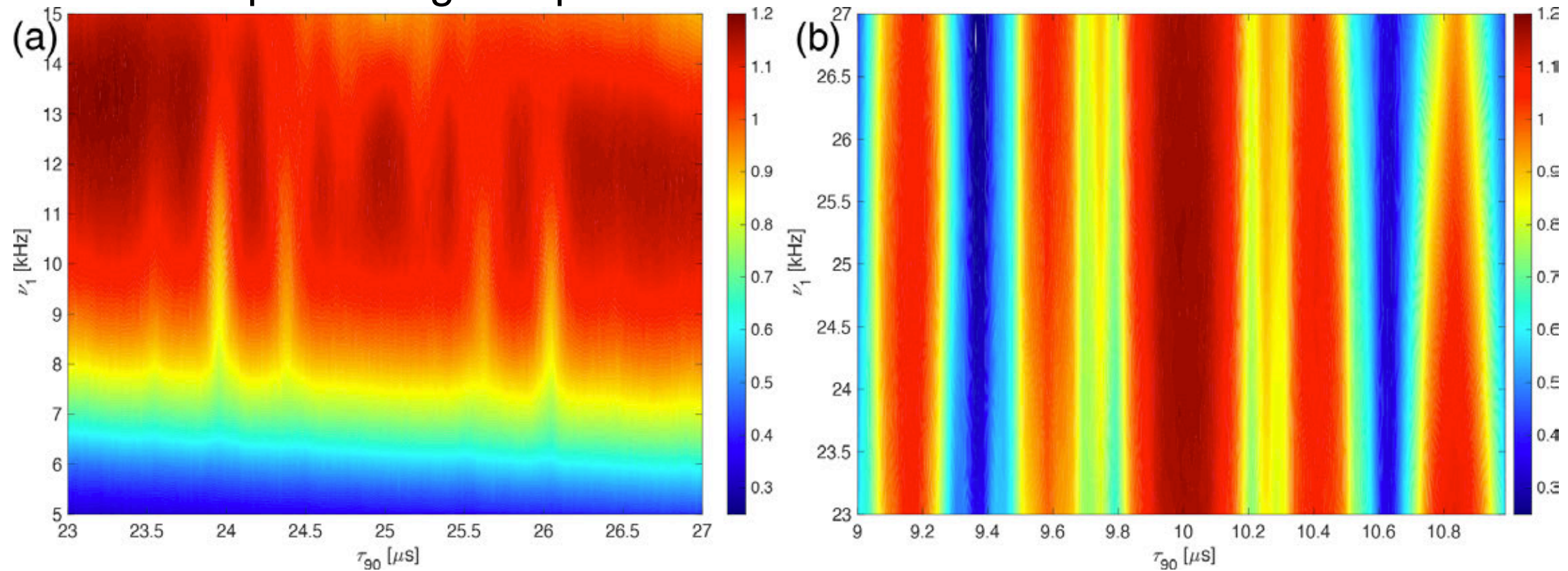
CH₂ group in 1,2-¹³C
glycine ethyl ester

There are narrow
ranges of pulse
lengths where we
have no resonance
conditions.

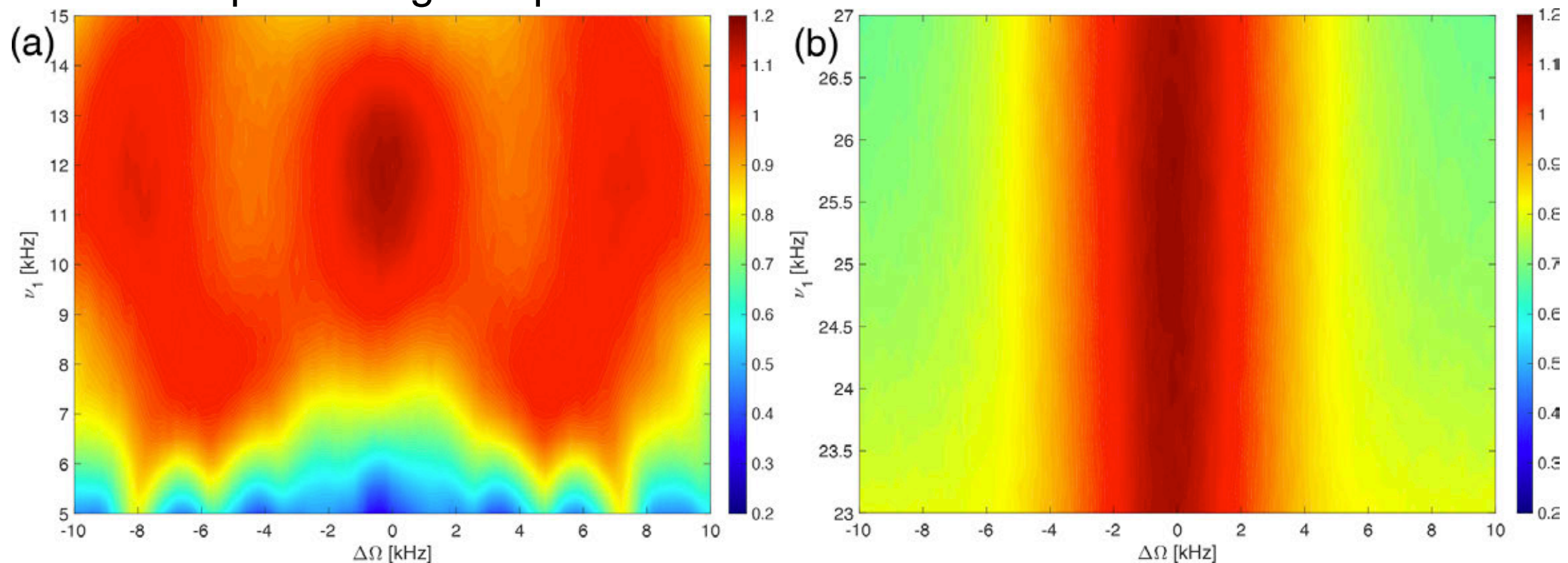
Low-Power WALTZ-64 Decoupling



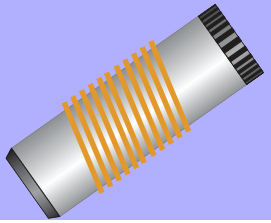
■ B_1 -field and pulse-length dependence



■ Offset and pulse-length dependence

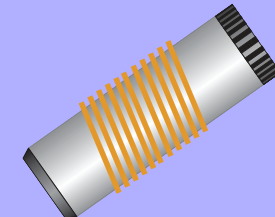


Practical Aspects of Heteronuclear Decoupling

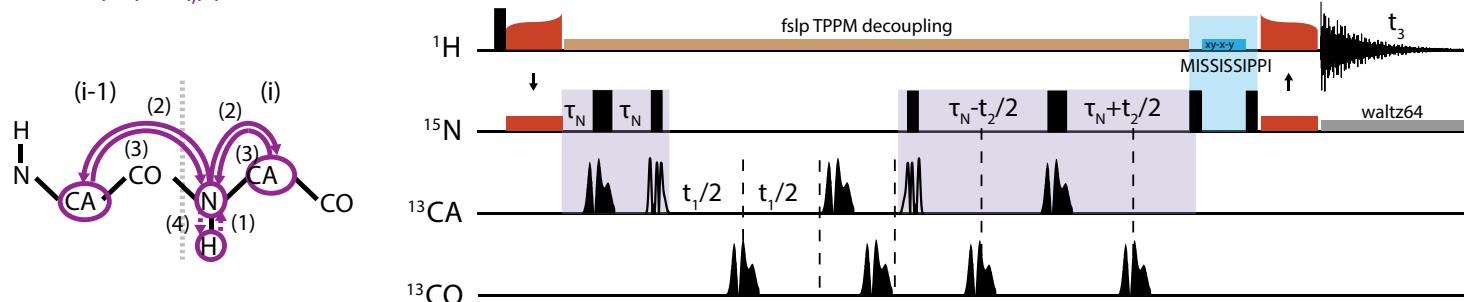


- ❑ At MAS frequencies 40 kHz and below use high-power decoupling with as high ω_1 as possible.
- ❑ At MAS frequencies 60 kHz and above use low-power decoupling with $\omega_1 < \omega_r/4$.
- ❑ In between there are no clear rules and the choice might depend on the available rf-field strength. Experimental comparison of high- and low-power decoupling is important in this regime.
- ❑ For high-power decoupling SW_f-TPPM and SPINAL-64 seem to be the most stable variants. At MAS frequency above 30 kHz and high enough rf fields, XiX can be a simple to optimize alternative.
- ❑ For low-power decoupling, WALTZ-64 with $\omega_1 = \omega_r/10$ or $\omega_1 = \omega_r/4$ needs almost no optimization. SW_f-TPPM also works quite well with $\omega_1 < \omega_r/4$ and optimizing the pulse length (roughly a π pulse).
- ❑ For samples with diluted proton density, low-power decoupling might also work for lower MAS frequencies.
- ❑ Decoupling of spins with large CSA tensors and large chemical-shift ranges (e.g., ^{19}F) is often difficult.

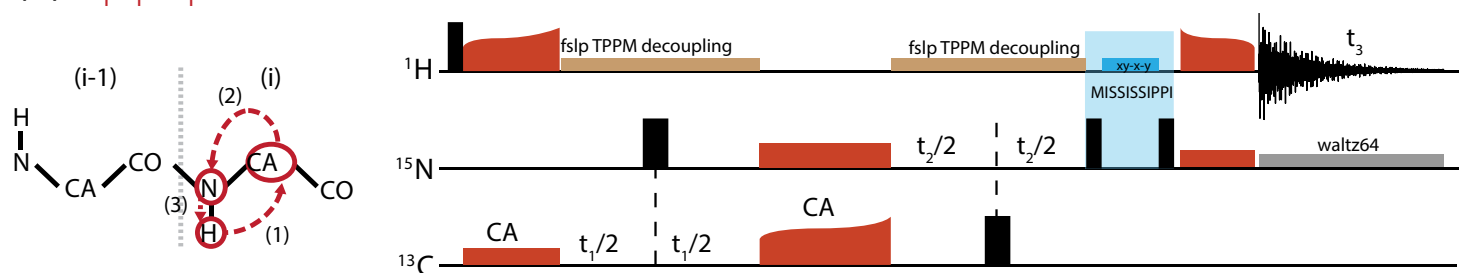
Important Building Blocks in MAS NMR



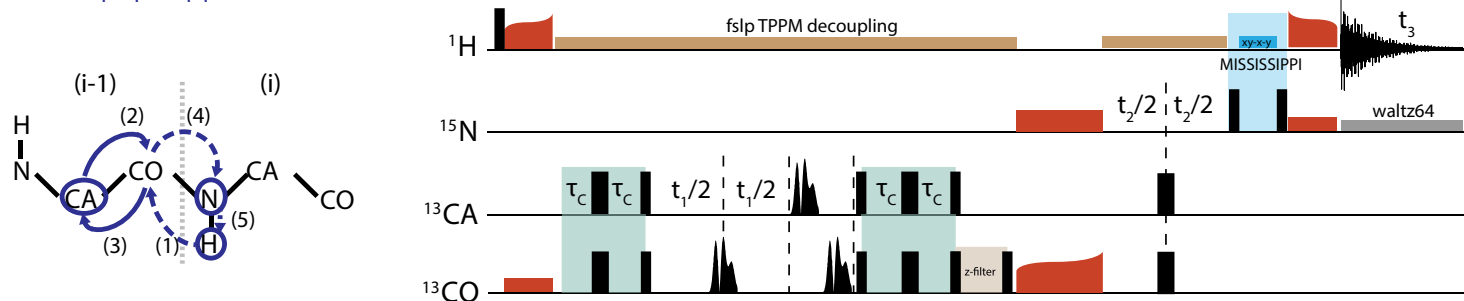
(a) $H_i N_i C\alpha_{i,i-1}$ correlation: (HN)CANH



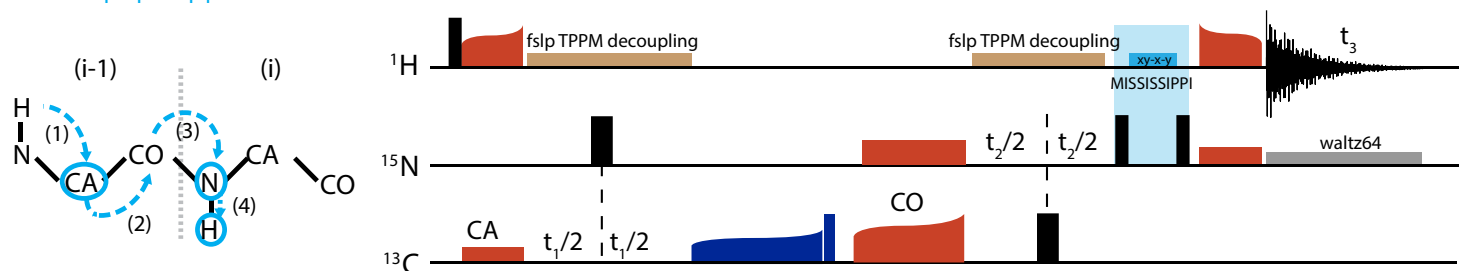
(b) $H_i N_i C\alpha_i$ correlation: (H)CANH



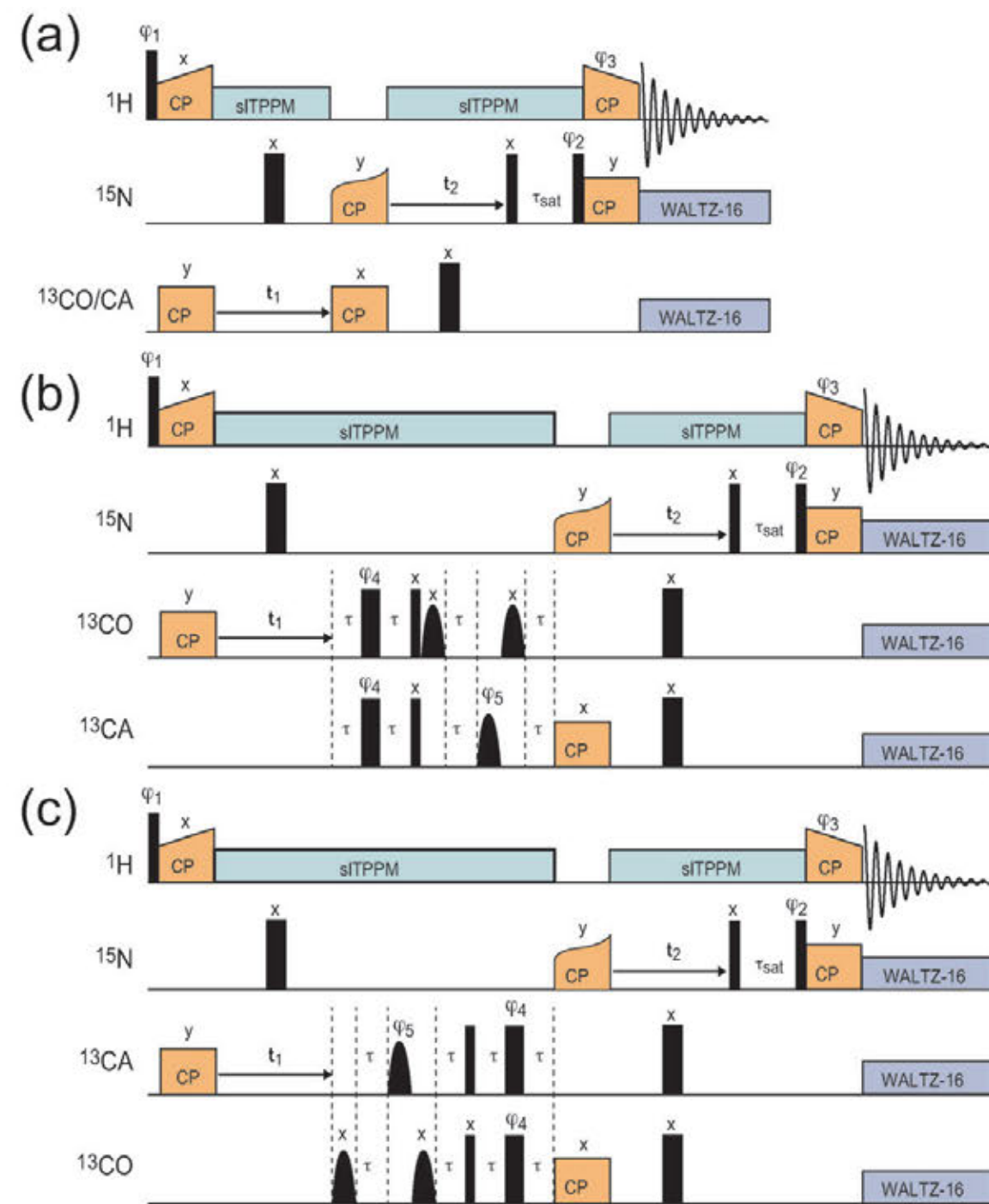
(c) $H_i N_i C\alpha_{i-1}$ correlation: (HCO)CA(CO)NH



(d) $H_i N_i C\alpha_i$ correlation: (H)CA(CO)NH



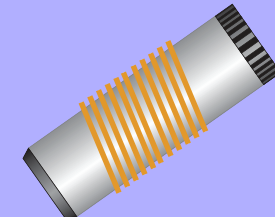
S. Penzel, ... , B.H. Meier, J. Biomol. NMR. 63 (2015) 165–186.
<https://doi.org/10.1007/s10858-015-9975-y>.



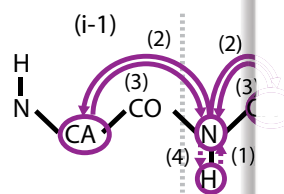
A. Marchetti, ..., G. Pintacuda, Angew. Chem. Int. Ed. Engl. 51 (2012) 10756–10759. <https://doi.org/10.1002/anie.201203124>.

Dipolar Recoupling

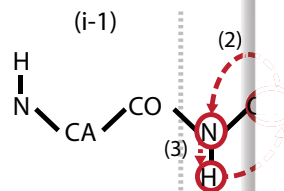
Important Building Blocks in MAS NMR



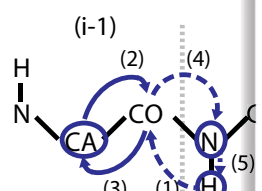
(a) $H_i N_i C\alpha_{i,i-1} CO_{i,i-1}$



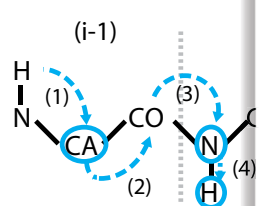
(b) $H_i N_i C\alpha_{i,i-1} CO_{i,i-1}$



(c) $H_i N_i C\alpha_{i,i-1} CO_{i,i-1}$

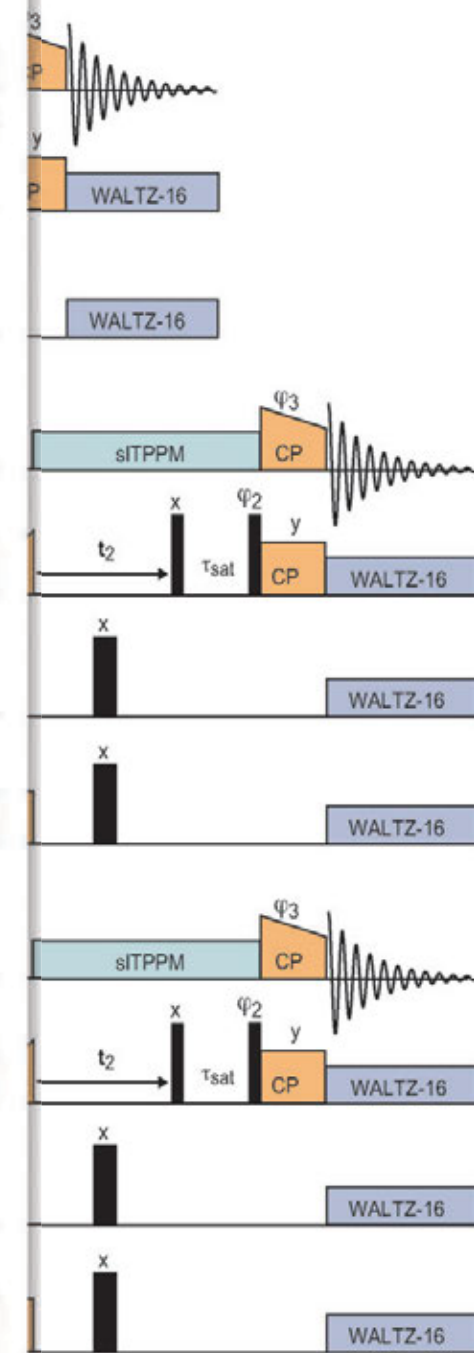
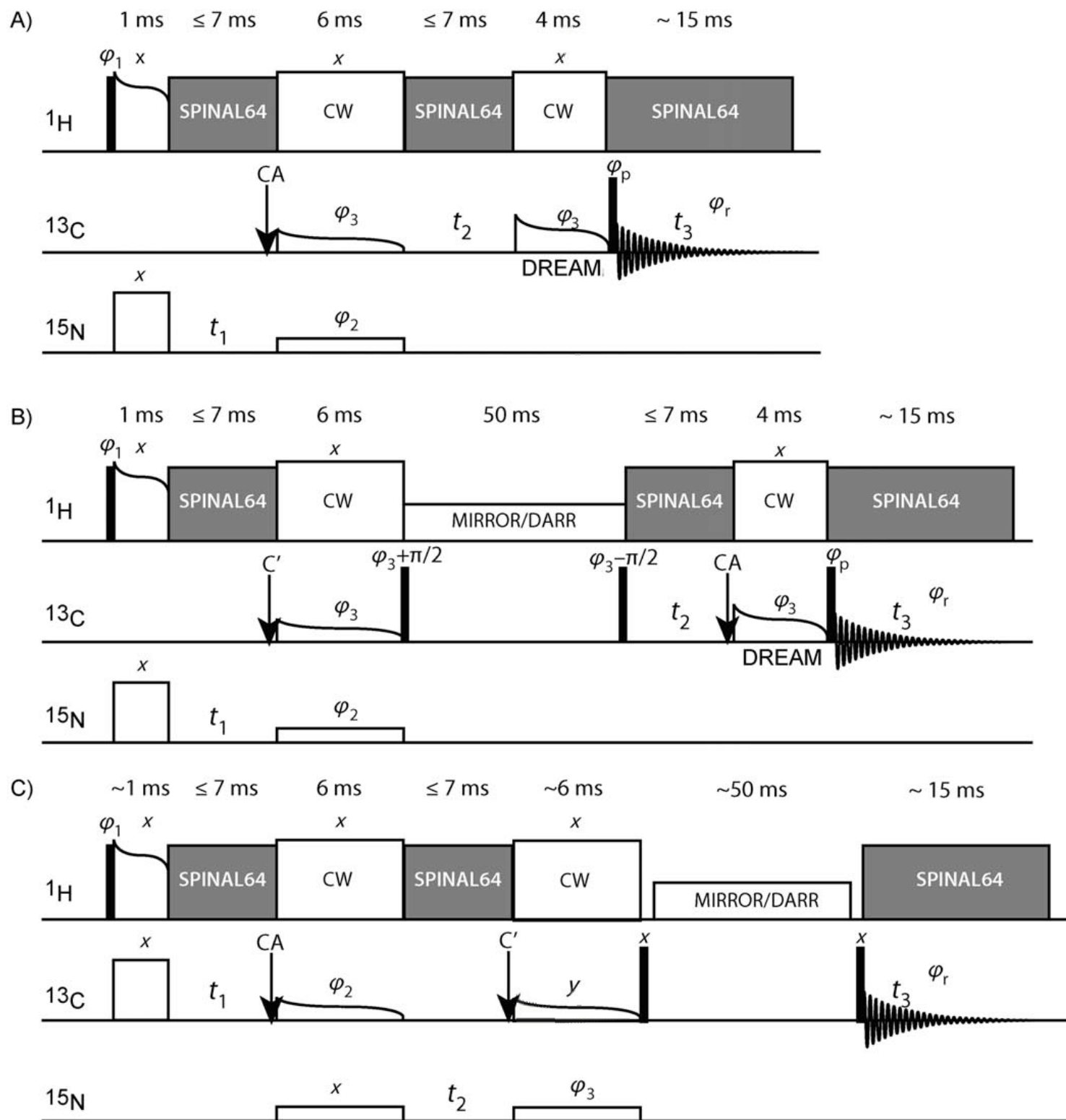


(d) $H_i N_i C\alpha_{i,i-1} CO_{i,i-1}$



S. Penzel
<https://doi.org/10.1002/anie.201203124>

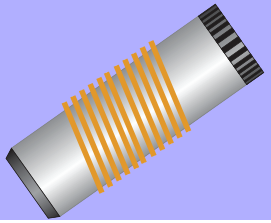
A.K. Schütz, ..., B.H. Meier, ChemBioChem 11 (2010) 1543–1551. <https://doi.org/10.1002/cbic.201000124>



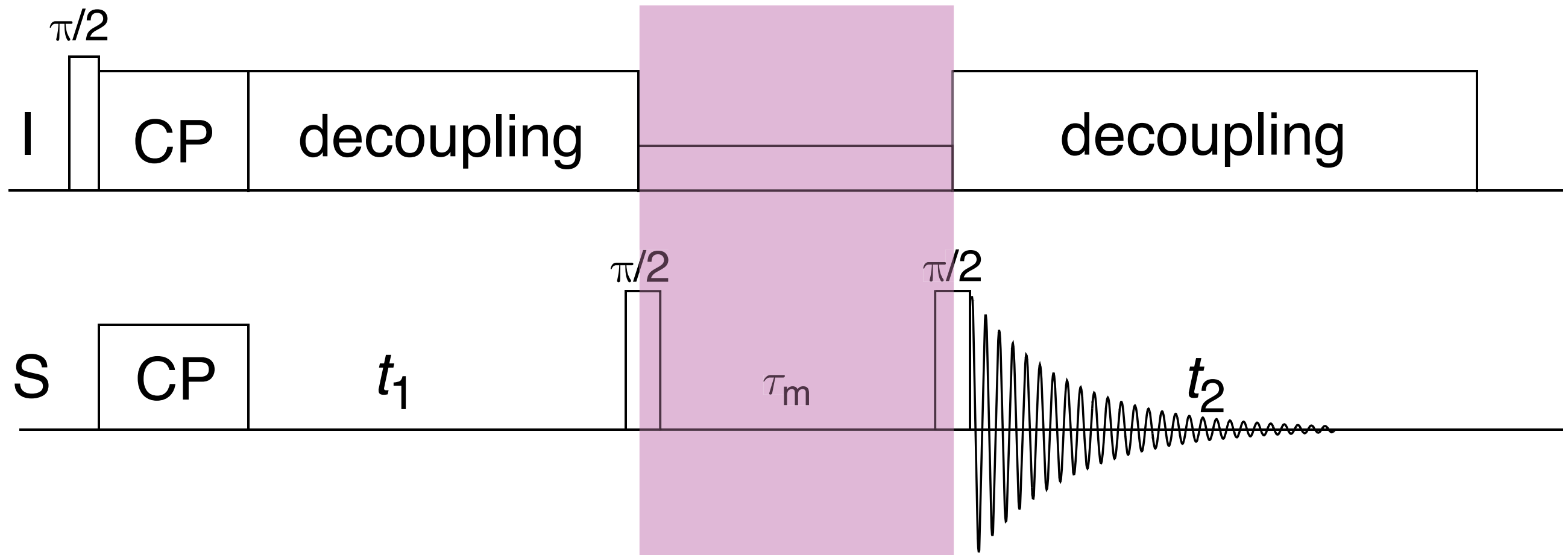
ew. Chem. Int. Ed. Engl. 51
g/10.1002/anie.201203124.

coupling

DARR - R³ Recoupling



❑ Proton-Driven Spin Diffusion under MAS (PDSD)/DARR



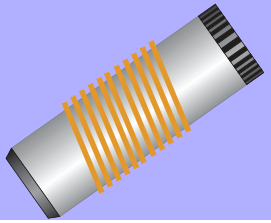
❑ The time-dependent Hamiltonian with the exception of the radio-frequency part is the same during all times of the experiment:

$$\hat{\mathcal{H}}(t) = \sum_i \sum_{\ell=0}^2 \mathbf{A}_{\ell,0}^{(i)}(t) \hat{\mathbf{T}}_{\ell,0}^{(i)} + \hat{\mathcal{H}}_{\text{rf}}(t) = \hat{\mathcal{H}}_{\text{D}}(t) + \hat{\mathcal{H}}_{\text{CS}}(t) + \hat{\mathcal{H}}_{\text{J}}(t) + \hat{\mathcal{H}}_{\text{rf}}(t)$$

❑ Effective Hamiltonian during spin-diffusion mixing time: homonuclear zero-quantum

Hamiltonian: $\hat{\mathcal{H}} \approx \omega_{\text{II}}^{(\text{eff})} (\hat{\mathbf{S}}_1^+ \hat{\mathbf{S}}_2^- + \hat{\mathbf{S}}_1^- \hat{\mathbf{S}}_2^+) \hat{I}_z$

Origin of Time-Dependent Hamiltonians



❑ The spin-system Hamiltonian in the rotating frame is static if the molecule is static.

sample rotation

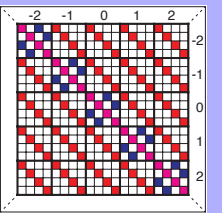
$$\hat{\mathcal{H}} = \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)} \hat{T}_{\ell,0}^{(i)}$$

$$\hat{\tilde{\mathcal{H}}}(t) = \sum_i \sum_{\ell=0}^2 A_{\ell,0}^{(i)}(t) \hat{\tilde{T}}_{\ell,0}^{(i)}(t) = \sum_{k=-\infty}^{\infty} \sum_{n=-2}^2 \hat{\tilde{\mathcal{H}}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_m t}$$

interaction-frame transformation

❑ Hamiltonians in solid-state NMR have often multiple time dependencies!

Effective Hamiltonians from Floquet Theory



□ We can calculate effective Hamiltonians for Hamiltonians with multiple time dependencies in a way very similar to AHT.

□ Appearance of *resonance conditions* for more than one frequency:

single frequency:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{(0)} - \frac{1}{2} \sum_{n \neq 0} \frac{[\hat{\mathcal{H}}^{(-n)}, \hat{\mathcal{H}}^{(n)}]}{n\omega_m} + \dots$$

two frequencies:

$$\hat{\mathcal{H}} = \sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} - \frac{1}{2} \sum_{n_0, k_0} \sum_{\nu, \kappa} \frac{[\hat{\mathcal{H}}^{(n_0 - \nu, k_0 - \kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)}]}{\nu\omega_r + \kappa\omega_m} + \dots$$

resonance conditions $n_0\omega_r + k_0\omega_m = 0$

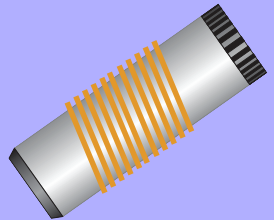
□ With multiple frequencies we have *resonant* and *non-resonant* contributions to the effective Hamiltonian in different orders:

$$\bar{\mathcal{H}} \approx \underbrace{\hat{\mathcal{H}}^{(0,0)} + \hat{\mathcal{H}}_{(2)}^{(0,0)} + \dots}_{\text{non-resonant: } n_0 = k_0 = 0} + \underbrace{\sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} + \sum_{n_0, k_0} \hat{\mathcal{H}}_{(2)}^{(n_0, k_0)} + \dots}_{\text{resonant: } n_0\omega_r + k_0\omega_m = 0}$$

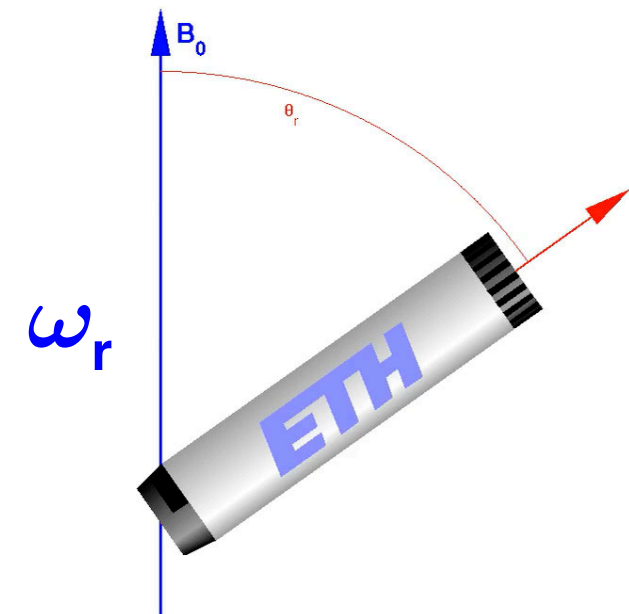
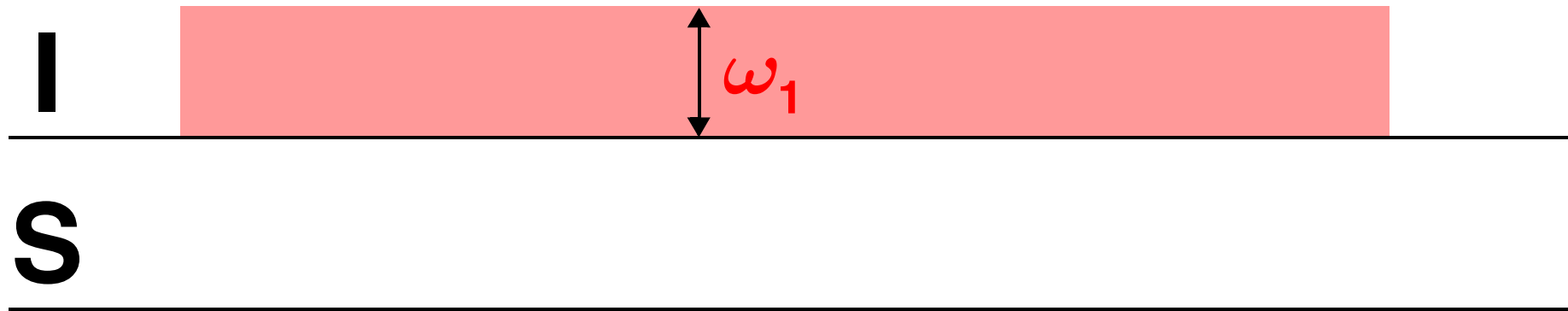
$$\hat{\mathcal{H}}_{(2)}^{(n_0, k_0)} = -\frac{1}{2} \sum_{\nu, \kappa} \frac{[\hat{\mathcal{H}}^{(n_0 - \nu, k_0 - \kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)}]}{\nu\omega_r + \kappa\omega_m}$$

□ At these resonance conditions, certain Fourier coefficients of the time-dependent interaction-frame Hamiltonian are time independent.

Example: MAS and CW Irradiation



- Heteronuclear coupled I-S two-spin system:
Continuous-wave (cw) irradiation on one spin under MAS.

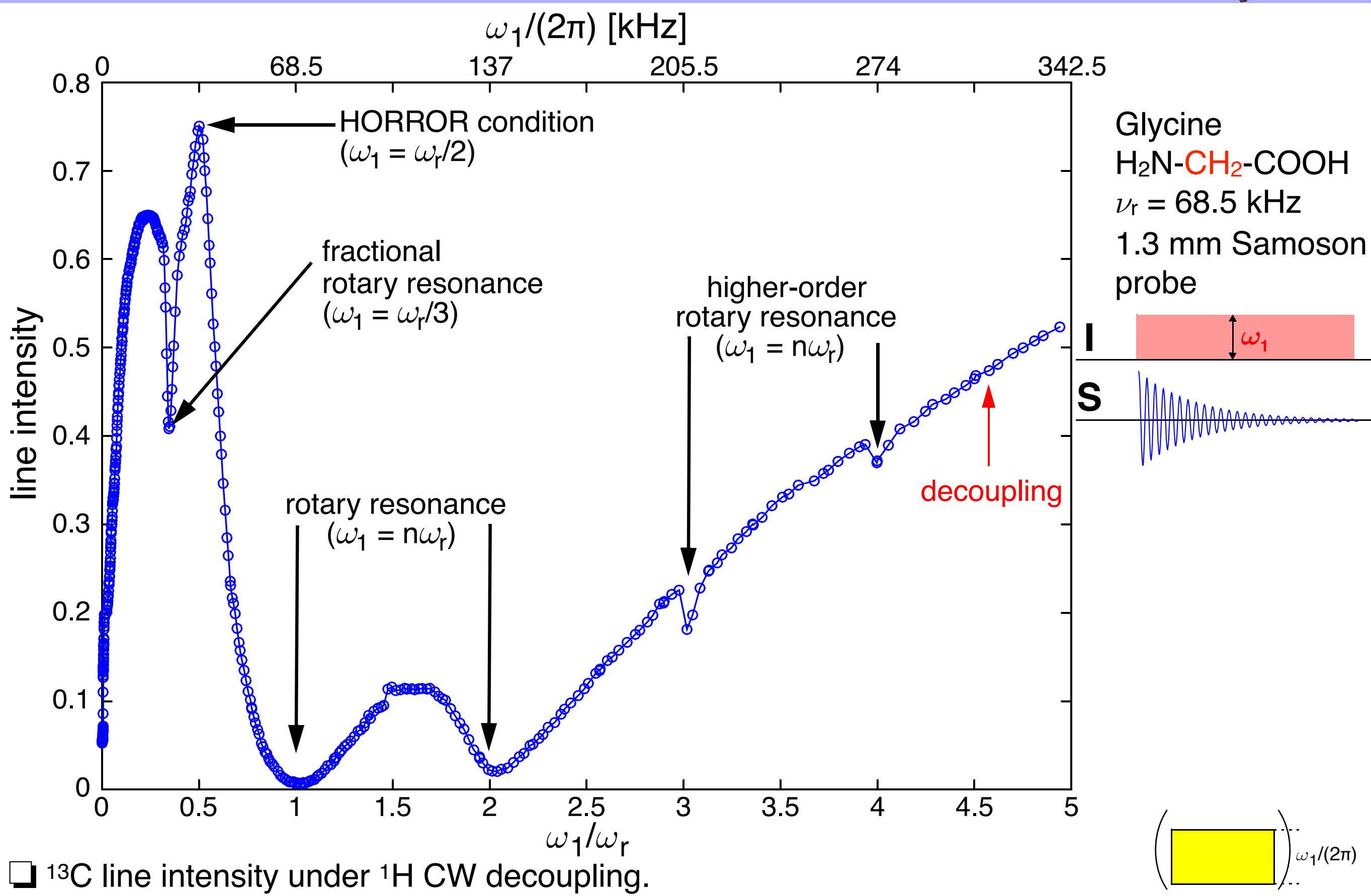
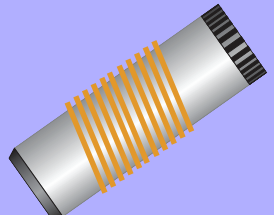


- Examples for such a situation:

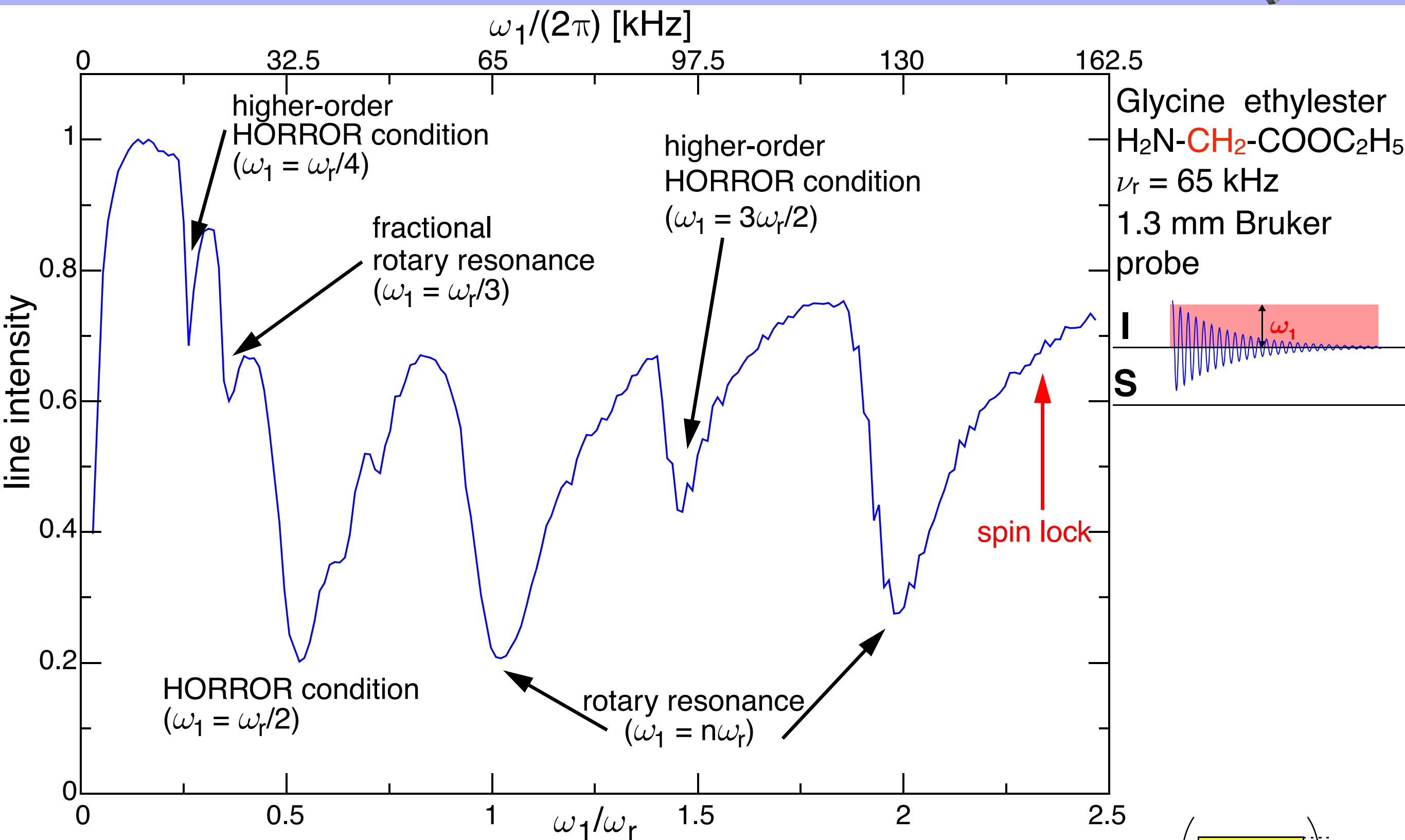
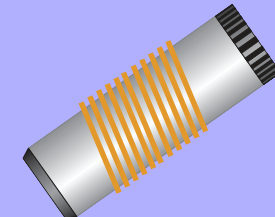
- Heteronuclear CW decoupling (non resonant)
- Rotary-resonance recoupling (R^3) ($n_0 \omega_r, \pm \omega_1 = 0, n_0 = \pm 1, \pm 2$)
- HORROR recoupling ($n_0 \omega_r, \pm k_0 \omega_1 = 0, n_0 = \pm 1, \pm 2, k_0 = \pm 2$)
- Higher-order R^3 experiments ($n_0 \omega_r, \pm \omega_1 = 0, n_0 = \pm 3, \pm 4$)
- DARR or MIRROR recoupling ($n_0 \omega_r, \pm \omega_1 + \ell_0 \Delta\Omega_{\text{iso}} = 0, n_0 = \pm 3, \pm 4, \ell_0 = \pm 1$)

M. Ernst, A. Samoson, B.H. Meier, Decoupling and recoupling using continuous-wave irradiation in magic-angle-spinning solid-state NMR: A unified description using bimodal Floquet theory, J. Chem. Phys. 123 (2005) 064102. doi:10.1063/1.1944291.

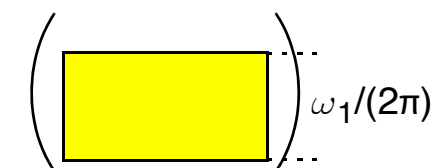
CW Irradiation in Rotating Solids: S-Spin Detection



CW Irradiation in Rotating Solids: I-Spin Detection



1H line intensity under 1H spin lock of 2.5 ms length.



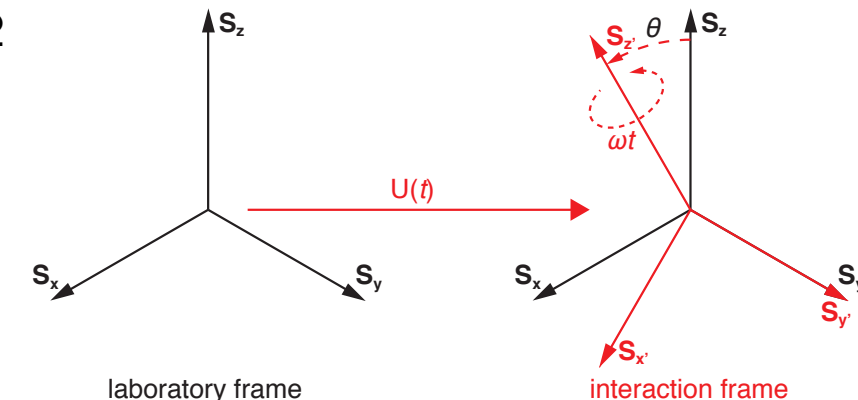
Theoretical Description of CW Irradiation in Rotating Solids $\hat{\mathcal{H}}(t)$

- Spin-system Hamiltonian in the rotating frame is time dependent due to magic-angle spinning (MAS).

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_I(t) + \hat{\mathcal{H}}_{IS}(t) + \hat{\mathcal{H}}_S(t) + \hat{\mathcal{H}}_{II}(t) + \hat{\mathcal{H}}_{SS}(t) = \sum_{n=-2}^2 \hat{\mathcal{H}}^{(n)} e^{in\omega_r t}$$

interaction-frame transformation:

$$\hat{U}(t) = \hat{T} \exp \left(-i \int_0^t \hat{\mathcal{H}}_{rf}(t_1) dt_1 \right) e^{i\pi/2 \hat{F}_y} = e^{-i\omega_1 \hat{F}_z t} e^{i\pi/2 \hat{F}_y}$$



$$\hat{\tilde{\mathcal{H}}}(t) = \hat{\tilde{\mathcal{H}}}_I(t) + \hat{\tilde{\mathcal{H}}}_{IS}(t) + \hat{\tilde{\mathcal{H}}}_S(t) + \hat{\tilde{\mathcal{H}}}_{II}(t) + \hat{\tilde{\mathcal{H}}}_{SS}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\tilde{\mathcal{H}}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$$

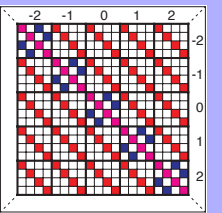
- Interaction-frame transformation with the rf-field introduces a second time-dependence in the Hamiltonian. There are now two frequencies: ω_r and ω_1 .

- Average Hamiltonian theory requires that

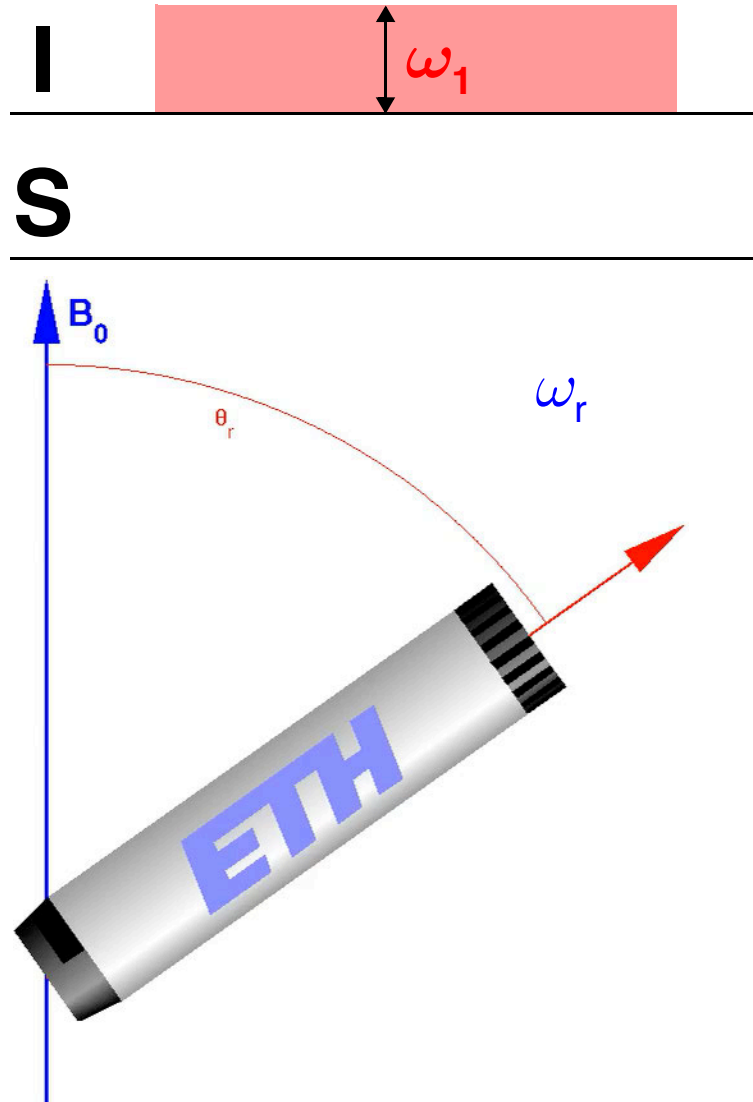
- the two frequencies are commensurate, i.e., $n \omega_r = k \omega_1$ (simultaneous averaging) or
- a separation of time scales, i.e., $\omega_r \ll \omega_1$ or $\omega_r \gg \omega_1$ (sequential averaging).

- Floquet theory allows a unified description for all values of ω_r and ω_1 .

Fourier Coefficients Under CW Irradiation

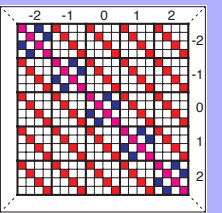


Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_1 t} e^{ik\omega_1 t}$

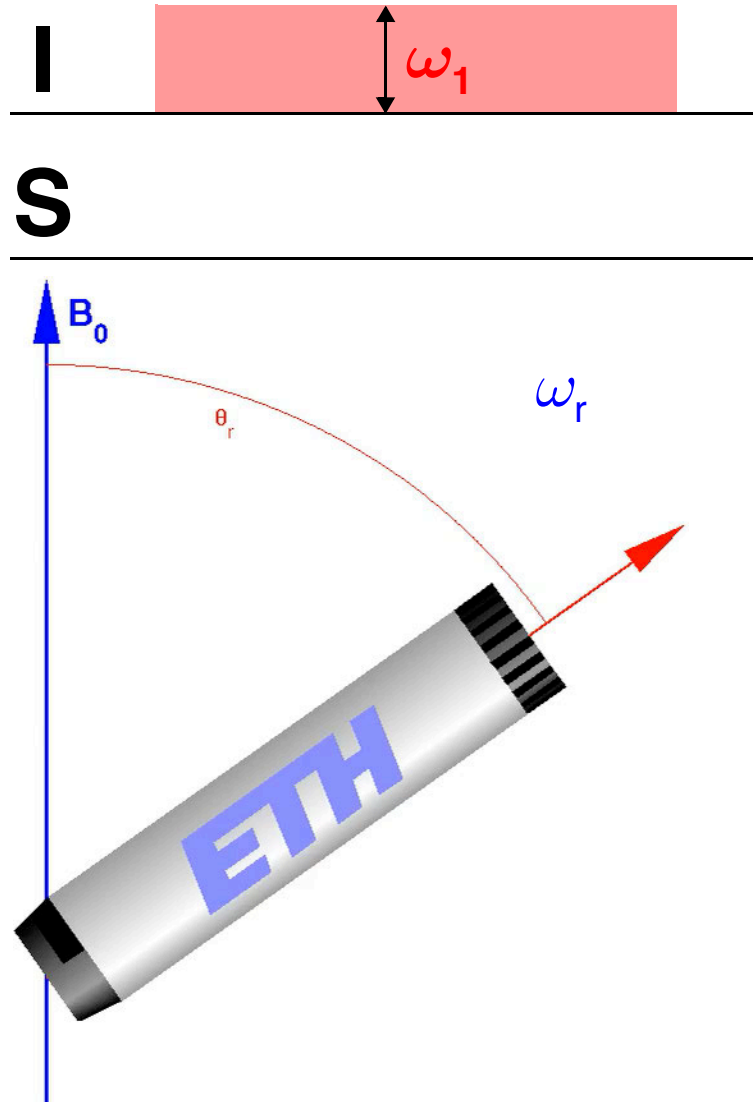


$$\left\{ \begin{array}{l} \hat{\mathcal{H}}^{(0,0)} = \omega_S^{(0)} S_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m) \\ \hat{\mathcal{H}}^{(n,0)} = \omega_S^{(n)} S_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right) \\ \hat{\mathcal{H}}^{(0,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp \\ \hat{\mathcal{H}}^{(n,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp \\ \hat{\mathcal{H}}^{(0,\pm 2)} = 0 \\ \hat{\mathcal{H}}^{(n,\pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp \end{array} \right.$$

Fourier Coefficients Under CW Irradiation



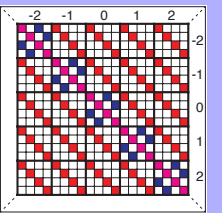
Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$



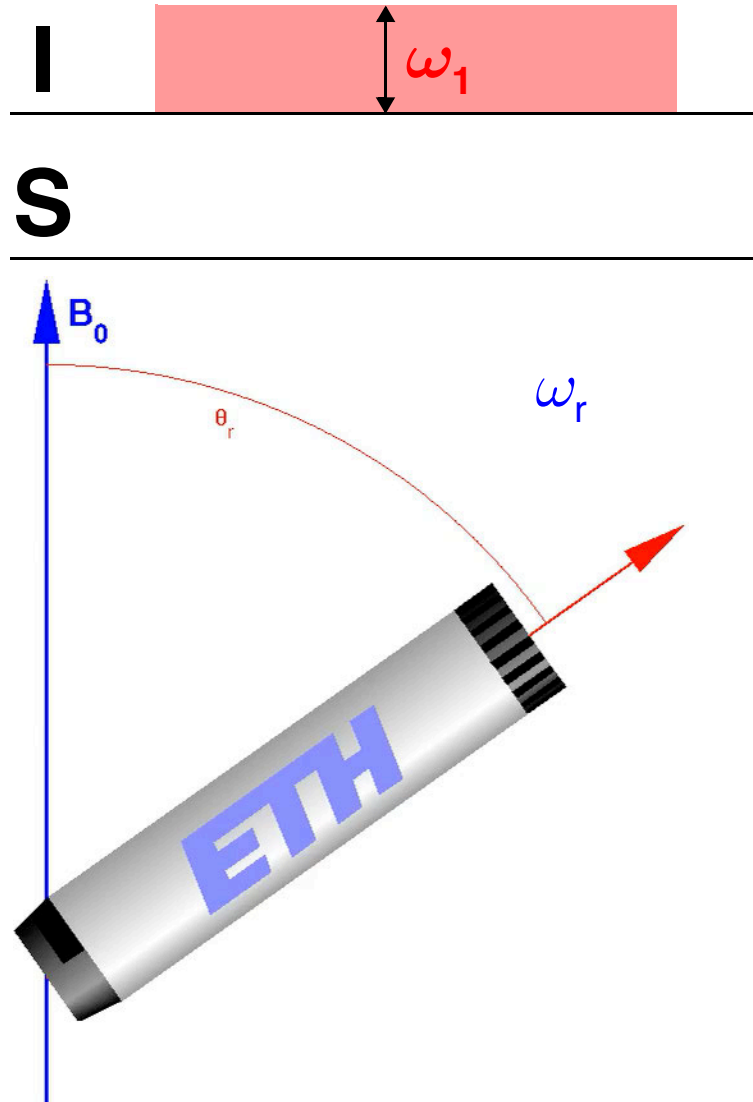
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Chemical shift of S spin: $\hat{\mathcal{H}}_S(t) = \hat{S}_z \sum_{n=-2}^2 \omega_S^{(n)} e^{in\omega_r t}$

Fourier Coefficients Under CW Irradiation



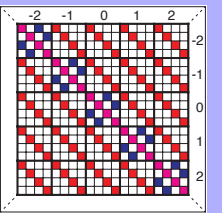
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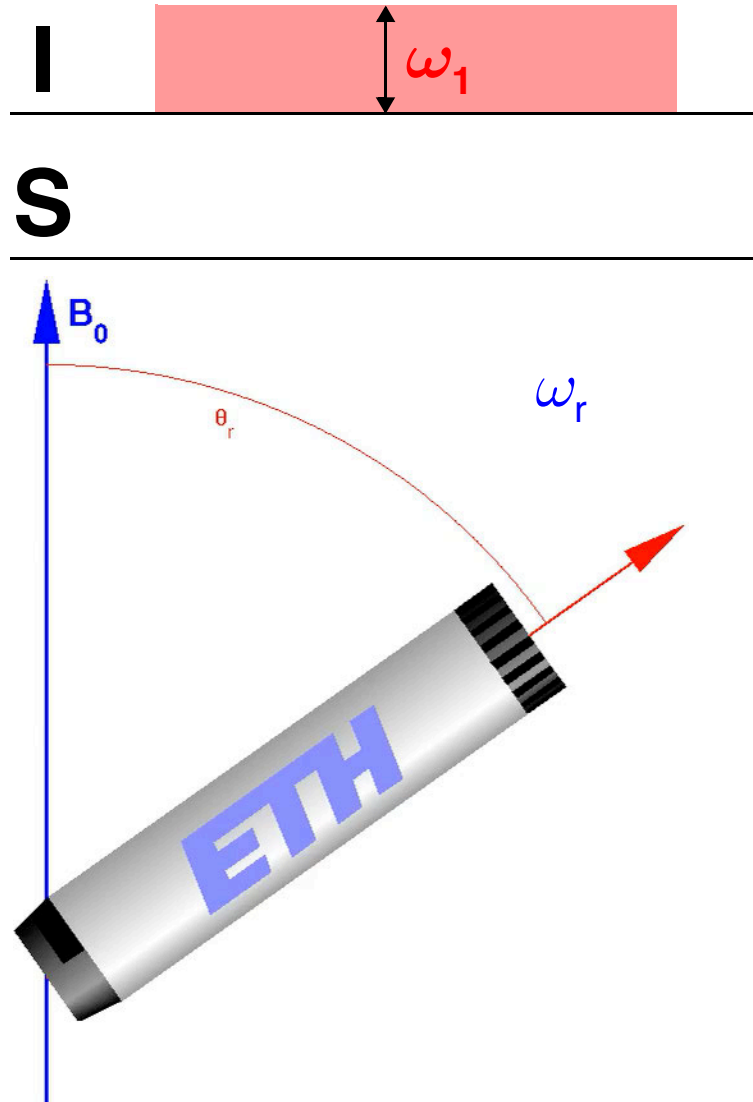
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Chemical shift of I spins: $\hat{\mathcal{H}}_I(t) = \sum_m \hat{I}_{mz} \sum_{n=-2}^2 \omega_m^{(n)} e^{in\omega_r t}$

Fourier Coefficients Under CW Irradiation



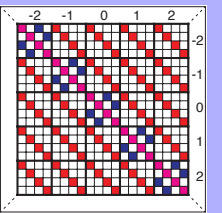
Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$



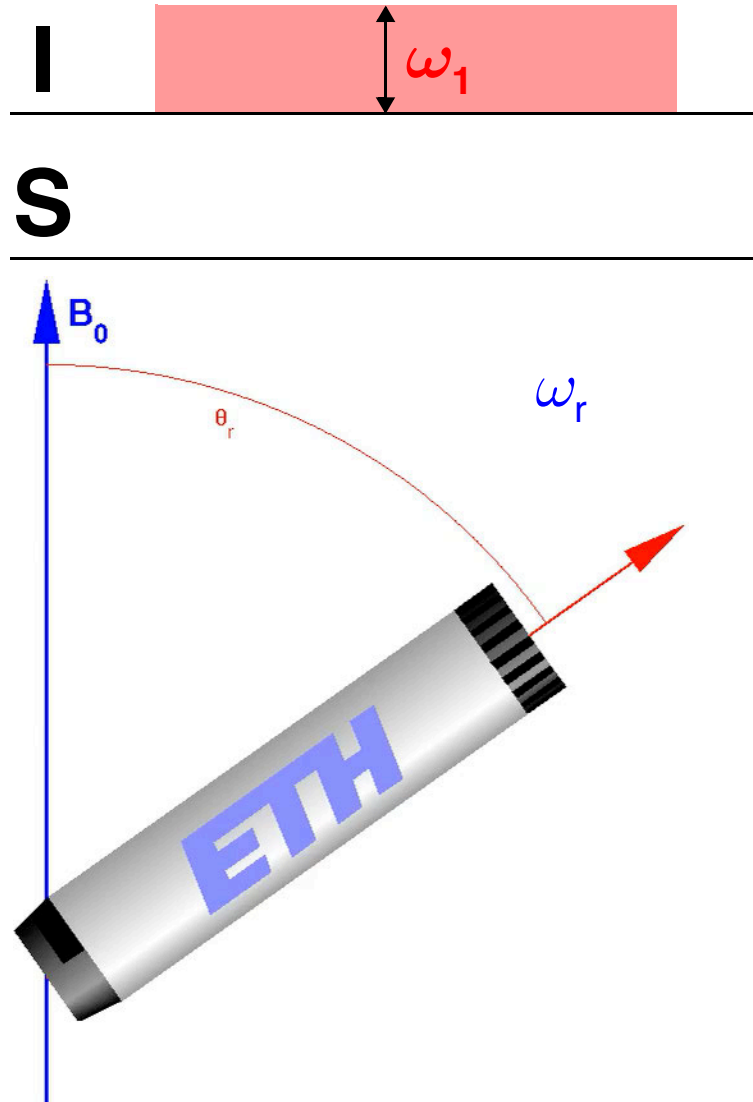
$$\left\{ \begin{aligned} \hat{\mathcal{H}}^{(0,0)} &= \omega_S^{(0)} S_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m) \\ \hat{\mathcal{H}}^{(n,0)} &= \omega_S^{(n)} S_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{mz} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{mx} + \hat{I}_{\ell y} \hat{I}_{my}) \right) \\ \hat{\mathcal{H}}^{(0,\pm 1)} &= -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp \\ \hat{\mathcal{H}}^{(n,\pm 1)} &= -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp \\ \hat{\mathcal{H}}^{(0,\pm 2)} &= 0 \\ \hat{\mathcal{H}}^{(n,\pm 2)} &= \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp \end{aligned} \right.$$

Homonuclear couplings (I-I): $\hat{\mathcal{H}}_{II}(t) = \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m) + \sum_{\ell < m} \left(2\hat{I}_{\ell z} \hat{I}_{mz} - (\hat{I}_{\ell x} \hat{I}_{mx} + \hat{I}_{\ell y} \hat{I}_{my}) \right) \sum_{\substack{n=-2 \\ n \neq 0}}^2 \omega_{\ell,m}^{(n)} e^{in\omega_r t}$

Fourier Coefficients Under CW Irradiation



Fourier coefficients: $\hat{\mathcal{H}}(t) = \sum_{n=-2}^2 \sum_{k=-2}^2 \hat{\mathcal{H}}^{(n,k)} e^{in\omega_r t} e^{ik\omega_1 t}$



$$\hat{\mathcal{H}}^{(0,0)} = \omega_S^{(0)} S_z + \sum_{\ell < m} \omega_{\ell,m}^{(0)} (\hat{I}_\ell \cdot \hat{I}_m)$$

$$\hat{\mathcal{H}}^{(n,0)} = \omega_S^{(n)} S_z - \sum_{\ell < m} \omega_{\ell,m}^{(n)} \left(\hat{I}_{\ell z} \hat{I}_{m z} - \frac{1}{2} (\hat{I}_{\ell x} \hat{I}_{m x} + \hat{I}_{\ell y} \hat{I}_{m y}) \right)$$

$$\hat{\mathcal{H}}^{(0,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(0)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(0)} \hat{S}_z \hat{I}_m^\mp$$

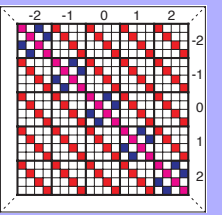
$$\hat{\mathcal{H}}^{(n,\pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^\mp - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^\mp$$

$$\hat{\mathcal{H}}^{(0,\pm 2)} = 0$$

$$\hat{\mathcal{H}}^{(n,\pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell,m}^{(n)} \hat{I}_\ell^\mp \hat{I}_m^\mp$$

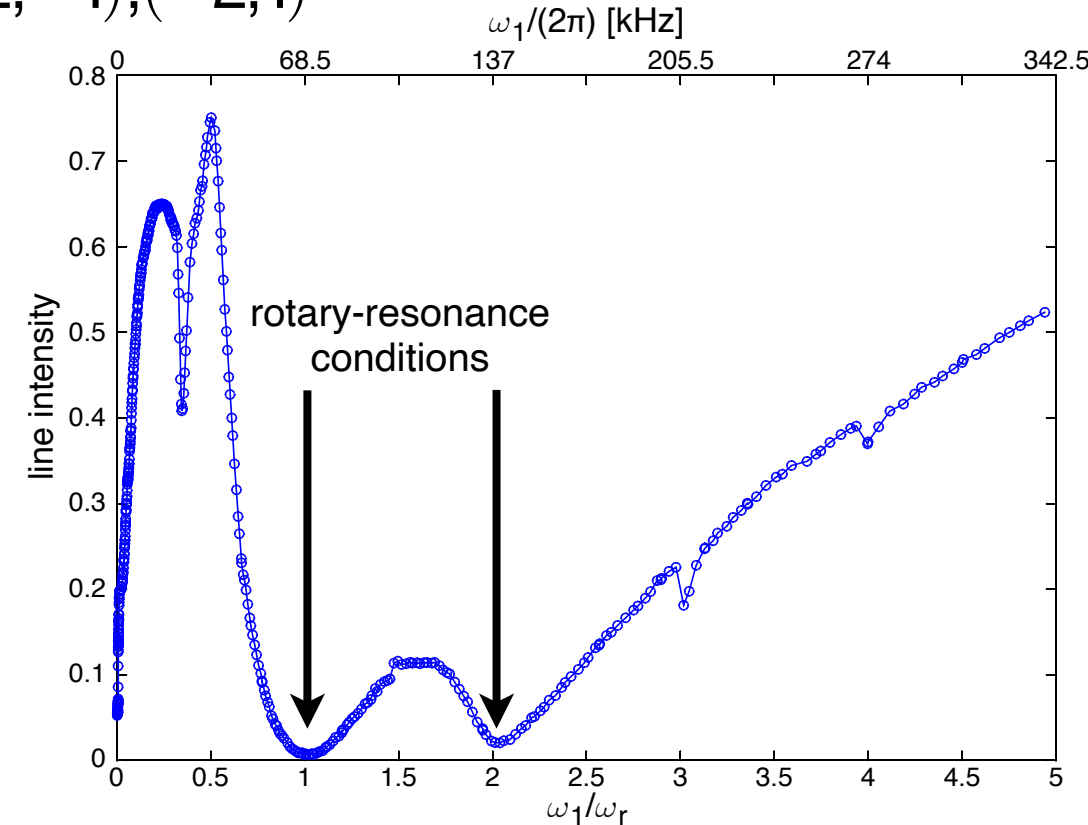
Heteronuclear couplings (I-S): $\hat{\mathcal{H}}_{IS}(t) = \sum_m 2\hat{S}_z \hat{I}_{mz} \sum_{\substack{n=-2 \\ n \neq 0}}^2 \omega_{S,m}^{(n)} e^{in\omega_r t}$

Rotary-Resonance Conditions



□ The resonance condition at the rotary-resonance conditions is $\omega_1/\omega_r = 1$ or $\omega_1/\omega_r = 2$.

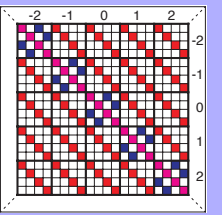
$$n_0\omega_r + k_0\omega_1 = 0 \left\{ \begin{array}{l} \omega_1 / \omega_r = -n_0 / k_0 = 1 \Rightarrow (n_0, k_0) = (1, -1), (-1, 1), (2, -2), (-2, 2) \\ \omega_1 / \omega_r = -n_0 / k_0 = 2 \Rightarrow (n_0, k_0) = (2, -1), (-2, 1) \end{array} \right.$$



$$\hat{\mathcal{H}}^{(n, \pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^{\mp} - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^{\mp}$$

$$\hat{\mathcal{H}}^{(n, \pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell, m}^{(n)} \hat{I}_\ell^{\mp} \hat{I}_m^{\mp}$$

Rotary-Resonance Conditions



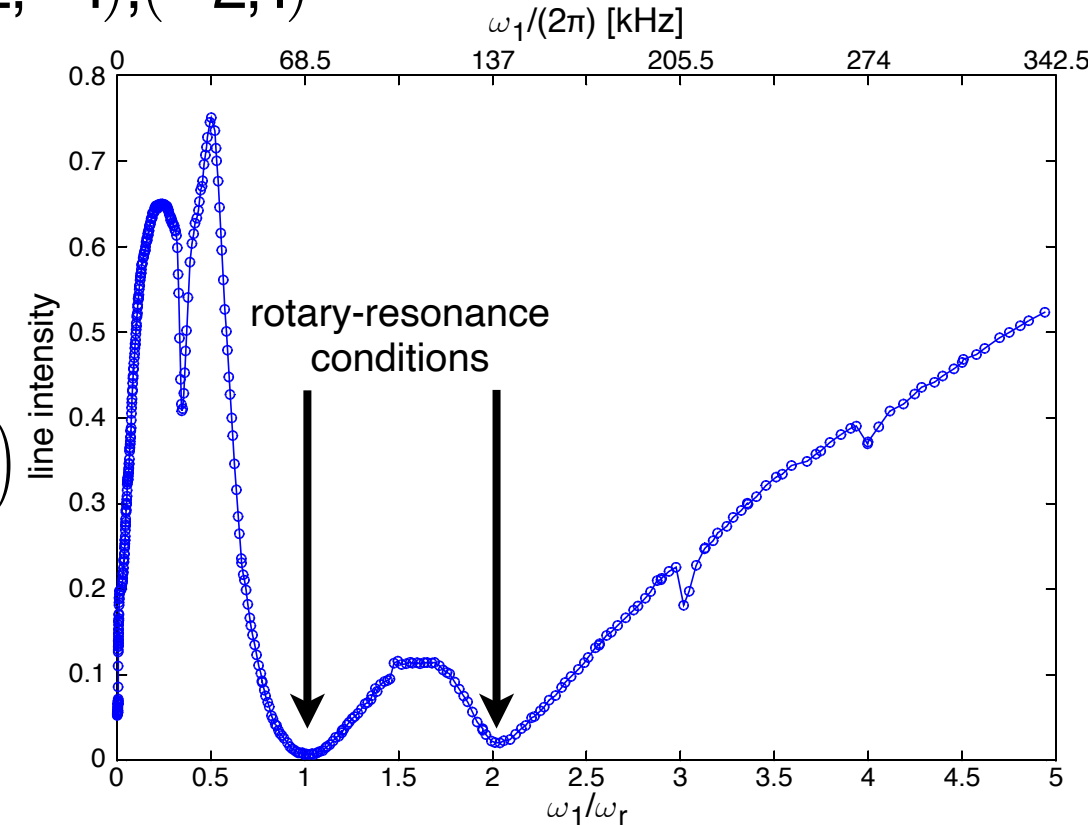
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□ $n = 1$ rotary-resonance condition:

$$\begin{aligned} \hat{\mathcal{H}}^{(1)} &= \sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} = \hat{\mathcal{H}}^{(1, -1)} + \hat{\mathcal{H}}^{(-1, 1)} + \hat{\mathcal{H}}^{(2, -2)} + \hat{\mathcal{H}}^{(-2, 2)} \\ &= -\frac{1}{2} \sum_m \left(\omega_m^{(1)} \hat{I}_m^+ + \omega_m^{(-1)} \hat{I}_m^- \right) - \frac{1}{2} \sum_m \left(\omega_{Sm}^{(1)} \hat{S}_z \hat{I}_m^+ + \omega_{Sm}^{(-1)} \hat{S}_z \hat{I}_m^- \right) \\ &\quad + \frac{3}{4} \sum_{\ell < m} \left(\omega_{\ell, m}^{(2)} \hat{I}_\ell^+ \hat{I}_m^+ + \omega_{\ell, m}^{(-2)} \hat{I}_\ell^- \hat{I}_m^- \right) \end{aligned}$$

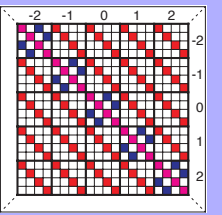
□ At the $n = 1$ rotary-resonance condition, we recouple the I-spin CSA tensor, the heteronuclear dipolar coupling and the homonuclear dipolar coupling.



$$\hat{\mathcal{H}}^{(n, \pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^{\mp} - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^{\mp}$$

$$\hat{\mathcal{H}}^{(n, \pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell, m}^{(n)} \hat{I}_\ell^{\mp} \hat{I}_m^{\mp}$$

Rotary-Resonance Conditions

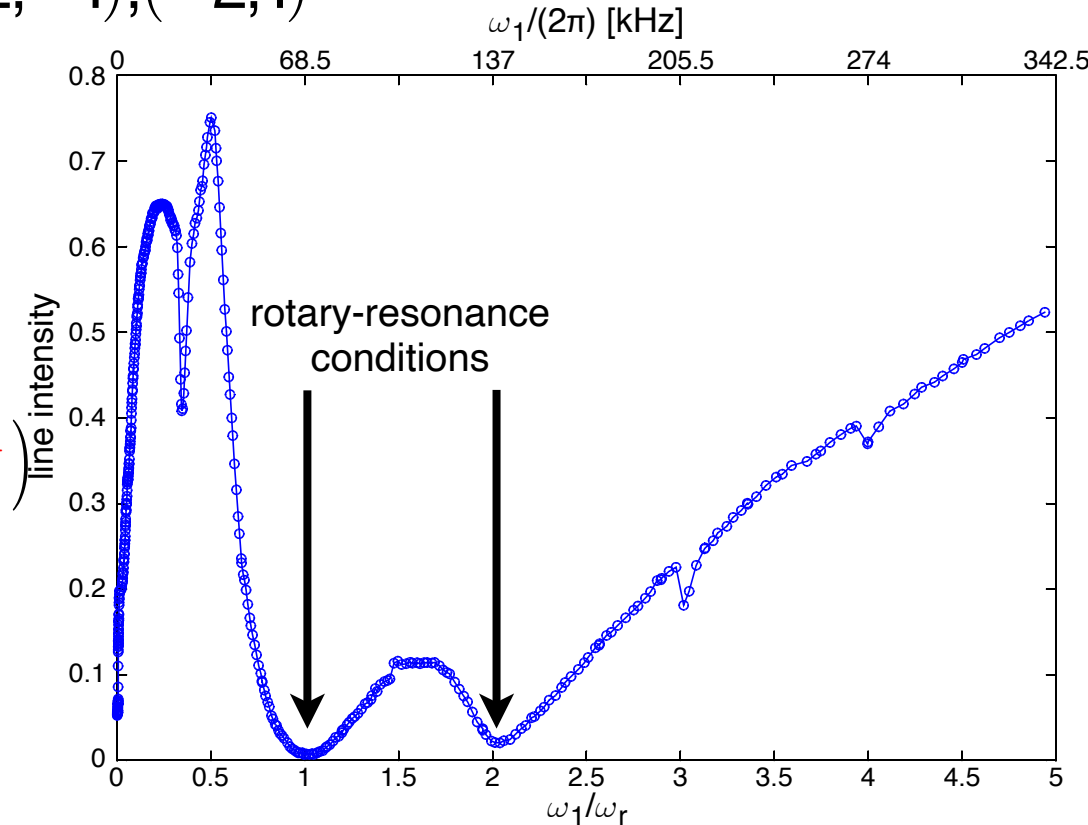


□ The resonance condition at the rotary-resonance conditions is $\omega_1/\omega_r = 1$ or $\omega_1/\omega_r = 2$.

$$n_0\omega_r + k_0\omega_1 = 0 \begin{cases} \omega_1/\omega_r = -n_0/k_0 = 1 \Rightarrow (n_0, k_0) = (1, -1), (-1, 1), (2, -2), (-2, 2) \\ \omega_1/\omega_r = -n_0/k_0 = 2 \Rightarrow (n_0, k_0) = (2, -1), (-2, 1) \end{cases}$$

□ $n = 2$ rotary-resonance condition:

$$\begin{aligned} \hat{\mathcal{H}}^{(1)} &= \sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} = \hat{\mathcal{H}}^{(2, -1)} + \hat{\mathcal{H}}^{(-2, 1)} \\ &= -\frac{1}{2} \sum_m \left(\omega_m^{(2)} \hat{I}_m^+ + \omega_m^{(-2)} \hat{I}_m^- \right) - \frac{1}{2} \sum_m \left(\omega_{Sm}^{(2)} \hat{S}_z \hat{I}_m^+ + \omega_{Sm}^{(-2)} \hat{S}_z \hat{I}_m^- \right) \end{aligned}$$



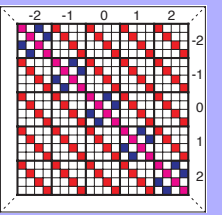
□ At the $n = 2$ rotary-resonance condition, we recouple the I-spin CSA tensor, the heteronuclear dipolar coupling *but not* the homonuclear dipolar coupling.

□ At the rotary-resonance conditions the S-spin line is broadened because the heteronuclear coupling is reintroduced.

$$\hat{\mathcal{H}}^{(n, \pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^{\mp} - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^{\mp}$$

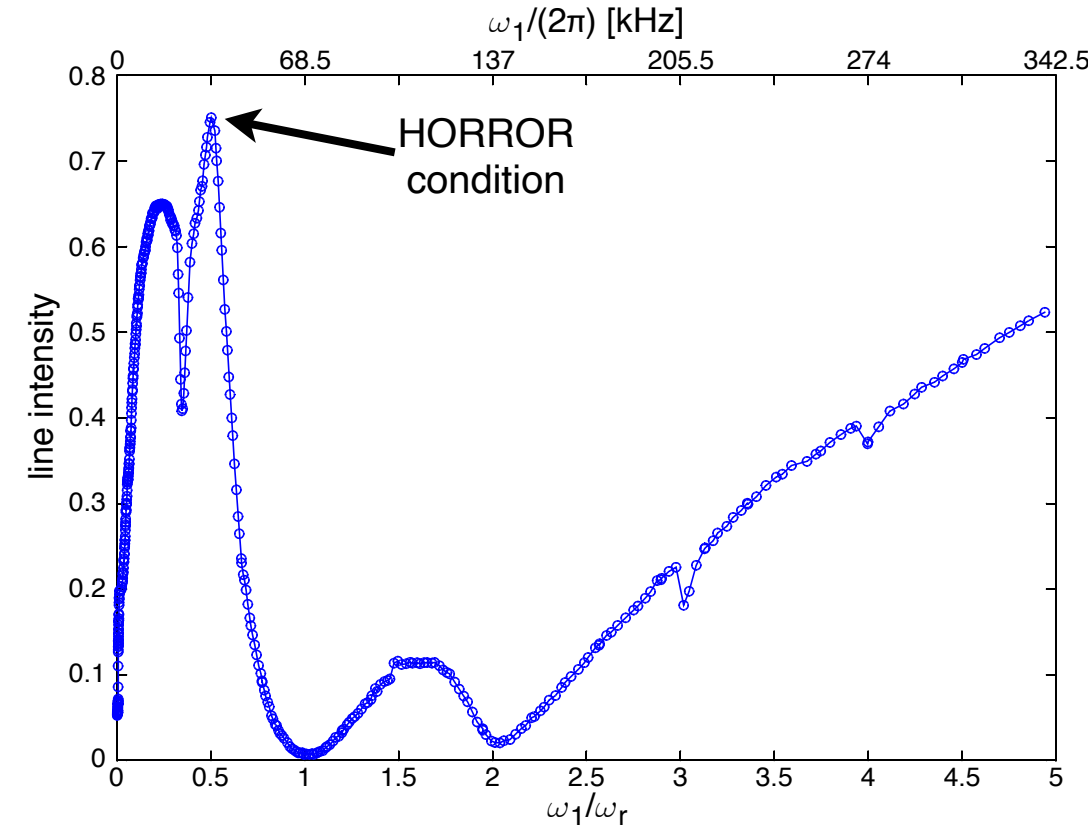
$$\hat{\mathcal{H}}^{(n, \pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell, m}^{(n)} \hat{I}_\ell^{\mp} \hat{I}_m^{\mp}$$

HORROR Condition



□ The resonance condition at the HORROR conditions is $\omega_1/\omega_r = 1/2$.

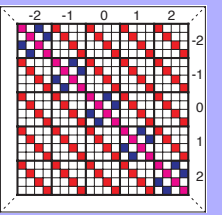
$$n_0\omega_r + k_0\omega_1 = 0: \quad \omega_1 / \omega_r = -n_0 / k_0 = 1/2 \quad \Rightarrow \quad (n_0, k_0) = (1, -2), (-1, 2)$$



$$\hat{\mathcal{H}}^{(n, \pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^{\mp} - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^{\mp}$$

$$\hat{\mathcal{H}}^{(n, \pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell, m}^{(n)} \hat{I}_\ell^{\mp} \hat{I}_m^{\mp}$$

HORROR Condition



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□ HORROR condition:

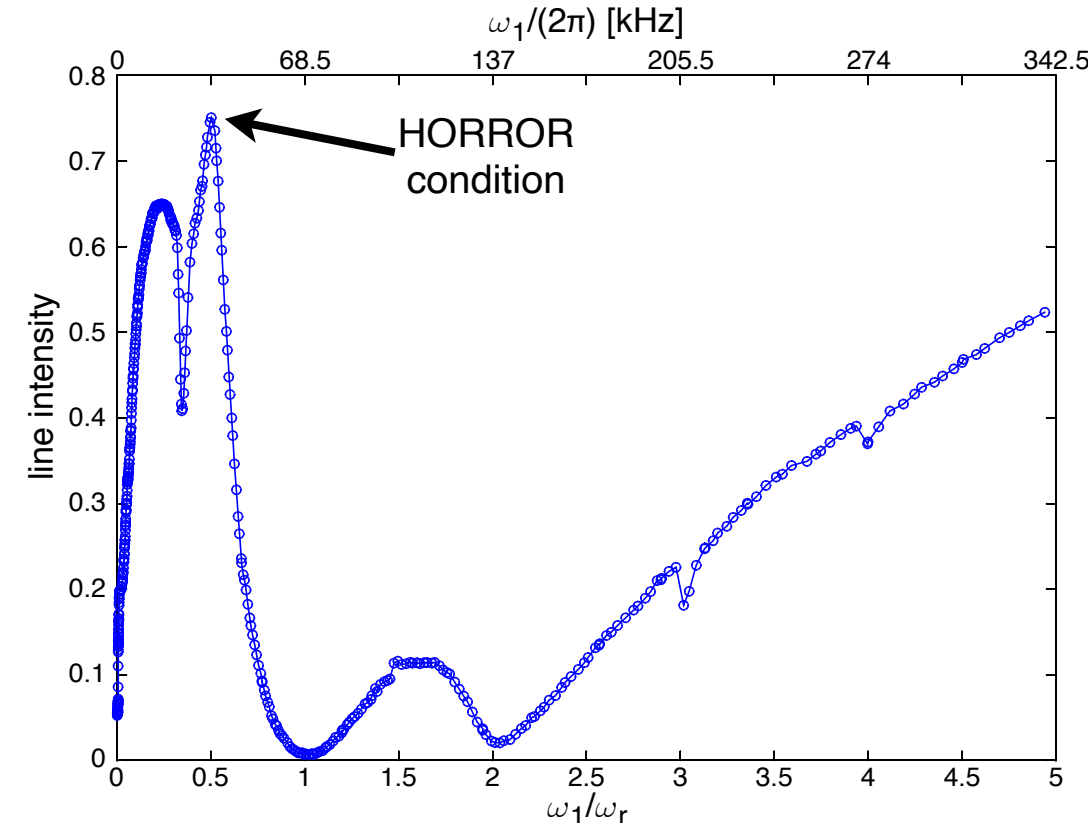
$$\begin{aligned} \hat{\mathcal{H}}^{(1)} &= \sum_{n_0, k_0} \hat{\mathcal{H}}^{(n_0, k_0)} = \hat{\mathcal{H}}^{(1, -2)} + \hat{\mathcal{H}}^{(-1, 2)} + \hat{\mathcal{H}}^{(2, -2)} + \hat{\mathcal{H}}^{(-2, 2)} \\ &= \frac{3}{4} \sum_{\ell < m} \left(\omega_{\ell, m}^{(1)} \hat{I}_{\ell}^{+} \hat{I}_{m}^{+} + \omega_{\ell, m}^{(-1)} \hat{I}_{\ell}^{-} \hat{I}_{m}^{-} \right) \end{aligned}$$

□ At the HORROR condition, we recouple *only* the homonuclear dipolar coupling.

□ Reintroducing the homonuclear coupling leads to faster spin diffusion.

□ This leads to “self decoupling” and narrower lines in the S-spin spectrum.

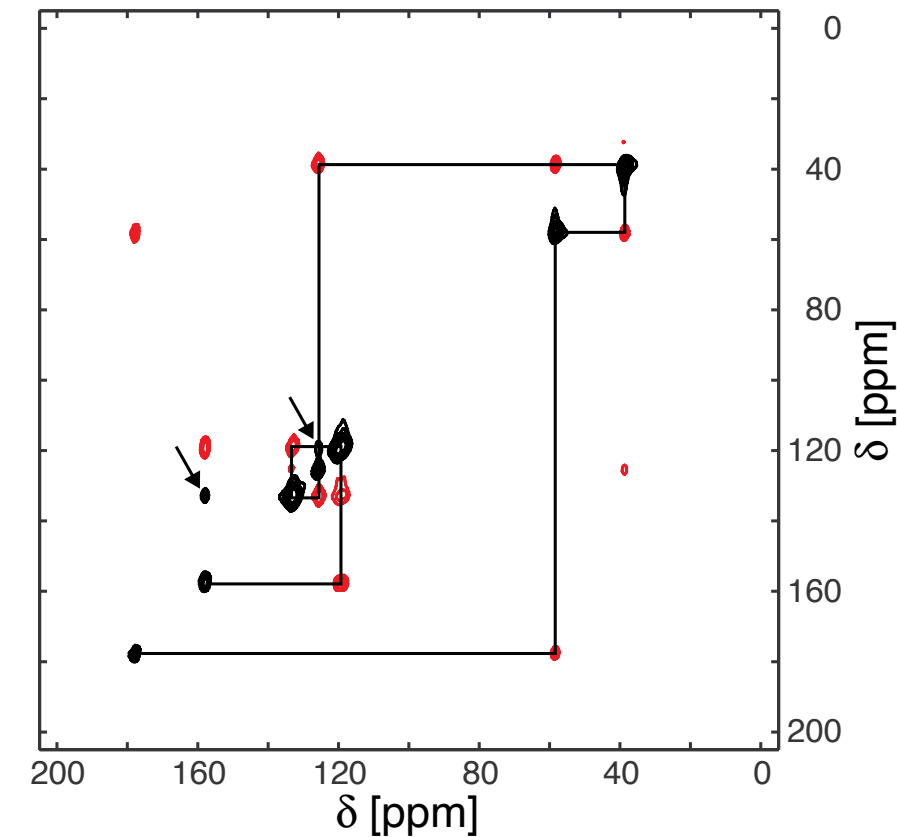
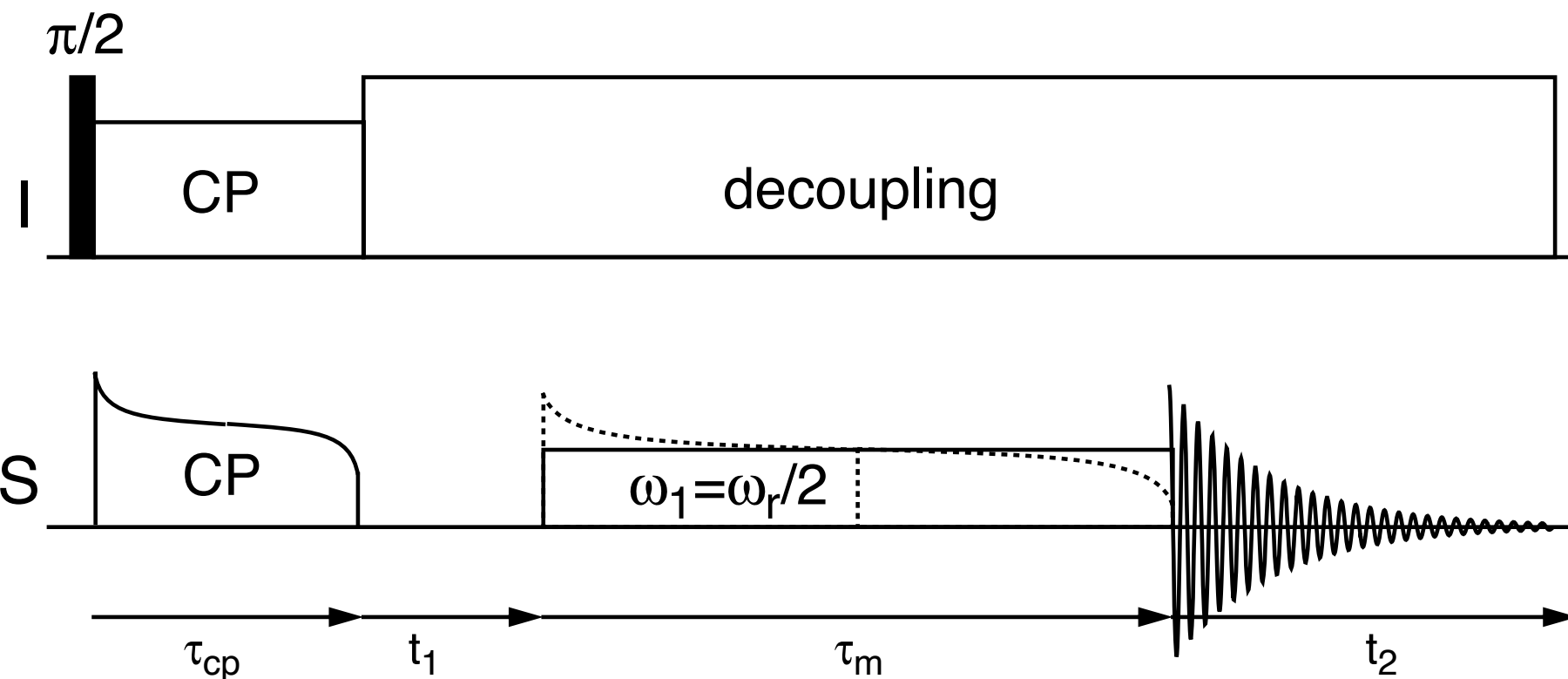
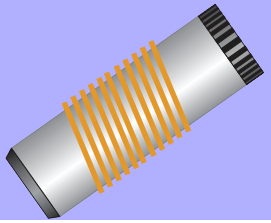
□ The Floquet formalism is for all three resonance conditions the same.



$$\hat{\mathcal{H}}^{(n, \pm 1)} = -\frac{1}{2} \sum_m \omega_m^{(n)} \hat{I}_m^{\mp} - \frac{1}{2} \sum_m \omega_{Sm}^{(n)} \hat{S}_z \hat{I}_m^{\mp}$$

$$\hat{\mathcal{H}}^{(n, \pm 2)} = \frac{3}{4} \sum_{\ell < m} \omega_{\ell, m}^{(n)} \hat{I}_{\ell}^{\mp} \hat{I}_m^{\mp}$$

HORROR and DREAM Recoupling: $\omega_r = 2 \omega_1$

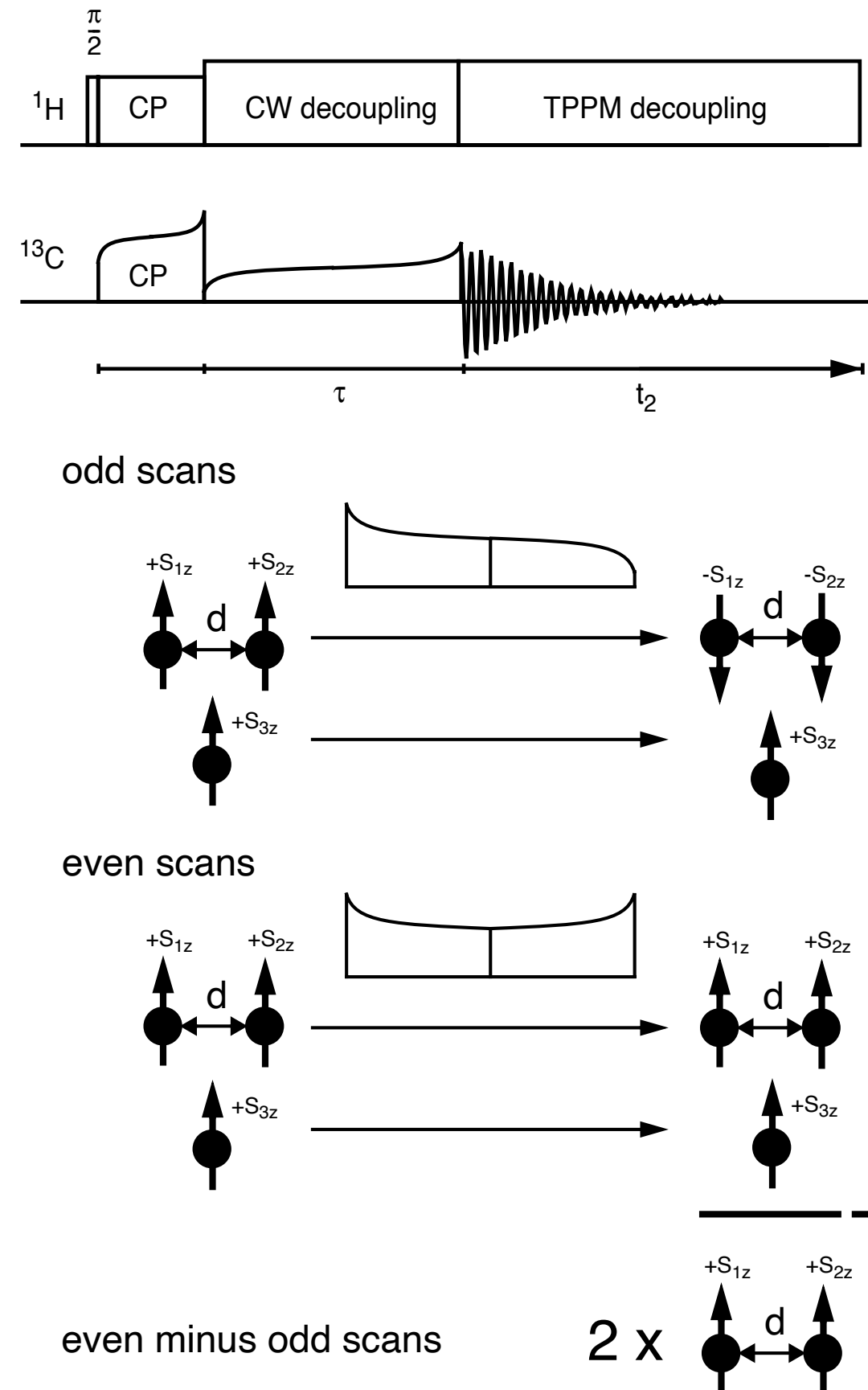
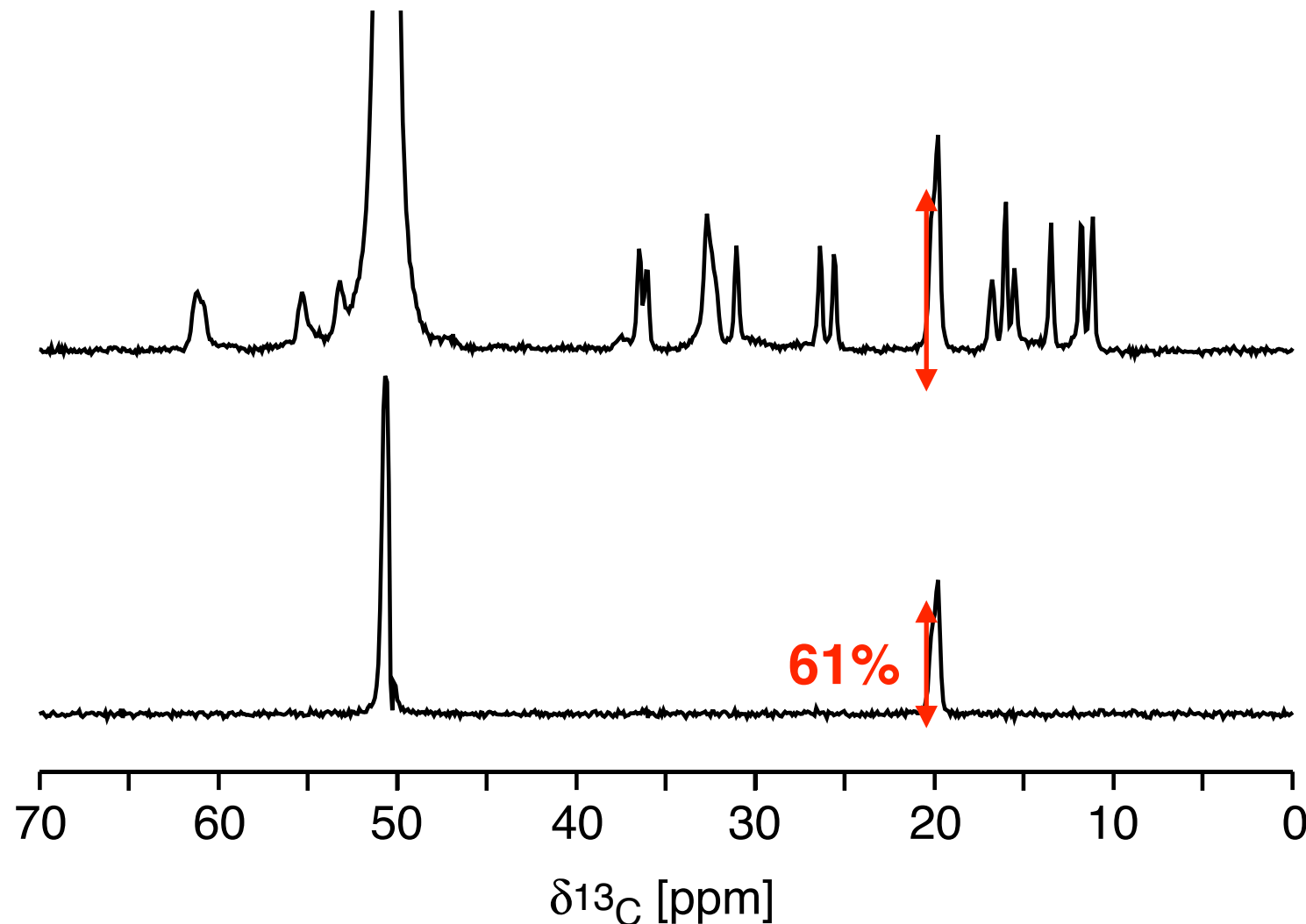


- ❑ DREAM (adiabatic version of HORROR) can be used for two-dimensional correlation spectra with DQ polarization transfer.
- ❑ DREAM has the advantage that the match condition is much broader and easier to implement in a broadband (large chemical-shift range) fashion.
- ❑ DREAM polarization transfer is very efficient at fast MAS where the rf-field amplitude is high enough to cover (part of) the interesting spectral range.
- ❑ At intermediate MAS frequencies the polarization transfer becomes strongly dependent on the chemical shifts of the spin pairs.

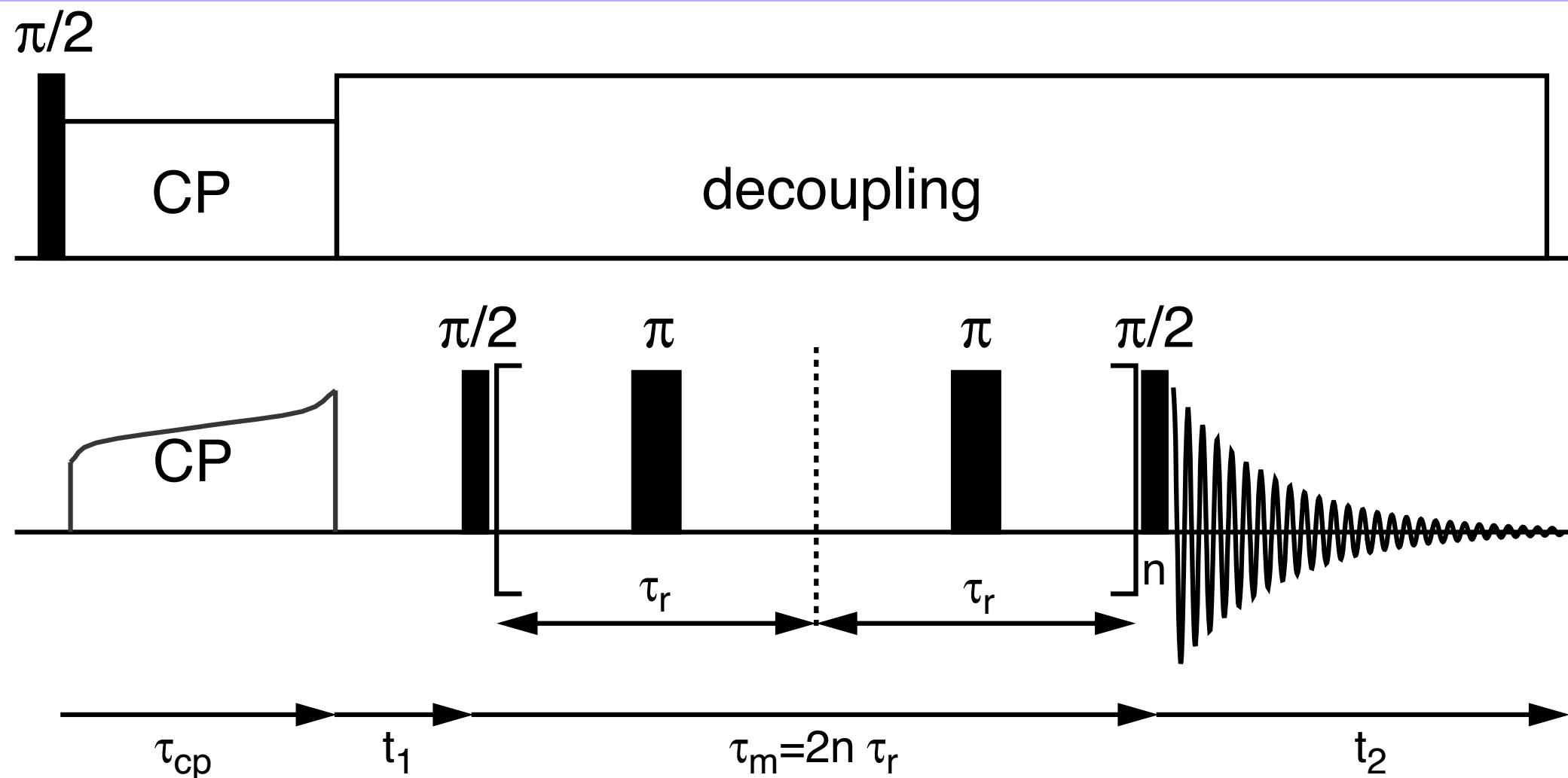
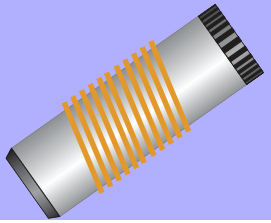
DREAM DQ Filtering



- Using different sweep profiles, DREAM can also be used as an efficient DQ filter to select ^{13}C neighboring spins.
- In a mixture of 1- ^{13}C alanine, nat. abundance methionine and iso-leucine, the efficiency is about 61% and the suppression of natural abundance peaks very good.

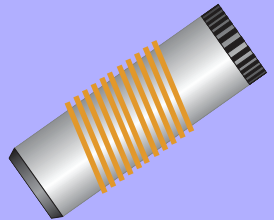


Radio-Frequency-Driven Recoupling (RFDR)



- ❑ RFDR is a homonuclear recoupling sequence where one π pulse per rotor cycle prevents the averaging of the homonuclear dipolar coupling.
- ❑ An xy-4 phase cycle compensates the effects of finite pulses.
- ❑ RFDR is simple to implement and quite robust method.
- ❑ It has seen renewed interest in recoupling protons under fast MAS.

Radio-Frequency-Driven recoupling (RFDR)



❑ In RFDR, recoupling is achieved by adding a 180° pulse during each rotor period.

❑ We can transform the ZQ part of the Hamiltonian into a toggling frame with the rf pulses (instantaneous rotations):

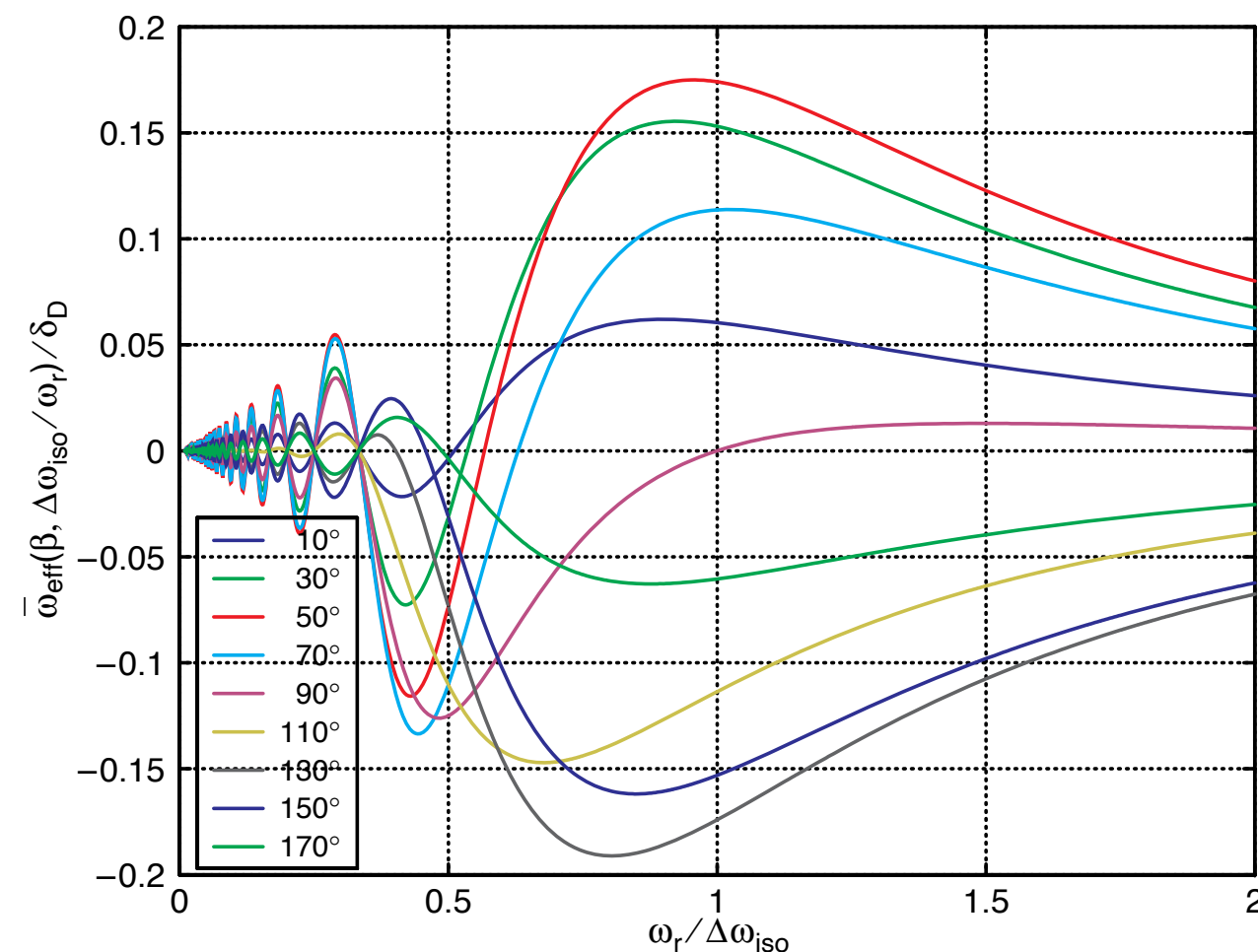
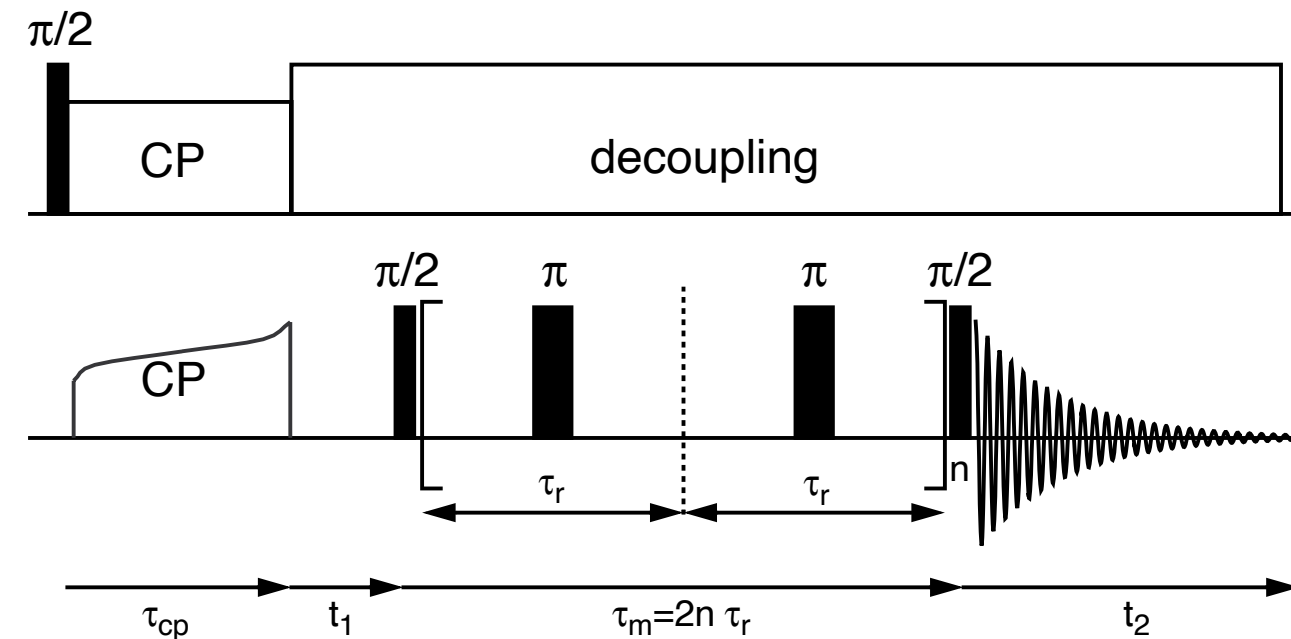
$$\hat{\mathcal{H}} = \begin{cases} +\Delta\omega_{\text{iso}}\hat{S}_z^\Delta - \omega_{12}(t)\hat{S}_x^\Delta & 0 < t < \tau_r/2 \\ -\Delta\omega_{\text{iso}}\hat{S}_z^\Delta - \omega_{12}(t)\hat{S}_x^\Delta & \tau_r/2 < t < 3\tau_r/2 \\ +\Delta\omega_{\text{iso}}\hat{S}_z^\Delta - \omega_{12}(t)\hat{S}_x^\Delta & 3\tau_r/2 < t < 2\tau_r \end{cases}$$

❑ Transforming into an interaction frame with the chemical-shift part of the Hamiltonian leads to an effective Hamiltonian of the form:

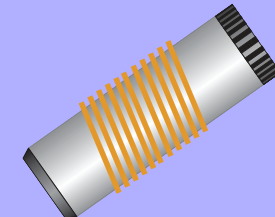
$$\bar{\hat{\mathcal{H}}}^{(1)} = \frac{\omega_{\text{eff}}(\beta, \Delta\omega_{\text{iso}}/\omega_r)}{2} (\hat{S}_1^+ \hat{S}_2^- + \hat{S}_1^- \hat{S}_2^+)$$

❑ The recoupling depends strongly on the chemical-shift difference.

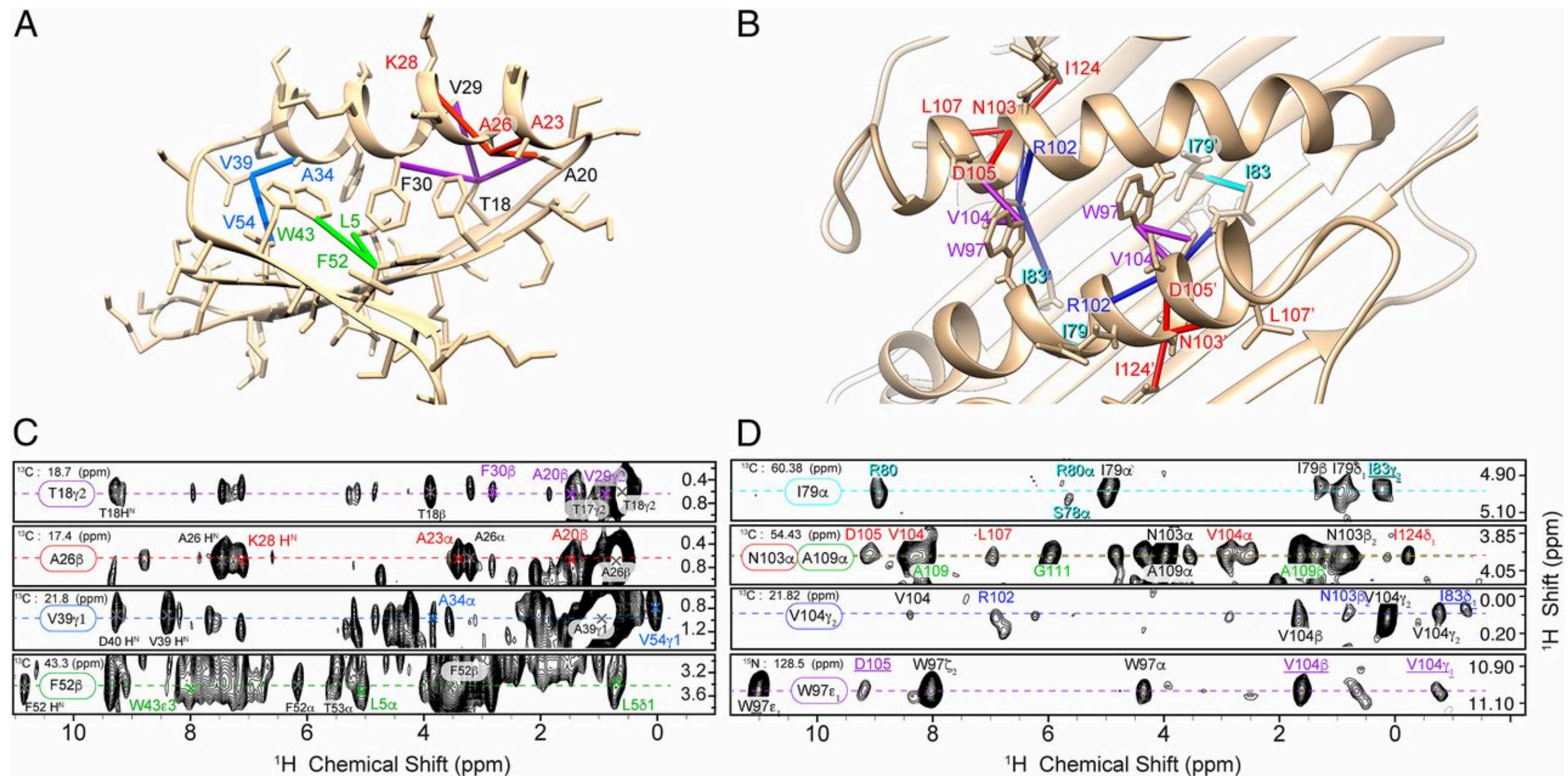
❑ RFDR is very stable and robust.



Examples of RFDR Spectra

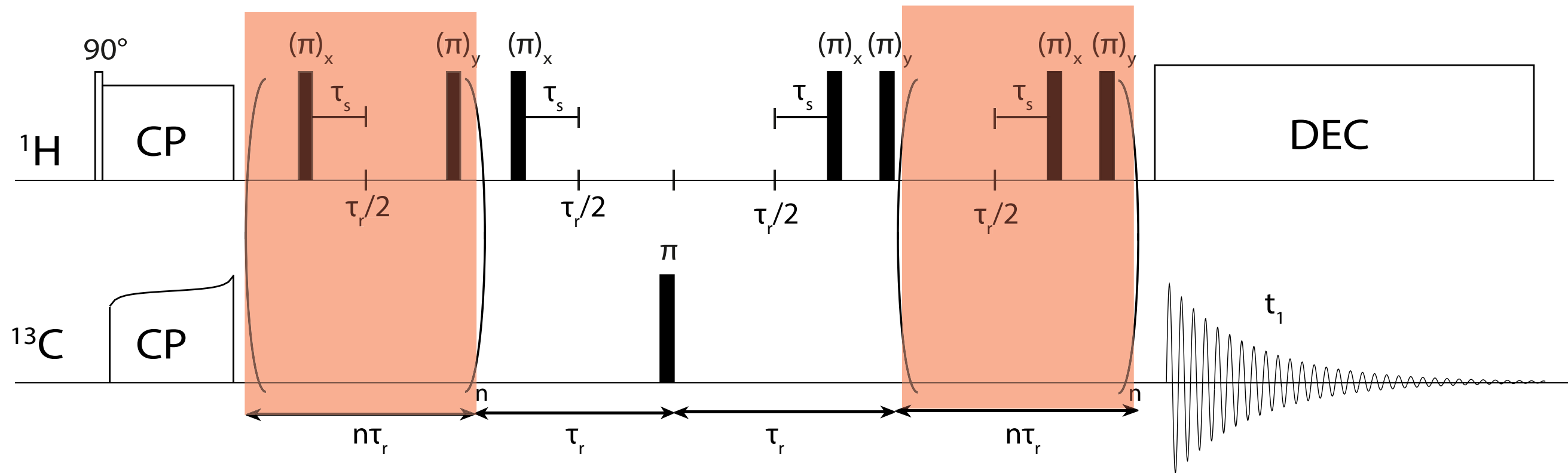
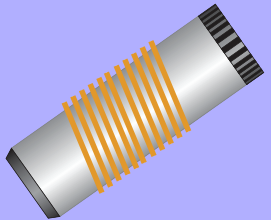


^1H RFDR, 100 kHz MAS, GB1, Structural Restraints from ^1H - ^1H Contacts



L.B. Andreas, ..., G. Pintacuda, Structure of fully protonated proteins by proton-detected magic-angle spinning NMR, Proc. Natl. Acad. Sci. USA 113 (2016) 9187–9192. <https://doi.org/10.1073/pnas.1602248113>.

Rotational-Echo Double Resonance (REDOR)

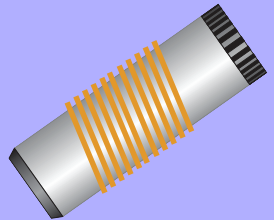


- ❑ REDOR (Rotational-Echo Double Resonance) is a periodic π -pulse sequence with two π pulses per rotor cycle.
- ❑ It recouples the heteronuclear dipolar coupling and leads to a dephasing of the magnetization under this coupling.
- ❑ Chemical shifts are refocused by the central π pulse.
- ❑ REDOR is typically measured with a reference experiment where all the pulses on one of the two spins are omitted.
- ❑ There are variants with shifted pulses to scale the dipolar coupling for measuring large couplings since sampling is only possible at multiples of $2\tau_r$.

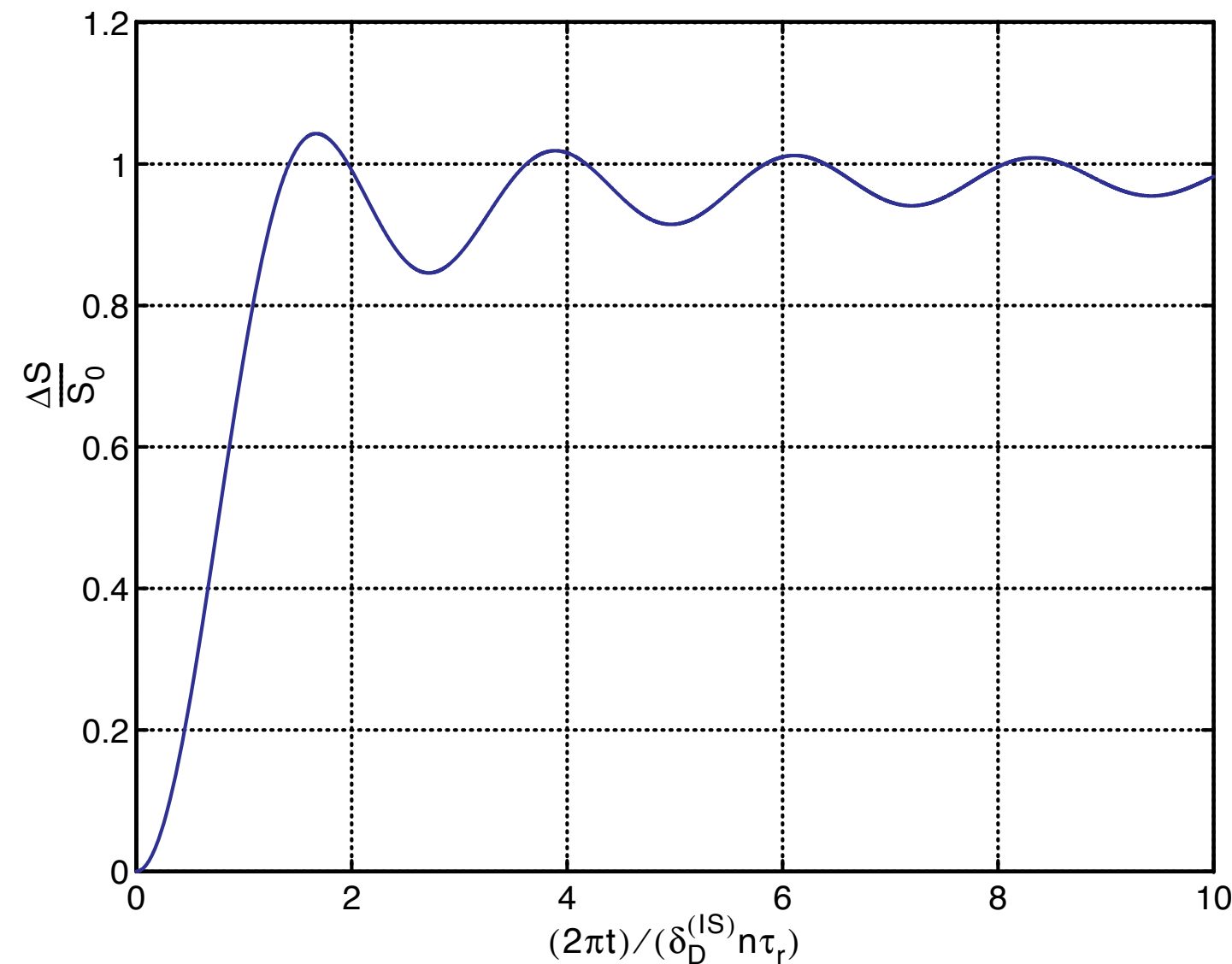
T. Gullion, J. Schaefer, Rotational-Echo Double-Resonance NMR, J. Magn. Reson. 81 (1989) 196–200.

T. Gullion, J. Schaefer, Detection of weak heteronuclear dipolar coupling by rotational-echo double-resonance NMR, Adv. Magn. Reson. 13 (1989) 57–83.

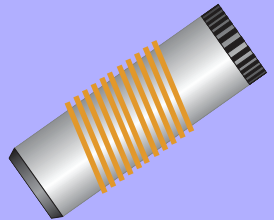
Rotational-Echo Double Resonance (REDOR)



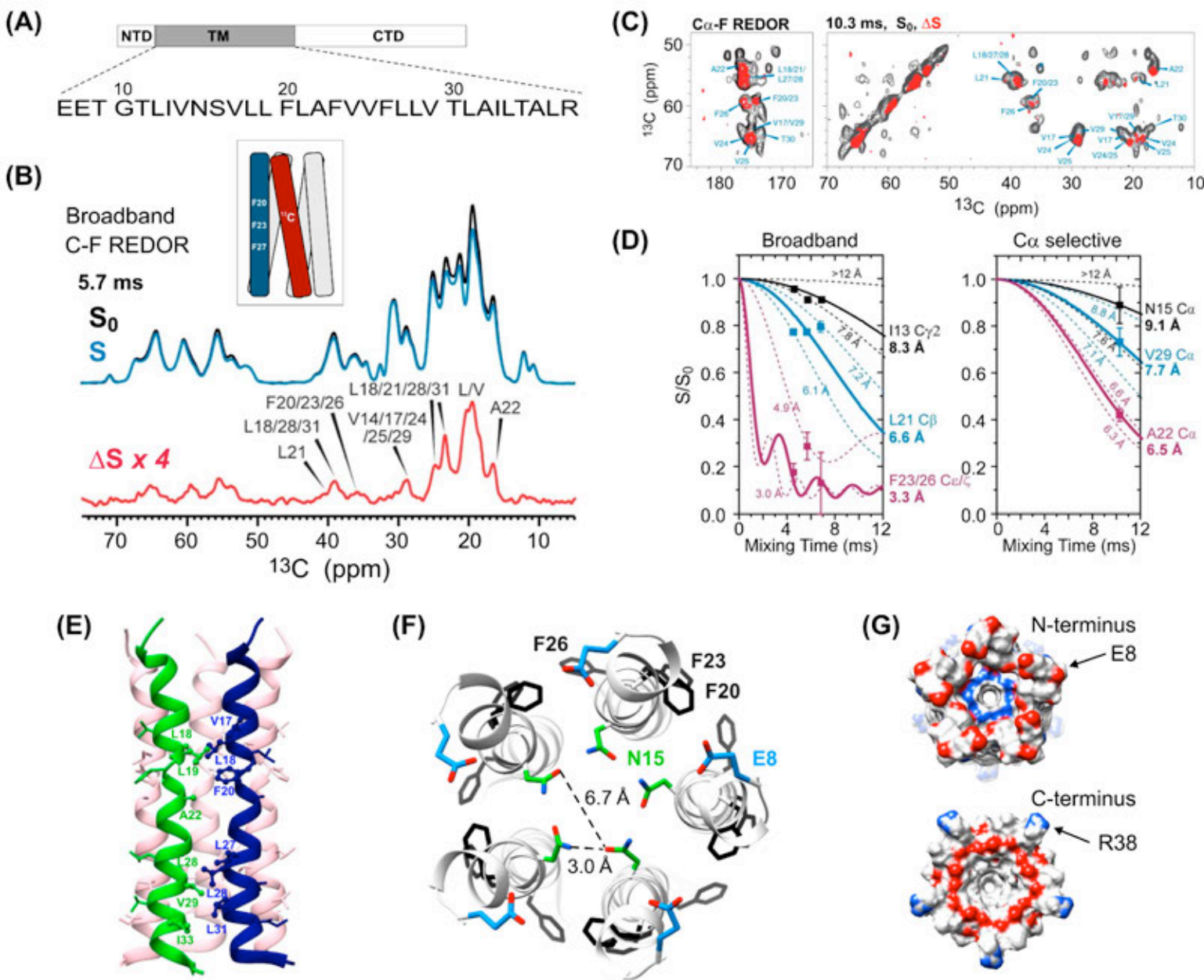
- REDOR is a heteronuclear dipolar recoupling sequence that uses two rotor-synchronized 180° pulses to prevent averaging of the dipolar coupling.
- REDOR is a robust sequence in isolated two-spin systems and can be used to measure relatively precise distances.
- The theoretical description uses again a toggling frame but here the 180° pulses changes the sign of the dipolar coupling.
- This prevents the averaging of the $n = 1$ Fourier component of the dipolar coupling leading to a dephasing under the Hamiltonian: $\bar{\mathcal{H}}^{(1)} = \omega_{\text{eff}}(\beta, \gamma) 2\hat{I}_z \hat{S}_z$
- The REDOR curve is universal since it scales with the anisotropy of the coupling.
- The Ising-type effective Hamiltonian distinguishes REDOR from most other recoupling sequences that have either a DQ or ZQ Hamiltonian.



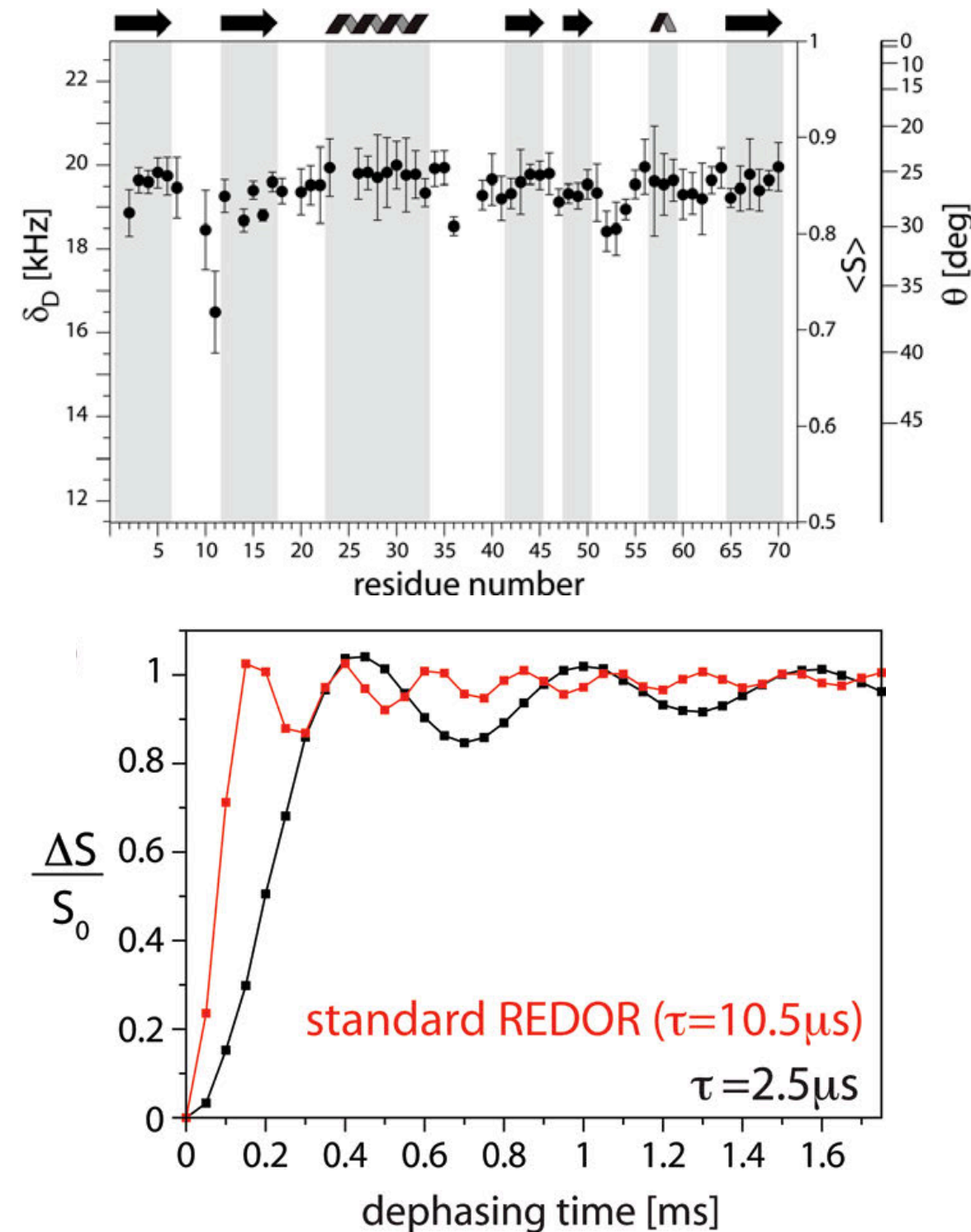
REDOR Examples



Distance Measurements: Domain Architecture of the SARS-CoV-2 Envelope Protein



Dynamics Characterization in Ubiquitin

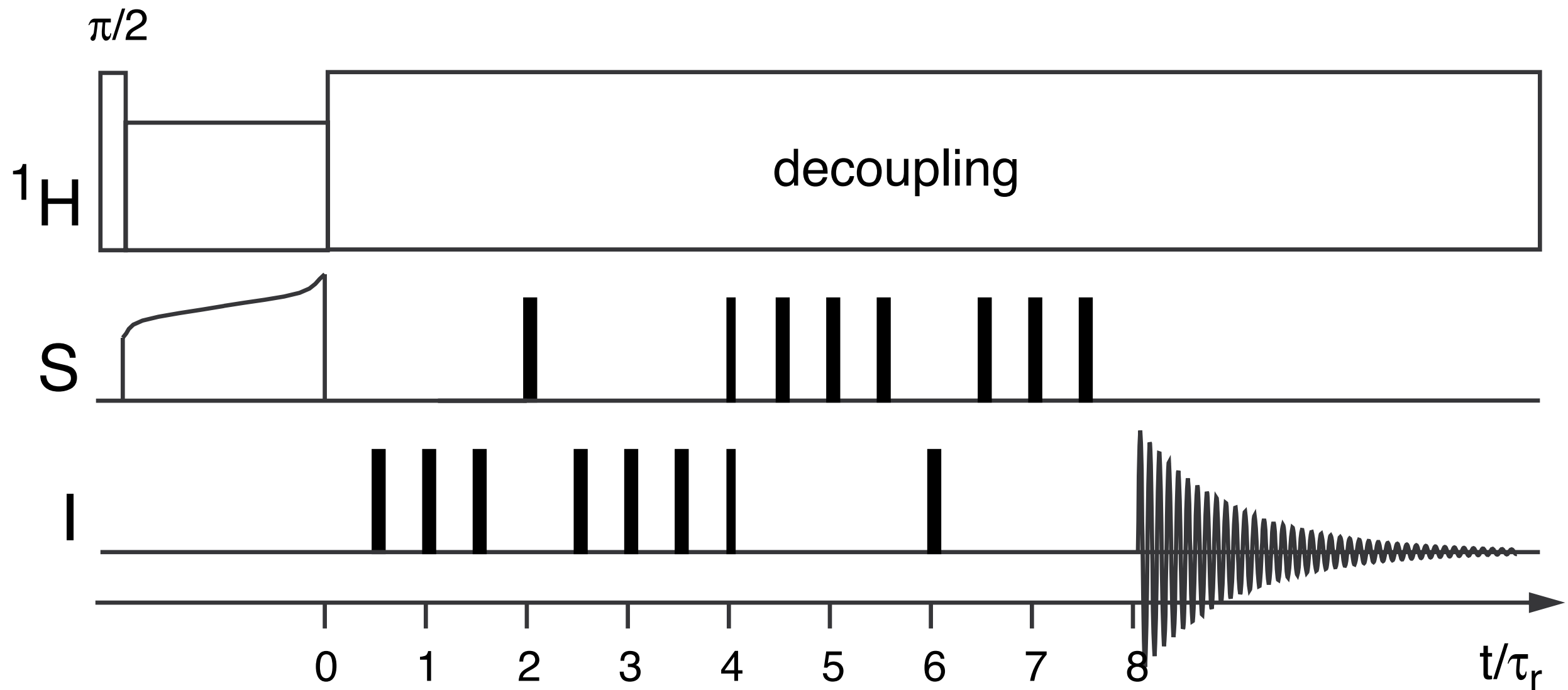
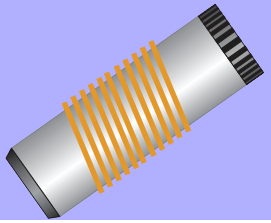


O. Toke, Int. J. Mol. Sci. 24 (2023) 13637. <https://doi.org/10.3390/ijms241713637>.

V.S. Mandala, ..., M. Hong, Nat. Struct. Mol. Biol. 27 (2020) 1202–1208. <https://doi.org/10.1038/s41594-020-00536-8>.

P. Schanda, ..., M. Ernst, J. Am. Chem. Soc. 132 (2010) 15957–15967. <https://doi.org/10.1021/ja100726a>.

Transferred Rotational-Echo Double Resonance (TEDOR)



- ❑ Including REDOR recoupling in an refocused INEPT-type pulse scheme allows us to use it for polarization transfer.
- ❑ The polarization transfer is less efficient than CP (56% vs 73% maximum efficiency) but it can sometimes be more robust and easier to set up.

Dipolar Truncation



- Most first-order dipolar recoupling sequences generate either a **DQ** (HORROR, DREAM, C7, ...) or **ZQ** (RFDR, R², ...) effective Hamiltonian of the form:

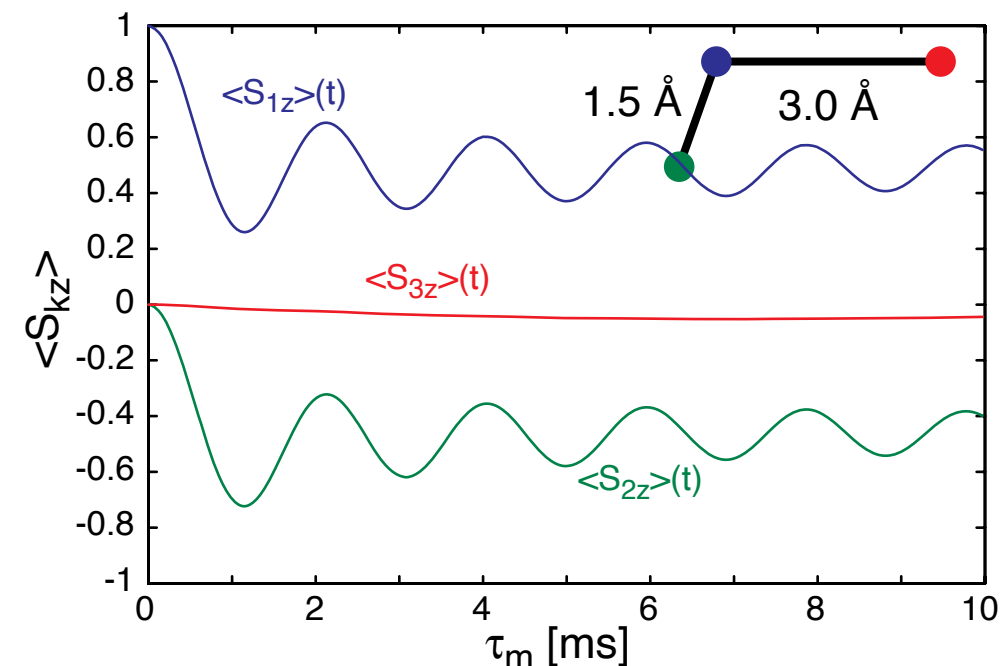
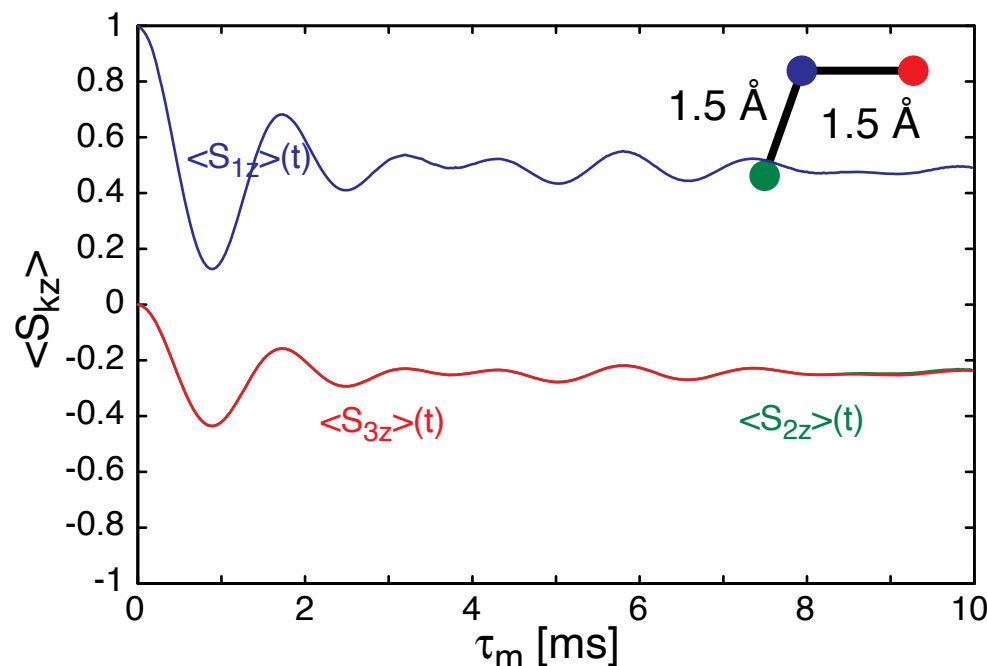
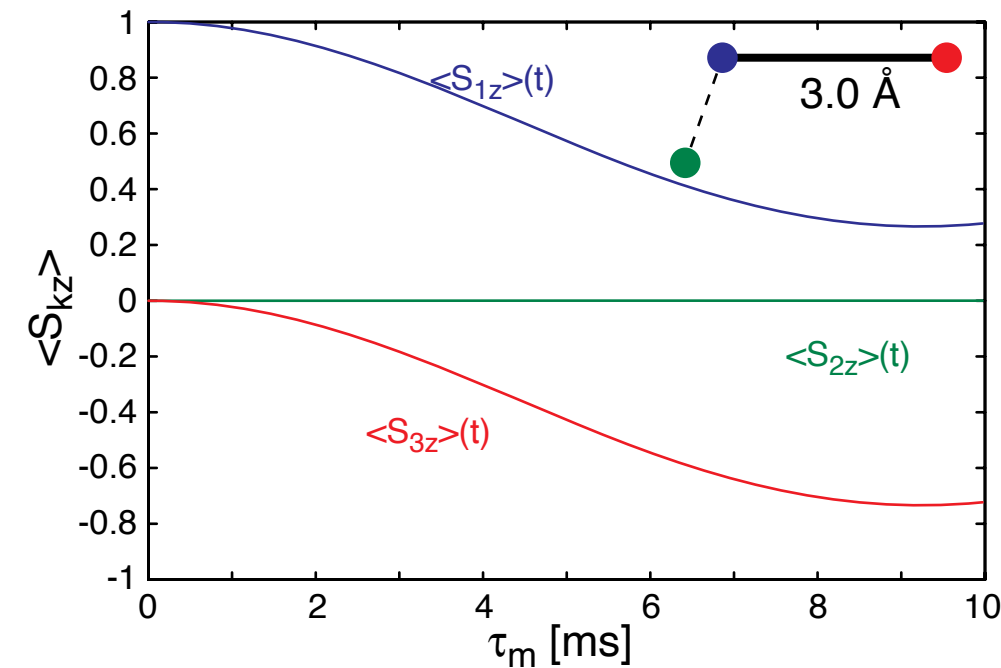
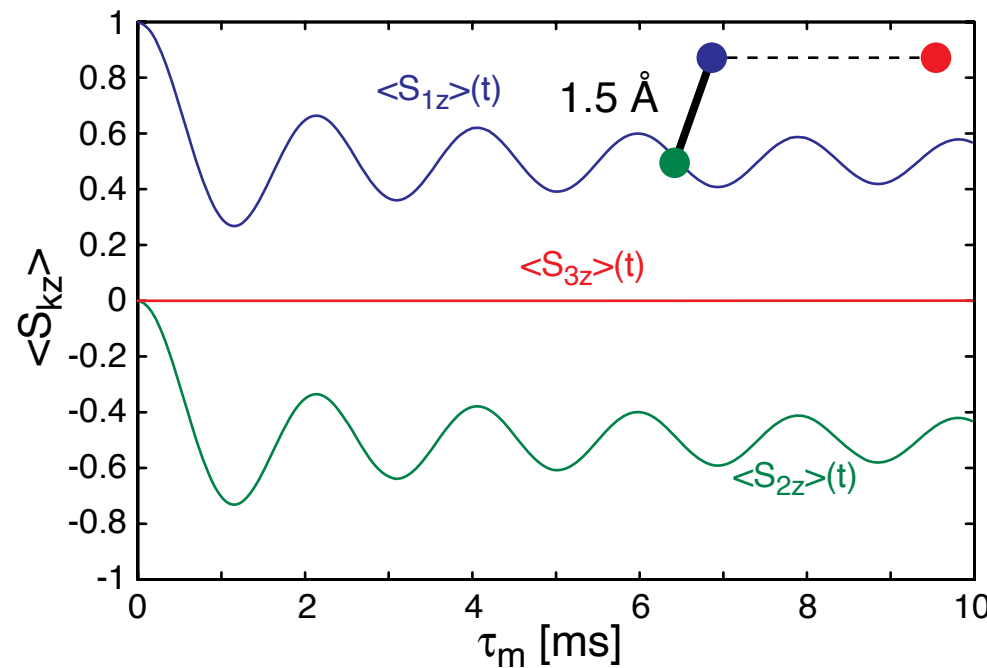
$$\hat{\mathcal{H}}^{(1)} = \omega_{\text{eff}}^{(12)} (S_1^+ S_2^+ + S_1^- S_2^-)$$

$$\hat{\mathcal{H}}^{(1)} = \omega_{\text{eff}}^{(12)} (S_1^+ S_2^- + S_1^- S_2^+)$$

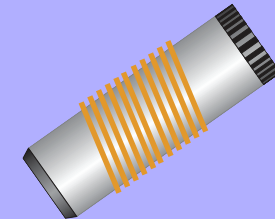
- Such recoupling sequences show dipolar truncation, i.e., large dipolar couplings truncate smaller dipolar couplings and we observe only transfer across the large coupling.

- REDOR is the exception with an Ising-type Hamiltonian

$$\hat{\mathcal{H}}^{(1)} = \omega_{\text{eff}}^{(12)} 2S_{1z} S_{2z}$$



Second-Order Recoupling Sequences



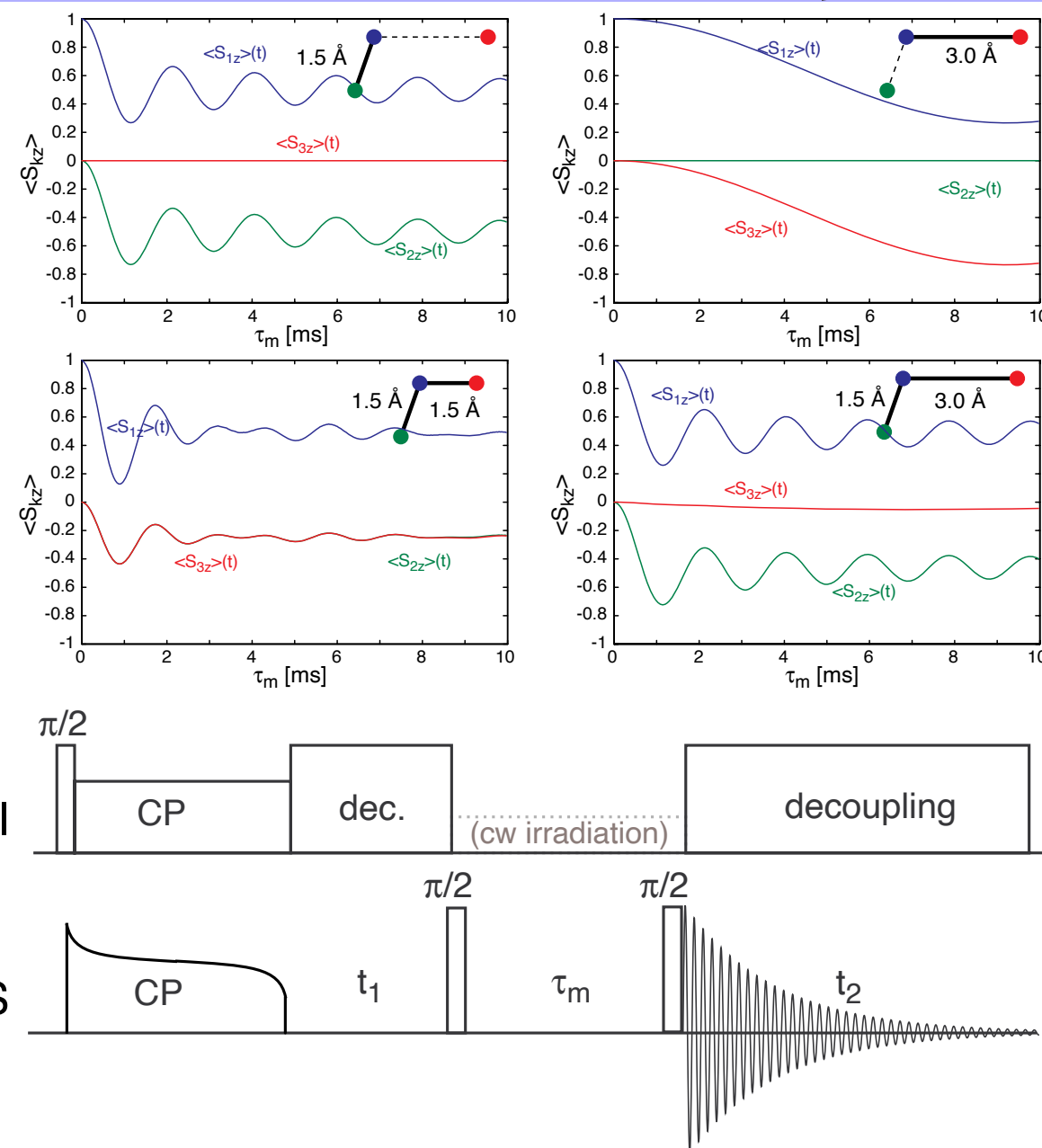
Second-order recoupling sequences are important because they are less susceptible to dipolar truncation than first-order recoupling sequences.

While first-order recoupling sequences directly lead to time-independent Fourier coefficients $\hat{\mathcal{H}}^{(n_0, k_0)}$, the second-order sequences lead to second-order contributions:

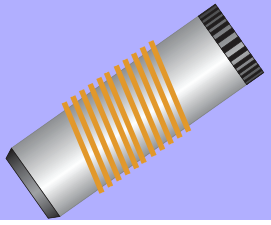
$$\hat{\mathcal{H}}_{(2)}^{(n_0, k_0)} = -\frac{1}{2} \sum_{\nu, \kappa} \frac{\left[\hat{\mathcal{H}}^{(n_0 - \nu, k_0 - \kappa)}, \hat{\mathcal{H}}^{(\nu, \kappa)} \right]}{\nu \omega_r + \kappa \omega_m}$$

The most widely used sequence is proton-driven spin diffusion where the incompletely averaged dipolar coupling by MAS is used for the polarization transfer.

Second-order recoupling sequences use three-spin terms that are the result of the commutator. This leads to an averaging of large and small couplings leading to smaller differences in the effective Hamiltonian.

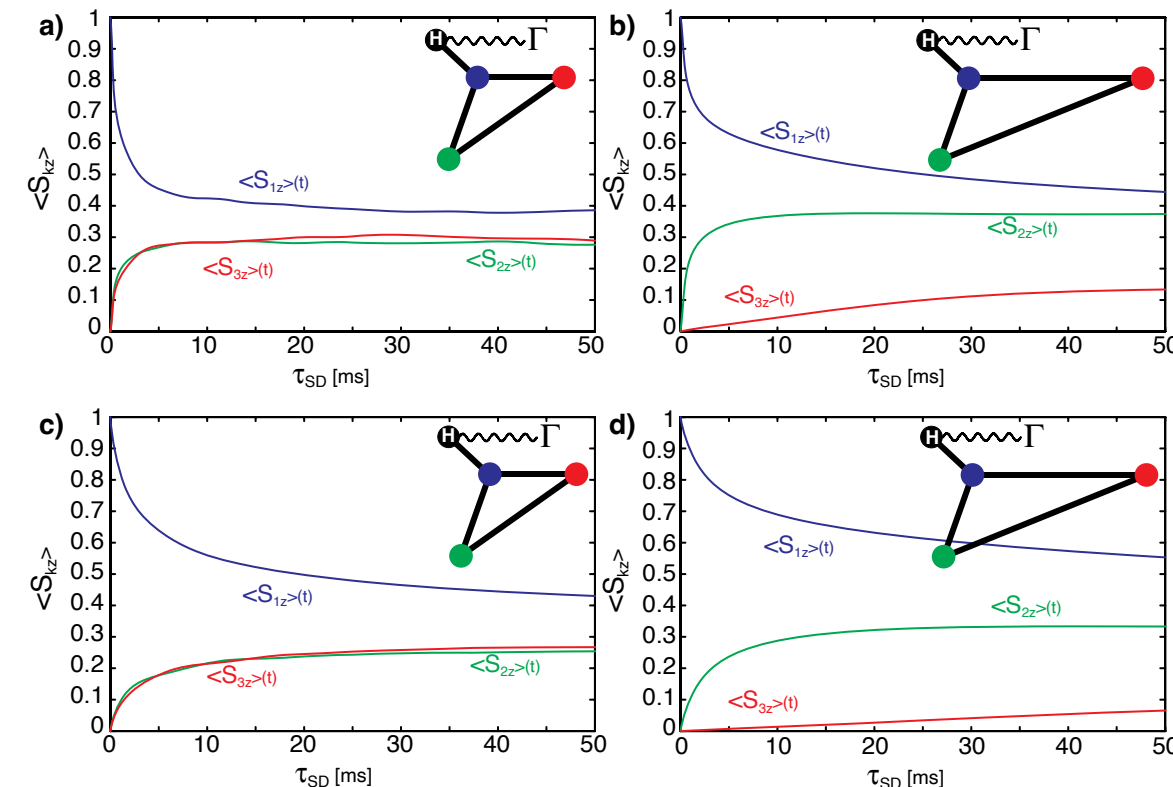


Proton-Driven Spin Diffusion

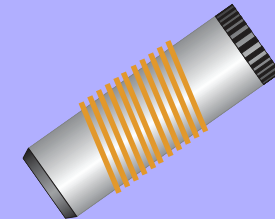


- ❑ The second-order effective Hamiltonian contains cross terms between two homonuclear couplings and between homo- and heteronuclear couplings.
- ❑ Both promote spin diffusion on the S spins.
- ❑ The magnitude of the effective couplings scales by $1/\omega_r$.
- ❑ Small chemical-shift differences can lead to a truncation of the coupling term.
- ❑ The chemical-shift differences on the S spins can be compensated by the densely coupled I-spin network.
- ❑ In other words: If the proton SQ lines overlap, the spin-diffusion process is possible.
- ❑ One can improve the overlap by irradiating the protons at the $n = 1$ R^3 condition.

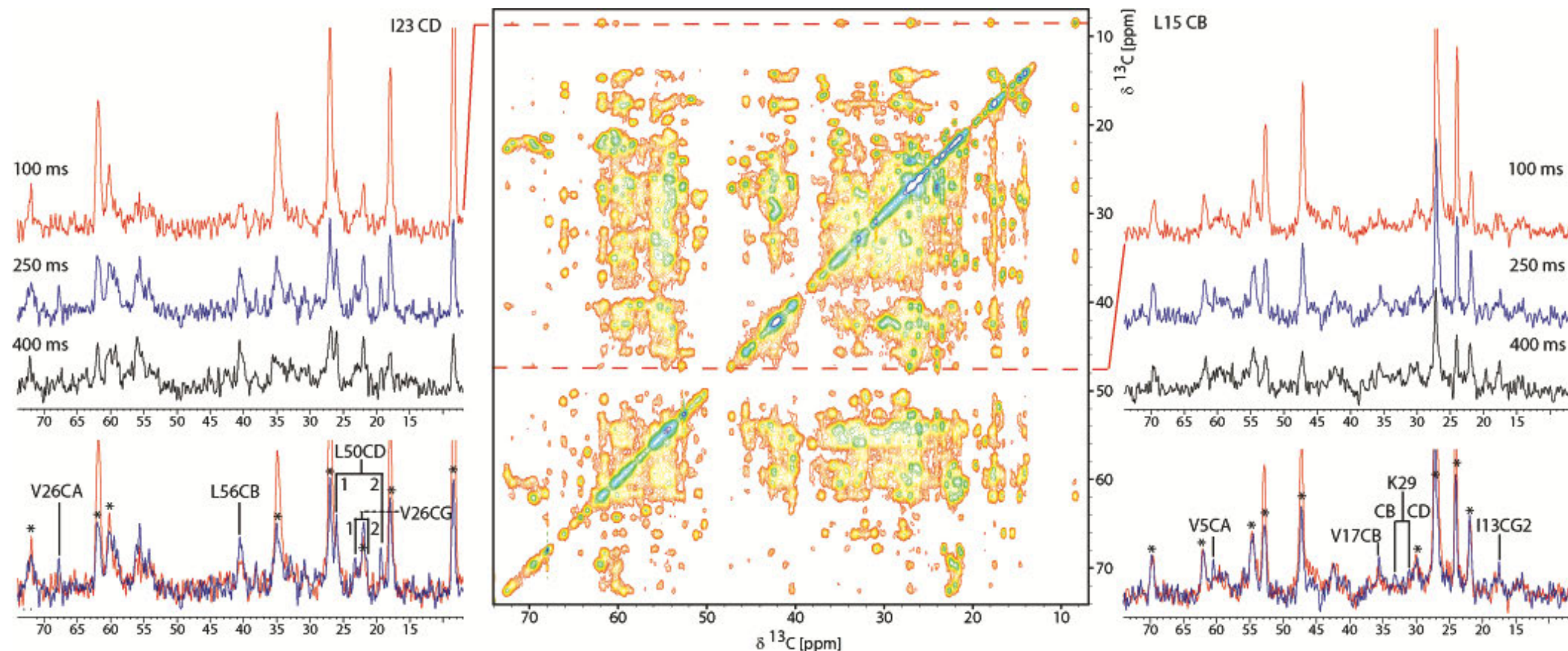
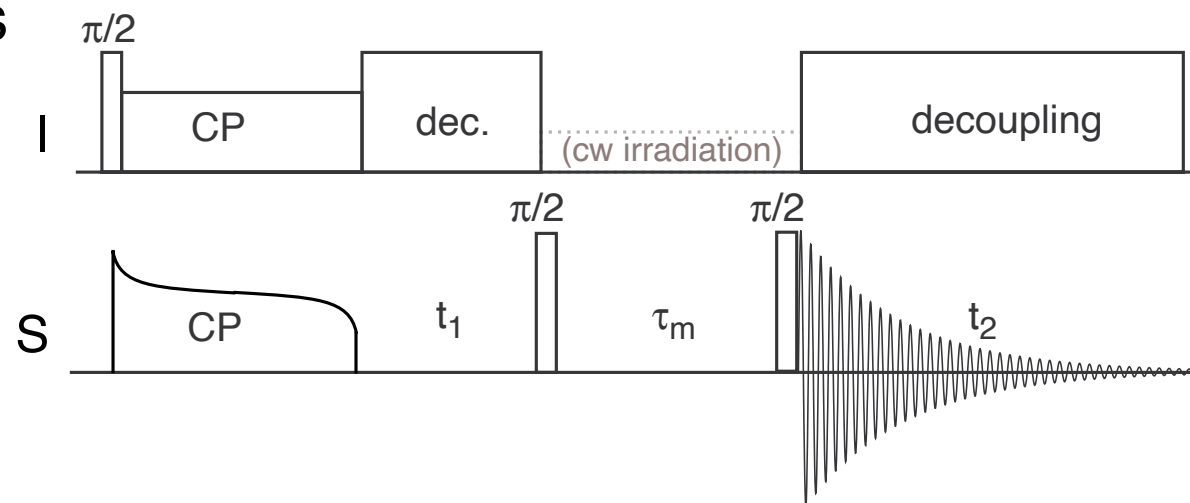
$$\begin{aligned} \hat{\mathcal{H}}_D^{(2)} = & \frac{-i}{36\omega_r} \sum_{a, k \neq \ell} 2\hat{I}_{az}(\hat{S}_k^+ \hat{S}_\ell^- - \hat{S}_\ell^+ \hat{S}_k^-) \sum_{q=1}^2 \frac{(-1)^q}{q^2} \text{Im}(A_{2,-q}^{(k,\ell)} A_{2,q}^{(k,a)}) \\ & - \frac{i}{36\omega_r} \sum_{k, a \neq b} 2\hat{S}_{kz}(\hat{I}_a^+ \hat{I}_b^- - \hat{I}_b^+ \hat{I}_a^-) \sum_{q=1}^2 \frac{(-1)^q}{q^2} \text{Im}(A_{2,-q}^{(a,b)} A_{2,q}^{(a,k)}) \\ & + \frac{i}{72\omega_r} \sum_{k \neq \ell \neq m} 2\hat{S}_{kz}(\hat{S}_\ell^+ \hat{S}_m^- - \hat{S}_m^+ \hat{S}_\ell^-) \\ & \quad \times \sum_{q=1}^2 \frac{(-1)^q}{q^2} [\text{Im}(A_{2,-q}^{(k,\ell)} A_{2,q}^{(k,m)}) + 4\text{Im}(A_{2,-q}^{(k,\ell)} A_{2,q}^{(\ell,m)})] \\ & + \frac{i}{72\omega_r} \sum_{a \neq b \neq c} 2\hat{I}_{az}(\hat{I}_b^+ \hat{I}_c^- - \hat{I}_c^+ \hat{I}_b^-) \\ & \quad \times \sum_{a=1}^2 \frac{(-1)^q}{q^2} [\text{Im}(A_{2,-q}^{(a,b)} A_{2,q}^{(a,c)}) + 4\text{Im}(A_{2,-q}^{(a,b)} A_{2,q}^{(b,c)})] \end{aligned}$$



Proton-Driven Spin Diffusion



- Proton-driven spin diffusion is one of the methods to obtain long-range correlations in proteins.
- Such methods can be used to generate distance restraints in order to calculate structures in solids by NMR.



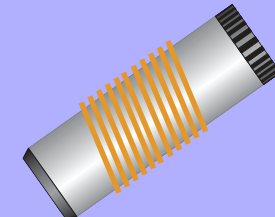
T. Manolikas, T. Herrmann, B.H. Meier, ..., J. Am. Chem. Soc. 130 (2008) 3959–3966.

Practical Aspects of (Dipolar) Recoupling

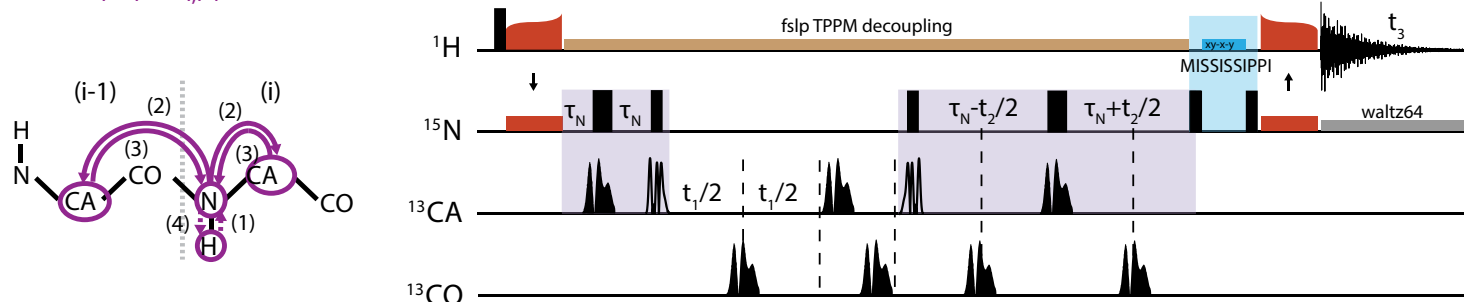


- ❑ There are many more sequences than I have discussed here.
- ❑ Use a robust, easy to implement, low-power, and well-characterized sequence.
- ❑ First-order recoupling sequences generate polarization transfer that is independent of the spinning frequency but show dipolar truncation.
- ❑ For distance measurements, REDOR is the best sequence available.
- ❑ For a large number of distance restraints in (bio-)molecules, use second-order sequences like PDSD, DARR, PAR, ...

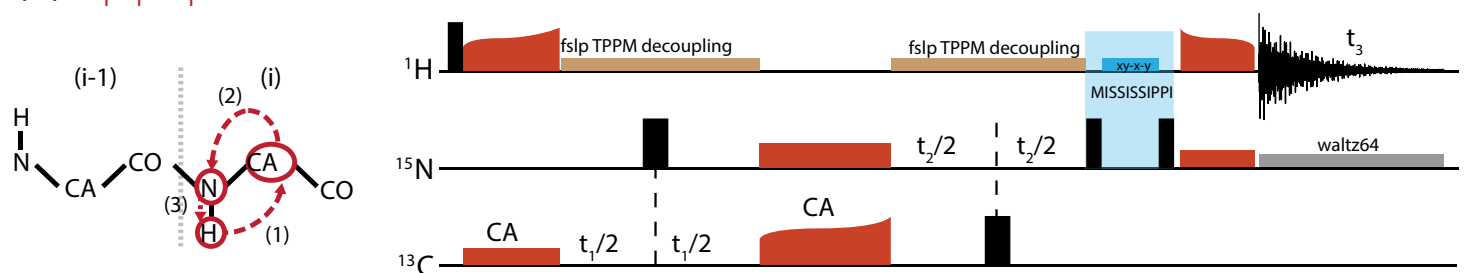
Important Building Blocks in MAS NMR



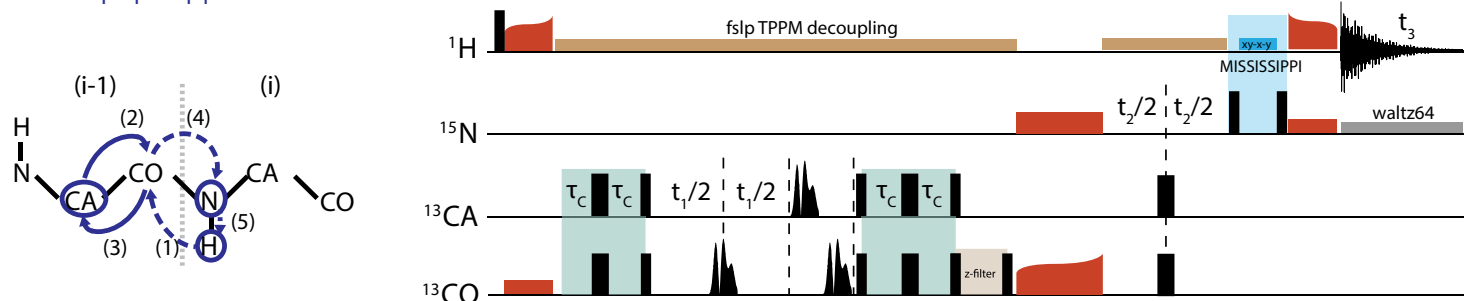
(a) $H_i N_i C\alpha_{i,i-1}$ correlation: (HN)CANH



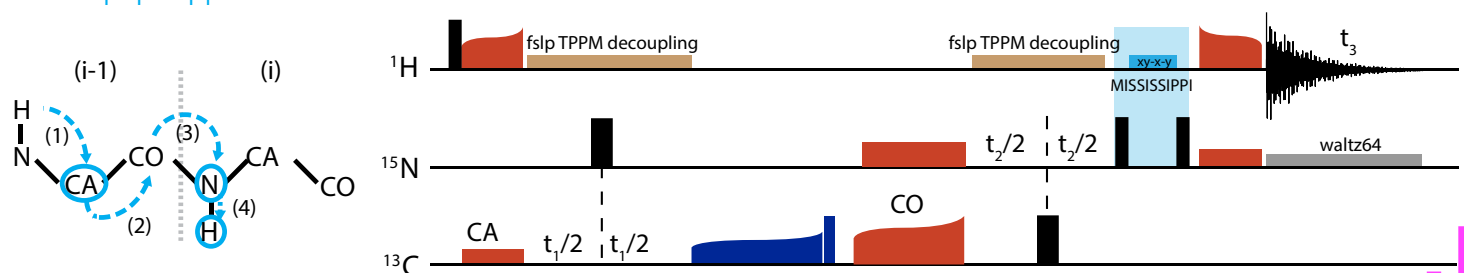
(b) $H_i N_i C\alpha_i$ correlation: (H)CANH



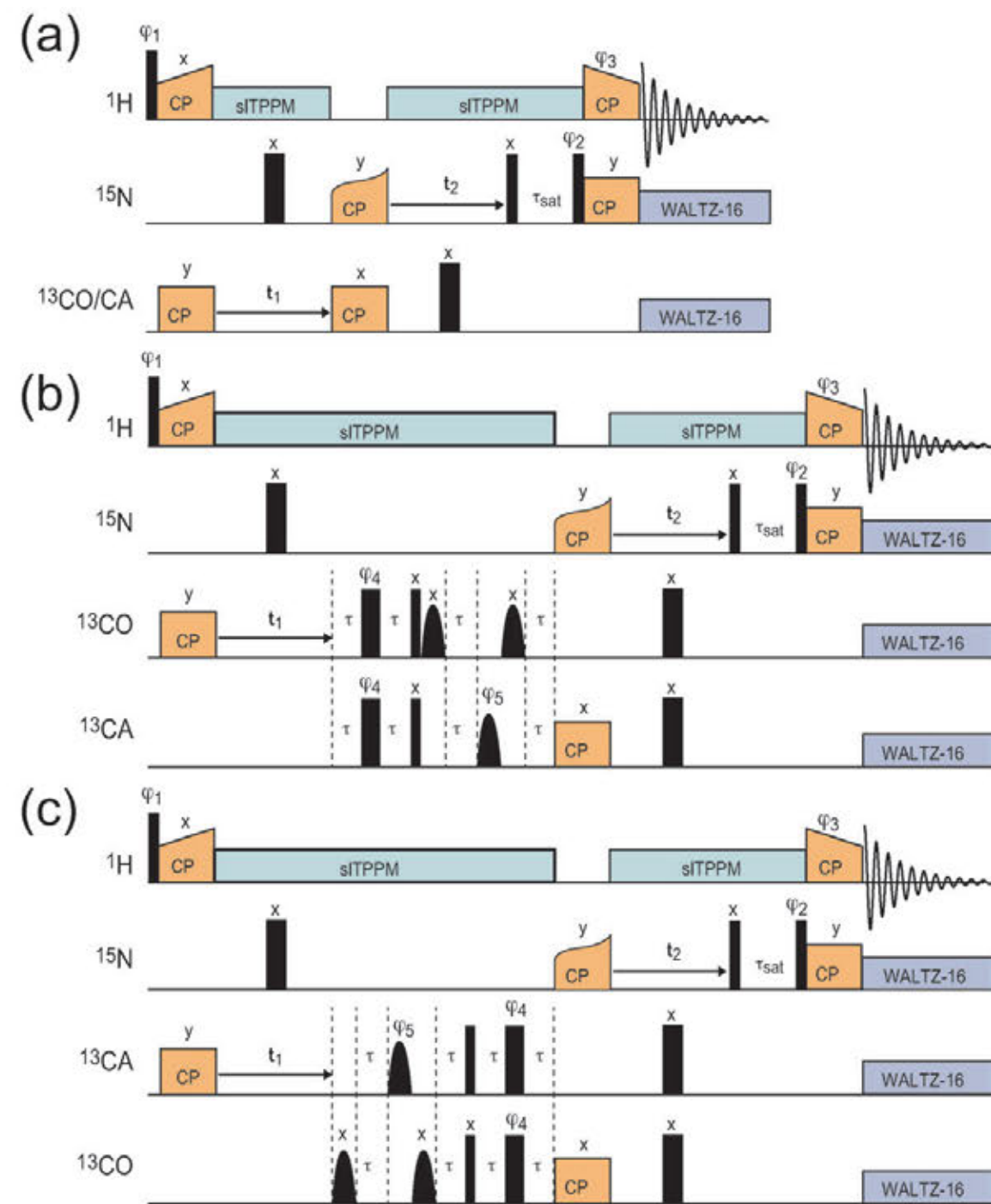
(c) $H_i N_i C\alpha_{i-1}$ correlation: (HCO)CA(CO)NH



(d) $H_i N_i C\alpha_i$ correlation: (H)CA(CO)NH



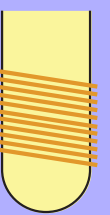
S. Penzel, ... , B.H. Meier, J. Biomol. NMR. 63 (2015) 165–186.
<https://doi.org/10.1007/s10858-015-9975-y>.



A. Marchetti, ..., G. Pintacuda, Angew. Chem. Int. Ed. Engl. 51 (2012) 10756–10759. <https://doi.org/10.1002/anie.201203124>.

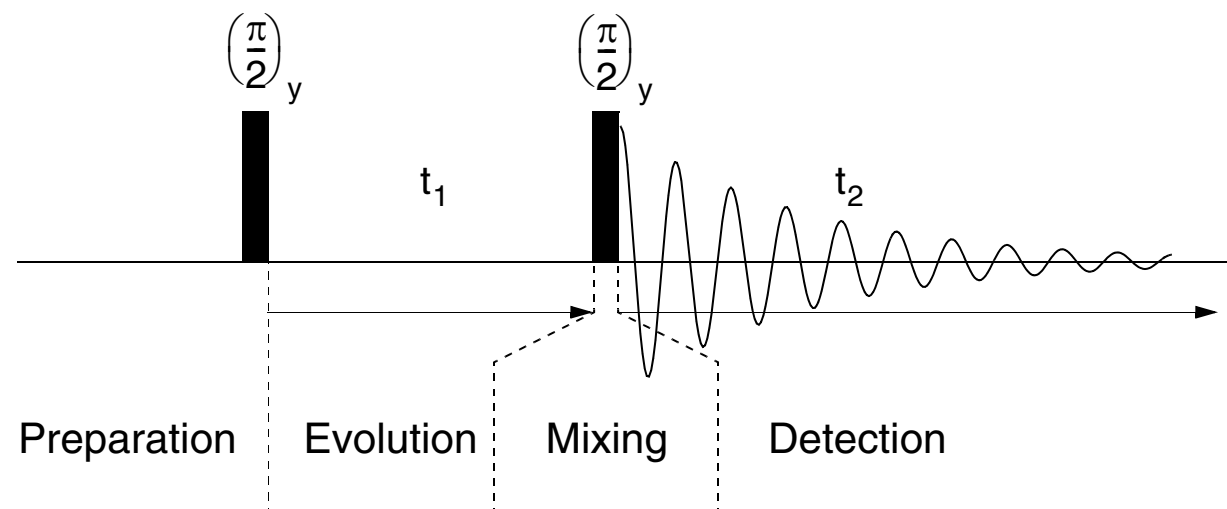
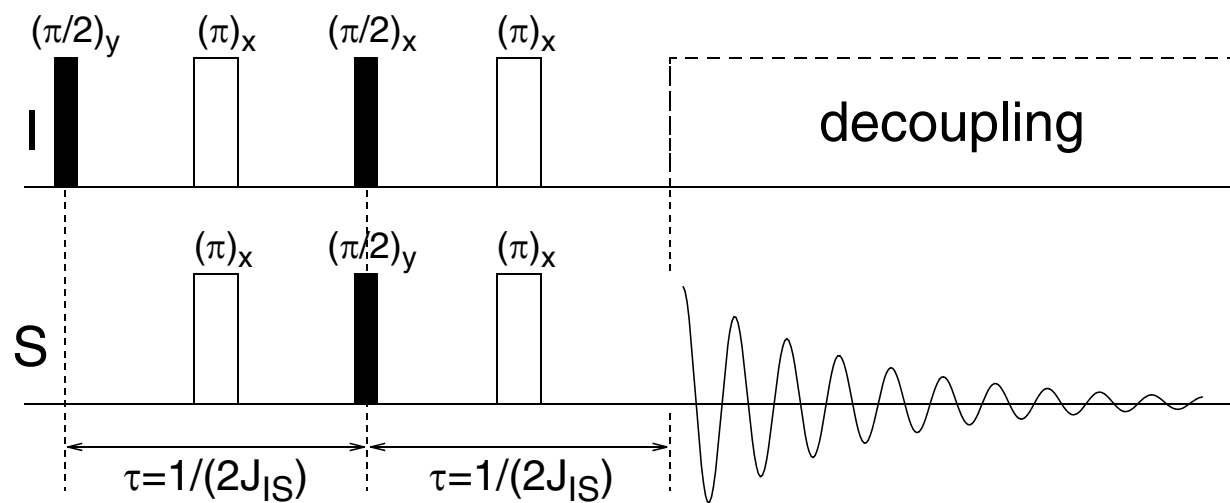
J-Coupling Based Transfer

J-Coupling Based Experiments in Liquids



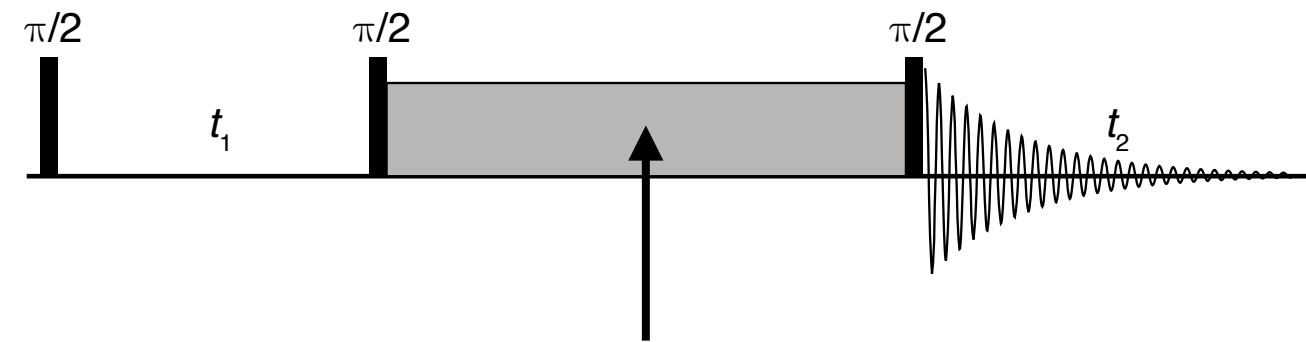
weak coupling: $\hat{\mathcal{H}}_J = 2\pi J_{12} \hat{I}_{1z} \hat{I}_{2z}$

- ❑ Hamiltonian allows dephasing of magnetization.
- ❑ Polarization transfer achieved by pulses.



strong coupling: $\hat{\mathcal{H}}_J = 2\pi J_{12} \vec{I}_1 \cdot \vec{I}_2$

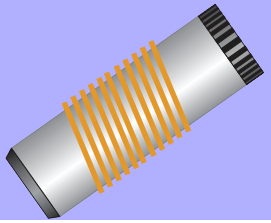
- ❑ Hamiltonian allows polarization transfer.
- ❑ Suppression of chemical shift is required.



Multiple Pulse Sequences:

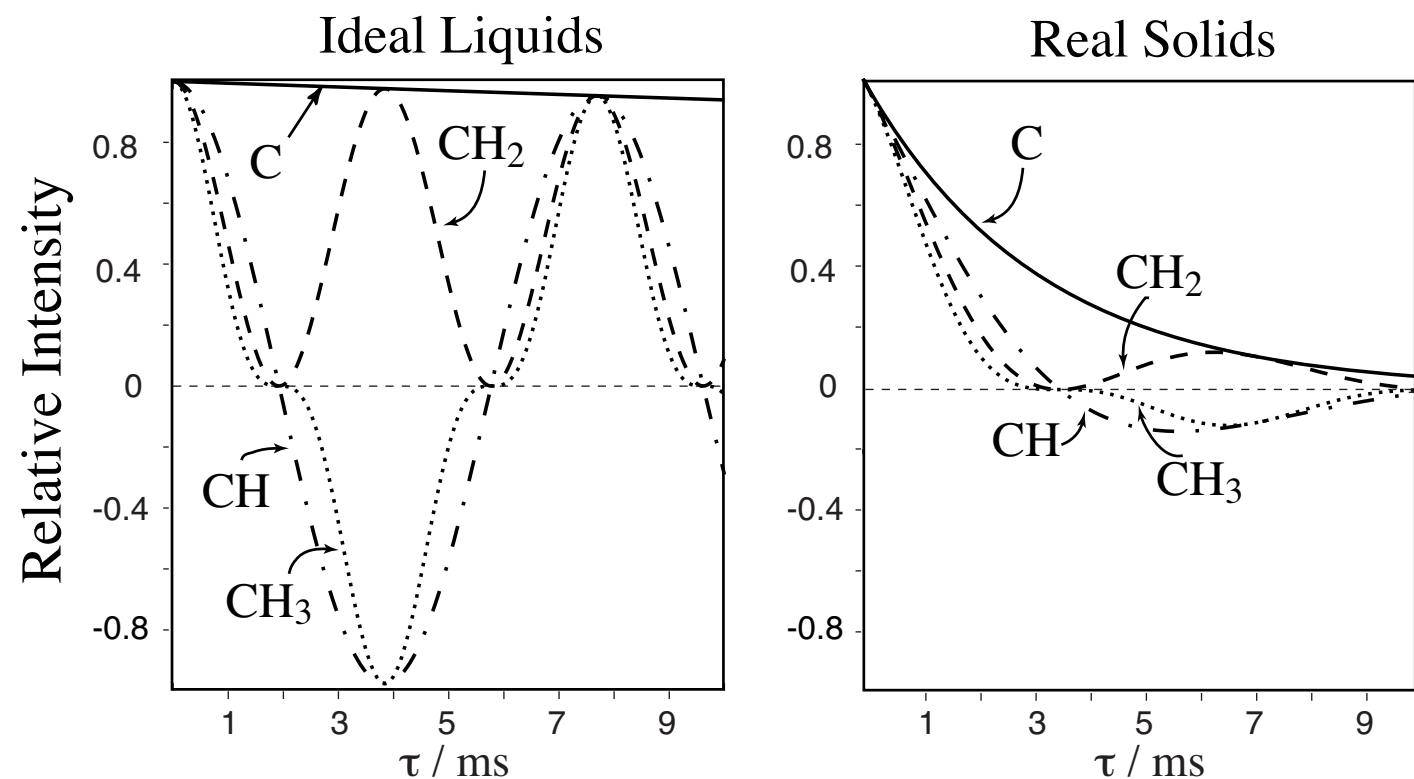
- WALTZ
- MLEV
- DIPSI
- FLOPSY

J-Coupling Based Experiments in Solids: INEPT



weak coupling: $\hat{\mathcal{H}}_J = 2\pi J_{12} \hat{I}_{1z} \hat{I}_{2z}$

- ❑ J-coupling experiments in solids require that dipolar couplings are partially averaged.
- ❑ This can be achieved by:
 - fast MAS: for fully protonated samples at least 100 kHz.
 - partial deuteration of the sample plus fast MAS of about 40 kHz.
 - homonuclear decoupling and MAS.
 - fast dynamics in the molecule.
- ❑ If the dephasing time of the magnetization under a spin-echo sequence (T_2') is slower than $1/2J$, pulsed polarization transfer is possible.
- ❑ Under such conditions, all INEPT-based experiments can be implemented.
- ❑ It is of advantage to use experiments that implement in-phase detection due to cancellation of the multiplet lines.
- ❑ INEPT vs. CP can be used to characterize dynamic vs. static parts of the molecule.

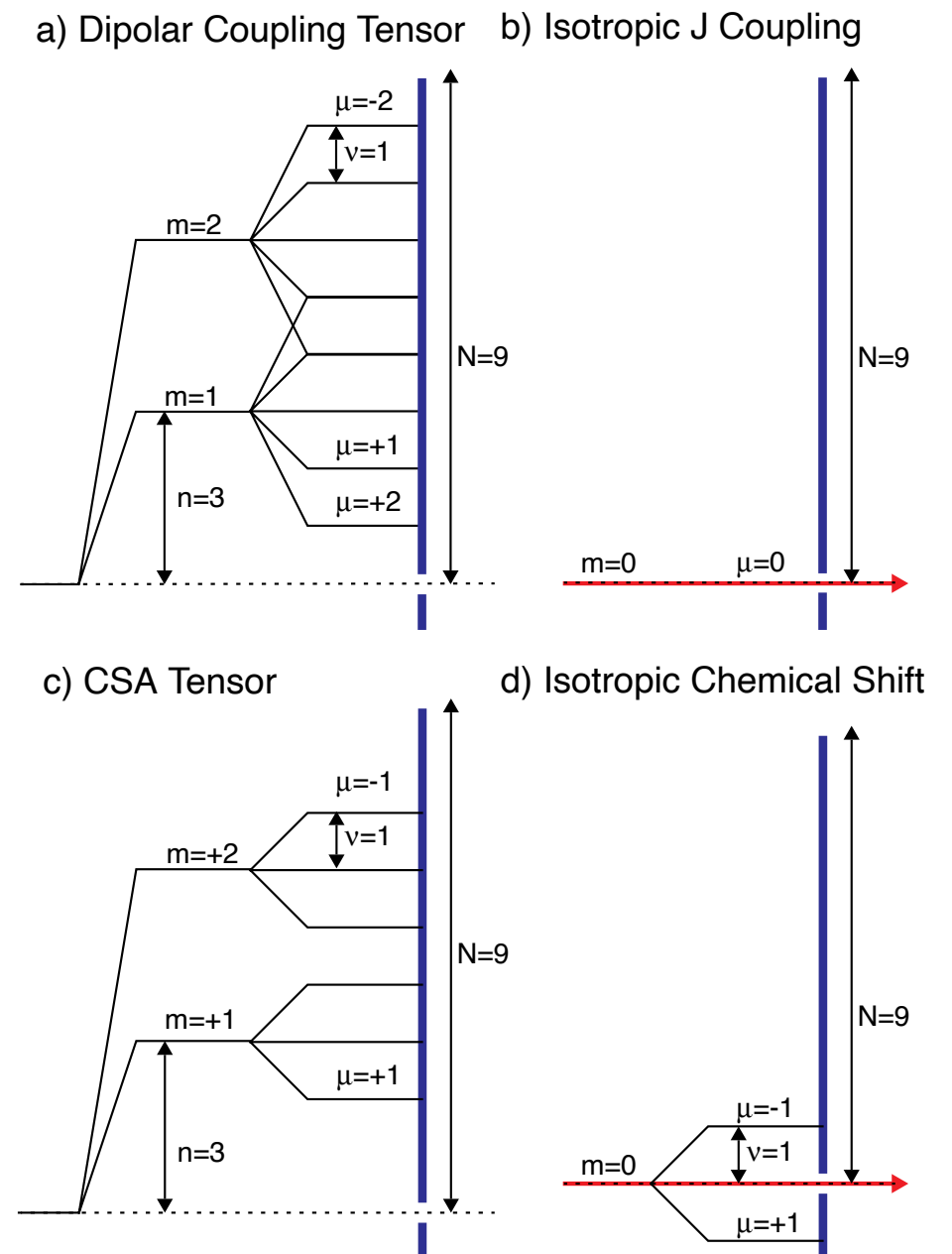
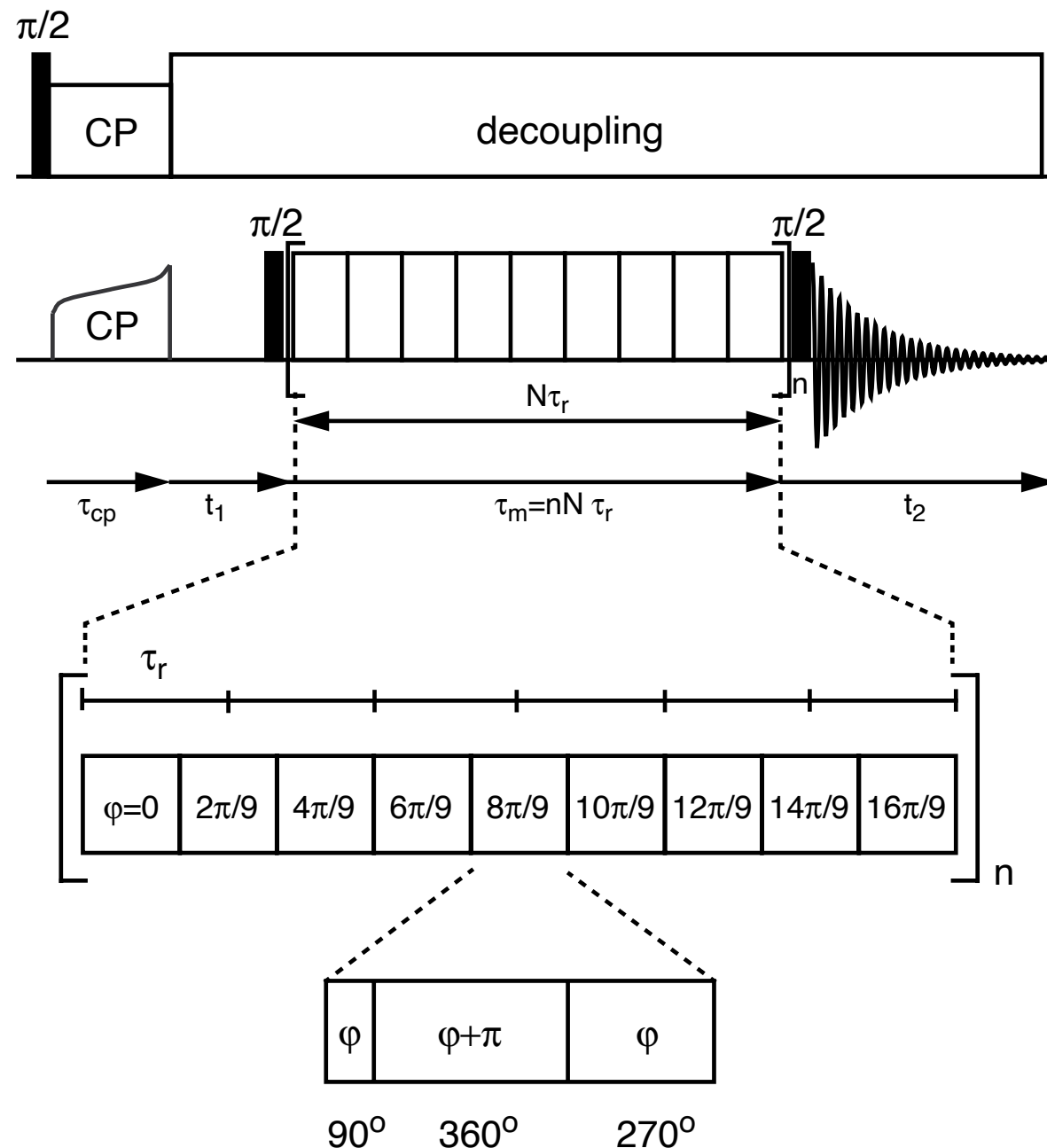


J-Coupling Based Experiments in Solids: TOBSY

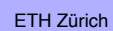


strong coupling: $\hat{\mathcal{H}}_J = 2\pi J_{12} \vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2$

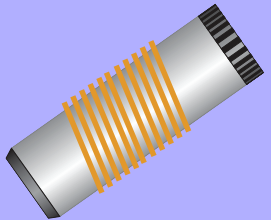
- ❑ To implement TOCSY-like experiments, all interactions except the homonuclear J coupling have to be suppressed.
- ❑ This can be achieved by symmetry-based C9 sequences.



- Matthias Ernst

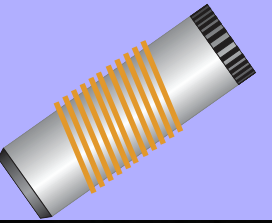


Practical Aspects of J-Coupling Transfer



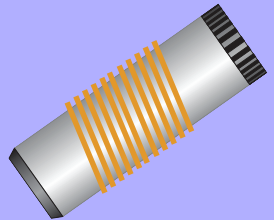
- ❑ J coupling sequences are mostly used to get signal from highly dynamic areas of molecules where the dipolar coupling is averaged out.
- ❑ Heteronuclear J coupling polarization transfer is an efficient alternative to CP at the highest MAS frequencies (> 100 kHz) or in samples with diluted proton networks (deuterated samples).
- ❑ Carefully optimize the length of the dephasing delays for optimum signal-to-noise ratio under short T_2' relaxation times.

Conclusions



Amritsar, 2015

Conclusions



- ❑ Divide pulse sequences into their basic building blocks for better understanding how they work.
- ❑ Each building block represents a different effective Hamiltonian that tells you what it does.
- ❑ If you want to implement efficient and good experiments, it is important to understand how pulse sequence building blocks work.
- ❑ Choose the best (high efficiency, easy to implement, low rf-field requirement, ...) building blocks available.
- ❑ The theory of solid-state NMR is complex.
- ❑ Know about experimental imperfections: phase transients, rf-field inhomogeneity, MAS modulations of rf-field inhomogeneity, amplifier droop, ...
- ❑ There is much more to solid-state NMR that I have not discussed or only mentioned in passing:
 - homonuclear dipolar decoupling
 - quadrupolar nuclei are an even bigger challenge
 - characterization of dynamics
 - sample preparation can have a big influence on the quality of spectra
 - DNP
- ❑ Remember that sensitivity is the most important issue in NMR.

Acknowledgements

