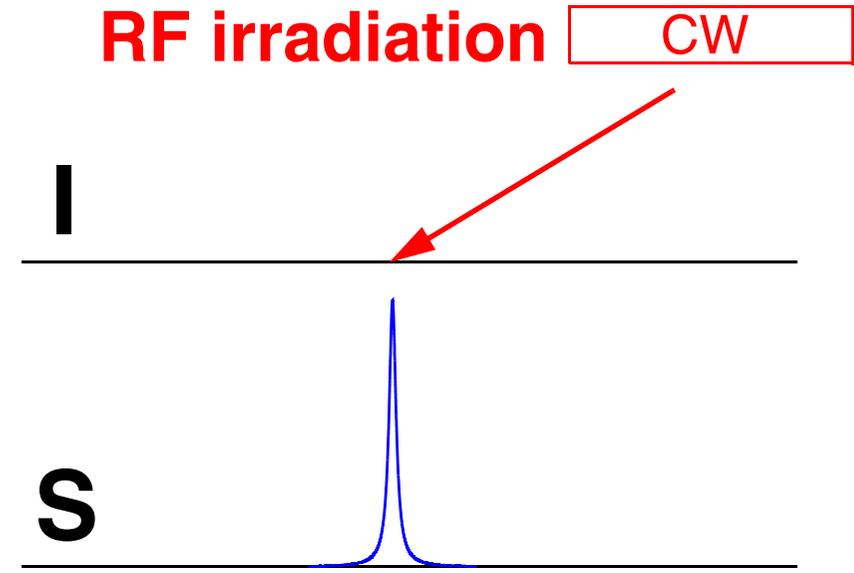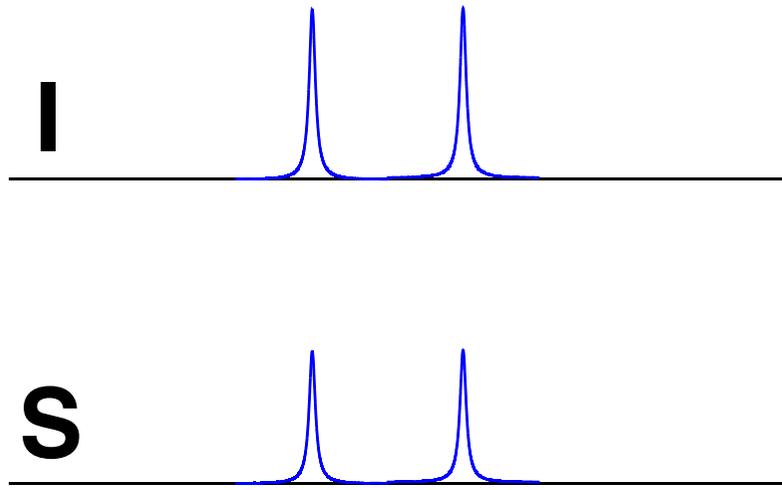# Heteronuclear Spin Decoupling in Magic-Angle-Spinning Solid-State NMR

Matthias Ernst
ETH Zürich

Heteronuclear Decoupling in Liquid-State NMR
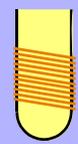
❏ Heteronuclear J-coupled two-spin system
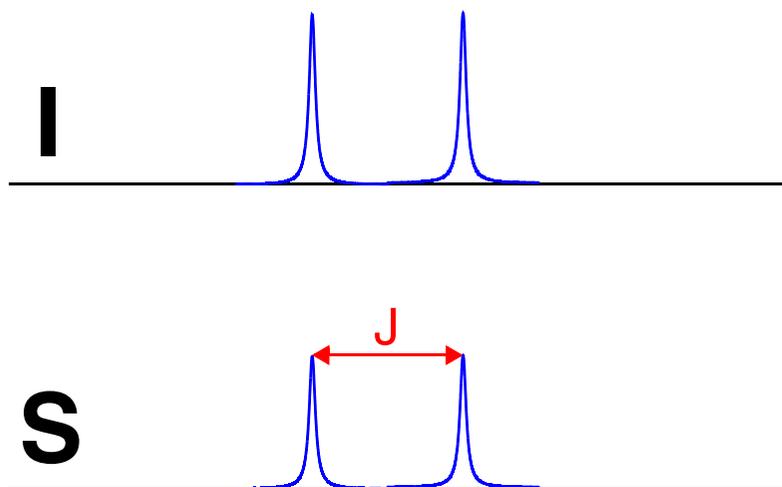
RF irradiation CW

I

S

I

S

❏ RF irradiation of the I spins leads to a collapse of the J-split multiplet on the S spins.

❏ Decoupling strategies:

- continuous-wave (cw) irradiation

- noise decoupling

- multiple-pulse sequences (MLEV, WALTZ, GARP, DIPSI, FLOPSY, ...)
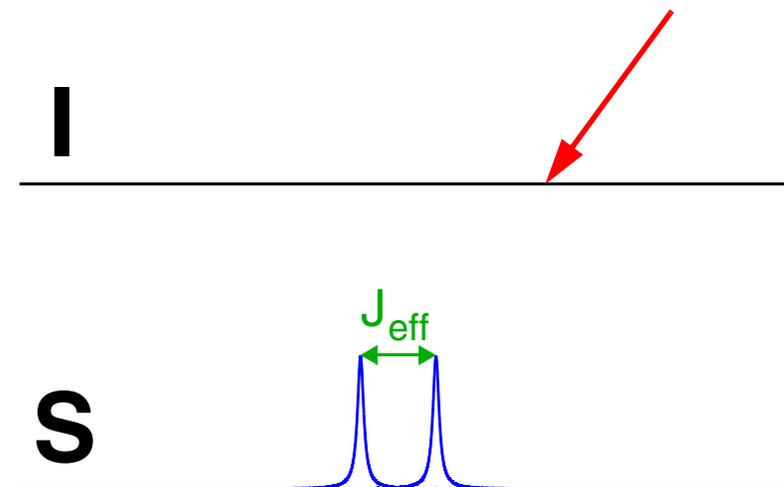
- adiabatic inversions (WURST, ...)

❏ CW irradiation: off-resonance effects

RF irradiation CW

I

I

S

J

S

J_{eff}
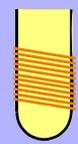
❏ Residual splitting is reduced to $J_{IS}\nu_I / \nu_1$ for off-resonance cw irradiation.

❏ Scaling corresponds to a projection of the heteronuclear J coupling onto the effective rf-field direction.

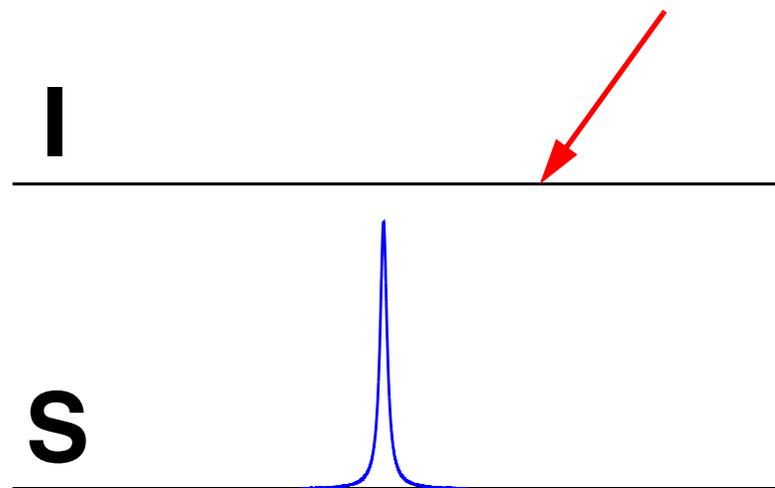❏ Typical magnitudes of such terms: J_{IS} = 150 Hz, ν_I < 5 kHz, $\nu_1 \approx$ 10 kHz.

I_z

ν_I

$+J/2$

ν_{eff}

$\pm J_{eff}/2$

ν_1

I_x

$-J/2$
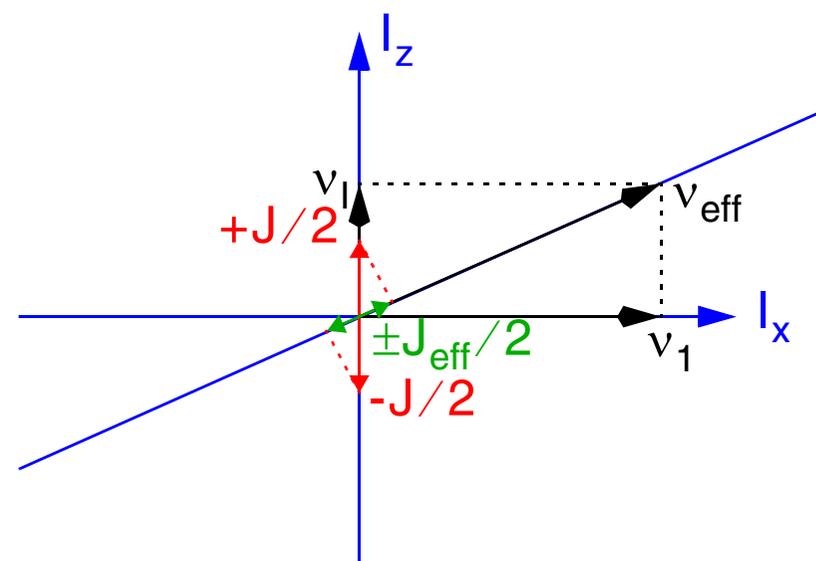
Heteronuclear Decoupling in Liquid-State NMR

❏ Composite pulses and multiple-pulse sequences

RF irradiation 🔴🔴🔴🔴🔴🔴🔴

I

S

I

S
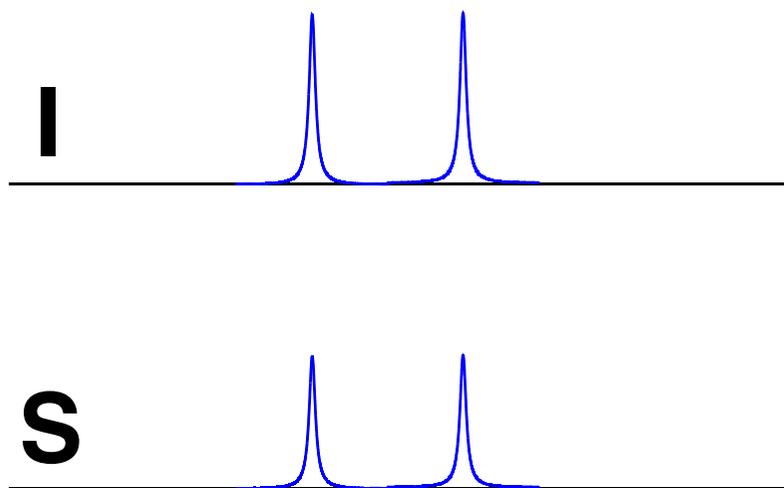
❏ Better inversion over a larger range of chemical-shift offsets.

❏ But now compensation of rf-field inhomogeneities or errors in the pulse length are necessary.
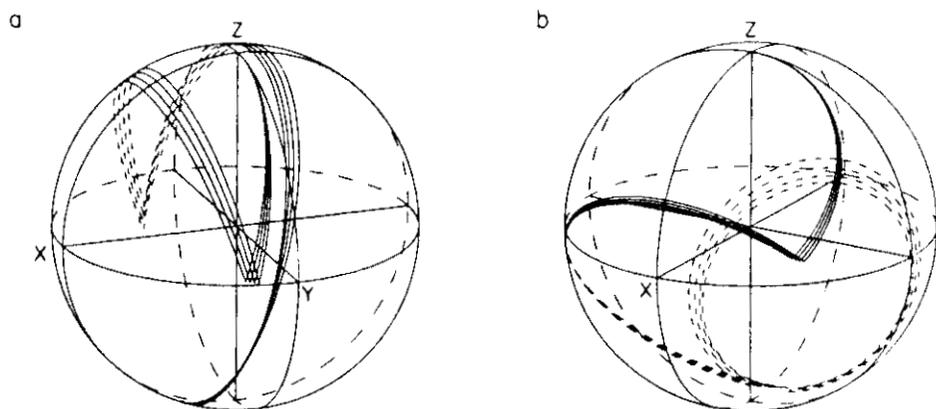
FIG. 5. Magnetization trajectories calculated for the spin inversion sequence $R = 1\bar{2}3$. (a) For small offsets from resonance (near $\Delta B \approx 0.25\ B_2$) the compensation is only moderate. (b) For offsets $\Delta B/B_2$ between 0.75 and 0.88, the first two pulses achieve the spin inversion and the last pulse merely rotates the magnetization through 360° about the tilted effective field.

A.J. Shaka, J. Keeler, and R. Freeman, "Evaluation of a New Broadband Decoupling Sequence: WALTZ-16" J. Magn. Reson. 53, 313-340 (1983).

❏ Adiabatic inversion pulses

RF irradiation 〜〜〜〜〜〜〜

I

S

I

S
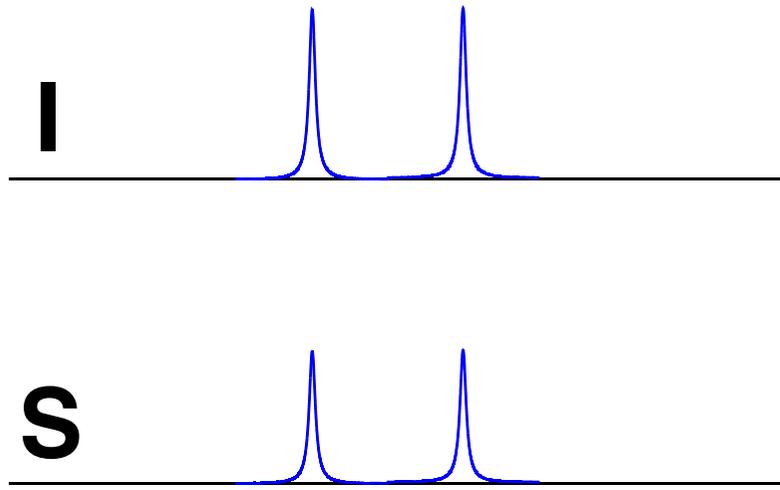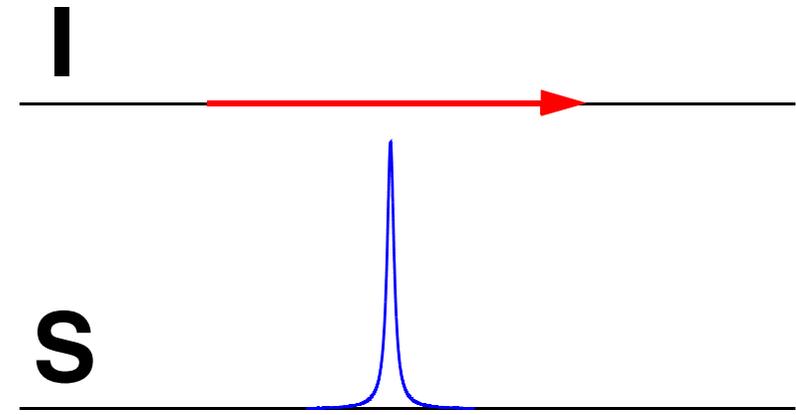
❏ Adiabatic inversion pulses give very good inversion over a large range of chemical shifts.

❏ RF-field amplitude is not a critical parameter in adiabatic pulses.

amplitude

$-T_p/2$ 0 $T_p/2$ T_p $3T_p/2$

phase

π

0

$-T_p/2$ 0 $T_p/2$ T_p $3T_p/2$

56 kHz

E. Kupce and R. Freeman, "Adiabatic Pulses for Wideband Inversion and Broadband Decoupling",
J. Magn. Reson. A115, 273-276 (1995).

Detour: Representation of Hamiltonians

❏ Cartesian notation of Hamiltonians:

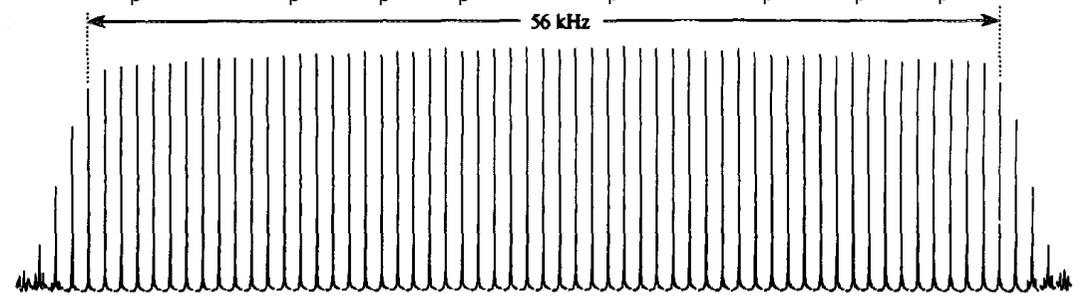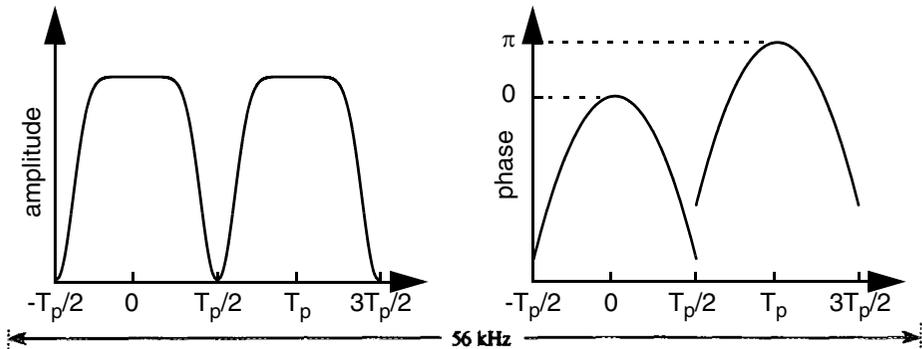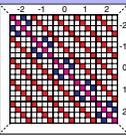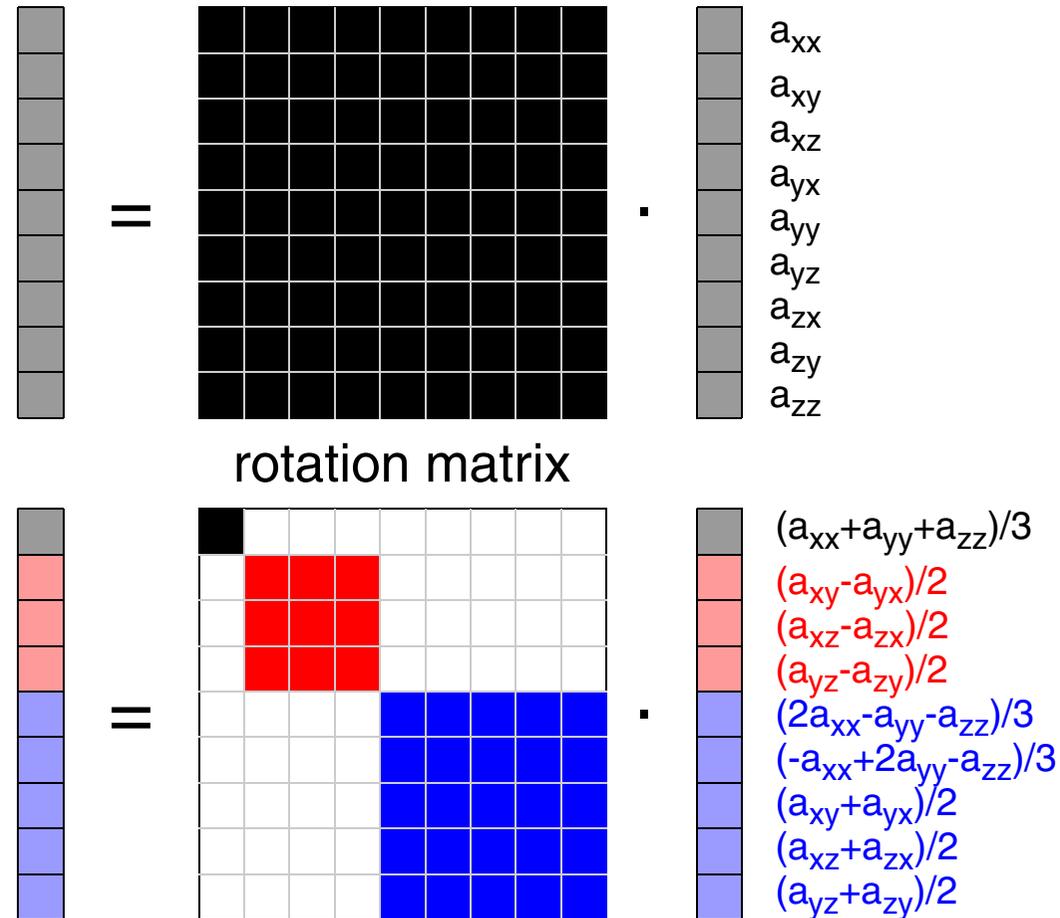$$\hat{\mathcal{H}}^{(k,n)} = \vec{\hat{I}}_k \cdot A^{(k,n)} \cdot \vec{\hat{I}}_n = \left(\hat{I}_{kx} \ \hat{I}_{ky} \ \hat{I}_{kz} \right) \cdot \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{pmatrix} \cdot \begin{pmatrix} \hat{I}_{nx} \\ \hat{I}_{ny}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

❏ **Scalar-product formulation** of the Hamiltonian in a Cartesian basis.

❏ Basis transformation leads to spherical-tensor representation:

$$\hat{\mathcal{H}}^{(k,n)} = \sum_{\ell=0}^{2} \vec{A}_\ell^{(k,n)} \cdot \vec{\hat{\mathcal{T}}}_\ell^{(k,n)}$$

❏ In spherical-tensor notation, rotations of the Hamiltonian are simpler due to the block structure of the rotation matrix.
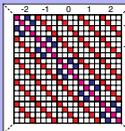
rotation matrix

a_{xx}
a_{xy}
a_{xz}
a_{yx}
a_{yy}
a_{yz}
a_{zx}
a_{zy}
a_{zz}

$(a_{xx}+a_{yy}+a_{zz})/3$
$(a_{xy}-a_{yx})/2$
$(a_{xz}-a_{zx})/2$
$(a_{yz}-a_{zy})/2$
$(2a_{xx}-a_{yy}-a_{zz})/3$
$(-a_{xx}+2a_{yy}-a_{zz})/3$
$(a_{xy}+a_{yx})/2$
$(a_{xz}+a_{zx})/2$
$(a_{yz}+a_{zy})/2$

❏ System Hamiltonian in the laboratory frame is static if the molecule is static.

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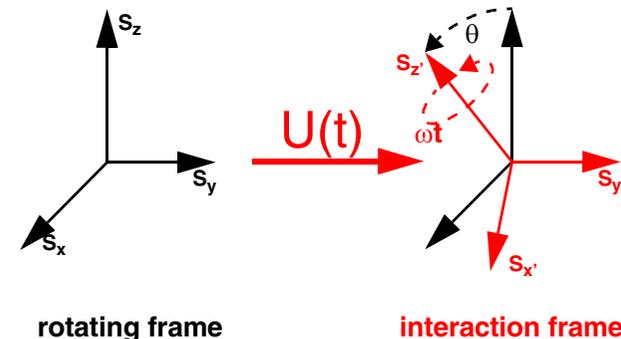
rotating frame

interaction frame

$U(t)$
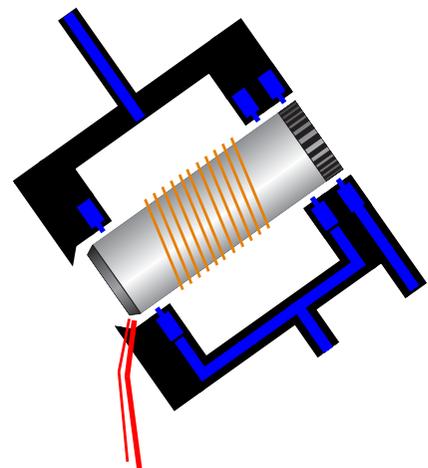
sample rotation

interaction-frame transformation

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

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

❏ spatial part of Hamiltonian is modulated

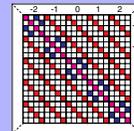❏ Examples:

- MAS, DAS, DOR

❏ spin part of Hamiltonian is modulated

❏ Examples:

- interaction-frame transformations

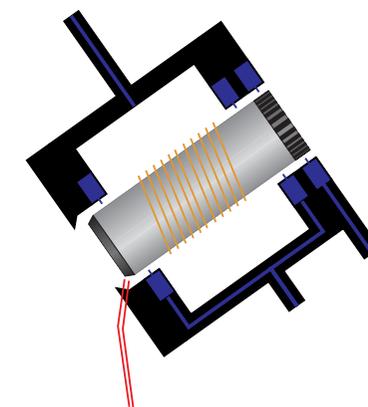❏ We need methods to deal with time-dependent Hamiltonians.

Detour: Average Hamiltonian Theory

❏ Time-dependent Hamiltonians $\mathscr{H}(t)$ are generated by

- interaction-frame transformations

- sample rotation, e.g. magic-angle spinning (MAS).

interaction frame

❏ For a single time dependence with a cycle time τ_m we can write the Hamiltonian as a Fourier series:
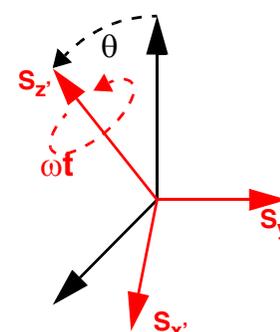
$$\mathscr{H}(t) = \sum_n \mathscr{H}^{(n)} e^{in\omega_m t}$$

Average Hamiltonian theory (AHT)

$$\overline{\mathscr{H}} = \mathscr{H}^{(0)} - \frac{1}{2}\sum_{n \neq 0} \frac{[\mathscr{H}^{(n)}, \mathscr{H}^{(-n)}]}{n\omega_m} + \frac{1}{2}\sum_{n \neq 0} \frac{[[\mathscr{H}^{(n)}, \mathscr{H}^{(0)}], \mathscr{H}^{(-n)}]}{(n\omega_m)^2} + \frac{1}{3}\sum_{k, n \neq 0} \frac{[\mathscr{H}^{(n)}, [\mathscr{H}^{(k)}, \mathscr{H}^{(-n-k)}]]}{kn\omega_m^2} + \dots$$

$$\overline{\mathscr{H}}^{(0)} \qquad\qquad \overline{\mathscr{H}}^{(1)} \qquad\qquad\qquad\qquad\qquad\qquad \overline{\mathscr{H}}^{(2)}$$

❏ Different orders of the AHT approximate the effective Hamiltonian with increasing accuracy.

❏ "Symmetric" sequences ($\mathscr{H}(t) = \mathscr{H}(\tau_c - t)$) eliminate the odd orders of the AHT expansion: $\overline{\mathscr{H}}^{(2)}$ is the leading term for the residual line width in all liquid-state decoupling sequences.
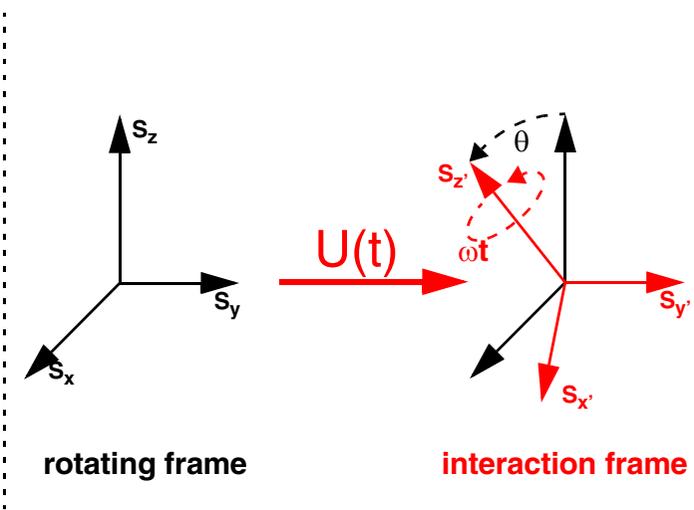
Theoretical Description of Decoupling in Liquids
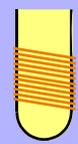
❑ Spin-system Hamiltonian in the rotating frame is static.

❑ Interaction-frame transformation with the rf-field leads to a time-dependent Hamiltonian.

$$\mathcal{H} = \mathcal{H}_I + \mathcal{H}_S + \mathcal{H}_{II} + \mathcal{H}_{SS} + \mathcal{H}_{IS}$$

interaction-frame transformation: $U(t) = \hat{T} \exp\left(-i\int_0^t \mathcal{H}_{rf}(t_1)dt_1\right)$

$$\tilde{\mathcal{H}}(t) = \tilde{\mathcal{H}}_I(t) + \tilde{\mathcal{H}}_S + \tilde{\mathcal{H}}_{II} + \tilde{\mathcal{H}}_{SS} + \tilde{\mathcal{H}}_{IS}(t) = \sum_k \mathcal{H}^{(k)} e^{ik\omega_m t}$$

rotating frame   **interaction frame**

❑ Only the chemical shifts of the I spins and the heteronuclear J couplings become time dependent in the rf-interaction frame.

❑ Single time dependence allows the use of average Hamiltonian theory (AHT).

❑ Only cross terms between the chemical shift and the heteronuclear coupling can appear in $\overline{\mathcal{H}}^{(1)}$ while $\overline{\mathcal{H}}^{(2)}$ can contain cross terms between all parts of the Hamiltonian.
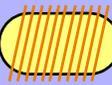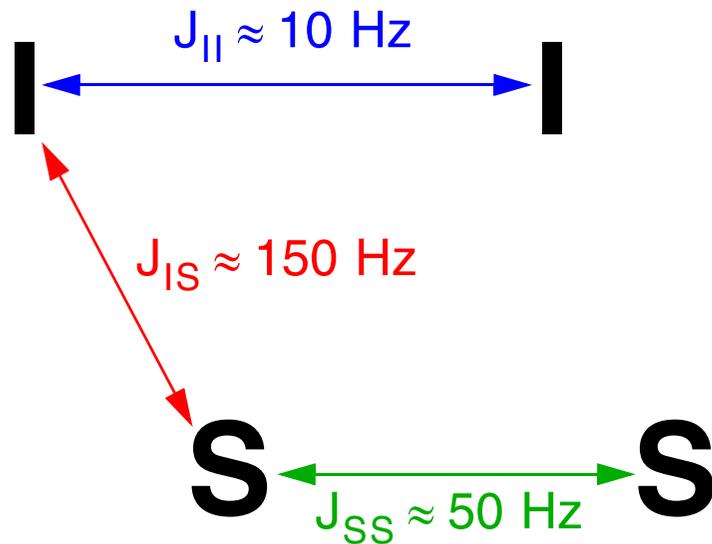
Heteronuclear Decoupling in Liquid-State NMR

❏ Decoupling in liquid-state NMR is mostly a question of perfectly inverting the spins over a large range of chemical shifts with minimum rf power.
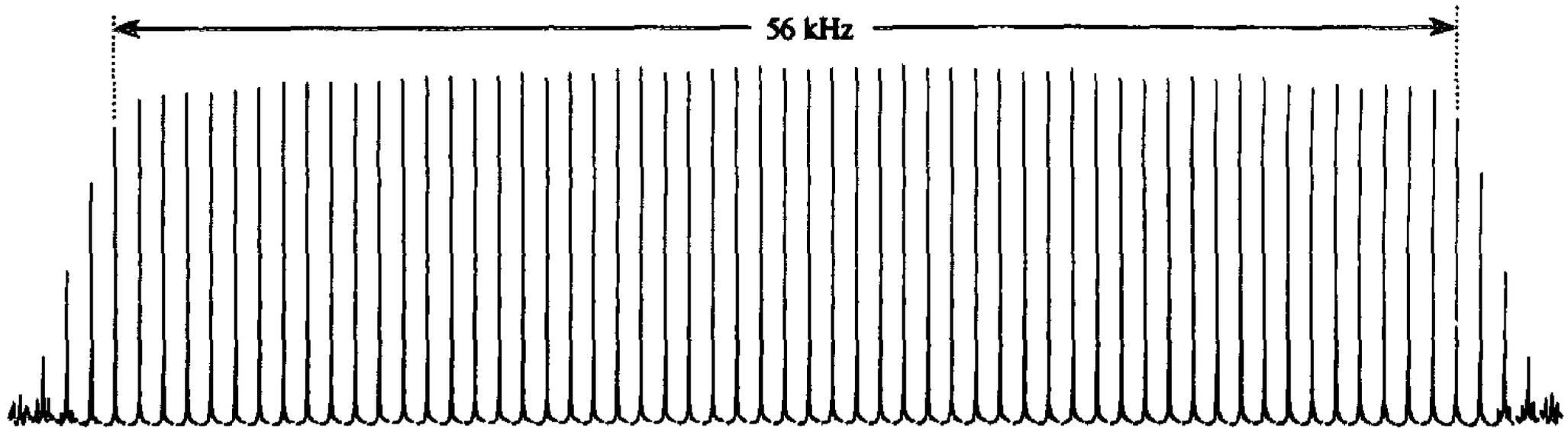
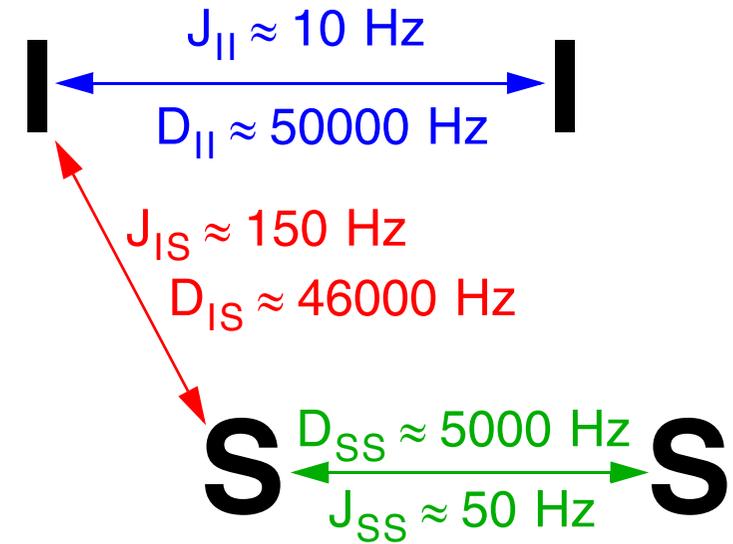❏ Decoupling sidebands can be observed at multiples of the inverse cycle time.

❏ Symmetric sequences ($\mathcal{H}(t) = \mathcal{H}(\tau_c - t)$) eliminate the first-order of the AHT. Residual splitting is determined by the second-order (double commutator) contributions.

❏ Homonuclear scalar couplings become important only in second-order AHT.
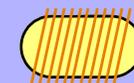DIPSI: Decoupling in the presence of scalar couplings.

Liquids

$J_{II} \approx 10$ Hz

$J_{IS} \approx 150$ Hz

$J_{SS} \approx 50$ Hz

Static Solids

$J_{II} \approx 10$ Hz

$D_{II} \approx 50000$ Hz

$J_{IS} \approx 150$ Hz

$D_{IS} \approx 46000$ Hz

$D_{SS} \approx 5000$ Hz

$J_{SS} \approx 50$ Hz
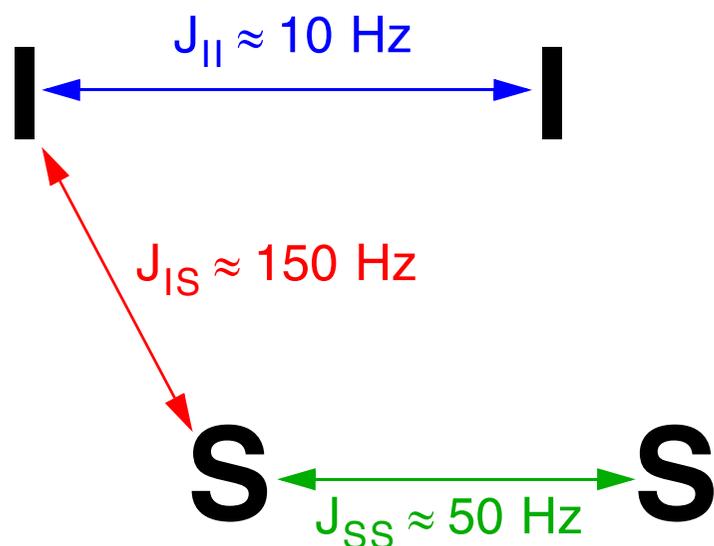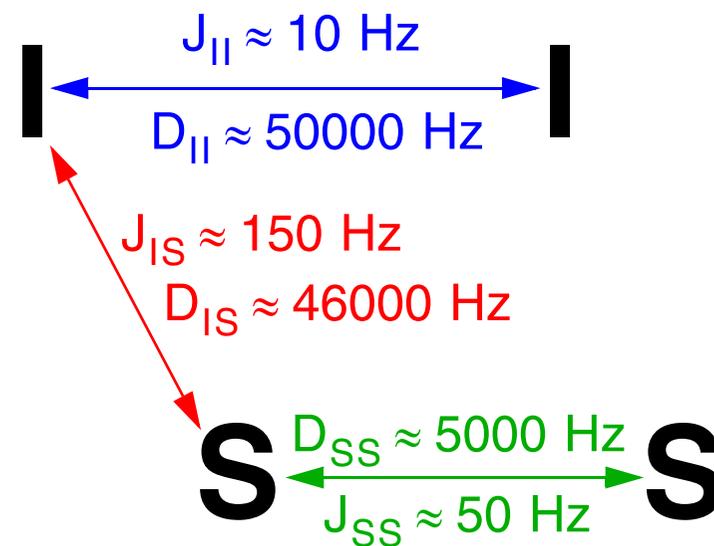
❑ Spin-spin couplings in solids (dipolar couplings) are roughly by a factor of 100-1000 larger than in liquids (J couplings) for rigid bio-organic substances.

- Higher rf-field amplitudes and better broadband inversion schemes are required.

- Typical rf-field amplitudes: ν_1 = 50-200 kHz

❑ Dipolar couplings are anisotropic and, therefore, orientation dependent.

Heteronuclear Decoupling in Static Solids

Liquids

$$I \xleftrightarrow{\quad J_{II} \approx 10 \text{ Hz} \quad} I$$

$J_{IS} \approx 150 \text{Z}$

$$S \xleftrightarrow{\quad} S$$
$J_{SS} \approx 50 \text{ Hz}$

Static Solids

$$I \xleftrightarrow{\quad J_{II} \approx 10 \text{ Hz} \quad} I$$
$D_{II} \approx 50000 \text{ Hz}$

$J_{IS} \approx 150 \text{ Hz}$
$D_{IS} \approx 46000 \text{ Hz}$

$D_{SS} \approx 5000 \text{ Hz}$
$$S \xleftrightarrow{\quad} S$$
$J_{SS} \approx 50 \text{ Hz}$
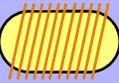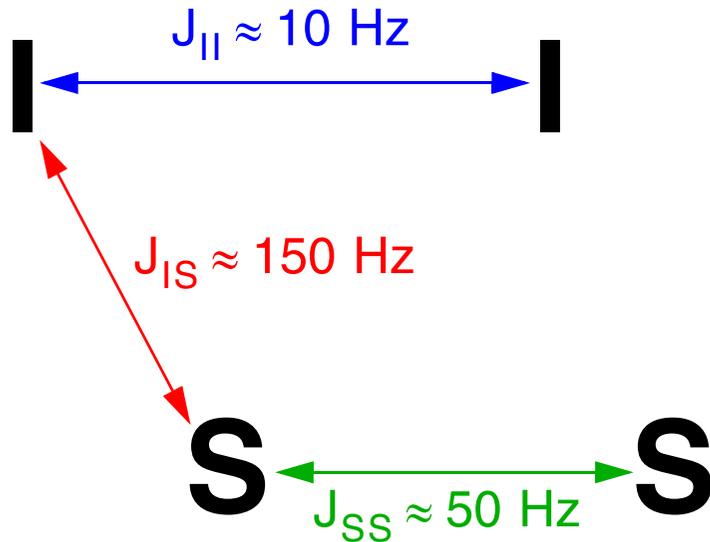
❑ Spin part of the homonuclear dipolar coupling $(3I_{1z}I_{2z} - \vec{I}_1 \cdot \vec{I}_2)$ is a second-rank tensor and not a scalar $(\vec{I}_1 \cdot \vec{I}_2)$ like in the J coupling.
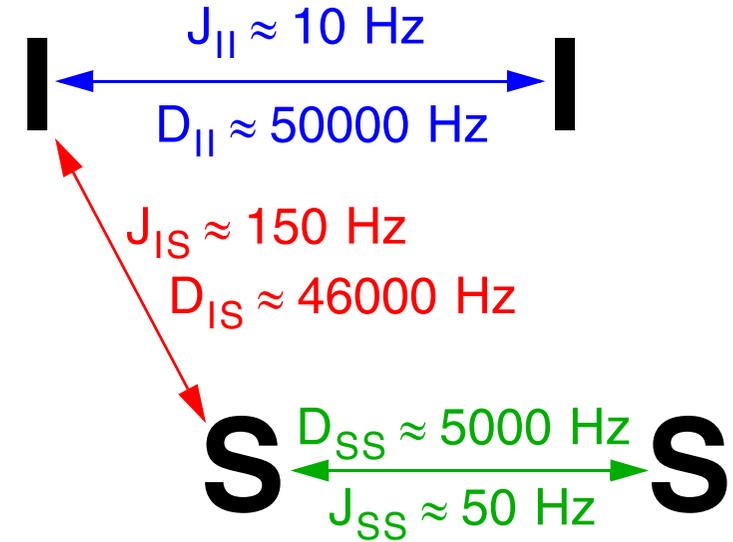
- Homonuclear dipolar couplings become time dependent in the rf-interaction frame.

- There can now be first-order cross terms in the AHT expansion between the homonuclear and the heteronuclear dipolar coupling that lead to residual line broadening.

- Special decoupling sequences optimized for homonuclear dipolar-coupled systems: COMARO (composite magic-angle rotation)
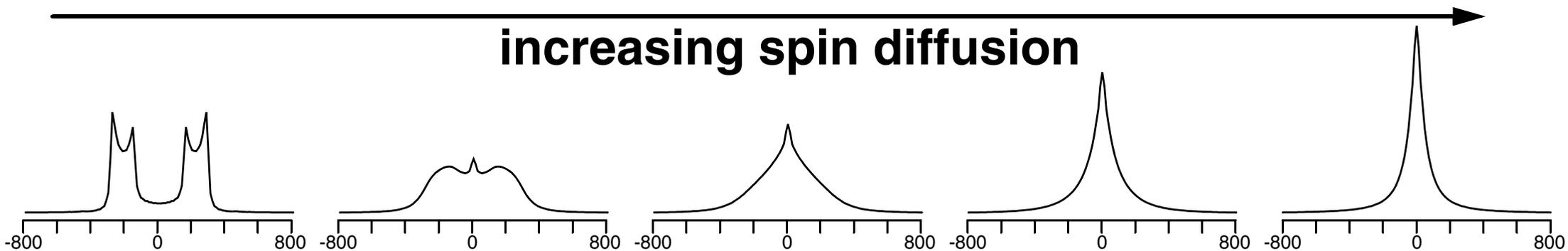
Heteronuclear Decoupling in Static Solids

Liquids

$J_{II} \approx 10$ Hz

$J_{IS} \approx 150$ Hz

$J_{SS} \approx 50$ Hz

Static Solids

$J_{II} \approx 10$ Hz

$D_{II} \approx 50000$ Hz

$J_{IS} \approx 150$ Hz

$D_{IS} \approx 46000$ Hz

$D_{SS} \approx 5000$ Hz

$J_{SS} \approx 50$ Hz

❏ Dense dipolar-coupling network on the I spins leads to spin diffusion among the I spins. "Self decoupling" can result in line narrowing due to an exchange-type process between the powder line shapes of the multiplet lines.
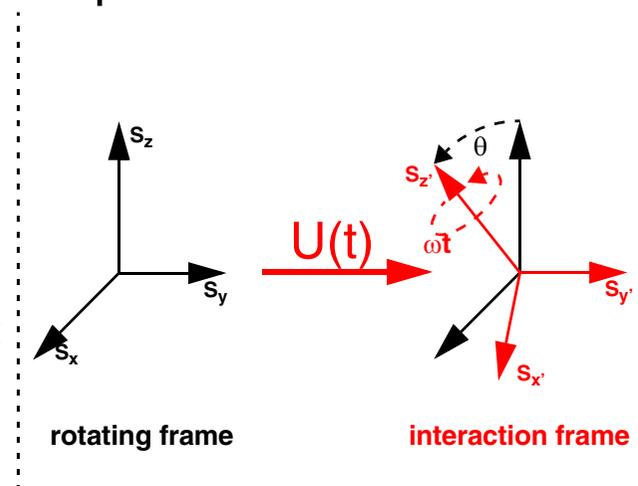
increasing spin diffusion

❏ Spin-system Hamiltonian in the rotating frame is static.

❏ Interaction-frame transformation with the rf-field leads to a time-dependent Hamiltonian.

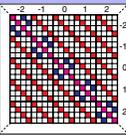$$\mathscr{H} = \mathscr{H}_I + \mathscr{H}_S + \mathscr{H}_{II} + \mathscr{H}_{SS} + \mathscr{H}_{IS}$$

interaction-frame transformation: $U(t) = \hat{T}\,\exp\left(-i\int_0^t \mathscr{H}_{rf}(t_1)\,dt_1\right)$

$$\tilde{\mathscr{H}}(t) = \tilde{\mathscr{H}}_I(t) + \tilde{\mathscr{H}}_S + \tilde{\mathscr{H}}_{II}(t) + \tilde{\mathscr{H}}_{SS} + \tilde{\mathscr{H}}_{IS}(t) = \sum_k \mathscr{H}^{(k)} e^{ik\omega_m t}$$

rotating frame   interaction frame

❏ Only the chemical shifts of the I spins, the heteronuclear J couplings, and the homonuclear dipolar couplings become time dependent in the rf-interaction frame.

❏ Single time dependence allows the use of average Hamiltonian theory (AHT).

❏ Cross terms between the heteronuclear coupling and the chemical shift or the homonuclear dipolar coupling can appear in $\overline{\mathscr{H}}^{(1)}$ while $\overline{\mathscr{H}}^{(2)}$ can contain cross terms between all parts of the Hamiltonian.

❏ "Symmetric" sequences ($\mathscr{H}(t) = \mathscr{H}(\tau_c - t)$) eliminate the first-order of the AHT. Residual splitting is determined by the second-order contributions.
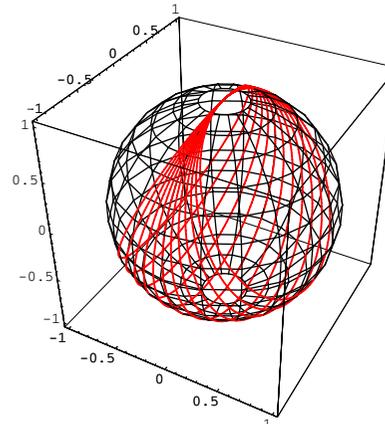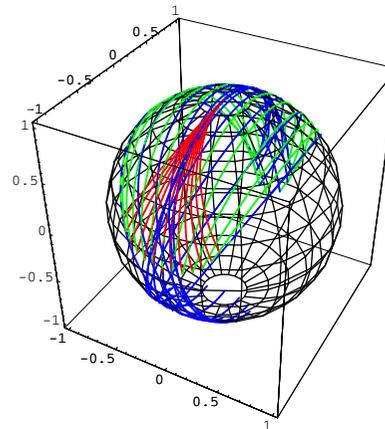
❏ **liquid-state NMR**

1950 cw decoupling

1966 noise decoupling

1981 multiple-pulse decoupling

1981 MLEV

1982 WALTZ

1985 GARP

1988 DIPSI

1995 adiabatic decoupling

1995 WURST

1997 SWIRL

cw decoupling

multiple pulse

solid-state NMR under MAS

1950 cw decoupling

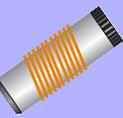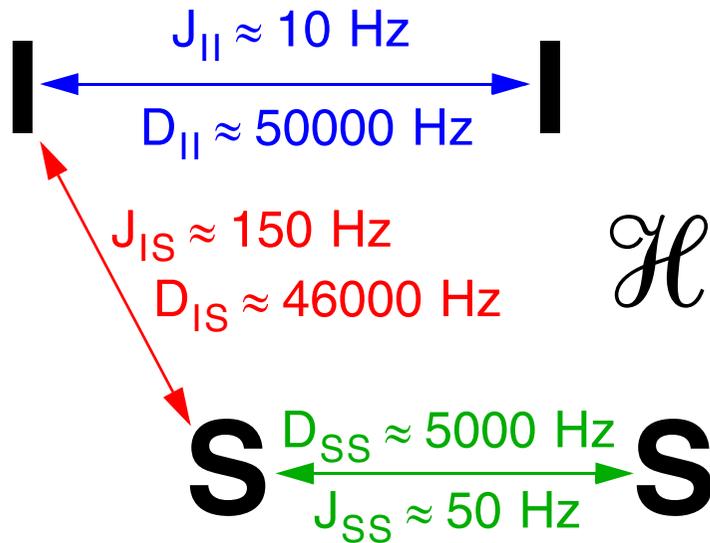1995 multiple-pulse decoupling

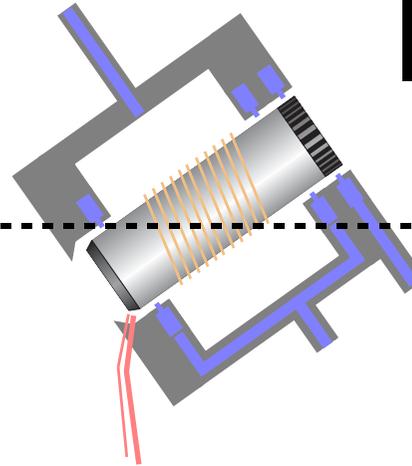1995 TPPM

2000 SPINAL

2001 XiX

2003 low-power decoupling

❏ Why was the development of decoupling techniques much slower in solid-state NMR under MAS conditions than in liquid-state NMR?
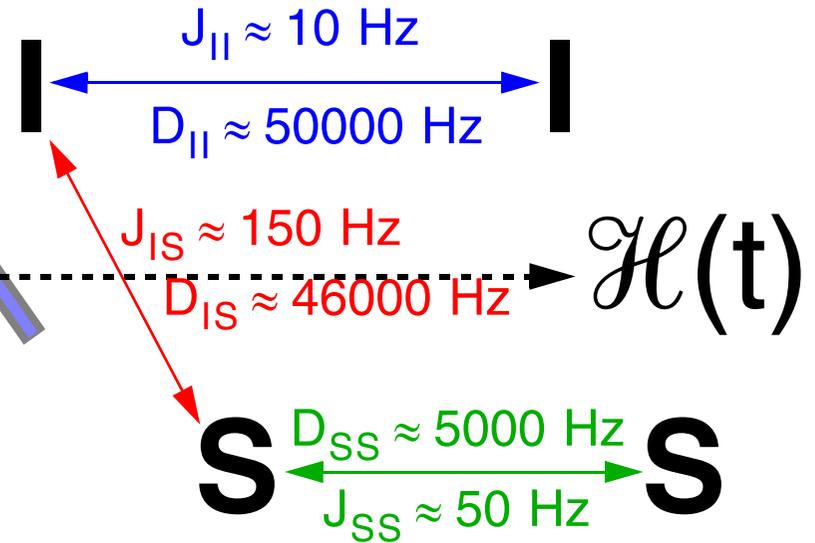
Heteronuclear Decoupling in Rotating Solids

Static Solids

$$J_{II} \approx 10 \text{ Hz}$$

I — I

$$D_{II} \approx 50000 \text{ Hz}$$

$$J_{IS} \approx 150 \text{ Hz}$$
$$D_{IS} \approx 46000 \text{ Hz}$$

$$D_{SS} \approx 5000 \text{ Hz}$$

S — S

$$J_{SS} \approx 50 \text{ Hz}$$

Rotating Solids

$$J_{II} \approx 10 \text{ Hz}$$

I — I

$$D_{II} \approx 50000 \text{ Hz}$$

$$J_{IS} \approx 150 \text{ Hz}$$
$$D_{IS} \approx 46000 \text{ Hz}$$

$$D_{SS} \approx 5000 \text{ Hz}$$

S — S

$$J_{SS} \approx 50 \text{ Hz}$$
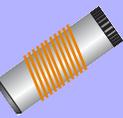
$\mathcal{H} \cdots\cdots \rightarrow \mathcal{H}(t)$

❏ Spin-system Hamiltonian in the rotating frame is time dependent due to magic-angle spinning (MAS).
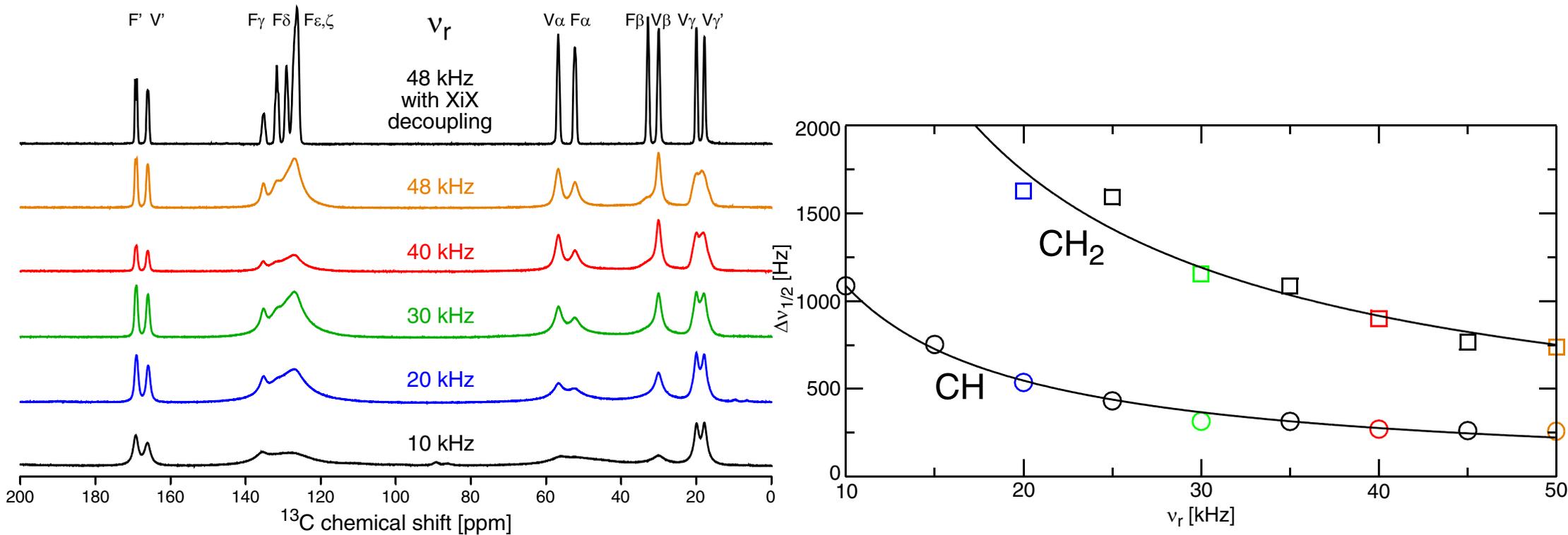
$$\mathcal{H}(t) = \mathcal{H}_I(t) + \mathcal{H}_S(t) + \mathcal{H}_{II}(t) + \mathcal{H}_{SS}(t) + \mathcal{H}_{IS}(t) = \sum_{n=-2}^{2} \mathcal{H}^{(n)} e^{in\omega_r t}$$

❏ This additional time dependence is the source of the difficulties in decoupling under sample rotation.

❏ MAS will average in zeroth-order approximation all anisotropic interactions.

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

❏ 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.

Theoretical Description of Decoupling in Rotating Solids
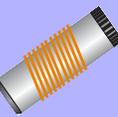
❑ Spin-system Hamiltonian in the rotating frame is time dependent due to magic-angle spinning (MAS).

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

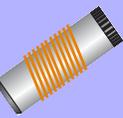interaction-frame transformation: $U(t) = \hat{T} \exp\left(-i\int_{0}^{t} \mathscr{H}_{rf}(t_1) dt_1\right)$

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

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

❑ Average Hamiltonian theory requires that

- the two frequencies are commensurate, i.e., $n\omega_m = k\omega_r$ (simultaneous averaging) or

- a separation of time scales, i.e., $\omega_m \gg \omega_r$ or $\omega_m \ll \omega_r$ (sequential averaging).
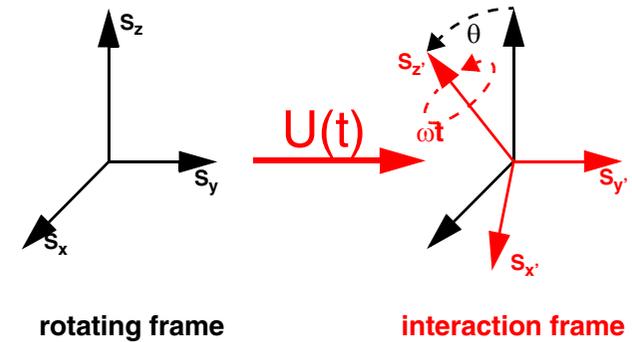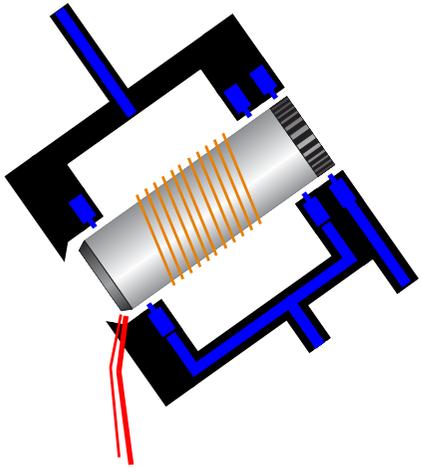
Detour: Origin Of Time-Dependent Hamiltonians

❏ System Hamiltonian in the laboratory frame is static if the molecule is static.

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

sample rotation + **interaction-frame transformation**

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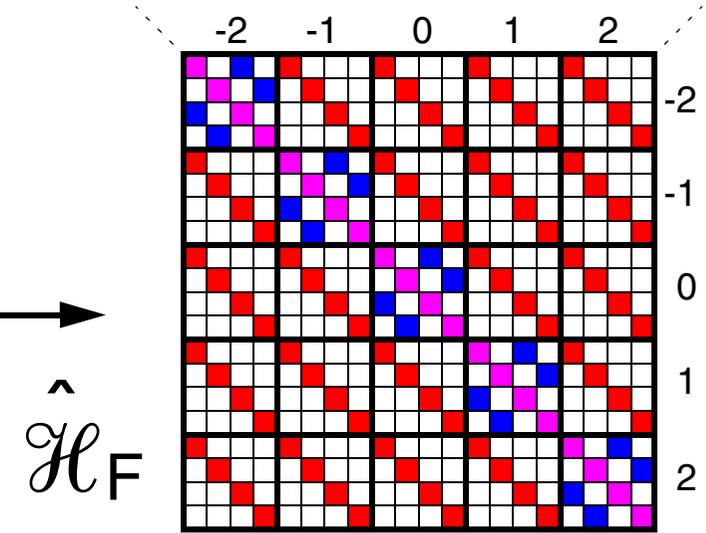
$U(t)$

rotating frame   interaction frame

❏ Spatial and Spin part of the Hamiltonian are modulated with different frequencies.

❏ We need methods to deal with Hamiltonians with multiple time dependencies.

❏ If multiples of the two frequencies are matched, we obtain again time-independent parts in the Hamiltonian.
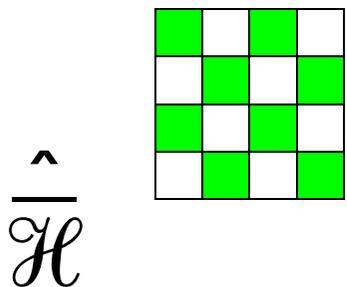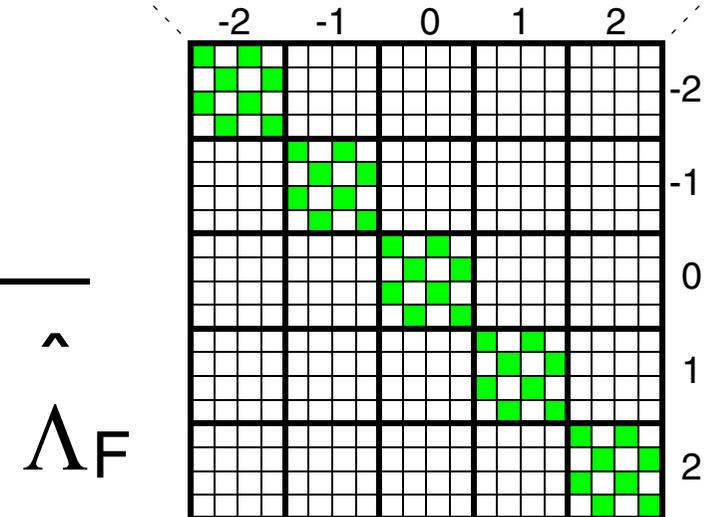
Construction of Floquet Hamiltonian

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

$\hat{\mathcal{H}}_F$
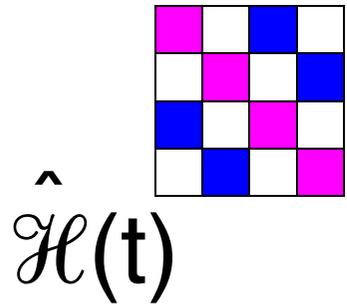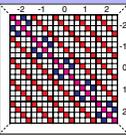
Block diagonalization using van-Vleck method

Projection back into Hilbert space
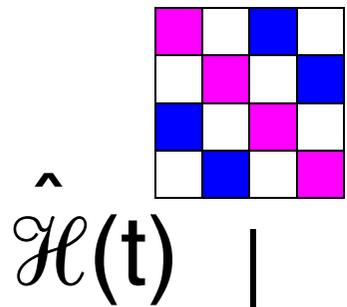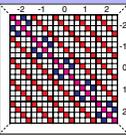
$\hat{\overline{\mathcal{H}}}$

$\hat{\Lambda}_F$

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

Construction of
Floquet Hamiltonian

$\hat{\mathscr{H}}_F$
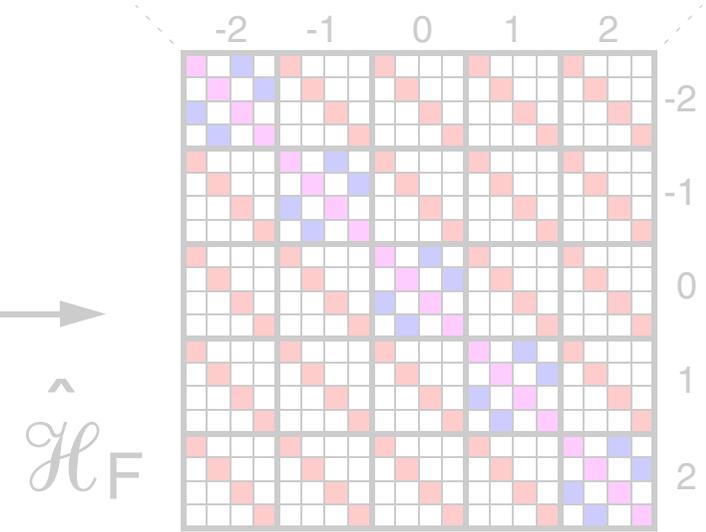
Calculation is independent
of the detailed structure of
the Hilbert-space blocks.

Block diagonalization
using van-Vleck method

$\hat{\overline{\mathscr{H}}}$

Projection back
into Hilbert space

$\hat{\Lambda}_F$
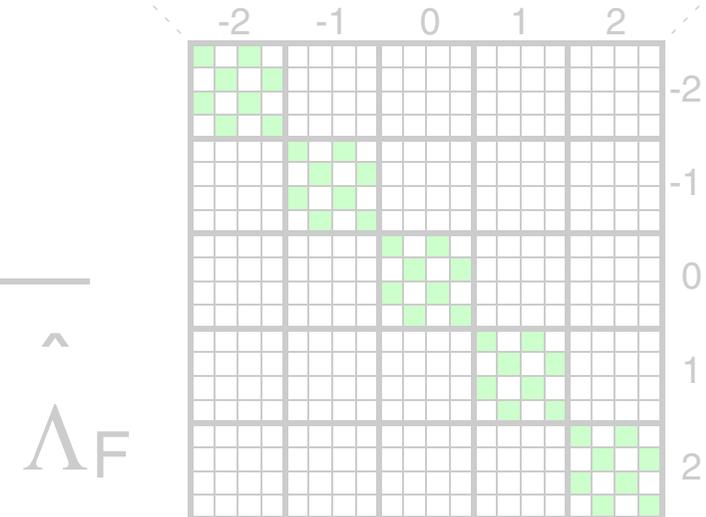
Single frequency ω_m

$$\mathcal{H}(t) = \sum_k \mathcal{H}^{(k)} e^{ik\omega_m t}$$

Calculation is independent of the detailed structure of the Hilbert-space blocks $\mathcal{H}^{(k)}$.

If we know $\mathcal{H}^{(k)}$ we can calculate $\overline{\mathcal{H}}$.
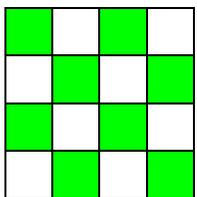
$$\overline{\mathcal{H}} = \mathcal{H}^{(0)} - \frac{1}{2}\sum_{n \neq 0} \frac{[\mathcal{H}^{(-n)}, \mathcal{H}^{(n)}]}{n\omega_m}$$

$$+ \frac{1}{2}\sum_{n \neq 0} \frac{[[\mathcal{H}^{(n)}, \mathcal{H}^{(0)}], \mathcal{H}^{(-n)}]}{(n\omega_m)^2} + \frac{1}{3}\sum_{k,\, n \neq 0} \frac{[\mathcal{H}^{(n)}, [\mathcal{H}^{(k)}, \mathcal{H}^{(-n-k)}]]}{kn\omega_m^2}$$

Two frequencies ω_r and ω_m

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

Construction of Floquet Hamiltonian $\hat{\mathcal{H}}_F$

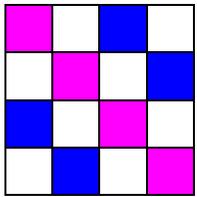**Calculation is independent of the detailed structure of the Hilbert-space blocks $\mathcal{H}^{(n,k)}$.**
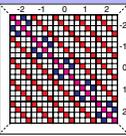
Block diagonalization using van-Vleck method

If we know $\mathcal{H}^{(n,k)}$ we can calculate $\overline{\overline{\mathcal{H}}}$.

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

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

Projection back into Hilbert space Λ_F
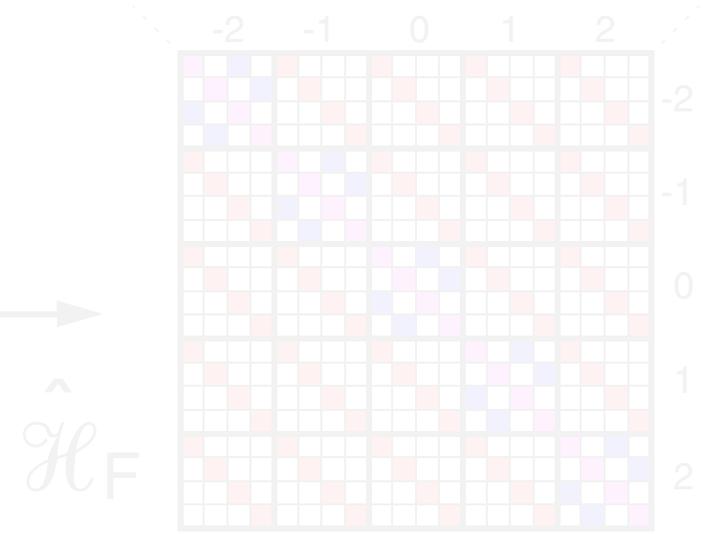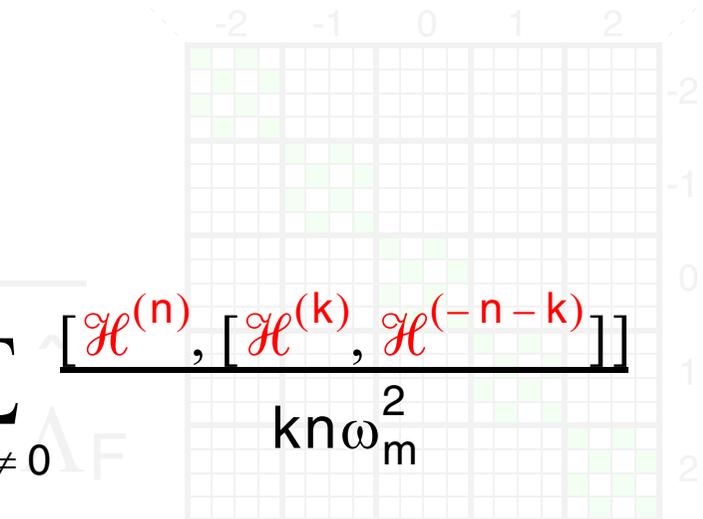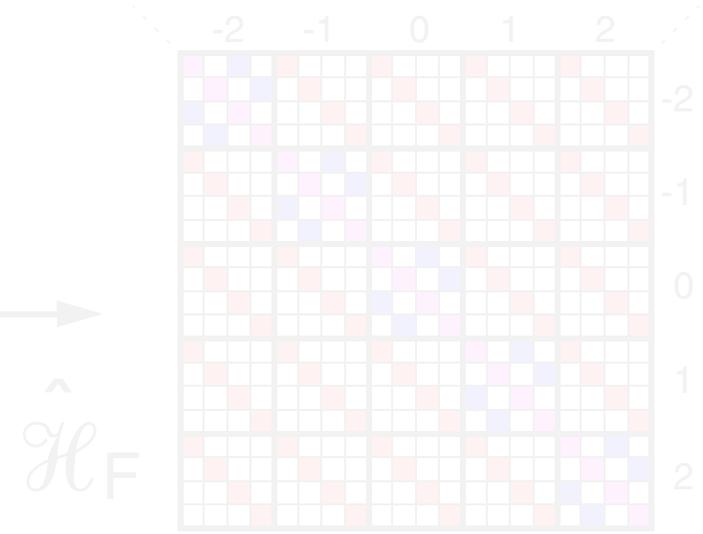
Effective Hamiltonians from Floquet Theory

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

❑ What is different when going from a single modulation frequency to two (or more) modulation frequencies?

one modulation frequency   two modulation frequencies

$$\overline{\mathcal{H}} = \mathcal{H}^{(0)} - \frac{1}{2}\sum_{n \neq 0} \frac{[\mathcal{H}^{(-n)}, \mathcal{H}^{(n)}]}{n\omega_m} + \dots \qquad\qquad \overline{\mathcal{H}} = \sum_{n_0, k_0} \mathcal{H}^{(n_0, k_0)} - \sum_{n_0, k_0} \frac{1}{2}\sum_{\nu, \kappa} \frac{[\mathcal{H}^{(n_0 - \nu, k_0 - \kappa)}, \mathcal{H}^{(\nu, \kappa)}]}{\nu\omega_r + \kappa\omega_m} + \dots$$

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

❑ With multiple modulation frequencies, resonance conditions at $n_0\omega_r + k_0\omega_m = 0$ appear. They lead to time-independent terms in first-order or second-order perturbation theory.

❑ At these resonance conditions we do not average out certain components $\mathcal{H}^{(n_0, k_0)}$ of the Hamiltonian.

❑ There are first-order $\mathcal{H}^{(n_0, k_0)}$ and second-order $\mathcal{H}_{(2)}^{(n_0, k_0)}$ resonance conditions.
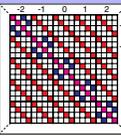
❑ Time-dependent interaction-frame Hamiltonian has (at least) two modulation frequencies

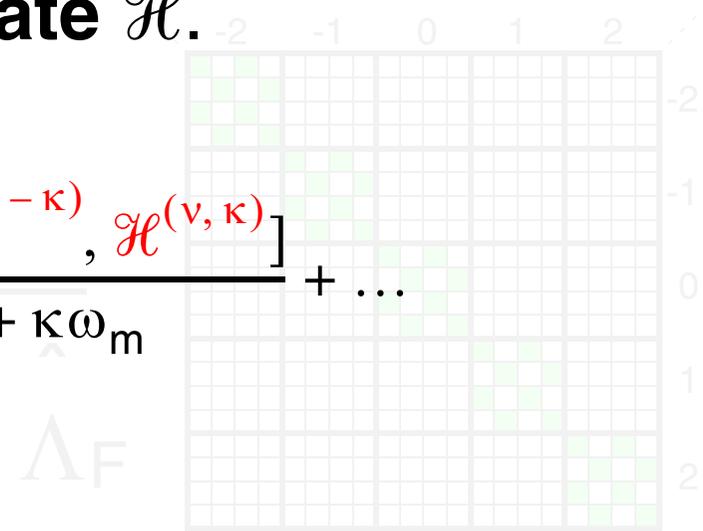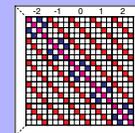$$\tilde{\mathcal{H}}(t) = \sum_{n=-2}^{2} \sum_{k} \tilde{\mathcal{H}}^{(n,k)} e^{ik\omega_m t} e^{in\omega_r t}$$
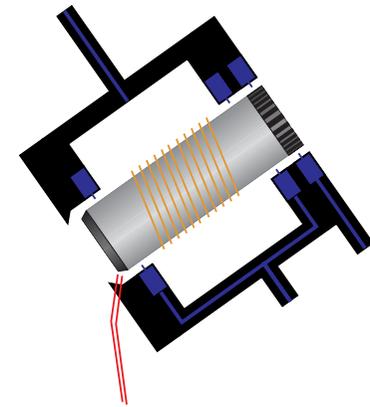
interaction frame

$$\overline{\tilde{\mathcal{H}}} = \sum_{n_0, k_0} \tilde{\mathcal{H}}^{(n_0, k_0)} - \sum_{n_0, k_0} \frac{1}{2} \sum_{\nu, \kappa} \frac{\left[\tilde{\mathcal{H}}^{(n_0 - \nu, k_0 - \kappa)}, \tilde{\mathcal{H}}^{(\nu, \kappa)} \right]}{\nu\omega_r + \kappa\omega_m} + \ldots$$
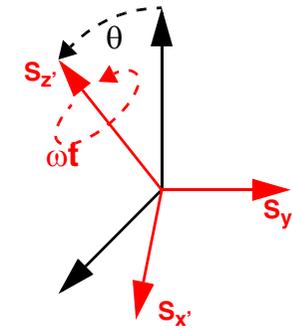
❑ Factors determining the observable line width in solid-state NMR decoupling:

- Residual coupling ($\tilde{\mathcal{H}}_{(2)}^{(0,0)}$) is given by the commutator term because the interaction-frame Hamiltonian is not "symmetric" due to the MAS rotation.

- Resonance conditions ($\tilde{\mathcal{H}}^{(n_0, k_0)}$ and $\tilde{\mathcal{H}}_{(2)}^{(n_0, k_0)}$) between the two modulation frequencies can lead to large terms which can be beneficial or detrimental to the decoupling process.

- I-spin spin diffusion leads to an additional averaging of the residual couplings.

Continuous-Wave Decoupling in Rotating Solids

Glycine:

H_2N-CH_2-COOH

$\nu_r = 68.5$ kHz
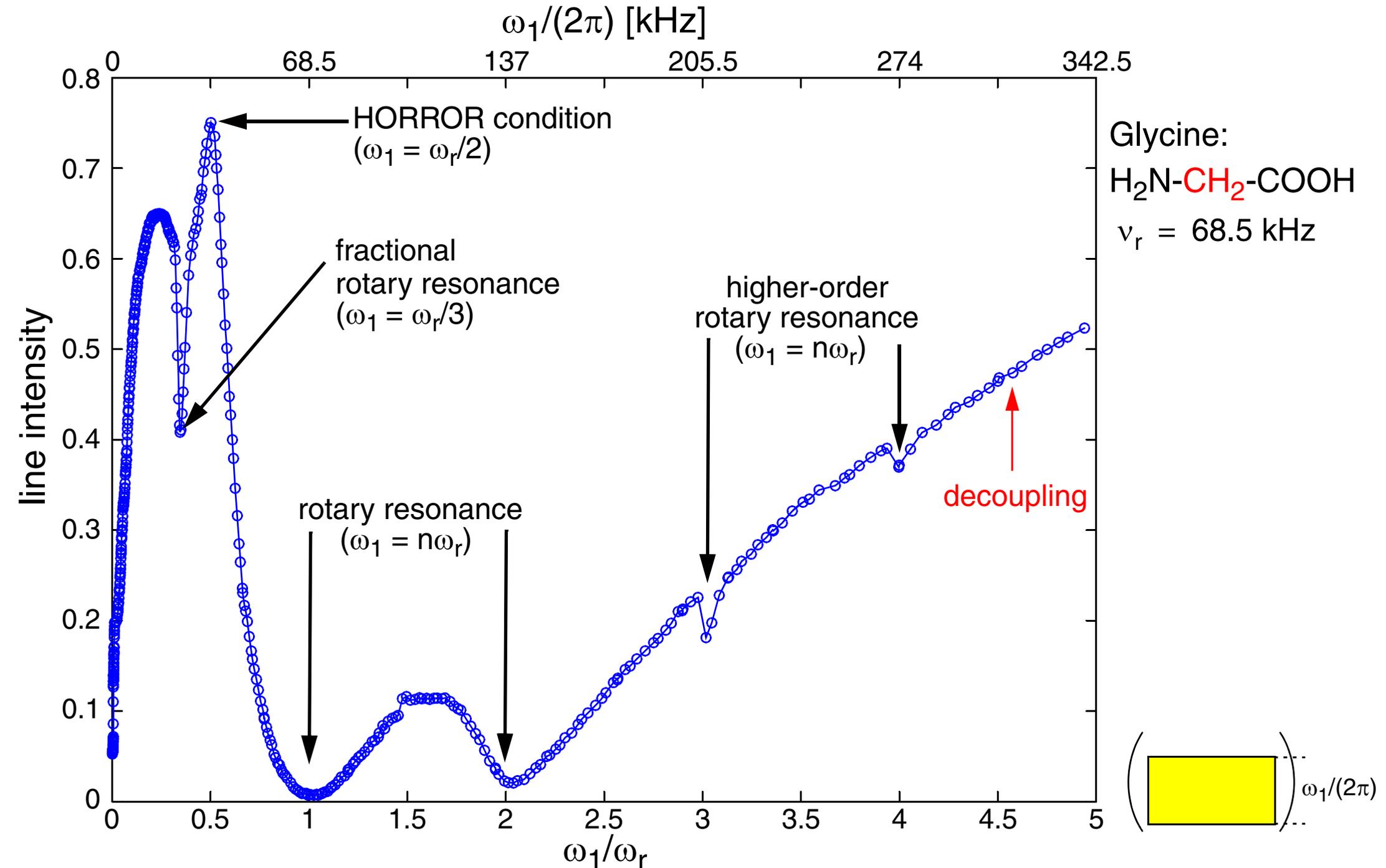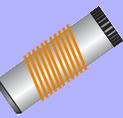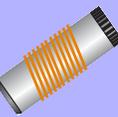
❏ Interaction-frame transformation with RF:

$$U(t) \; = \; \exp\left(-i\omega_1 \sum_{m=1}^{N} I_{mz}\right)$$

$$I_{mx} \rightarrow I_{mx}\cos(\omega_1 t) + I_{my}\sin(\omega_1 t)$$
$$I_{my} \rightarrow I_{my}\cos(\omega_1 t) - I_{mx}\sin(\omega_1 t)$$

❏ We find a single frequency ω_1 in the interaction frame:

interaction-frame representation

Fourier coefficients

FT

❏ Only the first side-diagonal in the rf-modulation space ($k = \pm 1$) is occupied.

❏ **Residual coupling** is given by a cross term between the **I**-spin CSA and the heteronuclear dipolar couplings.

$$\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(0,\,0)} = \frac{1}{4}\sum_{\nu,\,\kappa}\sum_{\ell}\kappa\left(\frac{\om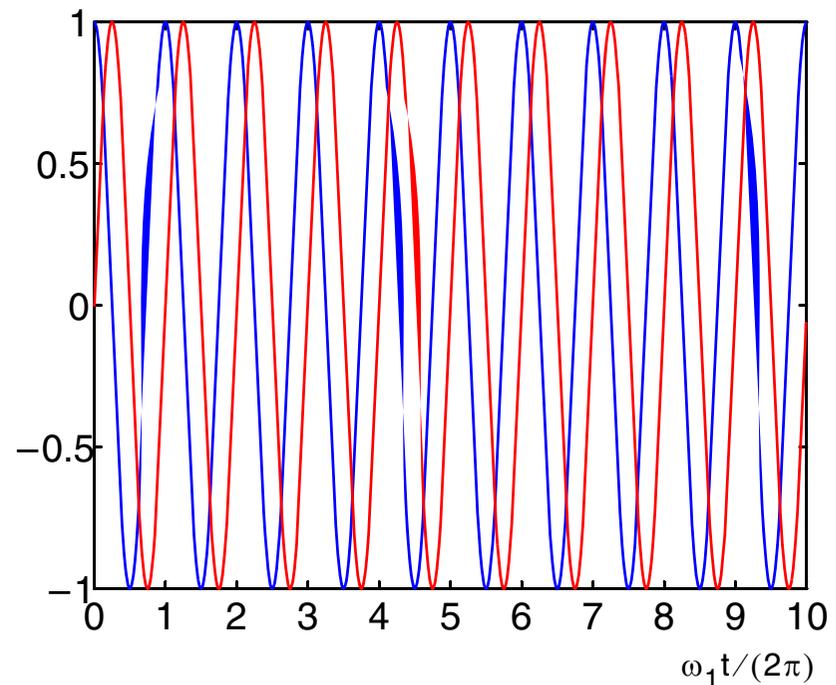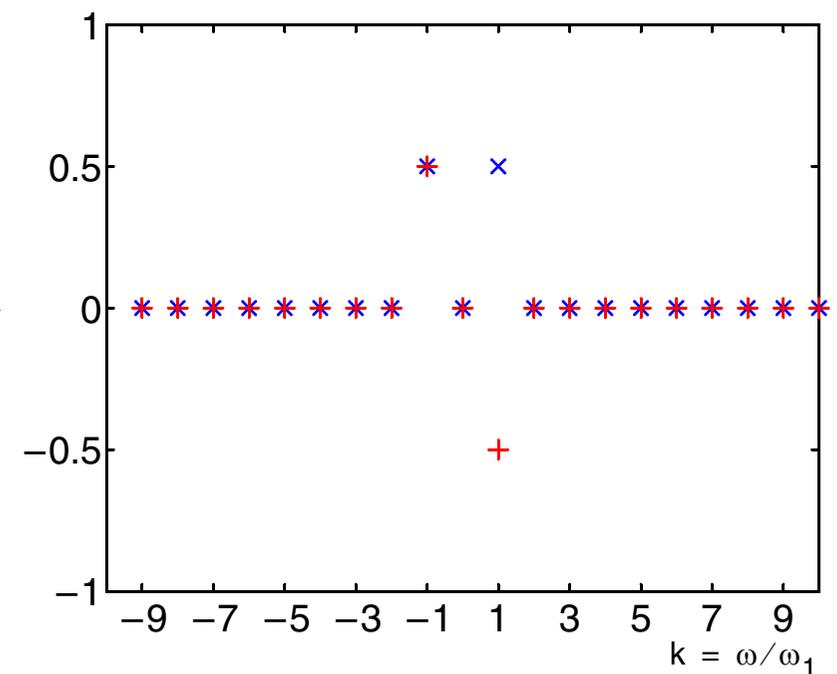ega_{I_\ell}^{(\nu)}\omega_{SI_\ell}^{(-\nu)} + \omega_{SI_\ell}^{(\nu)}\omega_{I_\ell}^{(-\nu)}}{\nu\omega_r + \kappa\omega_1}\right)2S_z I_{\ell z}$$

❏ **Resonance conditions**:

first-order resonance conditions with $\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}^{(n_0,\,k_0)} + \tilde{\mathcal{H}}^{(-n_0,\,-k_0)}$ and

second-order resonance conditions with $\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(n_0,\,k_0)} + \tilde{\mathcal{H}}_{(2)}^{(-n_0,\,-k_0)}$.

❏ **HORROR condition** at $\omega_1 = \omega_r/2$:

- Recouples **I**-spin homonuclear dipolar couplings.

- Line intensity is increased due to **I**-spin spin diffusion (self decoupling).

HORROR condition ($\omega_1 = \omega_r/2$)

$$\overline{\mathcal{H}} \approx \frac{3}{4}\sum_{\ell < m}(\omega_{\ell m}^{(-1)}I_\ell^+ I_m^+ + \omega_{\ell m}^{(1)}I_\ell^- I_m^-)$$

decoupling

❑ **Residual coupling** is given by a cross term between the **I**-spin CSA and the heteronuclear dipolar couplings.

$$\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}^{(0,0)}_{(2)} = \frac{1}{4}\sum_{\nu,\kappa}\sum_{\ell}\kappa\left(\frac{\omega^{(\nu)}_{I_\ell}\omega^{(-\nu)}_{SI_\ell} + \omega^{(\nu)}_{SI_\ell}\omega^{(-\nu)}_{I_\ell}}{\nu\omega_r + \kappa\omega_1}\right)2S_zI_{\ell z}$$

❑ **Resonance conditions**:

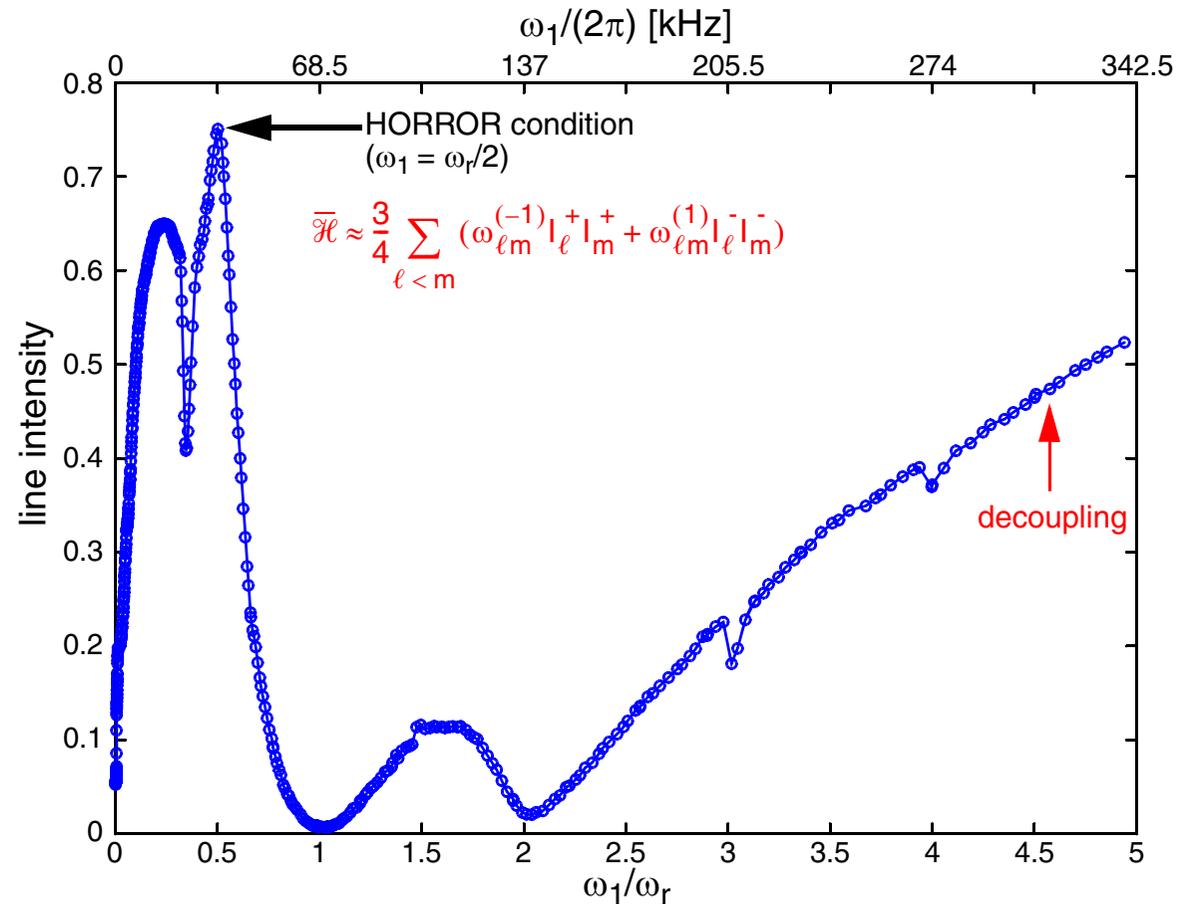first-order resonance conditions with $\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}^{(n_0,k_0)} + \tilde{\mathcal{H}}^{(-n_0,-k_0)}$ and

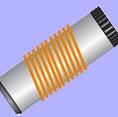second-order resonance conditions with $\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}^{(n_0,k_0)}_{(2)} + \tilde{\mathcal{H}}^{(-n_0,-k_0)}_{(2)}$.

❑ First-order rotary-resonance condition at $\omega_1 = 1\omega_r$ and $\omega_1 = 2\omega_r$.

- Recouples heteronuclear dipolar cou-plings.

- Lines are broadened and intensity is reduced.

$$\overline{\mathcal{H}} \approx -\frac{1}{2}\sum_{\ell}\left(\omega^{(-2)}_{I_\ell}I^+_\ell + \omega^{(2)}_{I_\ell}I^-_\ell + \omega^{(-2)}_{SI_\ell}2S_zI^+_\ell + \omega^{(2)}_{SI_\ell}2S_zI^-_\ell\right)$$

Continuous-Wave Decoupling in Rotating Solids

❏ **Residual coupling** is given by a cross term between the **I**-spin CSA and the heteronuclear dipolar couplings.

$$\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(0,\,0)} = \frac{1}{4}\sum_{\nu,\,\kappa}\sum_{\ell}\kappa\left(\frac{\omega_{I_\ell}^{(\nu)}\omega_{SI_\ell}^{(-\nu)} + \omega_{SI_\ell}^{(\nu)}\omega_{I_\ell}^{(-\nu)}}{\nu\omega_r + \kappa\omega_1}\right)2S_z I_{\ell z}$$

❏ **Resonance conditions**:

first-order resonance conditions with $\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}^{(n_0,\,k_0)} + \tilde{\mathcal{H}}^{(-n_0,\,-k_0)}$ and
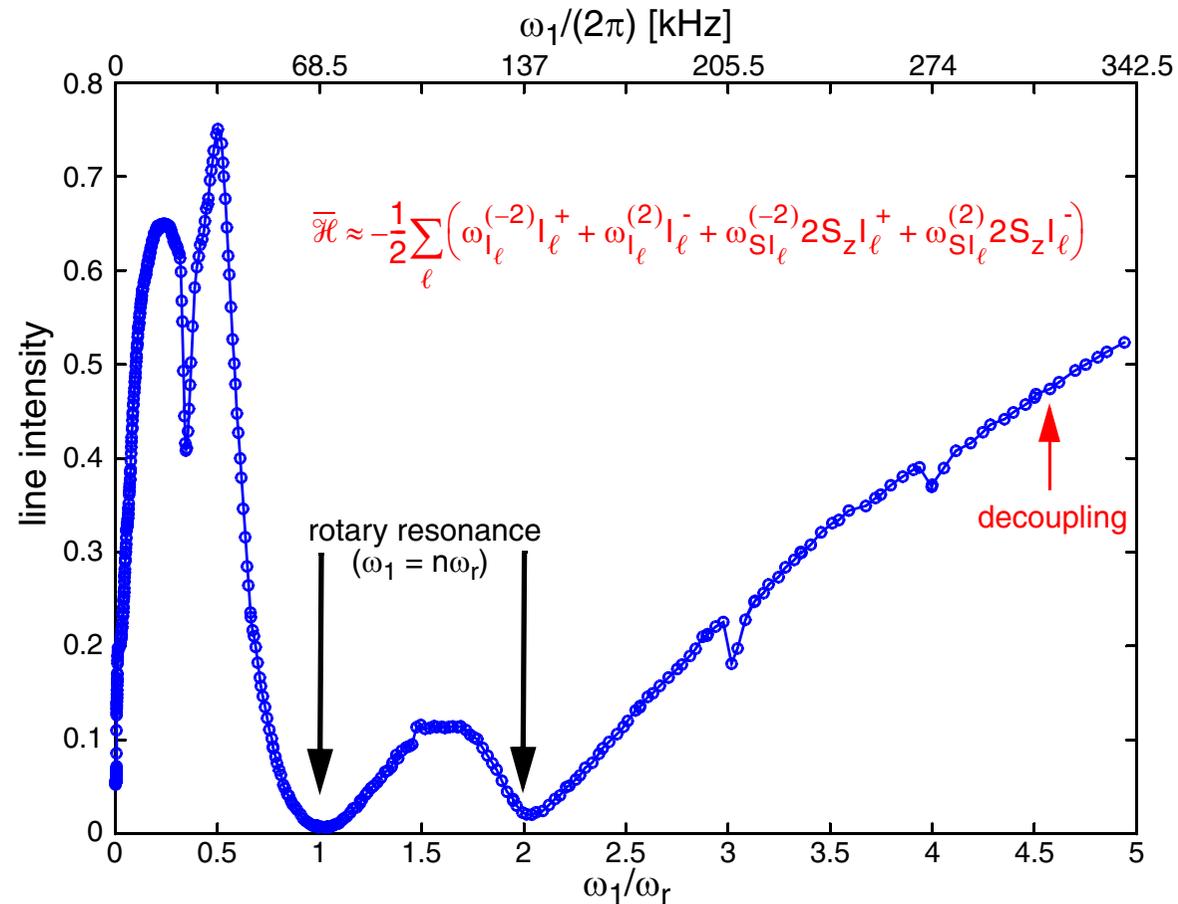
second-order resonance conditions with $\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(n_0,\,k_0)} + \tilde{\mathcal{H}}_{(2)}^{(-n_0,\,-k_0)}$.

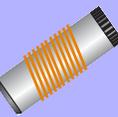❏ Second-order rotary-resonance condition at $\omega_1 = 3\omega_r$ and $\omega_1 = 4\omega_r$.

- Recouples heteronuclear dipolar couplings.

- Lines are broadened and intensity is reduced.

$$\overline{\mathcal{H}} \approx -\frac{1}{4\omega_r}\sum_{\ell,\,m}[\omega_{S\ell m}2S_z I_{\ell z}I_m^- + \omega_{S\ell m}^*2S_z I_{\ell z}I_m^+]$$

higher-order rotary resonance ($\omega_1 = n\omega_r$)

decoupling

❏ **Residual coupling** is given by a cross term between the **I**-spin CSA and the heteronuclear dipolar couplings.

$$\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(0,\,0)} = \frac{1}{4}\sum_{\nu,\,\kappa}\sum_{\ell}\kappa\left(\frac{\omega_{I_\ell}^{(\nu)}\omega_{SI_\ell}^{(-\nu)} + \omega_{SI_\ell}^{(\nu)}\omega_{I_\ell}^{(-\nu)}}{\nu\omega_r + \kappa\omega_1}\right)2S_z I_{\ell z}$$

❏ **Resonance conditions**:

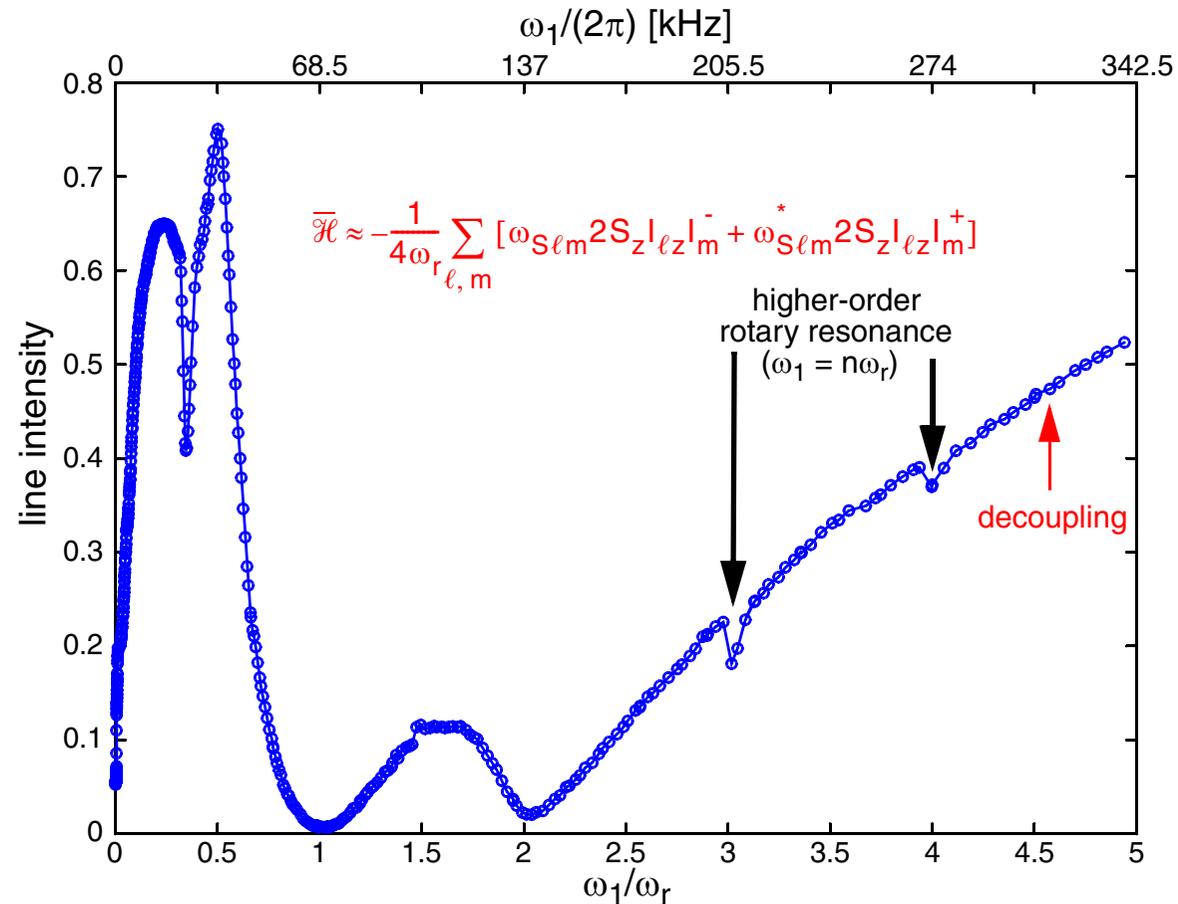first-order resonance conditions with $\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}^{(n_0,\,k_0)} + \tilde{\mathcal{H}}^{(-n_0,\,-k_0)}$ and
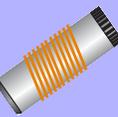
second-order resonance conditions with $\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(n_0,\,k_0)} + \tilde{\mathcal{H}}_{(2)}^{(-n_0,\,-k_0)}$.

- HORROR condition at $\omega_1 = \omega_r/2$.

- first-order rotary-resonance condition at $\omega_1 = 1\omega_r$ and $\omega_1 = 2\omega_r$.

- second-order rotary-resonance condition at $\omega_1 = 3\omega_r$ and $\omega_1 = 4\omega_r$.

❏ **I-spin spin diffusion** is active everywhere and scales with $1/\omega_r$.
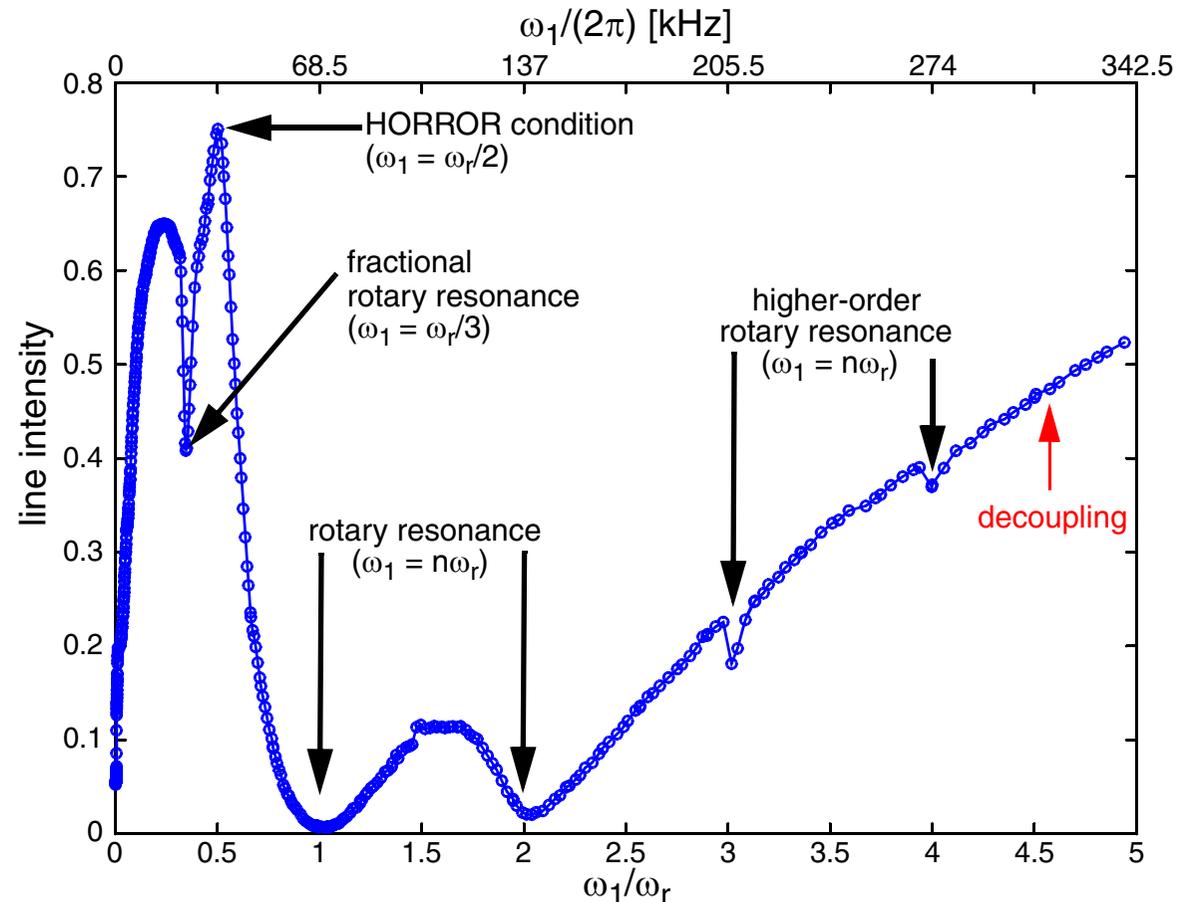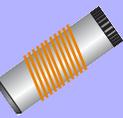
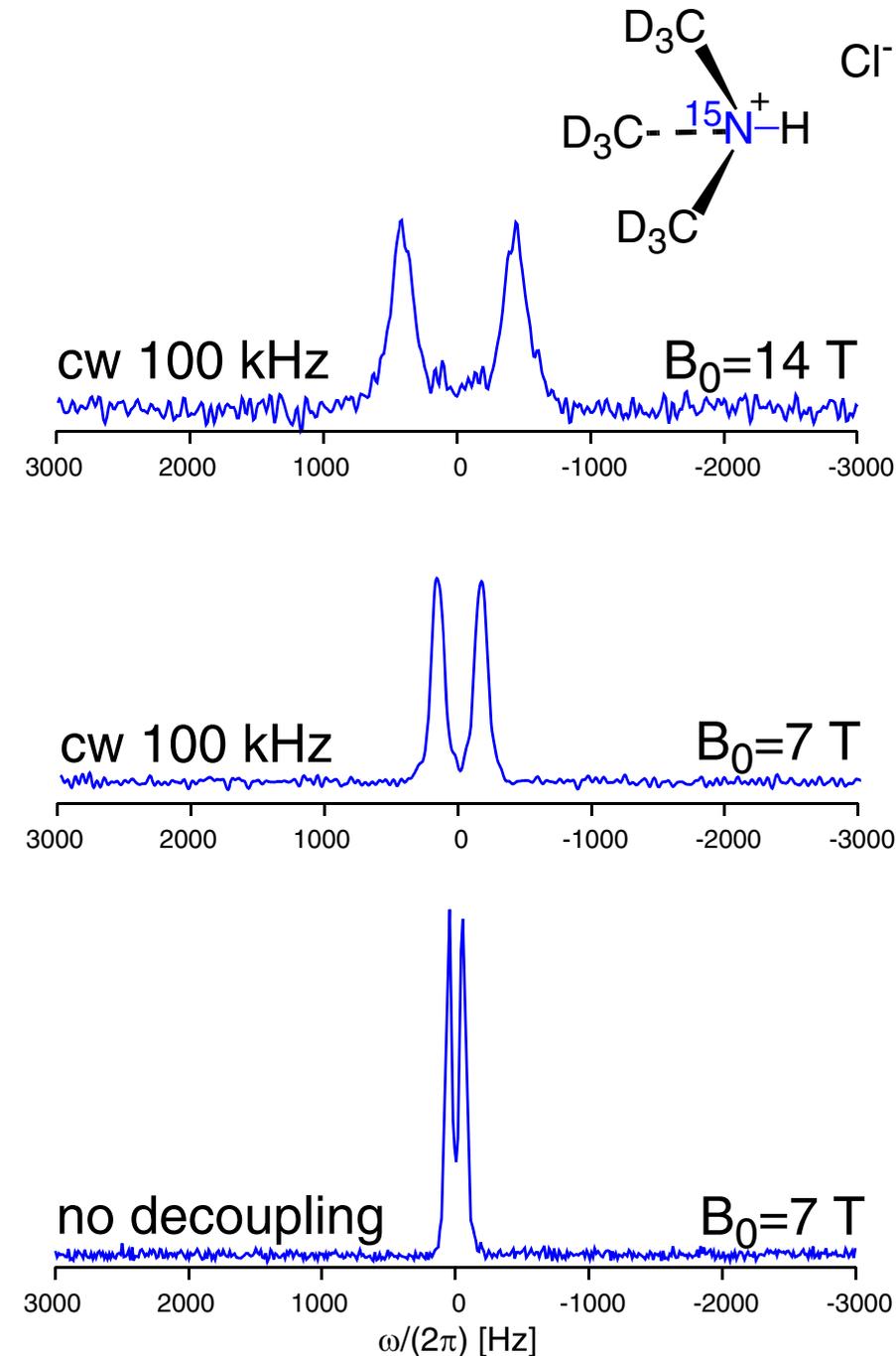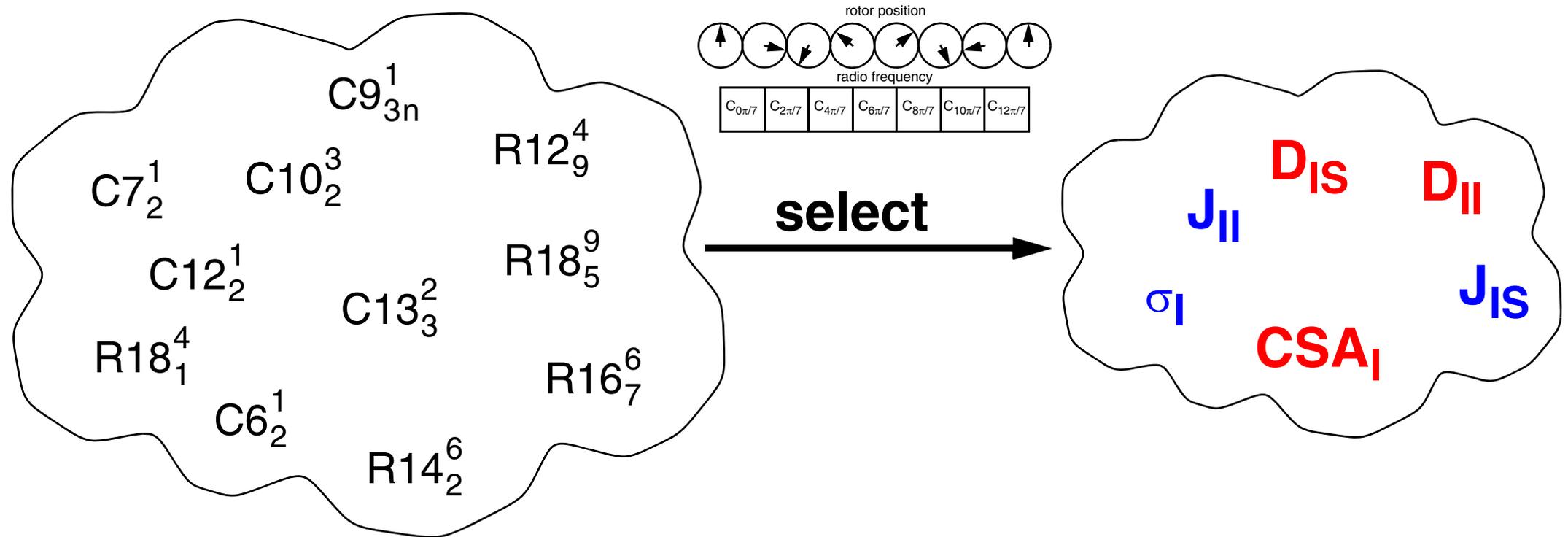❏ Continuous-wave decoupling is a terrible decoupling sequence with a large residual coupling.

❏ Residual coupling increases with increasing B_0 field strength (CSA!).

❏ Rotary-resonance conditions have to be avoided:

   - High-power decoupling: $\omega_1 > 3\omega_r$

   - Low-power decoupling: $\omega_1 \leq \omega_r/2$ 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: $\Delta\nu_{1/2}$ decreases with ν_1.

❏ Low-power decoupling: $\Delta\nu_{1/2}$ decreases with ν_r.

cw 100 kHz B_0=14 T

cw 100 kHz B_0=7 T

no decoupling B_0=7 T

$\omega/(2\pi)$ [Hz]

rotor position

radio frequency

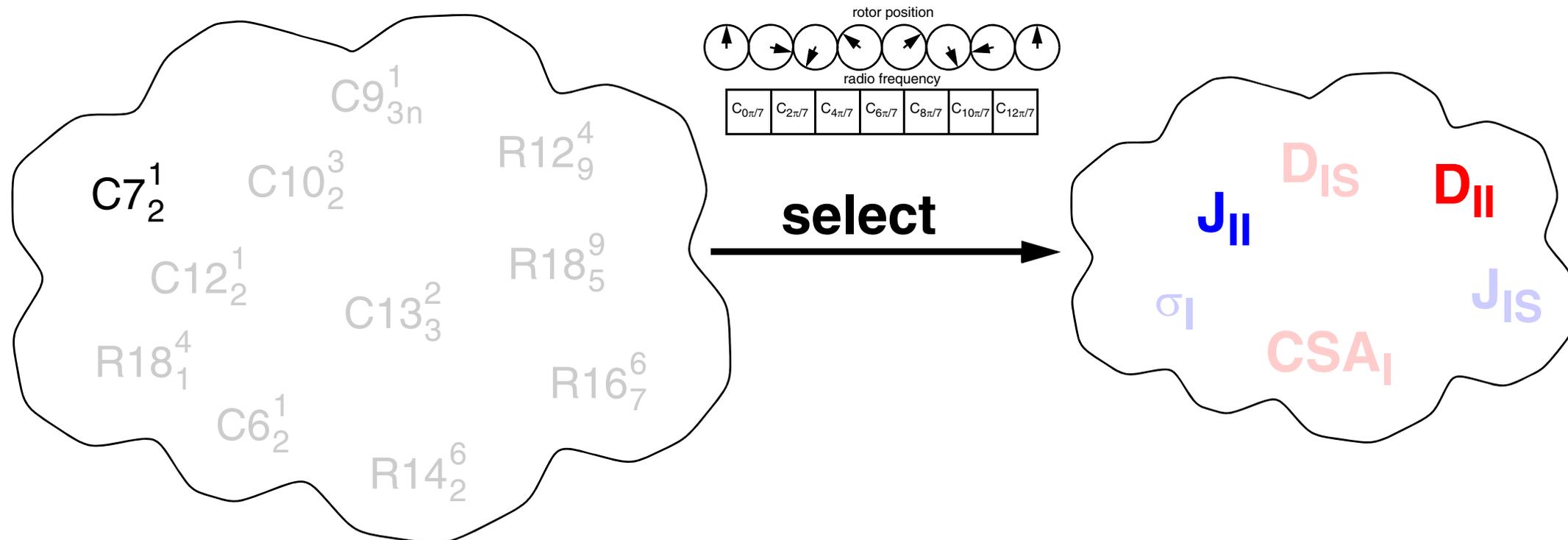| $C_{0\pi/7}$ | $C_{2\pi/7}$ | $C_{4\pi/7}$ | $C_{6\pi/7}$ | $C_{8\pi/7}$ | $C_{10\pi/7}$ | $C_{12\pi/7}$ |

$C9_{3n}^{1}$

$R12_{9}^{4}$

$C7_{2}^{1}$ $C10_{2}^{3}$

$C12_{2}^{1}$

$R18_{5}^{9}$

$C13_{3}^{2}$

$R18_{1}^{4}$

$R16_{7}^{6}$

$C6_{2}^{1}$

$R14_{2}^{6}$

select

J_{II} D_{IS} D_{II}

σ_{I} J_{IS}

CSA_{I}

❏   Rotor-synchronized R and C sequences allow us to select certain components of spin inter-actions.

❏   Analysis is based on a symmetry-driven version of average Hamiltonian theory.

❏   Very powerful tool for tailoring the effective Hamiltonian under MAS.

❏   Malcolm H. Levitt "Symmetry-Based Pulse Sequences in Magic-Angle Spinning Solid-State NMR", Encyclopedia of Nuclear Magnetic Resonance, Volume 9, 165-196 (2002).
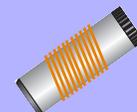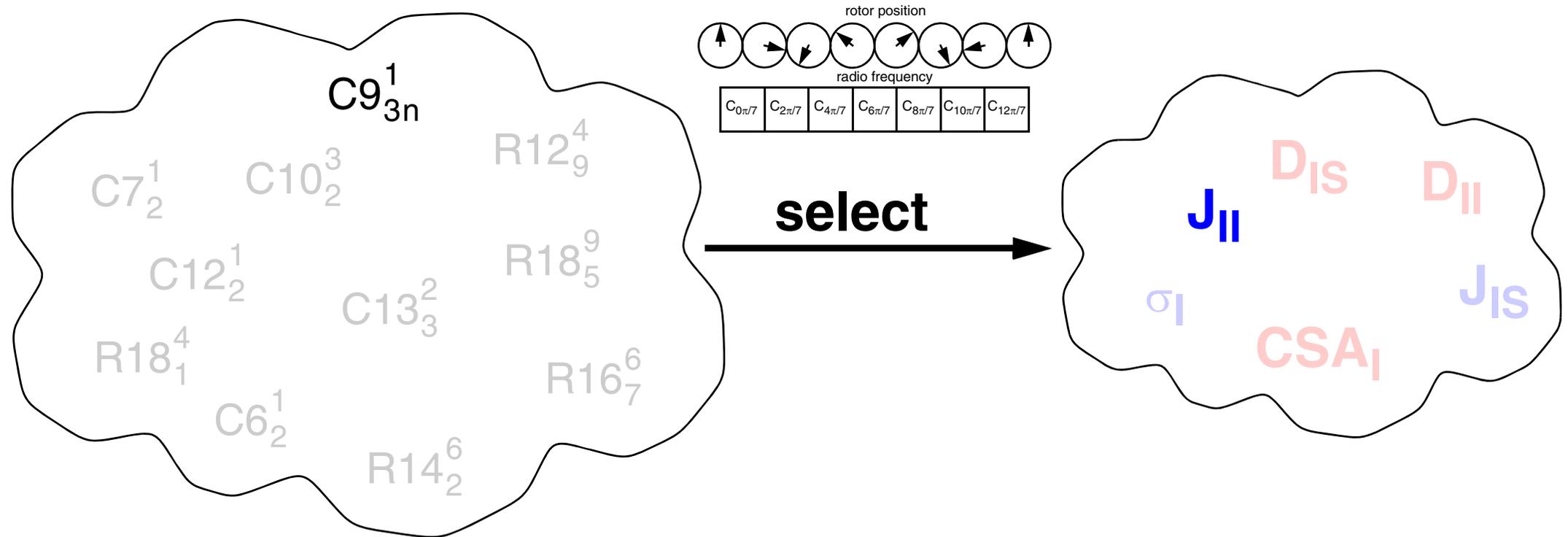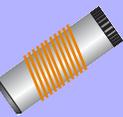
❏ Rotor-synchronized R and C sequences allow us to select certain components of spin interactions.

❏ Analysis is based on a symmetry-driven version of average Hamiltonian theory.

❏ Very powerful tool for tailoring the effective Hamiltonian under MAS.

❏ Malcolm H. Levitt "Symmetry-Based Pulse Sequences in Magic-Angle Spinning Solid-State NMR", Encyclopedia of Nuclear Magnetic Resonance, Volume 9, 165-196 (2002).
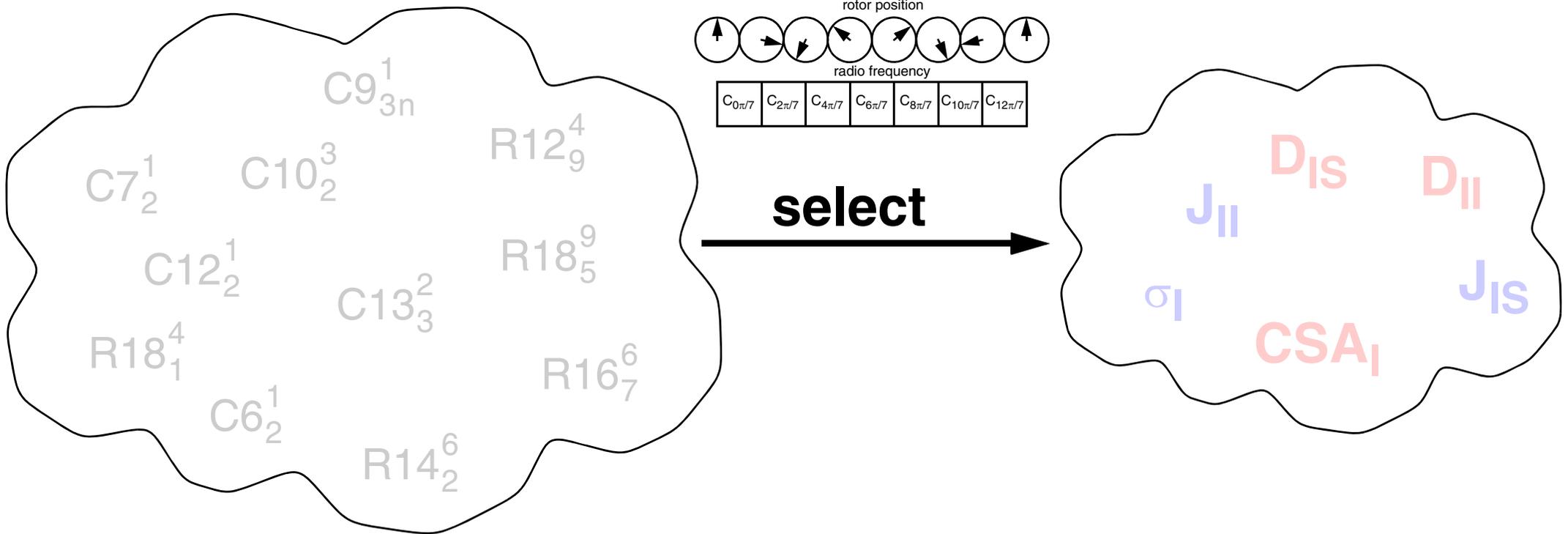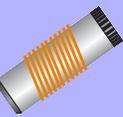
Rotor-Synchronized Sequences

$$C9_{3n}^1$$

$C7_2^1$ $C10_2^3$ $R12_9^4$

$C12_2^1$ $R18_5^9$

$C13_3^2$

$R18_1^4$

$R16_7^6$

$C6_2^1$

$R14_2^6$

rotor position

radio frequency

$C_{0\pi/7}$ $C_{2\pi/7}$ $C_{4\pi/7}$ $C_{6\pi/7}$ $C_{8\pi/7}$ $C_{10\pi/7}$ $C_{12\pi/7}$

select

D_{IS} D_{II}

J_{II}

σ_I J_{IS}

CSA_I

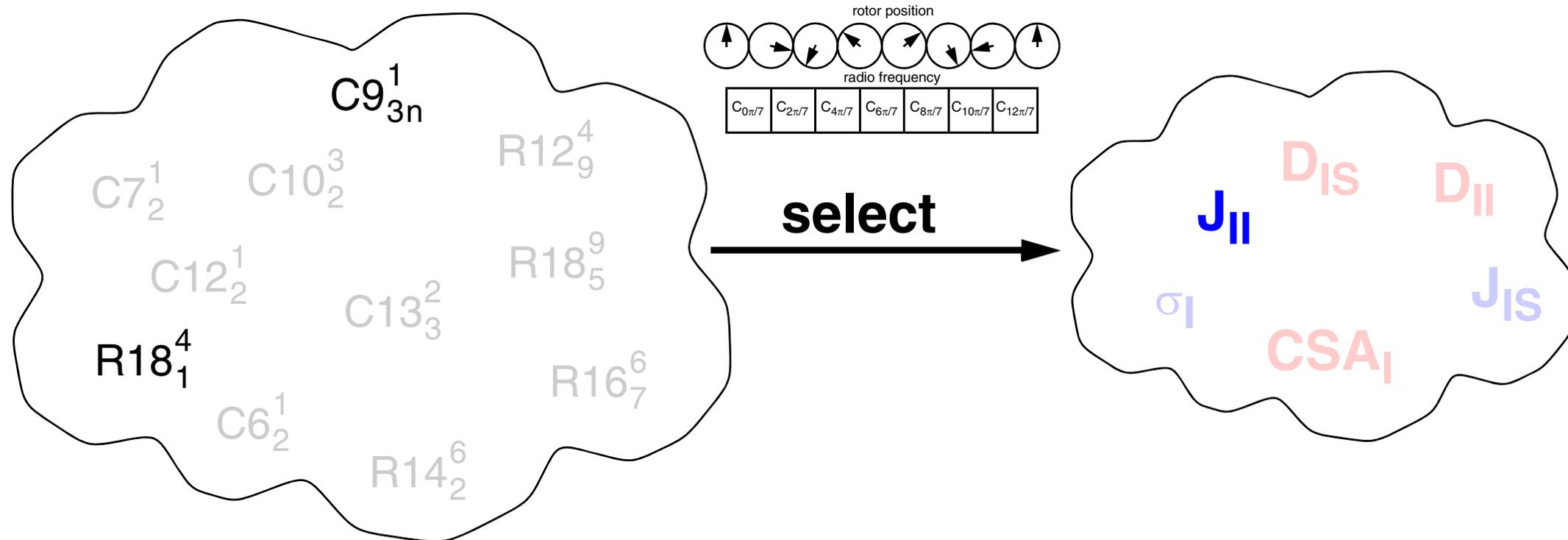❏ Rotor-synchronized R and C sequences allow us to select certain components of spin inter-actions.

❏ Analysis is based on a symmetry-driven version of average Hamiltonian theory.

❏ Very powerful tool for tailoring the effective Hamiltonian under MAS.

❏ Malcolm H. Levitt "Symmetry-Based Pulse Sequences in Magic-Angle Spinning Solid-State NMR", Encyclopedia of Nuclear Magnetic Resonance, Volume 9, 165-196 (2002).
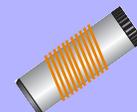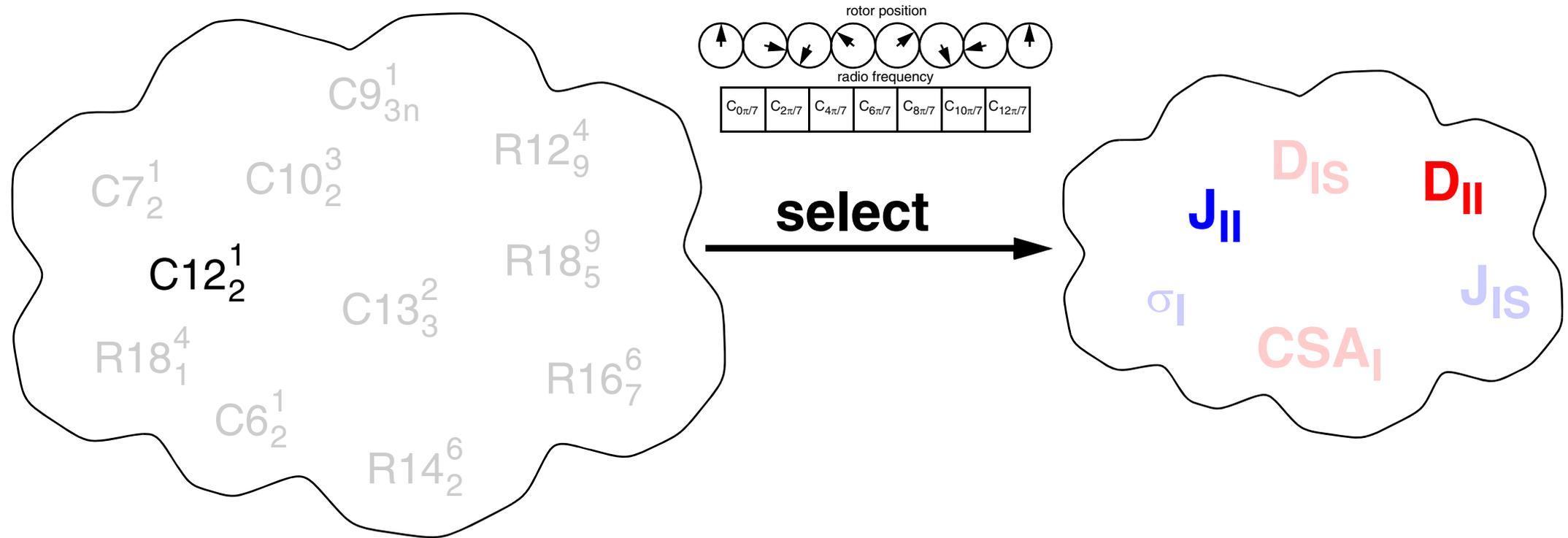
❏ Ideal case of eliminating all interactions (time suspension) does not exist.

Decoupling Using Rotor-Synchronized Sequences
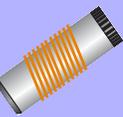
$C9_{3n}^1$

$C7_2^1$ $C10_2^3$ $R12_9^4$

$C12_2^1$ $R18_5^9$

$C13_3^2$

$R18_1^4$

$R16_7^6$

$C6_2^1$

$R14_2^6$

rotor position

radio frequency

$C_{0\pi/7}$	$C_{2\pi/7}$	$C_{4\pi/7}$	$C_{6\pi/7}$	$C_{8\pi/7}$	$C_{10\pi/7}$	$C_{12\pi/7}$

select

D_{IS} D_{II}

J_{II}

J_{IS}

σ_I

CSA_I

❏ Ideal case of eliminating all interactions (time suspension) does not exist.

❏ Isotropic homonuclear J_{II} coupling cannot be eliminated unless selective pulses are used.
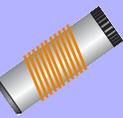
❏ Ideal case of eliminating all interactions (time suspension) does not exist.

❏ Isotropic homonuclear J_{II} coupling cannot be eliminated unless selective pulses are used.

❏ Recoupling the homonuclear dipolar coupling can have advantages for heteronuclear decoupling.

❏ $C12_2^{-1}$ performs quite well and gives comparable line widths to other decoupling sequences.

❏ RF-field requirement $\omega_1 = 6\omega_r$ dictates B_1-field strength for given MAS frequency.

❏ Synchronization is not a "strict" requirement: in the range of 120-145 kHz one obtains 90% of the maximum intensity.
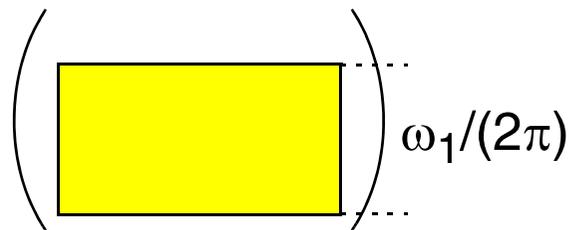
❏ Effective flip angle of 2π is very critical.
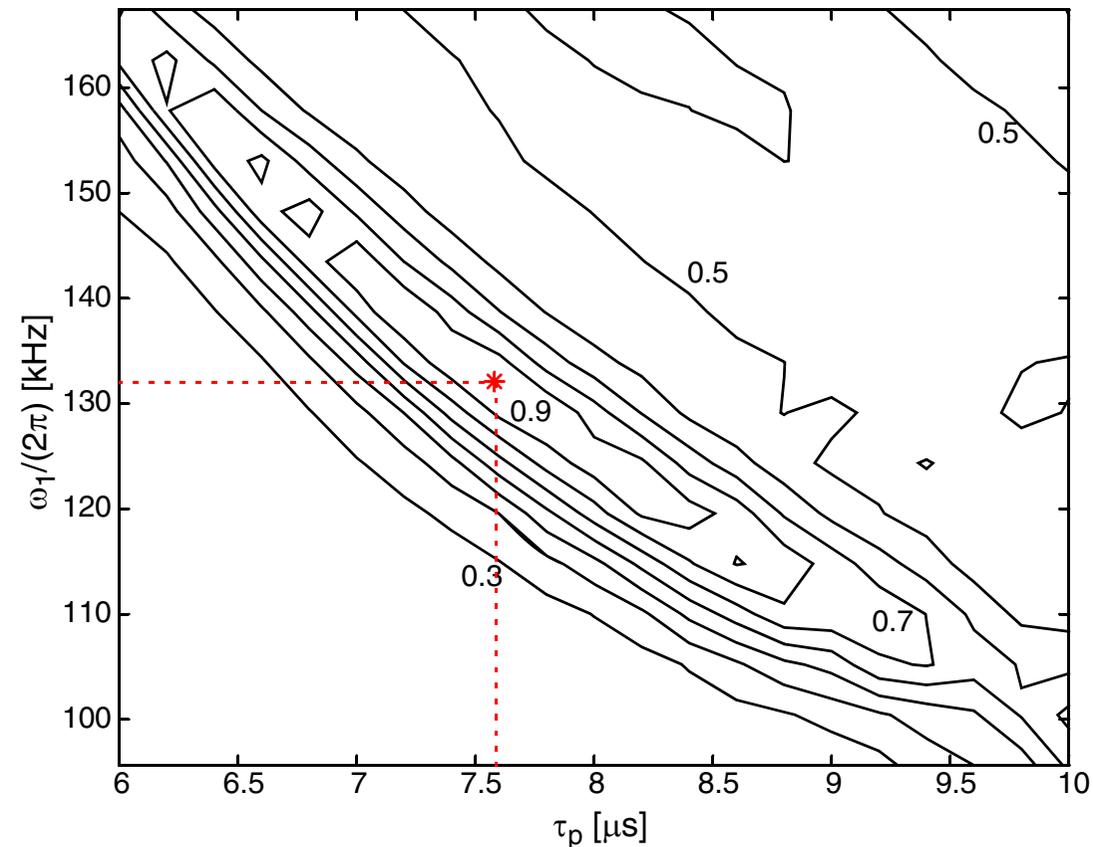
❏ Experimental line height of CH_2 group in sodium propionate.

❏ $\omega_r/(2\pi) = 22$ kHz, $\omega_1/(2\pi) = 132$ kHz, $\tau_p = 7.57$ µs. C = $(2\pi)_\phi$, $\Delta\phi = $ -30°, $B_0 = 9.4$ T.
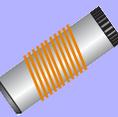
❏ Rotor synchronization of the pulse sequence is not always desirable.

CW

$\omega_1/(2\pi)$

$\omega_r, \ \omega_1$

TPPM

$+\phi$ $-\phi$

$\omega_1/(2\pi)$

τ_p n

$2\pi/\omega_m$

$\omega_r, \ \omega_m, \ \omega_\alpha$

XiX

0 π

$\omega_1/(2\pi)$

τ_p n

$2\pi/\omega_m$
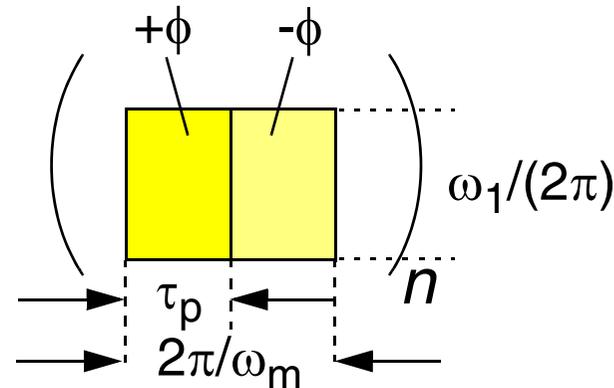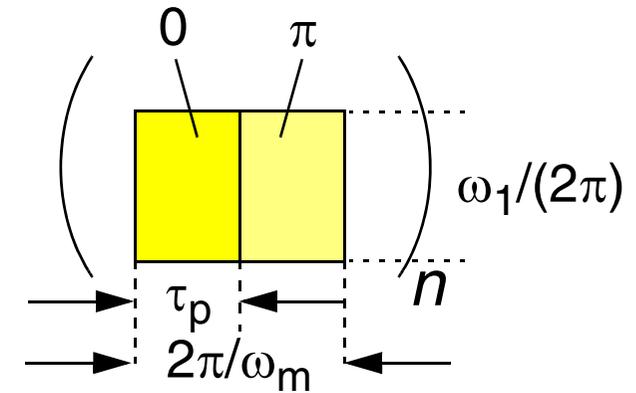
$\omega_r, \ \omega_m$

❏ There are many modifications of the TPPM sequence:

- frequency-modulated and phase-modulated (FMPM)

- 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 (SW_f-TPPM)

❏ Two pulses with 180° phase shift.

❏ Pulse duration is important not flip angle.

❏ Insensitive to rf-field inhomo-geneities.

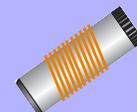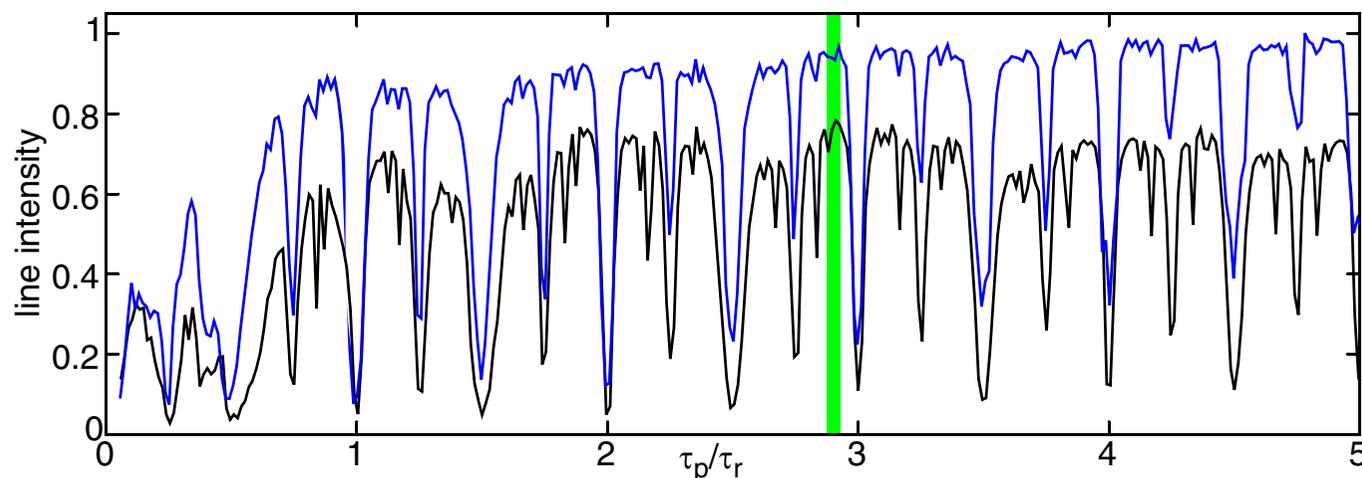❏ Optimum performance around $\tau_p \approx 2.85\tau_r$ and $\tau_p \approx 1.85\tau_r$.

❏ Performance minima at $\tau_p = n\tau_r/4$ (C2$_n^0$ recoupling sequence).

❏ Sample: [d9]-trimethyl-^{15}N-ammonium chloride, $\omega_r/(2\pi) = 30$ kHz, $\omega_1/(2\pi) = 100$ kHz (black), $\omega_1/(2\pi) = 150$ kHz (blue).
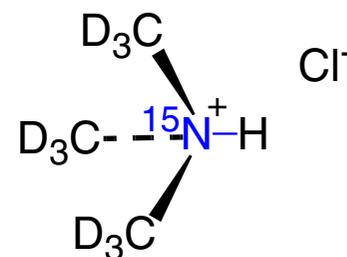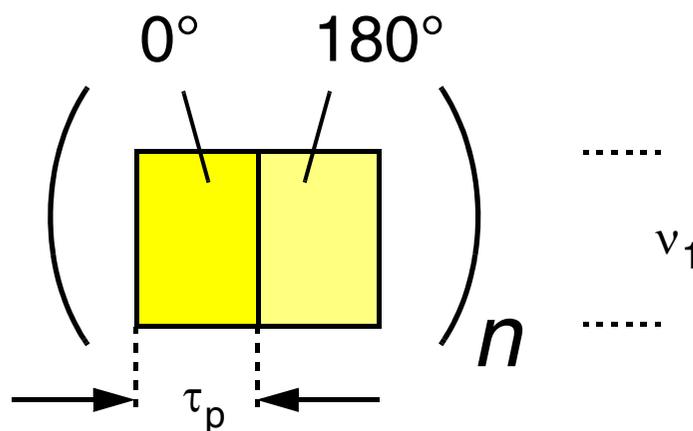
Theory of XiX Decoupling Under MAS
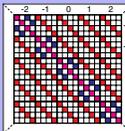
- Analytical interaction-frame transformation with RF:

$$U(t) = \exp\left(-i\beta(t)\sum_{m=1}^{N}I_{mz}\right)$$

$$I_{mx} \rightarrow I_{mx}\cos(\beta(t)) + I_{my}\sin(\beta(t))$$

$$I_{my} \rightarrow I_{my}\cos(\beta(t)) - I_{mx}\sin(\beta(t))$$

- Flip-angle is time dependent: $\beta(t) = \dfrac{\omega_1}{\omega_m}\left[\dfrac{\pi}{2} - \dfrac{4}{\pi}\sum_{k=0}^{\infty}\dfrac{1}{(2k+1)^2}\cos((2k+1)\omega_m t)\right]$

- We find integer multiples of the modulation frequency ω_m in the interaction frame:

interaction-frame representation

$\cos(\beta(t))$
$\sin(\beta(t))$
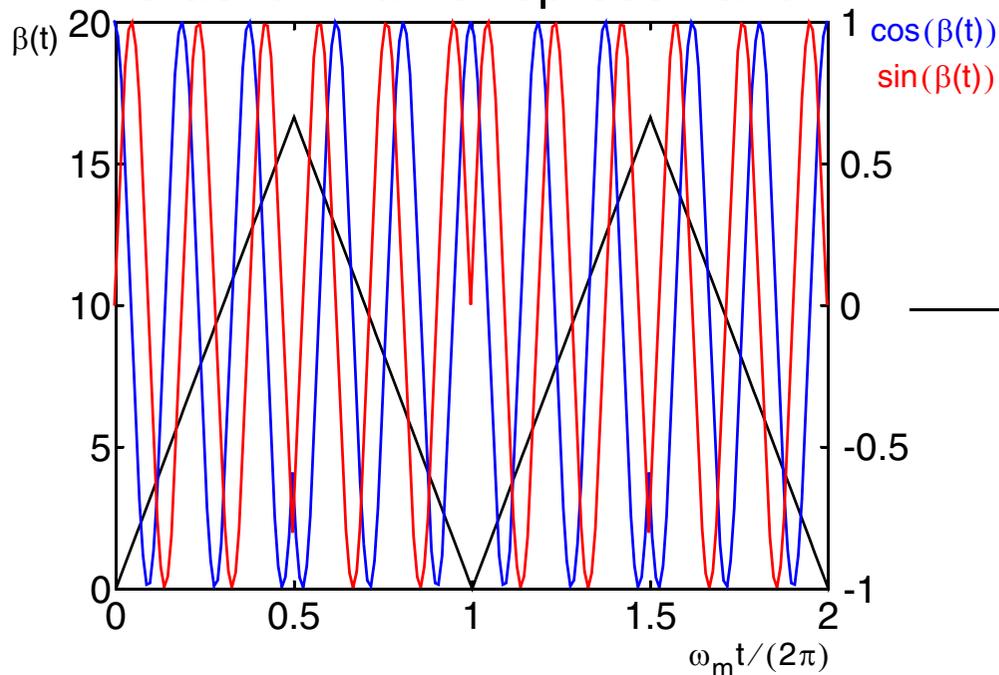
FT

Fourier coefficients

- We will find resonances between $\omega_m = \pi/\tau_p$ and ω_r.

XiX Decoupling Under MAS

❏ **Residual coupling** is given by a cross term between the homonuclear and the heteronuclear dipolar couplings.

$$\overline{\overline{\mathcal{H}}} \approx \tilde{\mathcal{H}}_{(2)}^{(0,0)} \approx -\frac{3}{8} \sum_{\nu,\kappa} \sum_{\ell \neq m} i \frac{\omega_{SI_\ell}^{(\nu)} \omega_{I_\ell I_m}^{(-\nu)} - \omega_{SI_\ell}^{(-\nu)} \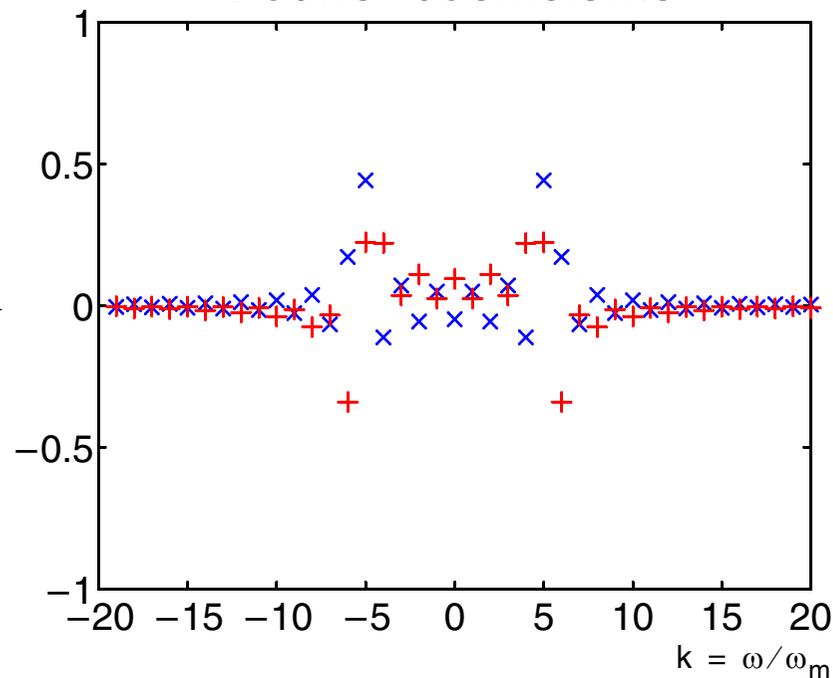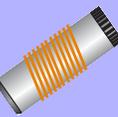omega_{I_\ell I_m}^{(\nu)}}{\nu \omega_r + \kappa \omega_m} (a_{\kappa,x} b_{\kappa,x} + a_{\kappa,y} b_{\kappa,y}) 4 S_z I_{\ell z} I_{my}$$

❏ **Resonance conditions**: first-order resonance conditions at $n_0 = \pm 1, \pm 2$.

❏ $\tau_p / \tau_r = -k_0 / 2$ (half rotor cycle) and $\tau_p / \tau_r = -k_0 / 4$ (quarter rotor cycle)

❏ First-order resonance conditions are very strong and rf-field and spinning frequency independent.

❏ Recouples heteronuclear dipolar couplings. Strength of recoupling depends on the Fourier coefficients a_k.

$$\tau_p / \tau_r = -k_0 / (2\, n_0)$$

$$\overline{\overline{\mathcal{H}}} = \tilde{\mathcal{H}}^{(n_0, k_0)} + \tilde{\mathcal{H}}^{(-n_0, -k_0)} = 2 \sum_\ell \mathrm{Re}\left(\omega_{SI_\ell}^{(n_0)} \right) (a_{k_0, x} 2 S_z I_{\ell x} + a_{k_0, y} 2 S_z I_{\ell y})$$

XiX Decoupling Under MAS

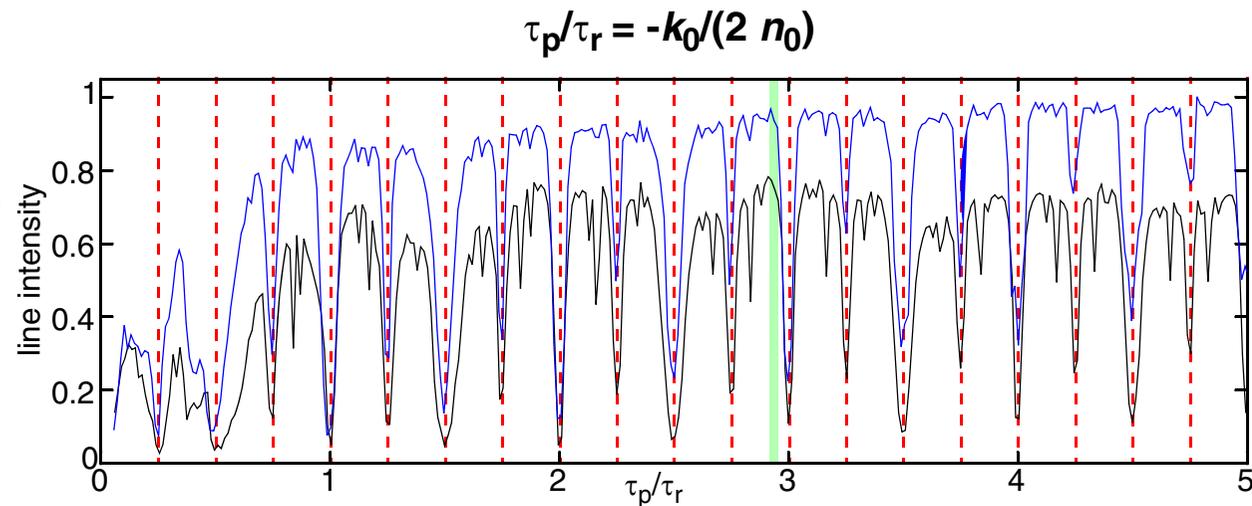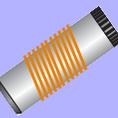❑ **Residual coupling** is given by a cross term between the homonuclear and the heteronuclear dipolar couplings.

$$\overline{\mathscr{H}} \approx \tilde{\mathscr{H}}_{(2)}^{(0,0)} \approx -\frac{3}{8}\sum_{\nu,\kappa}\sum_{\ell\neq m} i\frac{\omega_{SI_\ell}^{(\nu)}\omega_{I_\ell I_m}^{(-\nu)} - \omega_{SI_\ell}^{(-\nu)}\omega_{I_\ell I_m}^{(\nu)}}{\nu\omega_r + \kappa\omega_m}(a_{\kappa,x}b_{\kappa,x} + a_{\kappa,y}b_{\kappa,y})4S_z I_{\ell z}I_{my}$$

❑ **Resonance conditions**: second-order resonance conditions at $n_0 = \pm1, \pm2, \pm3, \pm4$.

❑ $\tau_p/\tau_r = -k_0/6$ (one sixth rotor cycle) and $\tau_p/\tau_r = -k_0/8$ (one eights rotor cycle)

❑ Second-order resonance conditions decrease with increasing MAS frequency and increasing rf-field amplitude.

❑ Cross terms between I-spin CSA tensors and heteronuclear dipolar couplings leads to a second-order coupling term.

$$\tau_p/\tau_r = -k_0/(2\,n_0)$$

$$\overline{\mathscr{H}} \approx \tilde{\mathscr{H}}_{(2)}^{(n_0,k_0)} + \tilde{\mathscr{H}}_{(2)}^{(-n_0,-k_0)}$$

$$\approx 2\sum_\ell \text{Im}\left(\omega_{SI_\ell}^{(+2)}\omega_{I_\ell}^{(+2)}\right)\sum_\kappa \frac{(a_{k_0-\kappa,x}a_{\kappa,y} - a_{\kappa,x}a_{k_0-\kappa,y})}{2\omega_r + \kappa\omega_m}2S_z I_{\ell z}$$

XiX Decoupling Under MAS

❏ Residual coupling is given by a cross term between the homonuclear and the heteronuclear dipolar couplings.
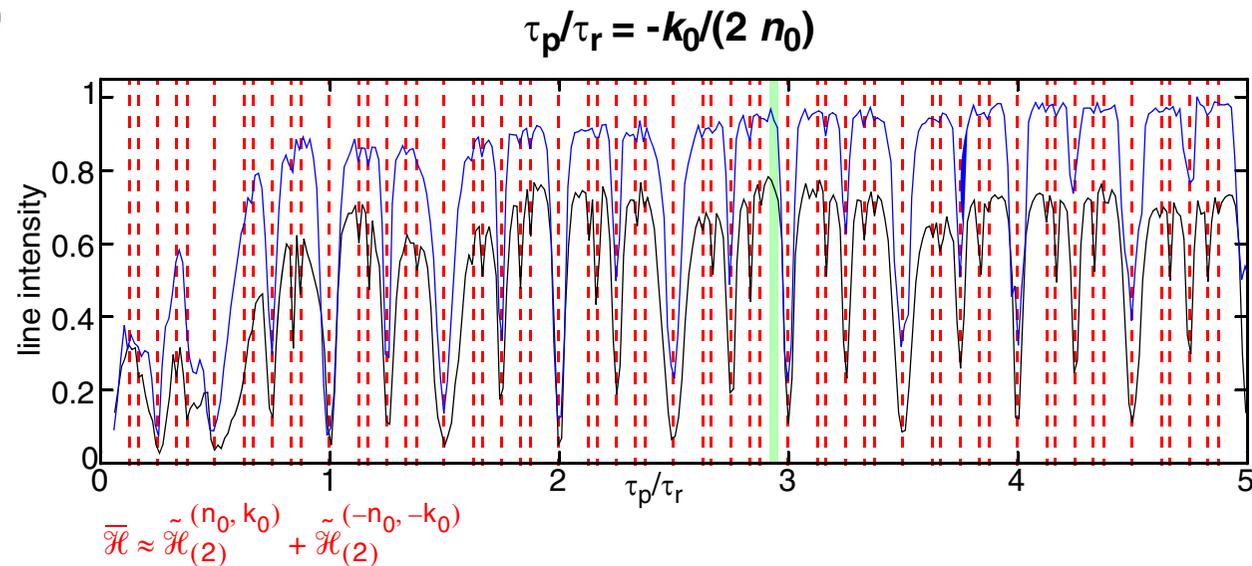
$$\overline{\overline{\mathcal{H}}} \approx \tilde{\mathcal{H}}^{(0,0)}_{(2)} \approx -\frac{3}{8}\sum_{\nu,\kappa}\sum_{\ell \neq m} i\frac{\omega^{(\nu)}_{SI_\ell}\omega^{(-\nu)}_{I_\ell I_m} - \omega^{(-\nu)}_{SI_\ell}\omega^{(\nu)}_{I_\ell I_m}}{\nu\omega_r + \kappa\omega_m}(a_{\kappa,x}b_{\kappa,x} + a_{\kappa,y}b_{\kappa,y})4S_z I_{\ell z}I_{my}$$

❏ Resonance conditions: first-order ($n_0 = \pm1, \pm2$) and second-order resonances at $n_0 = \pm3, \pm4$.

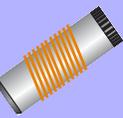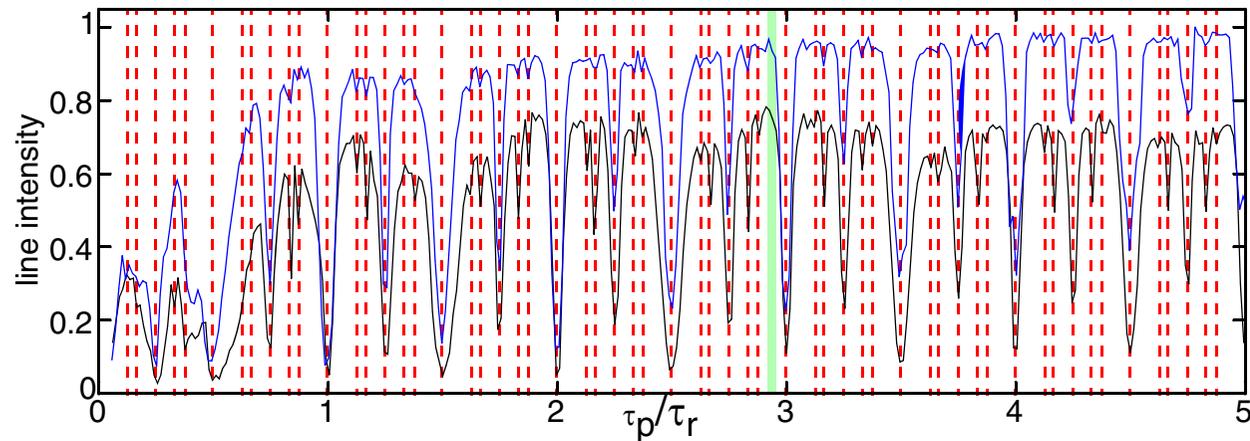❏ First-order resonance conditions are very strong and rf-field and spinning frequency independent.

❏ Second-order resonance conditions decrease with increasing MAS frequency and increasing rf-field amplitude.

❏ I-spin spin diffusion is present everywhere as a second-order contribution and scales with $1/\omega_r$.
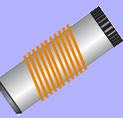
$$\tau_p/\tau_r = -k_0/(2\ n_0)$$


$$\overline{\overline{\mathcal{H}}} \approx \tilde{\mathcal{H}}^{(0,0)}_{(2)}$$

$$\approx -\frac{9}{32}\sum_{\nu,\kappa}\sum_{\ell \neq m < p}\frac{\left(\omega^{(\nu)}_{I_\ell I_m}\omega^{(-\nu)}_{I_\ell I_p} - \omega^{(-\nu)}_{I_\ell I_m}\omega^{(\nu)}_{I_\ell I_p}\right)}{\nu\omega_r + \kappa\omega_m}(b^2_{\kappa,x} + b^2_{\kappa,y})2I_{\ell z}(I^+_m I^-_p - I^-_m I^+_p)$$

❏ XiX decoupling is a sequence that gives a very small residual couplings for fast MAS and high rf-field amplitudes: CH$_2$ group $\tau_p/\tau_r = 2.85$, $\omega_r/(2\pi) = 30$ kHz, $\omega_1/(2\pi) = 150$.

❏ Resonance conditions at $\tau_p/\tau_r = -k_0/z$ with z = 2, 4, 6, and 8 have to be avoided. The proximity to resonance conditions and the strength of these resonance conditions limits the achievable line width in XiX decoupling.

❏ I-spin spin diffusion is present but does not play a major role due to the small magnitude of the residual couplings.

❏ XiX decoupling works best for high MAS frequencies ($\omega_r/(2\pi) > 25$ kHz) and large ratios of ω_1/ω_r. A good starting point for the local optimization is $\tau_p/\tau_r = 2.85$.
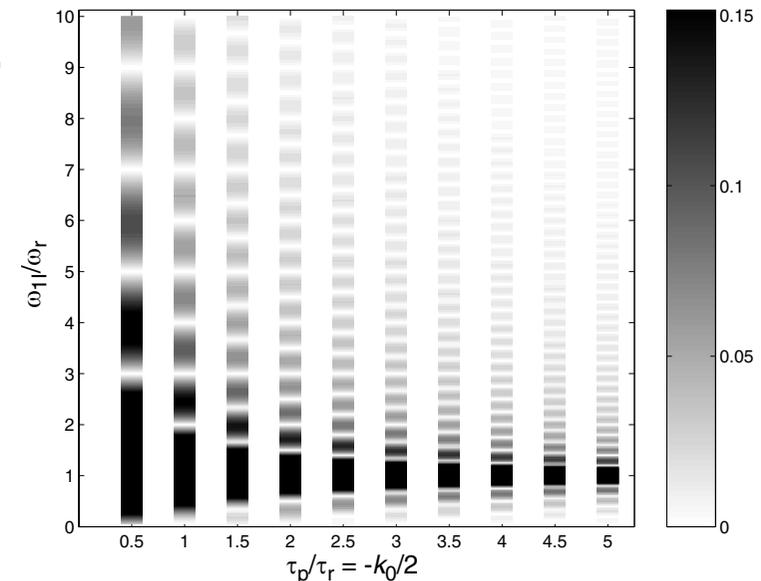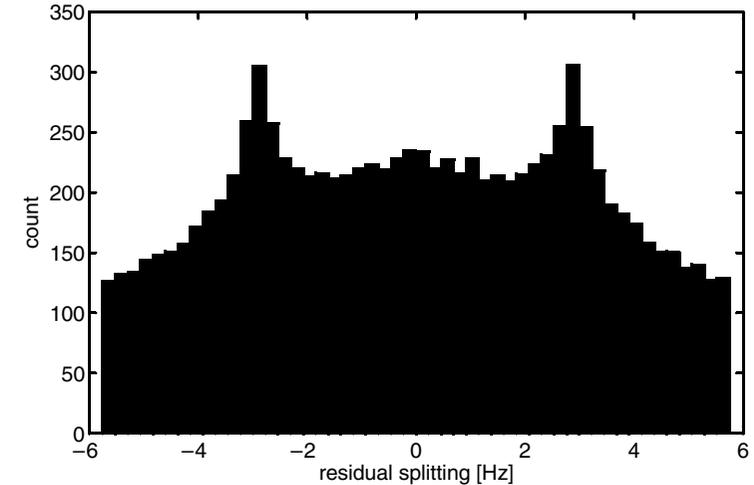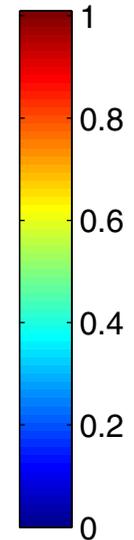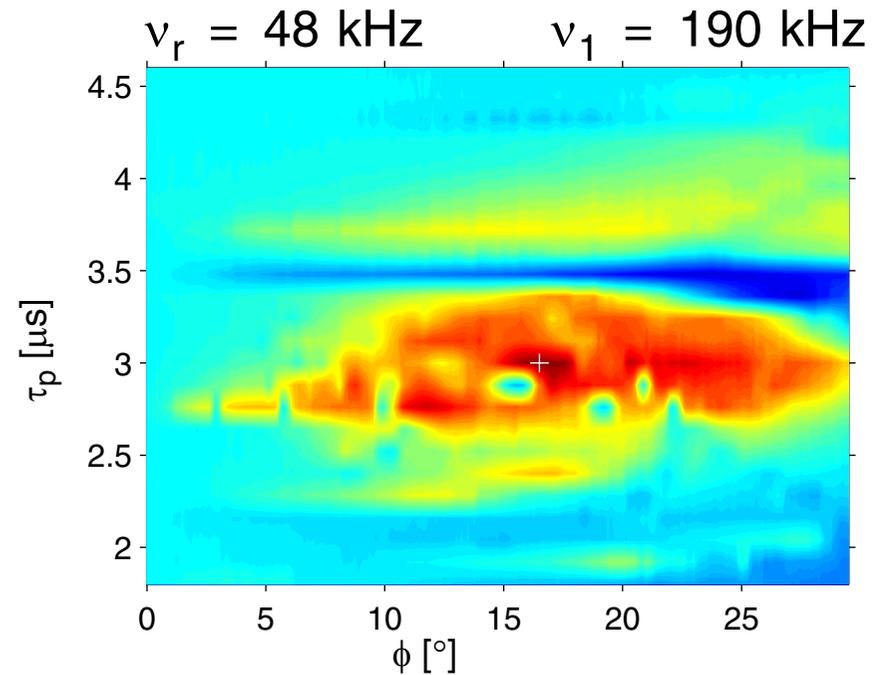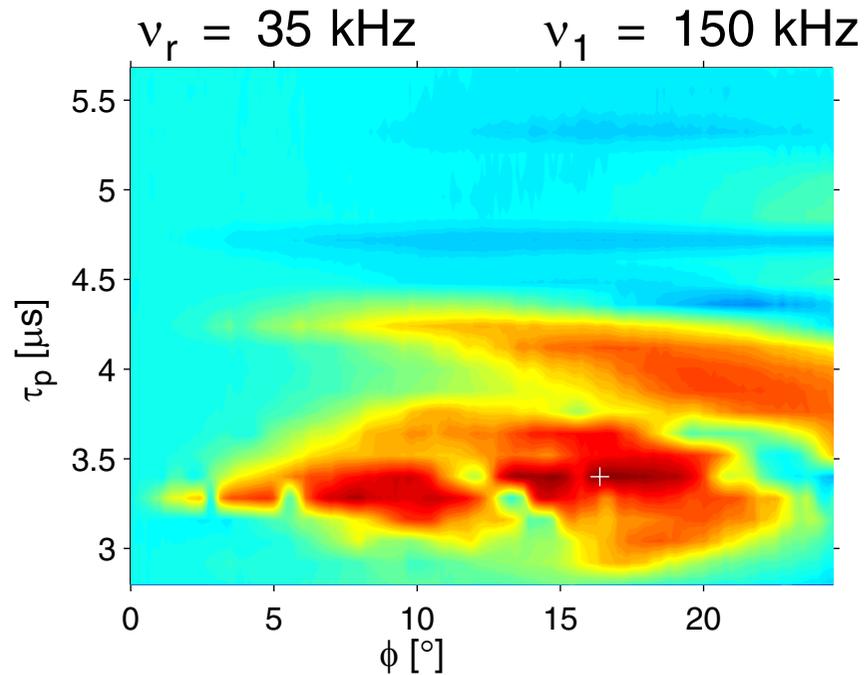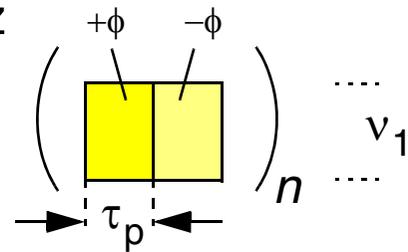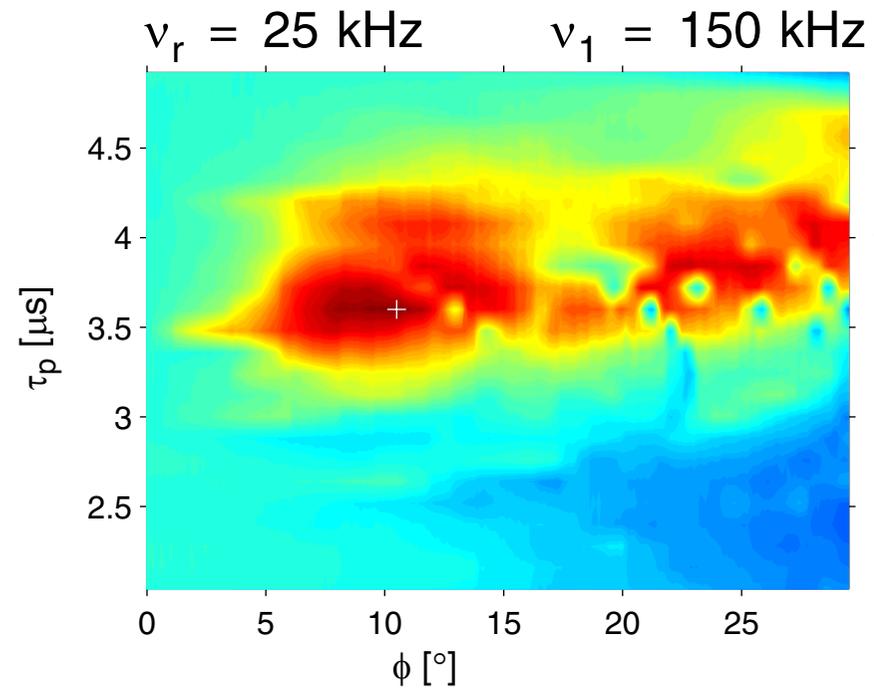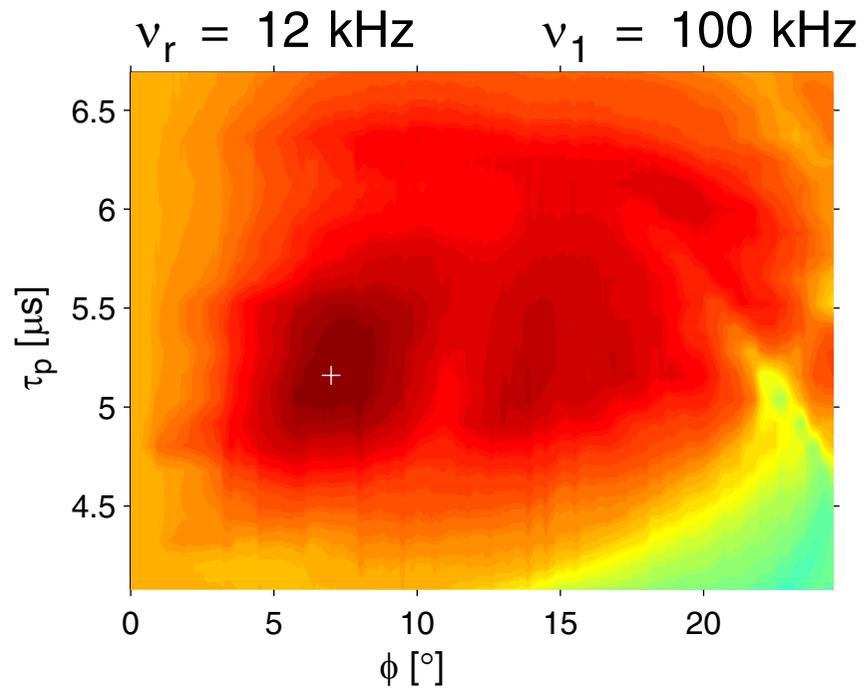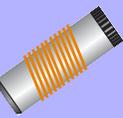
TPPM Decoupling Under MAS
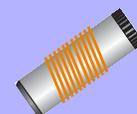
❏ TPPM consists of two pulses with a phase shift of 2ϕ.

❏ TPPM decoupling works well over a large range of spinning frequencies and rf-field amplitudes.

$\dfrac{\nu_1}{\text{kHz}}$	$\dfrac{\nu_r}{\text{kHz}}$	$\dfrac{\tau_p^{(\text{max})}}{\mu s}$	$\dfrac{\phi^{(\text{max})}}{^\circ}$	$\dfrac{\tau_p^{(\text{max})}}{\tau_\pi}$	$\dfrac{I(\tau_p^{(\text{max})}, \phi^{(\text{max})})}{I(\text{cw})}$
100	12	5.2	7.0	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	3.0	16.5	1.14	2.6
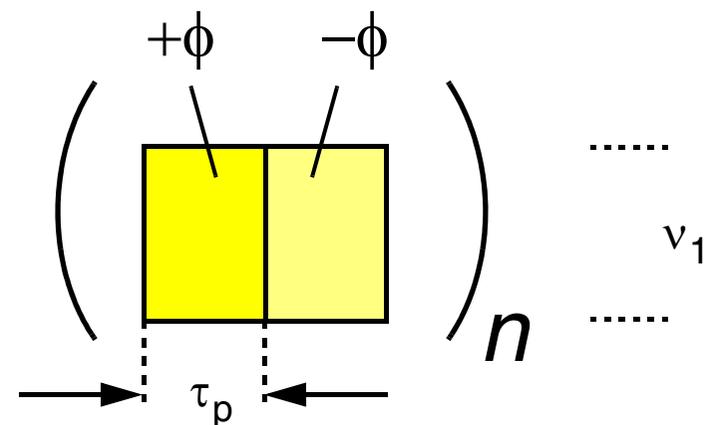
❏ Optimum phase angle changes significantly with experimental parameters.

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

❏ Improvement over cw decoupling increases with increasing spinning frequency.
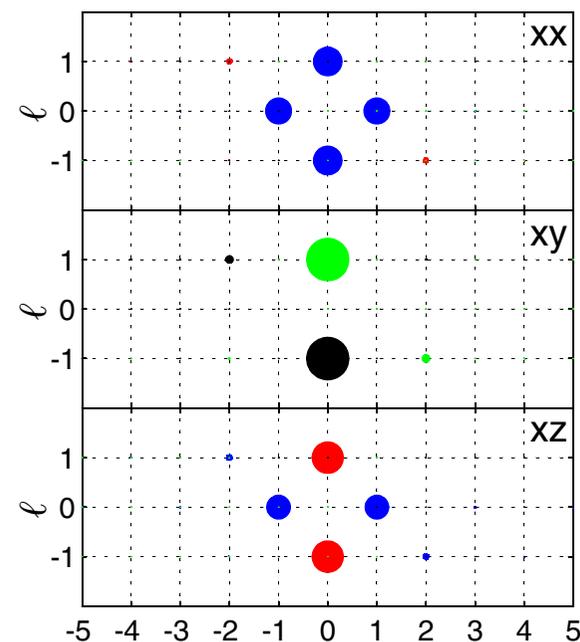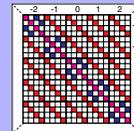
❑ There is no analytical interaction-frame transformation with the RF.

$$U(t) = \hat{T}\exp\left(-i\int_0^t \mathscr{H}_{rf}(t_1)dt_1\right)$$

$$I_{mx} \rightarrow I_{mx}f_{xx}(t) + I_{my}f_{xy}(t) + I_{mz}f_{xz}(t)$$

❑ One finds two frequencies $\omega_m = \pi/\tau_p$ and $\omega_\alpha = \frac{\alpha}{\pi}\omega_m$ with $\alpha = \mathrm{acos}(\cos\beta\cos^2\phi_0 + \sin^2\phi_0)$. Fourier coefficients can only be calculated numerically.

❑ Interaction-frame Hamiltonian has now three time dependencies

$$\tilde{\mathscr{H}}(t) = \sum_{n=-2}^{2}\sum_{k,\ell}\tilde{\mathscr{H}}^{(n,k,\ell)}e^{ik\omega_m t}e^{in\omega_r t}e^{i\ell\omega_\alpha t}$$
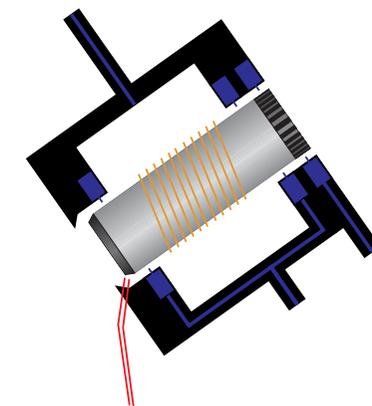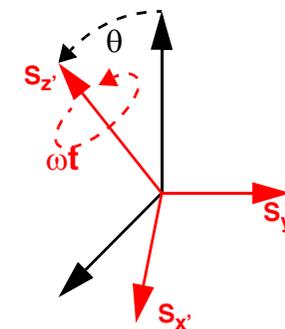
interaction frame

$$\overline{\mathscr{H}} = \sum_{n_0,k_0}\tilde{\mathscr{H}}^{(n_0,k_0,\ell_0)} - \sum_{n_0,k_0}\frac{1}{2}\sum_{\nu,\kappa}\frac{\left[\tilde{\mathscr{H}}^{(n_0-\nu,k_0-\kappa,\ell_0-\lambda)},\tilde{\mathscr{H}}^{(\nu,\kappa,\lambda)}\right]}{\nu\omega_r + \kappa\omega_m + \lambda\omega_\alpha} + \dots$$

❑ Triple-mode Floquet description is required.
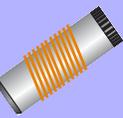
❏ Residual coupling is given by a cross term between the I-spin CSA tensor and the heteronuclear dipolar couplings.

$$\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(0,\,0)} \approx i\sum_p \sum_{\nu=-2}^{2} (\omega_{I_pS}^{(-\nu)}\omega_{I_p}^{(\nu)} + \omega_{I_pS}^{(\nu)}\omega_{I_p}^{(-\nu)})(q_{xx}^{(\nu)}I_{px}S_z + q_{xy}^{(\nu)}I_{py}S_z + q_{xz}^{(\nu)}I_{pz}S_z)$$

❏ Residual coupling has four parts which cannot be zeroed all simultaneously. The $q_{xy}^{(n)}$ component is always zero.

❏ The magnitude of the residual coupling depends on the relative orientation of the two tensors.

❏ The smallest residual couplings are found near a pulse length of a π pulse and for a phase angle between 5° and 20°.

❏ Residual coupling is given by a cross term between the I-spin CSA tensor and the heteronuclear dipolar couplings.

$$\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(0,0)} \approx i \sum_{p} \sum_{\nu=-2}^{2} (\omega_{I_pS}^{(-\nu)}\omega_{I_p}^{(\nu)} + \omega_{I_pS}^{(\nu)}\omega_{I_p}^{(-\nu)})(q_{xx}^{(\nu)}I_{px}S_z + q_{xy}^{(\nu)}I_{py}S_z + q_{xz}^{(\nu)}I_{pz}S_z)$$
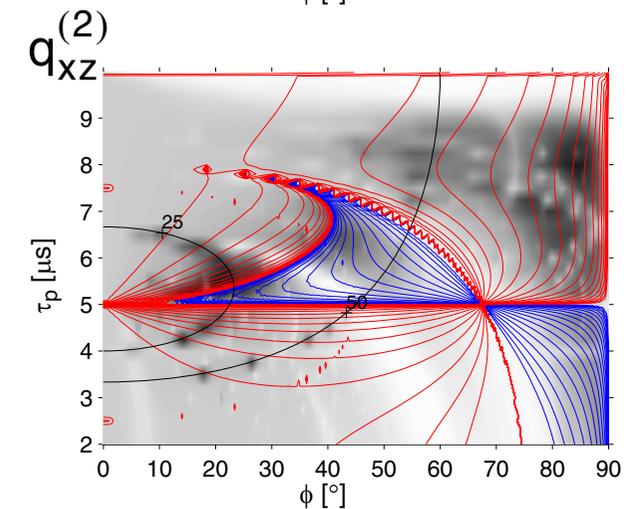
❏ Resonance conditions:

- $n_0\omega_r = \omega_m$ (straight lines in a)

- $n_0\omega_r = \omega_\alpha$ (curved lines in a)

❏ The heteronuclear dipolar coupling is recoupled in first order ($n_0 = 1,2$) or second order ($n_0 = 3,4$).

❏ These resonance conditions lead to a broadening of the lines and are detrimental to the decoupling.
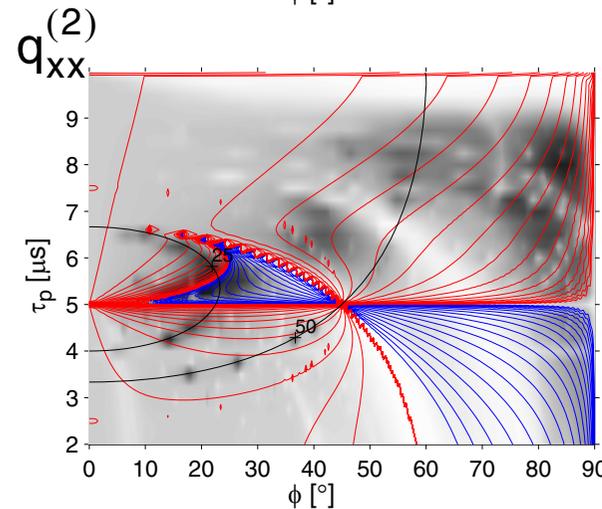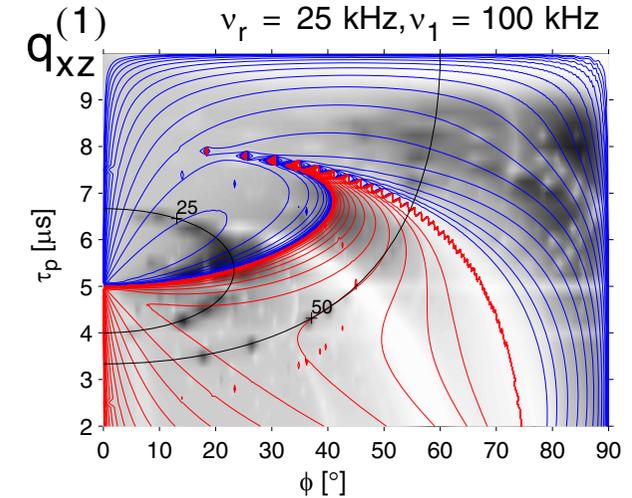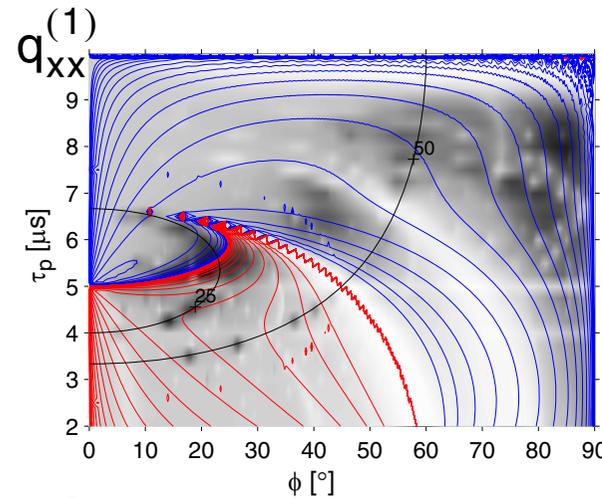
TPPM Decoupling Under MAS
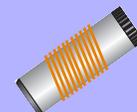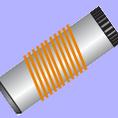
❏ **Residual coupling** is given by a cross term between the **I**-spin CSA tensor and the heteronuclear dipolar couplings.

$$\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(0,\,0)} \approx i\sum_{p}\sum_{\nu=-2}^{2}(\omega_{I_pS}^{(-\nu)}\omega_{I_p}^{(\nu)} + \omega_{I_pS}^{(\nu)}\omega_{I_p}^{(-\nu)})(q_{xx}^{(\nu)}I_{px}S_z + q_{xy}^{(\nu)}I_{py}S_z + q_{xz}^{(\nu)}I_{pz}S_z)$$

❏ **Resonance conditions**:

- $n_0\omega_r = \pm\omega_m \mp \omega_\alpha$ (b).

❏ This is a purely homonuclear recoupling condition because the $a_{x\mu}^{(\pm1,\,\mp1)}$ Fourier coefficients are always zero.

❏ The magnitude of the homonuclear terms determines the observed line width in connection with the residual coupling.

$\nu_r = 25$ kHz, $\nu_1 = 100$ kHz

❑ **Residual coupling** is given by a cross term between the **I**-spin CSA tensor and the heteronuclear dipolar couplings.

$$\overline{\mathcal{H}} \approx \tilde{\mathcal{H}}_{(2)}^{(0,\,0)} \approx i \sum_{p} \sum_{\nu\,=\,-2}^{2} (\omega_{I_pS}^{(-\nu)}\omega_{I_p}^{(\nu)} + \omega_{I_pS}^{(\nu)}\omega_{I_p}^{(-\nu)})(q_{xx}^{(\nu)}I_{px}S_z + q_{xy}^{(\nu)}I_{py}S_z + q_{xz}^{(\nu)}I_{pz}S_z)$$
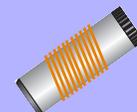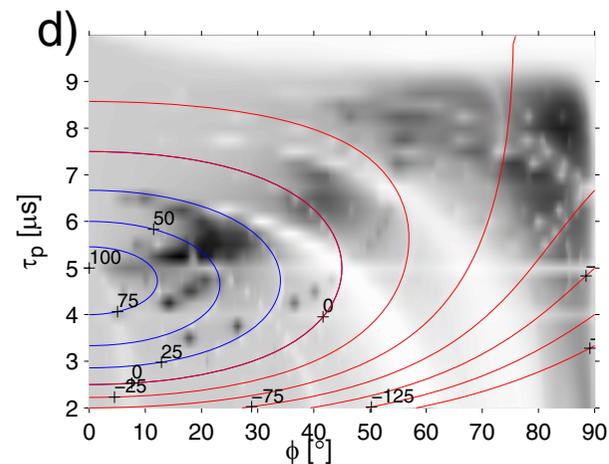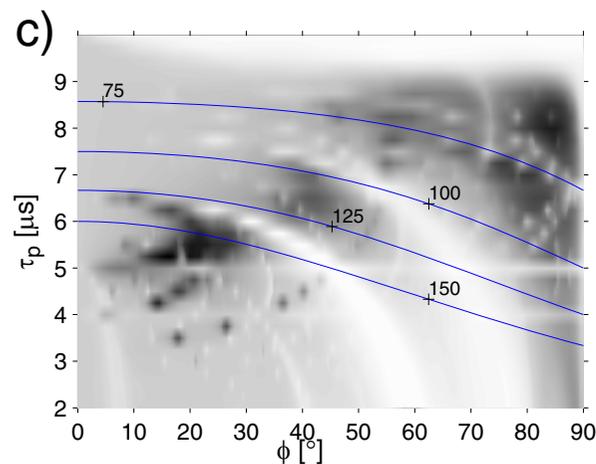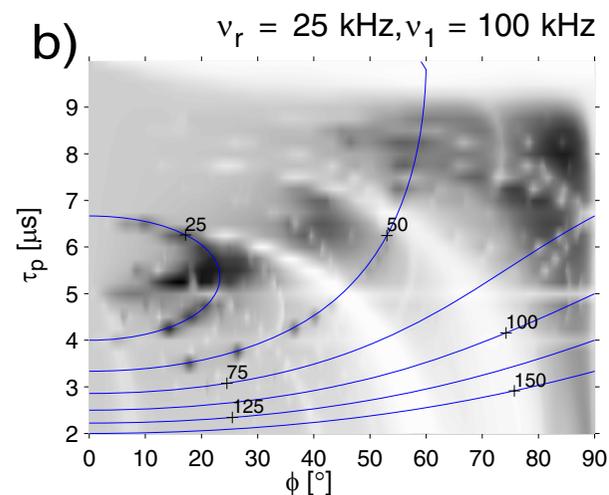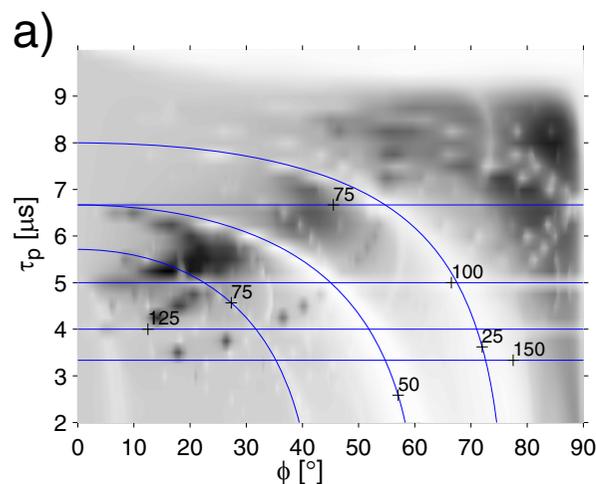
❑ **Resonance conditions**:

- $n_0\omega_r = \pm\omega_m\pm\omega_\alpha$ (c)

- $n_0\omega_r = \pm\omega_m\mp2\omega_\alpha$ (d)

❑ The heteronuclear dipolar coupling is recoupled in second order ($n_0 = 1,2,3,4$).

❑ These recoupling conditions are weaker than the first-order ones.
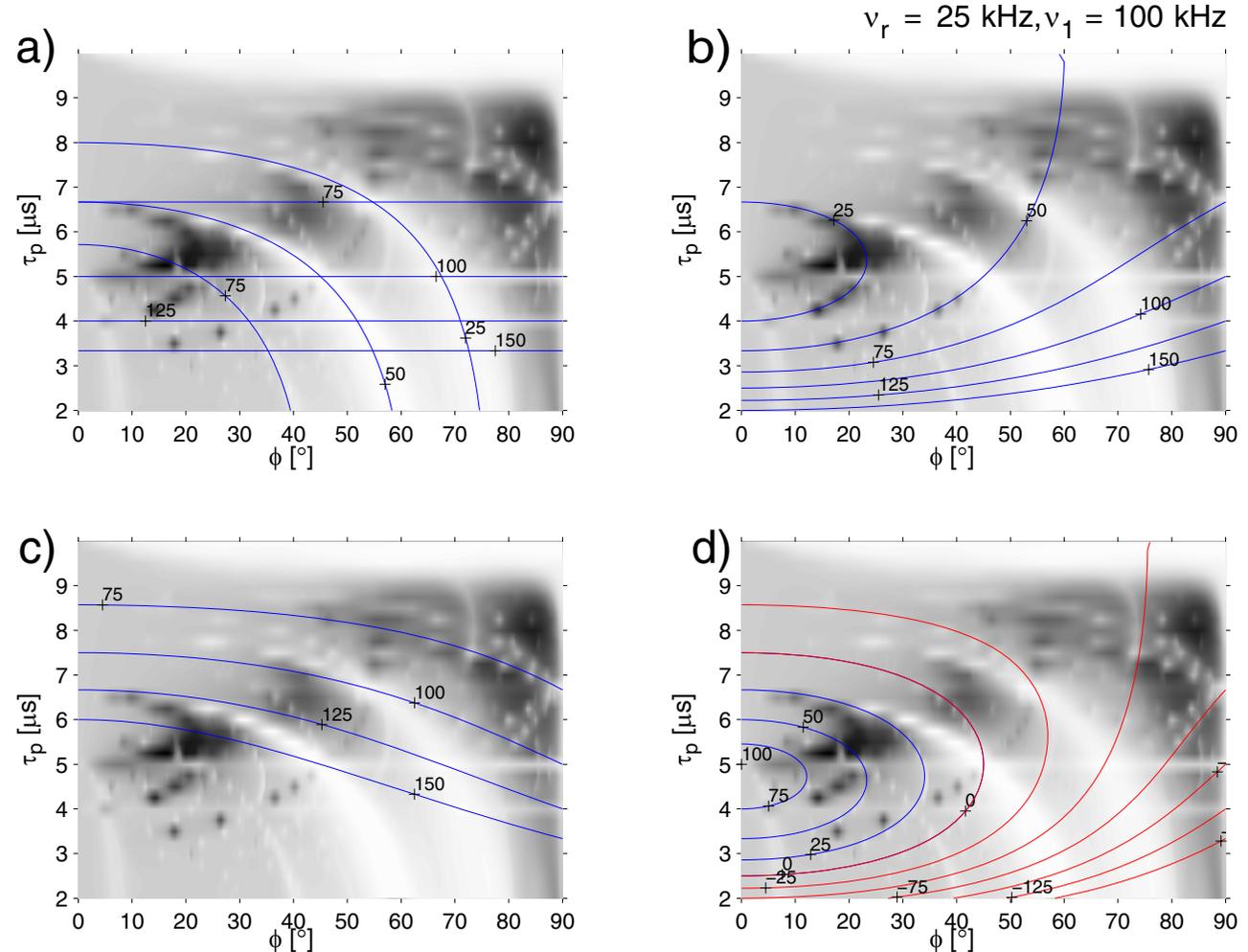
TPPM Decoupling Under MAS
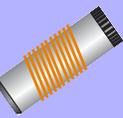
❏ TPPM decoupling is a sequence that has small residual couplings that come from cross term between I-spin CSA and dipolar-coupling tensors. Cross terms between the heteronuclear and the homonuclear dipolar couplings are only important for $\phi = 90°$.

❏ Some resonance conditions reintroduce the heteronuclear dipolar coupling ($n_0\omega_r = \omega_\alpha$) and have to be avoided. Others reintroduce the homonuclear dipolar couplings of the I spins ($n_0\omega_r = \pm\omega_m\mp\omega_\alpha$) and are beneficial for the decoupling process.

❏ I-spin spin diffusion is present everywhere but is emphasized on the homonuclear resonance conditions.

simulations for a CH$_2$ system ν_r = 25 kHz, ν_1 = 100 kHz

all interactions

no I-spin CSA tensors

no homonuclear dipolar couplings
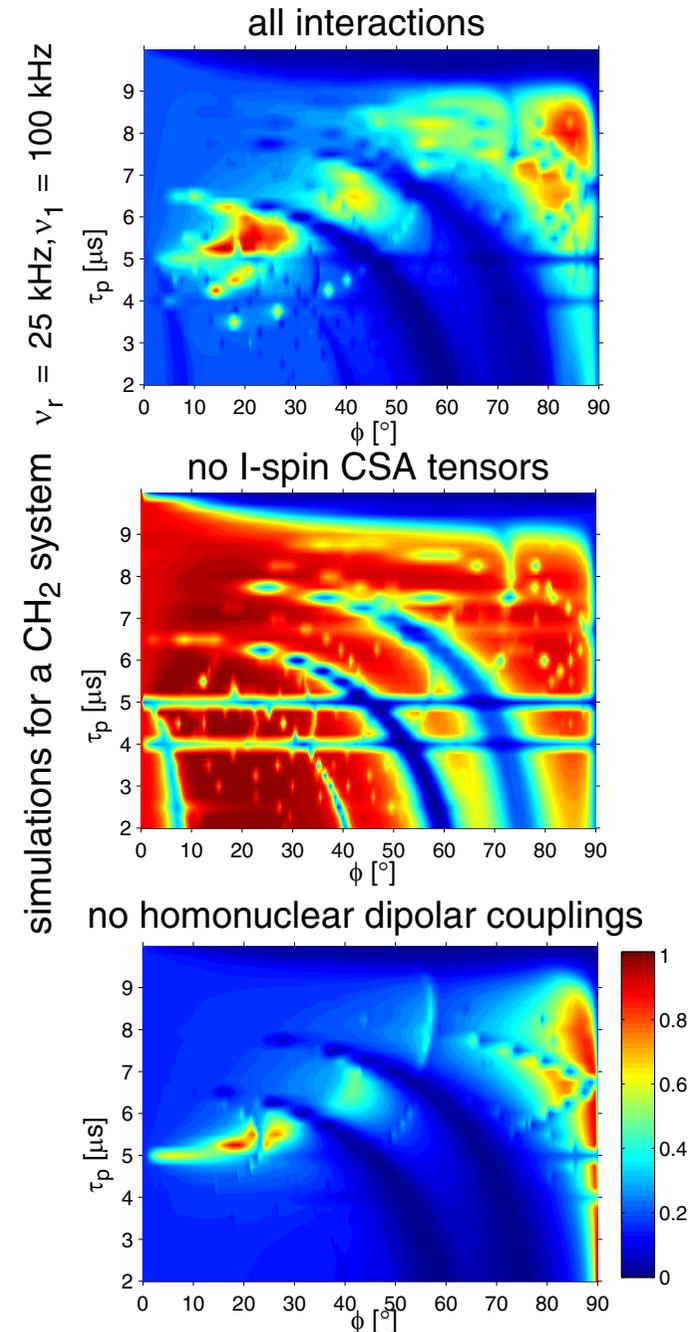
Conclusions
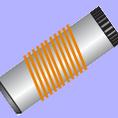
❑ Resonance conditions between sample spinning and spin rotations makes decoupling in solid-state NMR under sample rotation more complicated.

❑ Observable line width in rotating solids is determined by

- the residual coupling terms $\tilde{\mathscr{H}}_{(2)}^{(0,\,0)}$.
- the influence of nearby resonance conditions $\tilde{\mathscr{H}}^{(n_0,\,k_0)}$ and $\tilde{\mathscr{H}}_{(2)}^{(n_0,\,k_0)}$
- the I-spin spin diffusion induced "self decoupling".

❑ Leading term for the residual coupling in solids is the commutator term while in static samples the double commutator determines the line width.

❑ The residual coupling in TPPM and cw decoupling is dominated by the I-spin CSA cross term with the heteronuclear dipolar coupling. In XiX decoupling, the cross term between homonuclear and a heteronuclear dipolar couplings is the most important term.

❑ Resonance conditions can be bad, e.g., heteronuclear couplings leading to additional line broadening or good, e.g., homonuclear couplings leading to "self decoupling".

❑ "Self decoupling" due to I-spin spin diffusion leads to additional narrowing of the residual couplings.

Practical Considerations
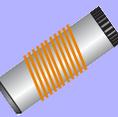
❏ CW decoupling should not be used in rotating solids.

❏ TPPM decoupling and XiX decoupling give both better performance (smaller residual couplings).

❏ TPPM decoupling can be used over a large range of spinning frequencies and rf-field amplitudes. Optimization of TPPM is critical: two-parameter optimization of pulse length τ_p and phase angle ϕ!

❏ Modified TPPM sequences like SPINAL or SW_f-TPPM are more stable under certain experimental conditions. There are no experimental studies that compare the performance of these sequences over a large range of experimental parameters (B_0, ν_r, and ν_1)

❏ XiX decoupling works best for high MAS frequencies (ν_r > 20 kHz) and high rf-field amplitudes (ν_1 > 5ν_r). Optimization of XiX decoupling is a local one parameter optimization around τ_p = 2.85 τ_r.

Other Contributions To Experimental Line Width
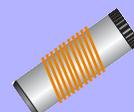
- ❏ Technical problems:

  - Temperature gradients

  - B_0-field homogeneity (shim)

  - Setting of magic angle

- ❏ Sample preparation

  - Sample heterogeneity

  - Susceptibility effects

- ❏ Spin-dynamics

  - Decoupling efficiency

  - S-spin homonuclear couplings (rotational-resonance effects)

  - Relaxation effects
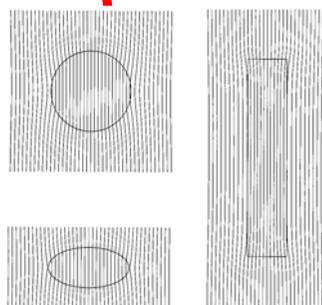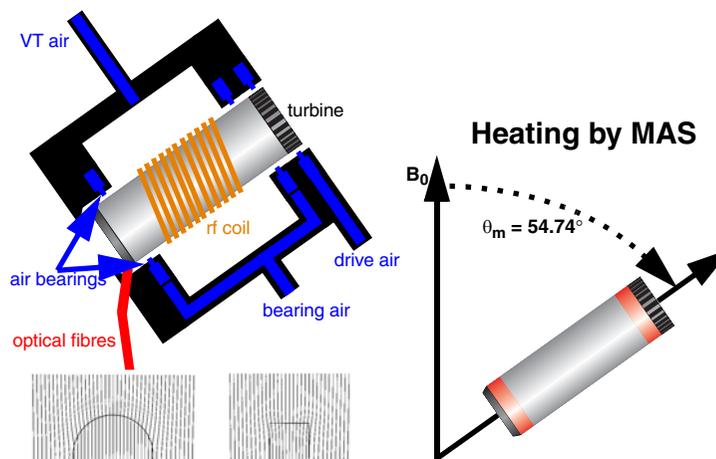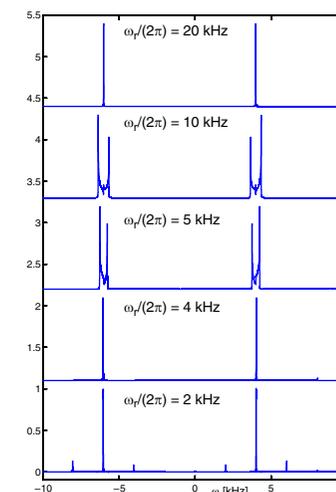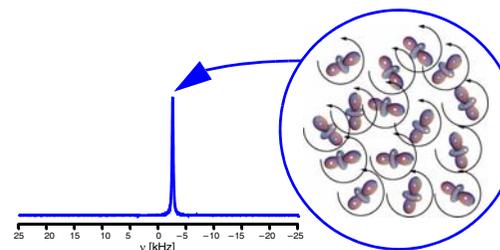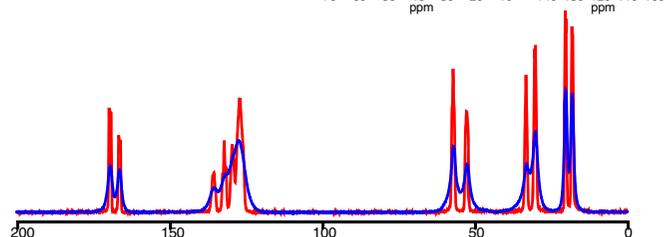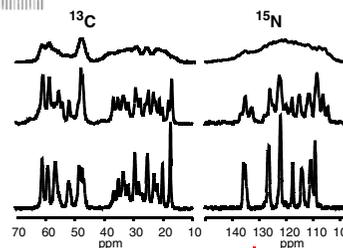
Acknowledgements
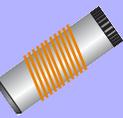
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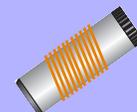
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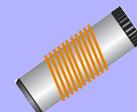
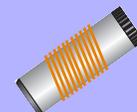## CW decoupling

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