Polarization Transfer & Recoupling (R sequences)

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Outline

1. Basics of recoupling
2. Sensitivity & NMR
3. Cross Polarization
4. CP & AHT
5. CP under MAS
6. Some variations of CP
7. REDOR
8. Rotational Resonance
9. PDSD & similar
10. $R N^\nu_n$ sequences
11. Applications
To suppress undesired, sizeable interactions in powder sample, it is important to:

- spin the sample fast about the magic angle
- apply RF pulses to eliminate the unwanted terms from $\mathcal{H}$
- Consider the combined effect of sample and spin rotations
MAS and Recoupling

The design of sequences to recouple specific spin interactions under MAS involves the control of the space & spin part of $\mathcal{H}$:

- Polarization transfer methods and heteronuclear recoupling.
- Rotary resonance condition for heteronuclear recoupling, $\omega_r = n\omega_{\text{nut}}$, with $n = 1, 2$
- Rotational resonance: $n \omega_r = \omega_{\Delta}^{\text{iso}} = |\omega_{i}^{\text{iso}} - \omega_{j}^{\text{iso}}|$
- Proton-mediated X recoupling methods.
- Use symmetry principles build rotor synchronised sequences with the desired properties, i.e, $CN_h^\nu$ and $RN_h^\nu$ sequences
- ... many many more ...

P.S. several images provided from Dr Phil Williamson in what follows
Polarization Transfer
Polarization transfer (PT) in liquids is achieved via the $J$-couplings through the INEPT sequence.

Due to short $T_2$ problems in solids (even in refocussed versions), methods based on DD interactions are often preferred.
Low Sensitivity of NMR and Cross-Polarization

- NMR is a technique with intrinsically low sensitivity: the NMR signal is due to spin magnetization which depends on the population difference among closely spaced energy levels.

\[
\text{NMR Signal} \propto \Delta E \propto \gamma B_0 \rightarrow \text{high} \quad \frac{k_B T}{\rightarrow \text{cold}}
\]

- Cross Polarization (CP) enhances the NMR signal of low-\(\gamma\) nuclei in dipolar contact with high-\(\gamma\) nuclei \([1, 2, 3]\).
Polarization transfer takes place when the $I$ and $S$ fields satisfy the so-called Hartmann-Hahn (HH) condition [4]

$$
\omega^S_{\text{nut}} = \omega^I_{\text{nut}}
$$

HH conditions (Hahn ingenious concept): equalize energy gaps in the double-rotating frame for both the $I$ and $S$ species, by $\gamma_I B_{1I} = \gamma_S B_{1S}$.

In this frame, the IS dipole-dipole coupling can induce transitions [3, 5, 6].
Cross Polarization (2)

- Generate transverse magnetization on the $I$ channel and apply a field $\omega^I_{\text{nut}}$, sufficient to lock it.

- **Satisfy the HH condition** with a suitable field $\omega^S_{\text{nut}}$. The width of the matching profile is proportional to $d_{IS}$. Weakly coupled systems (i.e., very mobile, distant spins, low $\gamma$) require a very fine optimization of the power levels.

- **Contact time** = time for which the two fields are applied. It depends upon $d_{IS}$, hence it is short for strong interactions (near spins) and long for weak interactions.
Cross Polarization (3)

\[ \beta\text{-carotene} \]

Variable-contact time experiment

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$T_{HC}$ [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1.79 ± 0.03</td>
</tr>
<tr>
<td>C2</td>
<td>0.78 ± 0.03</td>
</tr>
<tr>
<td>5-Me</td>
<td>1.45 ± 0.09</td>
</tr>
</tbody>
</table>

Kolodziejski, Chem. Rev. 2002
\[ \tilde{\mathcal{H}}_B = \tilde{\mathcal{H}}_{IS} + \omega_{\text{nut}}^I \mathbf{i}_x + \omega_{\text{nut}}^S \mathbf{s}_x \]

The rf terms are the main quantization direction and \( \mathcal{H}_{IS} \) is a perturbation orthogonal to them. In this frame the spin Temp for \( I \) is

\[ T_I = \frac{\omega_{\text{nut}}^I}{\omega_0} T_{\text{Lattice}} = \frac{B_I}{B_0} T_{\text{Lattice}} \]

If \( \omega_{\text{nut}}^I = \omega_{\text{nut}}^S \), a resonance condition is met and energy transfer takes place. At equilibrium, the spin Temp during CP is expected to be

\[ T_{CP} \approx T_I = \frac{B_I}{B_0} T_{\text{Lattice}} = \frac{\gamma_S B_S}{\gamma_I B_0} T_{\text{Lattice}} \]

hence \( T_S \) is lower than achieved by \( S \) spin locking by a factor \( \gamma_S / \gamma_I \)

\[ \frac{M_S^{(CP)}}{M_{S,eq}} = \frac{\gamma_I}{\gamma_S} \]

See on Slichter [3] and Stejskal [7].
\[ \hat{H} = \omega_0 \hat{I}_z + \omega_{\text{nut}}^l (\hat{I}_x \cos \omega_1 t + \hat{I}_y \sin \omega_1 t) \]
\[ = \omega_0 \hat{I}_z + \omega_{\text{nut}}^l R_z(\omega_1 t) \hat{I}_x R_z(-\omega_1 t) \]

A convenient separation of $\hat{H}_A$ and $\hat{H}_B$ terms is

\[ \hat{H} = \omega_1 \hat{I}_z + (\omega_0 - \omega_1) \hat{I}_z + \omega_{\text{nut}}^l (\hat{I}_x \cos \omega_1 t + \hat{I}_y \sin \omega_1 t) \]

hence

\[ \hat{U}_A = \exp\{-i \omega_1 \hat{I}_z t\} = \hat{R}_z(\omega_1 t) \]
\[ \hat{H}_B = \Delta \omega \hat{I}_z + \omega_{\text{nut}}^l R_z(\omega_1 t) \hat{I}_x \hat{R}_z(\omega_1 t) = \omega_{\text{nut}}^l \hat{I}_x \]

For $\Delta \omega = 0$

\[ \tilde{\hat{H}}_B = \omega_{\text{nut}}^l \hat{I}_x \]
Simplified description of CP: Rotating Frame

Consider a spin pair, I and S. The Hamiltonian during CP in the L frame using resonant rf fields is

\[ \hat{H}_{Tot} = \hat{H}_Z + \hat{H}_{IS} + \hat{H}_{RF} \]
\[ \hat{H}_Z = \omega_0 \hat{I}_z + \omega_0 \hat{S}_z \]
\[ \hat{H}_{IS} = \omega_{IS} \hat{I}_z \hat{S}_z \]
\[ \hat{H}_{RF} = \omega_{nut} \hat{R}_{lz}(\omega_0 t) \hat{I}_x + \omega_{nut} \hat{R}_{sz}(\omega_0 t) \hat{S}_x \]

Transform to the interaction frame of both nuclei, with
\[ \hat{H}_B = \hat{H}_{IS} + \hat{H}_{RF} \]
\[ \tilde{\hat{H}}_B = \hat{R}_{lz}(\omega_0 t) \hat{R}_{sz}(\omega_0 t) \left( \hat{H}_{IS} + \hat{H}_{RF} \right) \]
\[ \tilde{\hat{H}}_{IS} = \tilde{\hat{H}}_{IS} \]
\[ \tilde{\hat{H}}_{RF} = \omega_{nut} \hat{I}_x + \omega_{nut} \hat{S}_x \]
Simplified description of CP: Toggling frame & AHT

Move to the interaction frame of the two rf fields, using $\hat{\mathcal{H}}_B = \hat{\mathcal{H}}_{IS}$

\[
\tilde{\hat{\mathcal{H}}}_B = \tilde{\hat{\mathcal{H}}}_{RF} + \tilde{\hat{\mathcal{H}}}_{IS} \\
\tilde{\hat{\mathcal{H}}}_{tog} = \hat{R}_{lx}(-\omega_I^n t) \hat{R}_{sx}(-\omega_S^n t) \hat{\mathcal{H}}_{IS} \\
= \omega_{IS} \hat{R}_{lx}(-\omega_I^n t) \hat{R}_{sx}(-\omega_S^n t) \hat{I}_z \hat{S}_z \\
= \omega_{IS} \left( \hat{I}_z \cos \omega_I^n t + \hat{I}_y \sin \omega_I^n t \right) \times \\
\times \left( \hat{S}_z \cos \omega_S^n t + \hat{S}_y \sin \omega_S^n t \right)
\]

The Hartmann-Hahn conditions is $\omega_S^n = \omega_I^n$. With some trigonometric tricks, the average $\hat{\mathcal{H}}$ comes out as

\[
\tilde{\hat{\mathcal{H}}}^{(1)}_{tog} \approx \omega_{IS} \left( \hat{I}_z \hat{S}_z + \hat{I}_y \hat{S}_y \right)
\]
Simplified description of CP: Evolution under $\hat{H}$

The heteronuclear average $\hat{H}$ relevant in the CP for a pair of spins is

$$\hat{H}_{CP} = \omega_{IS}(\hat{I}_z \hat{S}_z + \hat{I}_y \hat{S}_y)$$

The evolution of the initial state $\hat{\rho}(0) = \hat{I}_x$ due to $\hat{H}_{CP}$ is (see Spiess [2])

$$\frac{1}{2} \hat{I}_x(1 + \cos \omega_{IS}t) + \frac{1}{2} \hat{S}_x(1 - \cos \omega_{IS}t) + (\hat{I}_y \hat{S}_z - \hat{I}_z \hat{S}_y) \sin \omega_{IS}t$$

The sign of the S signal depends on the sign of the initial transverse I signal.

Only the highlighted term is retained from conventional 2-step phase cycling on the proton 90° pulse.
Under MAS, the matching condition becomes

\[ \omega^S_{\text{nut}} = \omega^I_{\text{nut}} \pm k \omega_r \]

This is due to the time dependence of the \( I-S \) DD interactions. See Stejskal \textit{et al.} [8]
CP Profile for Adamantane at 5 kHz

\( \frac{(\omega_{1I} - \omega_{1S})}{(2\pi)} \) [kHz]

\( \tau_m = 16 \text{ ms} \)

\( \tau_m = 1 \text{ ms} \)
CP: Main Advantages

- S signal increased theoretically up to a maximum of $(\gamma_I/\gamma_S)$. On powders this is scaled down to 73% of that.

- For $^1$H-$^{13}$C the signal increase routinely corresponds to a factor between 3 and 4.

- The pulse delay is determined by the $T_1$ of the high-$\gamma$, I species. This is typically much shorter than the $T_1$ for low-$\gamma$, S species.

- Decrease in pulse delay, so many more scans can be acquired within a fixed amount of time.

- Suppression of back-ground signal. Useful for nuclei like $^{13}$C, which occur naturally in some of the materials in the probe, around and within the sample.
CP: Limitations

- Spin-lock not fulfilled efficiently for system with strong internal interactions, i.e., quadrupolar nuclei: both $\omega^I_{\text{nut}}$ and $\omega^S_{\text{nut}}$ have to be larger than all other interactions.

- The condition $\omega^S_{\text{nut}} = \omega^I_{\text{nut}} \pm k\omega_r$ may be difficult to practically achieve for nuclei with very different Larmor frequencies.

  This is apparent when writing explicitly the rf fields on the two channels.

  $$B^S = \frac{\gamma^I}{\gamma^S} B^I \pm k\omega_r/\gamma^S$$

- Difficult to set-up CP on highly mobile systems.
Polarization Transfer with PRESTO

$R_{\nu}N_{n}$ for heteronuclear recoupling and CSA recoupling of $I$.

Can be used for $I$ to $S$ polarization transfer [9, 10]

Take $\hat{\rho}_1 = B_I \hat{I}_z$ to see how it works.

If CSA is neglected and $|\kappa \omega_{IS} \tau_1 / 2| = \pi / 2$, we get:

$$\hat{H}_{S_0} \approx \frac{|\kappa \omega_{IS}|}{2} e^{-i\phi_{IS}} \hat{I}_z^2 \hat{I}_x \hat{S}_z e^{i\phi_{IS}} \hat{I}_z$$

$$\hat{H}_{S_{\pi/2}} \approx \frac{|\kappa \omega_{IS}|}{2} e^{-i\phi_{IS}} \hat{I}_z^2 \hat{I}_y \hat{S}_z e^{i\phi_{IS}} \hat{I}_z$$

$$\hat{\rho}_2 = B_I e^{-i\phi_{IS}} \hat{I}_z - 2 \hat{I}_y \hat{S}_z e^{i\phi_{IS}} \hat{I}_z$$

$$\hat{\rho}_3 = -B_I e^{-i\phi_{IS}} \hat{I}_z 2 \hat{I}_y \hat{S}_x e^{i\phi_{IS}} \hat{I}_z$$

$$\hat{\rho}_4 = -B_I \hat{S}_y$$
PT with PRESTO - worked out

The PRESTO calculations use the product operator commutators. $\hat{\rho}_2$ is worked out below to show how it is done.

\[
\mathcal{H}_{S_0} \approx |\kappa \omega_{IS}/2| e^{-i\phi_{IS}} \hat{I}_z^2 \hat{I}_x \hat{S}_z e^{i\phi_{IS}} \hat{I}_z
\]

\[
\rho_2 = e^{-i\mathcal{H}_{S_0} \tau} (B_I \hat{I}_z) e^{-i\mathcal{H}_{S_0} \tau}
\]

\[
= e^{-i\phi_{IS} \hat{I}_z} e^{-i \hat{I}_x \hat{S}_z \pi/2} e^{i\phi_{IS} \hat{I}_z} (B_I \hat{I}_z) e^{-i\phi_{IS} \hat{I}_z} e^{i \hat{I}_x \hat{S}_z \pi/2} e^{i\phi_{IS} \hat{I}_z}
\]

\[
= e^{-i\phi_{IS} \hat{I}_z} e^{-i \hat{I}_x \hat{S}_z \pi/2} (B_I \hat{I}_z) e^{i \hat{I}_x \hat{S}_z \pi/2} e^{i\phi_{IS} \hat{I}_z}
\]

\[
= B_I e^{-i\phi_{IS} \hat{I}_z} \left( \hat{I}_z \cos(\pi/2) - 2 \hat{I}_y \hat{S}_z \sin(\pi/2) \right) e^{i\phi_{IS} \hat{I}_z}
\]

\[
= B_I e^{-i\phi_{IS} \hat{I}_z} - 2 \hat{I}_y \hat{S}_z e^{i\phi_{IS} \hat{I}_z}
\]
When to use PRESTO

- Alternative to CP

- Advantageous in most cases which are difficult for CP because it does not require irradiation of the two channels at the same time.

- All "difficult stuff" done on the $I$ channel.

- Works also on quadrupolar nuclei (PRESTO-II version of the sequence).

If your problem is motion, PRESTO has the same limitations as CP.
Example: AgSbF$_6$

\[ \gamma_F / \gamma_{Ag} \approx 20 \]

600 scans, direct Ag observation versus PRESTO
Some CP-based sequences:

RampCP [11]

Adiabatic CP, [12]

Lee-Goldburg CP [13, 14]

CP with $I$ field off-resonance by

$$\Delta \omega = \frac{\omega^I_{\text{nut}}}{\tan \beta_m} \approx 0.71 \omega^I_{\text{nut}}$$

Useful to measure $IS$ distances under fast MAS

Broader condition, more efficient & robust w.r.t. rf inhomogeneity and variations in $\omega_r$.

Many more CP sequences available ...
Homonuclear & Heteronuclear recoupling methods
REDOR (1)

REDOR = rotational echo double resonance. Dephase X through $d_{XY}$, using rotor-synchronized $\pi$ pulses on both X and Y channels [15].
REDOR (2)

- $1.54 \text{ Å}$
- $2.5 \text{ Å}$
- $4.0 \text{ Å}$

Graph showing the dephasing period versus the relative spin order $\Delta S/S_0$. The graph includes three peaks at different dephasing periods corresponding to the distances $1.54 \text{ Å}$, $2.5 \text{ Å}$, and $4.0 \text{ Å}$. The x-axis represents the dephasing period in seconds, while the y-axis represents the relative spin order.
Rotational Resonance

By matching $\omega_r$ to the chemical shift difference of two homonuclear sites, we reintroduce selectively their DD coupling [16], reflected in the lineshape distortion.

Fully $^{13}$C labelled Alanine

$\omega_r/2\pi = 12.750$ kHz

9.4 T
Magnetization exchange through RR

\[ \omega_r \]

From P. Williamson

\[
\begin{array}{c}
\text{O} \\
1 \quad 2 \quad 3 \\
\text{O} \\
\quad 4 \\
\text{N}
\end{array}
\]
Rotational Resonance pro’s and con’s

(+): Measure selectively a particular internuclear distance out of many.

(+): it can provide high resolution information for favourable cases.

(-): RR requires a reasonably large CS difference, as most applications require moderate to high spinning frequency.

(-): RR is not very selective, so it requires the sites to be well resolved in order to perform an accurate measurement.

(-): lineshape distortion.

(-): poor CSA compensation.
I-mediated S recoupling. PDSD & DARR

Proton Driven Spin Diffusion (PDSD) [17]

Dipolar assisted rotary resonance recoupling (DARR) [18]

- $S$ transverse magnetization evolves during $t_1$, then is sent back along $z$.
- $S$ spin far apart "talk" via their mutual couplings to $I$ spins during $\tau_{mix}$.
- Pulse and observation during $t_2$ reveals $S$-$S$ correlations.
Fibrillar $\beta_2m, \tau_{mix} = 20$ ms.
\[ \hat{\mathcal{H}}^\Lambda = c^\Lambda \sum_{k=0}^{2} \sum_{m=-k}^{k} \left[ \hat{A}_{km}^\Lambda \right]^R e^{-im(\alpha_{RL}^0 - \omega_r t)} d^k_{m0}(\beta_{RL}) \left[ \hat{T}^\Lambda_{k-m} \right] \]

Spin interaction are classified according to their rank-component as: \{l, m\} for space, \{\lambda, \mu\} for spin, field terms are rank 1.

Notation change below: spin/field contributions in \(T\) are separated, so from here on \(T\) just refers to spin, \(l = k\) and \(\lambda \leq k\). The numerical value of the field in \(\mathcal{H}_{\text{int}}\) and \(c^\Lambda\) are included in \(A\).

A generic term in \(\hat{\mathcal{H}}_{\text{int}}\) will have the form

\[ \hat{\mathcal{H}}_{lm\lambda\mu}^\Lambda = \left[ \hat{A}_{lm}^\Lambda \right]^R e^{-im(\alpha_{RL}^0 - \omega_r t)} d^l_{m0}(\beta_{RL}) \hat{T}^\Lambda_{\lambda\mu} \]
Spin interactions for spin 1/2 nuclei

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Space Rank</th>
<th>Space Component</th>
<th>Spin Rank</th>
<th>Spin Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso J</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Iso CS</td>
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<td>-1,0,1</td>
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<tr>
<td>DD</td>
<td>2</td>
<td>-2,-1,0,1,2</td>
<td>2</td>
<td>-2,-1,0,1,2</td>
</tr>
</tbody>
</table>

RANK 0

RANK 1

RANK 2
Intro to $\mathbb{R}N^\nu_n$ sequences

For $Z_u = odd$ (take $Z_u = 1$ below), choose a pair of propagators such that

$$E^0 = R_z(\phi_0) R_x(\pi) R_z(-\phi_0)$$

$$E^{0'} = \prod_x E^0 \prod_x^\dagger$$

where the basic element is an effective $\pi$ rotation, with alternating $\mathbb{R}$ and $\mathbb{R}'$ elements. Hat from operators are omitted [19].
$\mathcal{R}N_n^\nu$: symmetries and selection rules

- The $\mathcal{R}N_n^\nu$ sequence is periodic and $\tilde{\mathcal{H}}^{(1)}_{lm\lambda\mu} \neq 0$ if $mn - \mu\nu = \frac{N}{2}Z_\lambda$
- $Z_\lambda$ has the same parity as the spin rank, $\lambda$.

As an example of how to use these rules, $\mathcal{R}14_6^6$ selects $2m - 6\mu = 7Z_\lambda$, fulfilled by the dipolar components $(m, \mu) = (\mp 1, \pm 2)$

No solution for the CSA components.
$R N^\nu_n$: Spin-space selection diagram

$R 14^6_2$

Part a: Spin-space selection diagram

Part b: Spin-space selection diagram

DD  CSA
How to get the selection rules? I.F.

The total Hamiltonian for the system is

\[ \mathcal{H} = \mathcal{H}_{RF}(t) + \mathcal{H}_{int} = \mathcal{H}_A + \mathcal{H}_B \]

The procedure is similar to what we did for WAHUHA. We want

\[
\tilde{\mathcal{H}}_B(t_q) = U_A^\dagger(t_q, t_0^0) \mathcal{H}_B U_A(t_q, t_0^0)
\]

\[ = U_{RF}^\dagger(t_q, t_0^0) \mathcal{H}_{int} U_{RF}(t_q, t_0^0) \]

The tensorial spin part of each term in \( \mathcal{H}_{int} \) is \( T^\Lambda_{\lambda_0} \).

Only the action of \( U_{RF} \) on this needs to be accounted for (the rest are scalars w.r.t. \( U_{RF} \)).
I.F. and propagators needed

The $R N^\nu_n$ sequence is built by concatenating $N/2$ pair of elements of the form

$$E_q = (\prod x)^q R_{\phi_0} (\prod x^\dagger)^q = (\hat{\prod}_x)^q R_{\phi_0}$$

with a proper choice of $\phi_0$. We need to define the following propagators:

- $S_q = U(t_q, t^0_q) =$ Prop. at a generic time $t_q$ within $E_q$, starting from the beginning of the element.
- $E_q = U(t^0_{q+1}, t^0_q) =$ Prop. over one complete $E_q$
- $A_q = U(t_q, t^0_0) = S_q E_{q-1} \ldots E_0 =$ Accumulated prop from $t^0_0$ to $t_q$
Explicit form of accumulated $E_q$

Use $R_z(\phi_k)\prod_x = \prod_x R_z(-\phi_k)$ to work out everything below.

\begin{align*}
E_0 &= R_z(\phi_0) R_x(\pi) R_z(-\phi_0) \\
&= R_x(\pi) R_z(-2\phi_0) \\
E_1 E_0 &= \prod_x R_z(\phi_0) R_x(\pi) R_z(-\phi_0) \prod_x^\dagger R_z(\phi_0) R_x(\pi) R_z(-\phi_0) \\
&= \prod_x R_x(\pi) R_z(-2\phi_0) \prod_x^\dagger R_x(\pi) R_z(-2\phi_0) \\
&= R_z(-2\phi_0) \prod_x^\dagger R_x(\pi) R_z(-2\phi_0) \\
&= R_z(-4\phi_0) \\
E_{q-1} \ldots E_0 &= R_x(q\pi) R_z(-2q\phi_0)
\end{align*}
Explicit form of $A_q$

\[
S_q = (\hat{\Pi}_x)^q \hat{R}_z(\phi_0) S_0^0 \\
= (\hat{\Pi}_x)^q \hat{R}_z(\phi_0) R_x(\omega_{\text{nut}}^S \tau_0), \quad t_0 \in [t_0^0, t_1^0]
\]

\[
S_{q+1} = \Pi_x S_q \Pi_x^\dagger
\]

\[
S_0 = S_{\text{even}}
\]

\[
S_1 = S_{\text{odd}}
\]

The accumulated propagator over the first $q$ elements, $A_q$, is

\[
A_0 = S_0
\]

\[
A_1 = S_1 E_0 = \Pi_x S_0 \Pi_x^\dagger \Pi_x R_z(-2\phi_0) = \Pi_x S_0 R_z(-2\phi_0)
\]

\[
A_2 = S_2 E_1 E_0 = S_0 (\Pi_x)^2 R_z(-4\phi_0) = (\Pi_x)^2 S_0 R_z(-4\phi_0)
\]

\[
A_q = (\Pi_x)^q S_0 R_z(-2q\phi_0)
\]
Derivation of selection rules (1)

We evaluate the $\hat{\mathcal{H}}$ in the I.F. and then apply A.H.T. over one period. The interaction frame Hamiltonian, considering only $T_{\lambda 0}$ terms, is given by:

$$\hat{A}_q^\dagger T_{\lambda 0} = \hat{R}_z(2q\phi_0) \hat{S}_0^\dagger \left(\hat{\Pi}_x^\dagger\right)^q T_{\lambda 0}$$

In the derivation which follows, use the conditions:

$$\hat{\Pi}_x T_{\lambda \mu} = (-1)^\lambda T_{\lambda - \mu}$$

$$\hat{S}_0^\dagger T_{\lambda \mu} = \sum_{\mu'} T_{\lambda \mu'} D_{\mu' \mu}^\lambda \left(\Omega_{\text{rf}}(t_0)\right)$$

$$\hat{R}_z(\alpha) T_{\lambda \mu} = T_{\lambda \mu} e^{-i\mu \alpha}$$
Derivation of selection rules (2)

For an R element, we have \( \Omega_{\text{rf}}(t) = \left( -\frac{\pi}{2} + \phi_0, -\beta_{\text{nut}}(t), \frac{\pi}{2} - \phi_0 \right) \).

\[
\hat{A}_{q}^\dagger T_{\lambda 0} = (-)^{\lambda q} \hat{R}_z(2q\phi_0) \hat{S}_0^\dagger T_{\lambda 0}
\]

\[
= (-)^{\lambda q} \sum_{\mu} \hat{R}_z(2q\phi_0) T_{\lambda \mu} D_{\mu 0}^\lambda (\Omega_{\text{rf}}(t_0))
\]

\[
= e^{i\pi \lambda q} \sum_{\mu} T_{\lambda \mu} e^{-i2q\mu\phi_0} D_{\mu 0}^\lambda (\Omega_{\text{rf}}(t_0))
\]

For a certain set of quantum numbers \( \tilde{\mathcal{H}} \) is given by terms of the form:

\[
\tilde{\mathcal{H}}_{lm\lambda\mu}(t_q) = [A_{lm}]^R D_{m0}^l (\Omega_{RL}^{R}) e^{i\pi \lambda q} e^{-2iq\mu\phi_0} T_{\lambda \mu} D_{\mu 0}^\lambda (\Omega_{\text{rf}}(t_0)) e^{im\omega_r t_q}
\]

\[
= [A_{lm}]^R d_{m0}^l (\beta_{RL}^{R}) e^{-im(\alpha_{RL} + \omega_r t_0)} e^{im\omega_r t_0} T_{\lambda \mu} D_{\mu 0}^\lambda (\Omega_{\text{rf}}(t_0)) \times \exp \{ iq(\pi \lambda - 2\mu \phi_0 + m\omega_r \tau_R) \}
\]
Derivation of selection rules (3)

\[ \tilde{\mathcal{H}}_{lm\lambda\mu}(t_q) = \left[A_{lm}\right]^R d_{m0}^l (\beta_{RL}) e^{-im(\alpha_{RL} + \omega_r t_0)} e^{im\omega_r t_0} T_{\lambda\mu} D_{\mu0}^\lambda (\Omega_{rf}(t_0)) \times \]
\[ \exp \{iq(\pi\lambda - 2\mu\phi_0 + m\omega_r \tau_R)\} \]

Spin interaction and on the form of R & Quantum numbers and \( q \).

The first order A.H. over one period is given by:

\[ \tilde{\mathcal{H}}^{(1)}_{lm\lambda\mu} = \left[A_{lm}\right]^R \kappa_{lm\lambda\mu} e^{-im(\alpha_{RL} + \omega_r t_0)} T_{\lambda\mu} S \]

with

\[ \kappa_{lm\lambda\mu} = d_{m0}^l (\beta_{RL}) \tau_R^{-1} \int_{t_0}^{t_0 + \tau_R} D_{\mu0}^\lambda (\Omega_{rf}(t)) e^{im\omega_r t} dt \]

\[ S = \frac{1}{N} \sum_{q=0}^{N-1} \exp (iq \{\pi \lambda q - 2\mu\phi_0 + m\omega_r \tau_R\}) \]
Derivation of selection rules (4)

It is possible to rewrite $\phi_0 = \frac{\pi \nu}{N}$, $\nu \in \mathbb{R}$, without losing generality. Moreover, $\omega_r \tau_R = 2\pi n/N$, which gives

$$S = \frac{1}{N} \sum_{q=0}^{N-1} \exp \left\{ \frac{i2\pi q}{N} \left( \frac{\lambda N}{2} - \mu \nu + mn \right) \right\}$$

which is 0 unless the exponential argument is a multiple of $i2\pi$. If $Z_{\lambda}$ is any integer with the same parity as $\lambda$, then

$$S = \begin{cases} 
0 & mn - \mu \nu \neq \frac{N}{2} Z_{\lambda} \\
1 & mn - \mu \nu = \frac{N}{2} Z_{\lambda}
\end{cases}$$

At the end of the period, all terms which do not satisfy it, are to zero to first order.
Scaling factor & $\gamma$ encoding

The $\kappa_{lm\lambda\mu}$ term in $\tilde{\mathcal{H}}^{(1)}_{lm\lambda\mu}$ is with

$$\kappa_{lm\lambda\mu} = d^l_{m0} \left( \beta^{RL} \right) \tau_R^{-1} \int_{t_0^0}^{t_0^0 + \tau_R} D^\lambda_{\mu0}(\Omega_{rf}(t)) e^{im\omega_r(t_0 - t_0^0)} dt_0$$

$$= d^l_{m0} \left( \beta^{RL} \right) \tau_R^{-1} \int_{t_0^0}^{t_0^0 + \tau_R} d^\lambda_{\mu0}(-\beta_0) e^{i(\mu \gamma_0 + m\omega_r t_0 - m\omega_r t_0^0)} dt_0$$

If only one set of quantum numbers $\left\{ l, m, \lambda, \mu \right\}$ is symmetry allowed in $\tilde{\mathcal{H}}^{(1)}_{lm\lambda\mu}$, then

$$\tilde{\mathcal{H}}^{(1)}_{lm\lambda\mu} = [A_{lm}]^R \kappa_{lm\lambda\mu} e^{-im(\alpha_{RL} + \omega_r t_0^0)} T_{\lambda\mu}$$

$$= \sum_{m'} [A_{lm'}]^M e^{-im'\alpha_{MR}} d^l_{m'm}(\beta_{MR}) e^{-im(\gamma_{MR} + \alpha_{RL} + \omega_r t_0^0)} \kappa_{lm\lambda\mu} T_{\lambda\mu}$$

The dependence on the $\gamma_{MR}$ powder angle goes together with other terms relating the RL frames and the powder averaging can be simplified.
Examples of $\mathcal{R}N^n$ applications

- Homonuclear DD DQ recoupling: $R_{14}^6$, $R_{20}^9$, $R_{26}^{11}$, ...
  Have a look at Maria Concistrè & co. work on rhodopsin

- Heteronuclear Recoupling and CSA recoupling: $R_{18}^5$, $R_{18}^7$, ...

- Heteronuclear Decoupling: $R_{24}^1$, $R_{24}^2$, ...

- ZQ Dipolar Recoupling: $R_{4}^1$, ...
DQ DD recoupling of endohedral $\text{H}_2@\text{C}_{60}$

Best fits:
DD(293K) = $-610$ Hz, 
DD(240K) = $-660$ Hz, 
DD(175K) = $-730$ Hz

Reintroduce selectively $^1\text{H} - ^1\text{H}$ couplings under MAS. The DD has a mild T dependence.
Spin Counting

The purpose is to determine if the DQF signals are due to *inter* or *intra*molecular $^1\text{H}-^1\text{H}$ interactions.

$$\tau_c = 8\tau_r$$

SR26$^{11}_4$
Spin Counting

Spin rank up to $\lambda = 5$: intermolecular contacts in $\text{H}_2@\text{C}_{60}$ [20].
DQC are created (not necessarily with $CN_n^\nu$ or $RN_n^\nu$ sequences), then evolve in presence of $I$-$S$ interaction over a variable interval, to obtain $I$-$S$-$S$-$I$ torsion angle.
Torsion angle measurements (2)

The protons are expected to be in trans position and the measurement is in good agreement.
Suitable recoupling sequences can be applied to provide a correlation mediated directly by the $S$-$S$ interactions. This method provides improved resolution in the second dimension.
DQ-SQ experiment example

Tyrosine, 20 kHz [19]
Selected Reading (1)


Selected Reading (2)


