Using Symmetry To Design Pulse Sequences in Solid-State NMR

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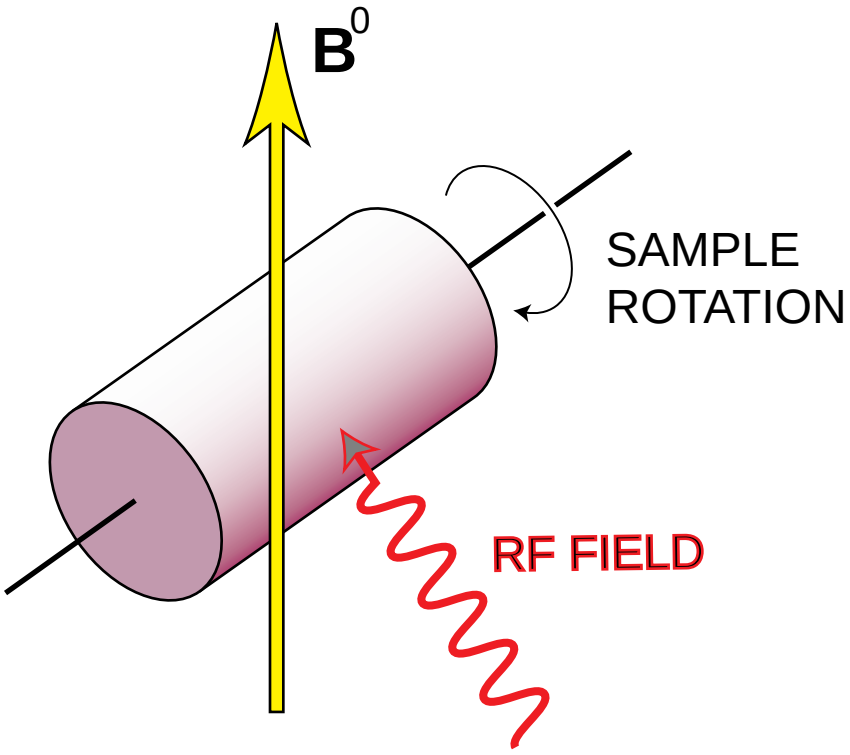
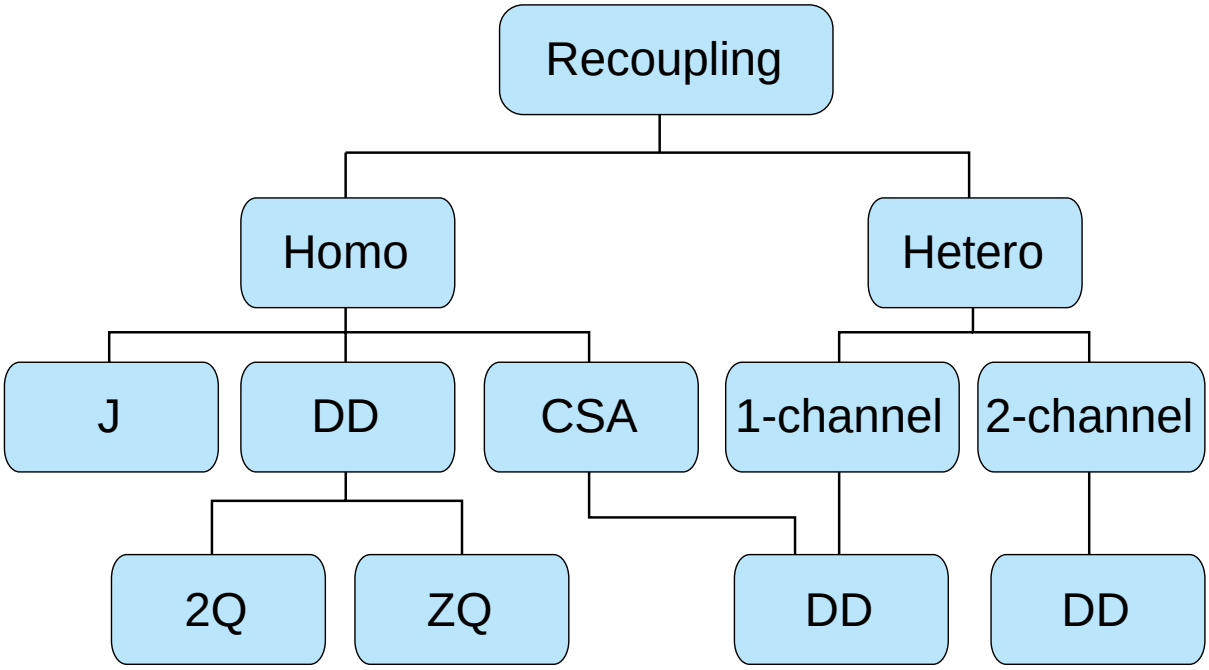
Overview

- Symmetry principles of recoupling
- Double-quantum homonuclear recoupling
- Zero-quantum homonuclear recoupling
- Heteronuclear recoupling: distances and polarization transfer

MAS + Rf → Recoupling



Types of Recoupling



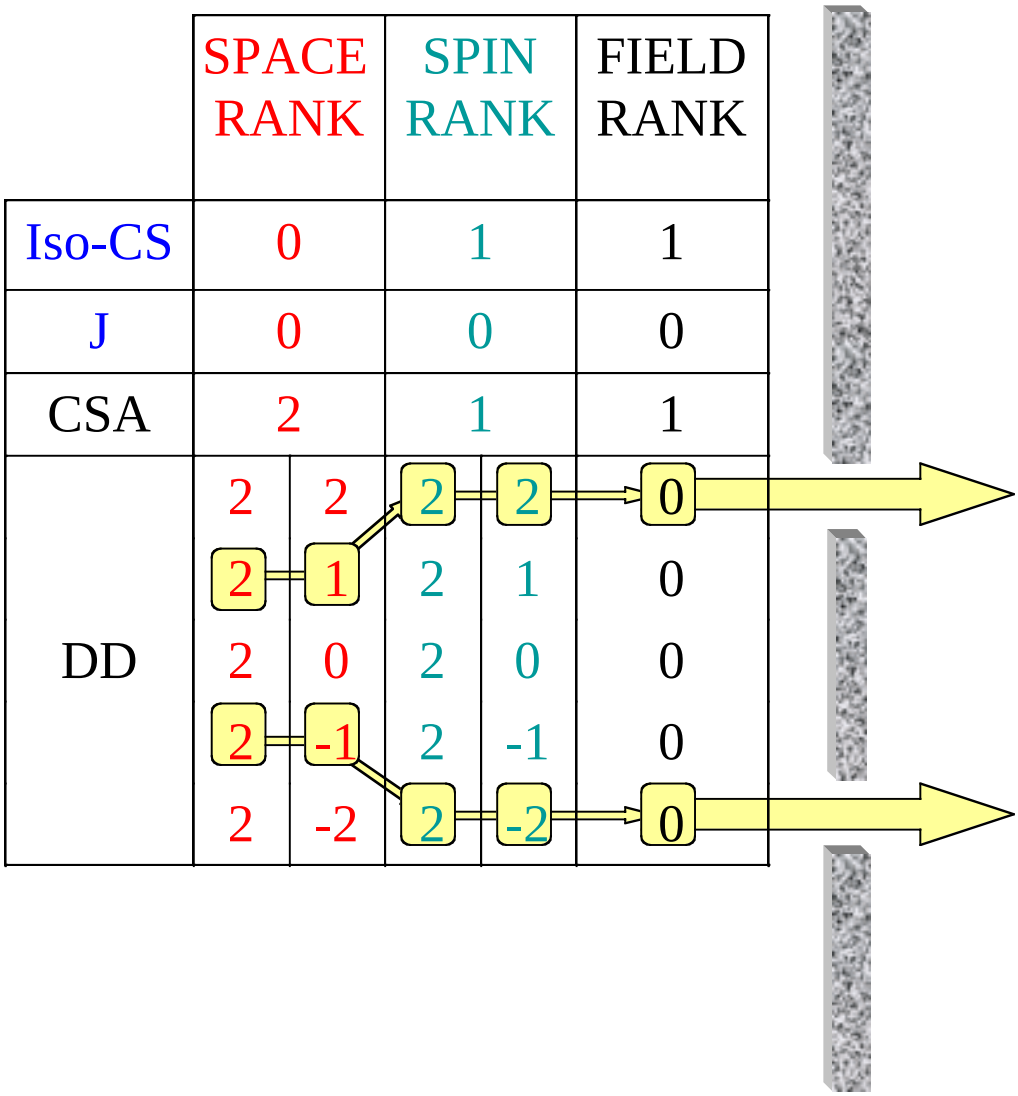
Spin Interactions and their Rotational Symmetries

	SPACE RANK	SPIN RANK	FIELD RANK
Iso-CS	0	1	1
J	0	0	0
CSA	2	1	1
DD	2	2	0

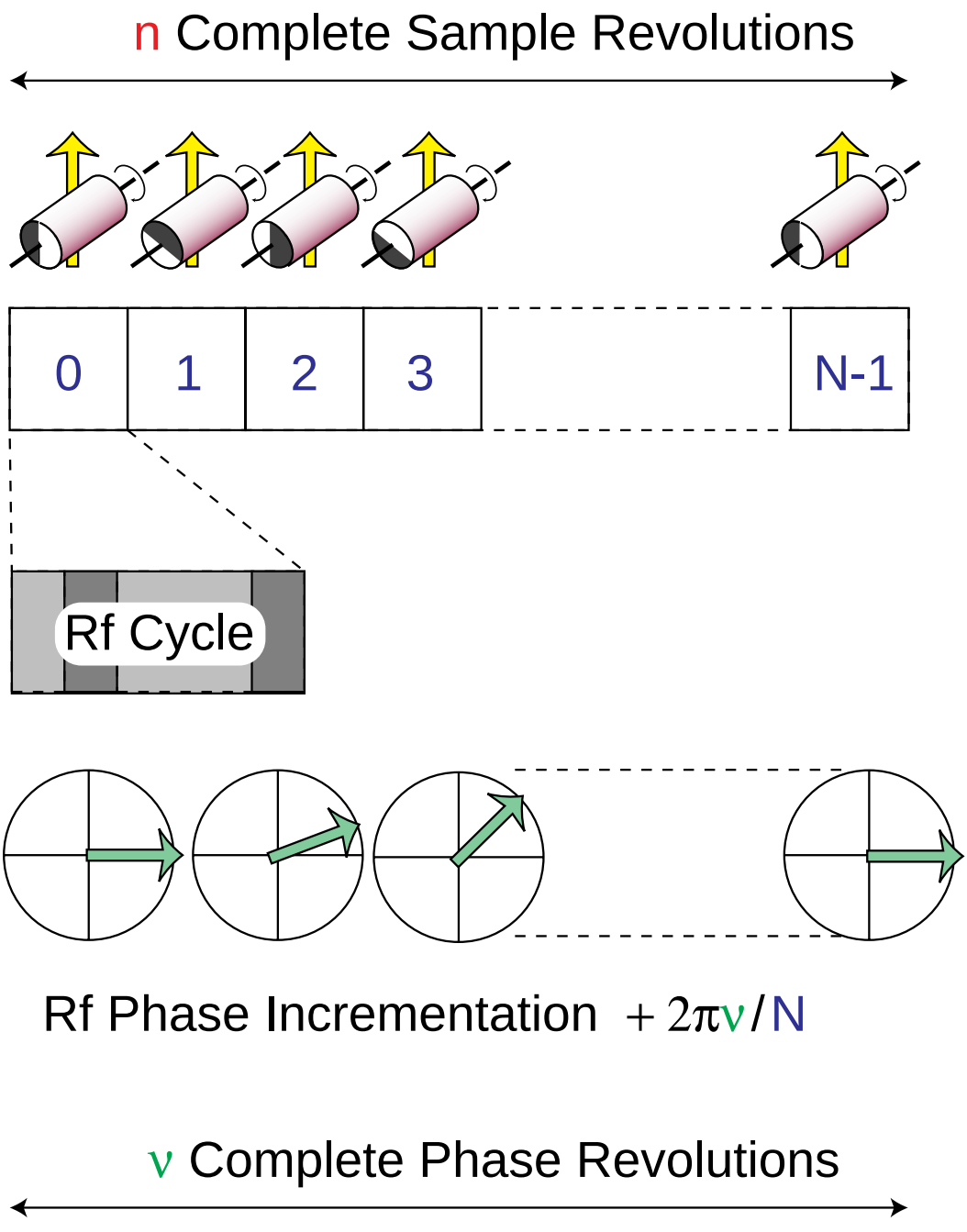
Rotational Components

	SPACE RANK		SPIN RANK		FIELD RANK
Iso-CS	0		1		1
J	0		0		0
CSA	2		1		1
DD	2	2 1 0 -1 -2	2	2 1 0 -1 -2	0

Component Selection for 2Q Homonuclear Recoupling



Structure of $\mathbb{C}N_n^{\nu}$ Sequences

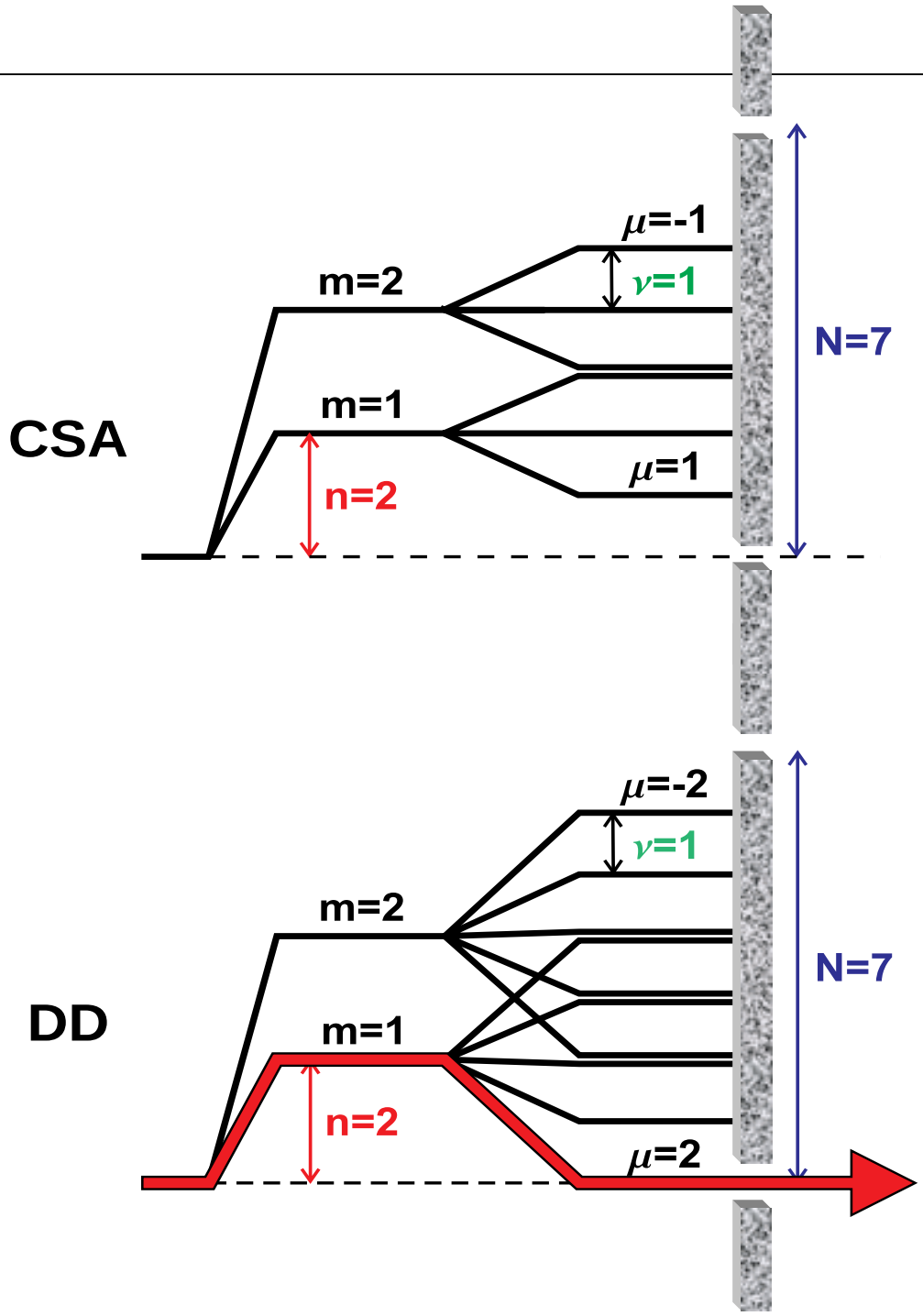


Average Hamiltonian Selection Rules

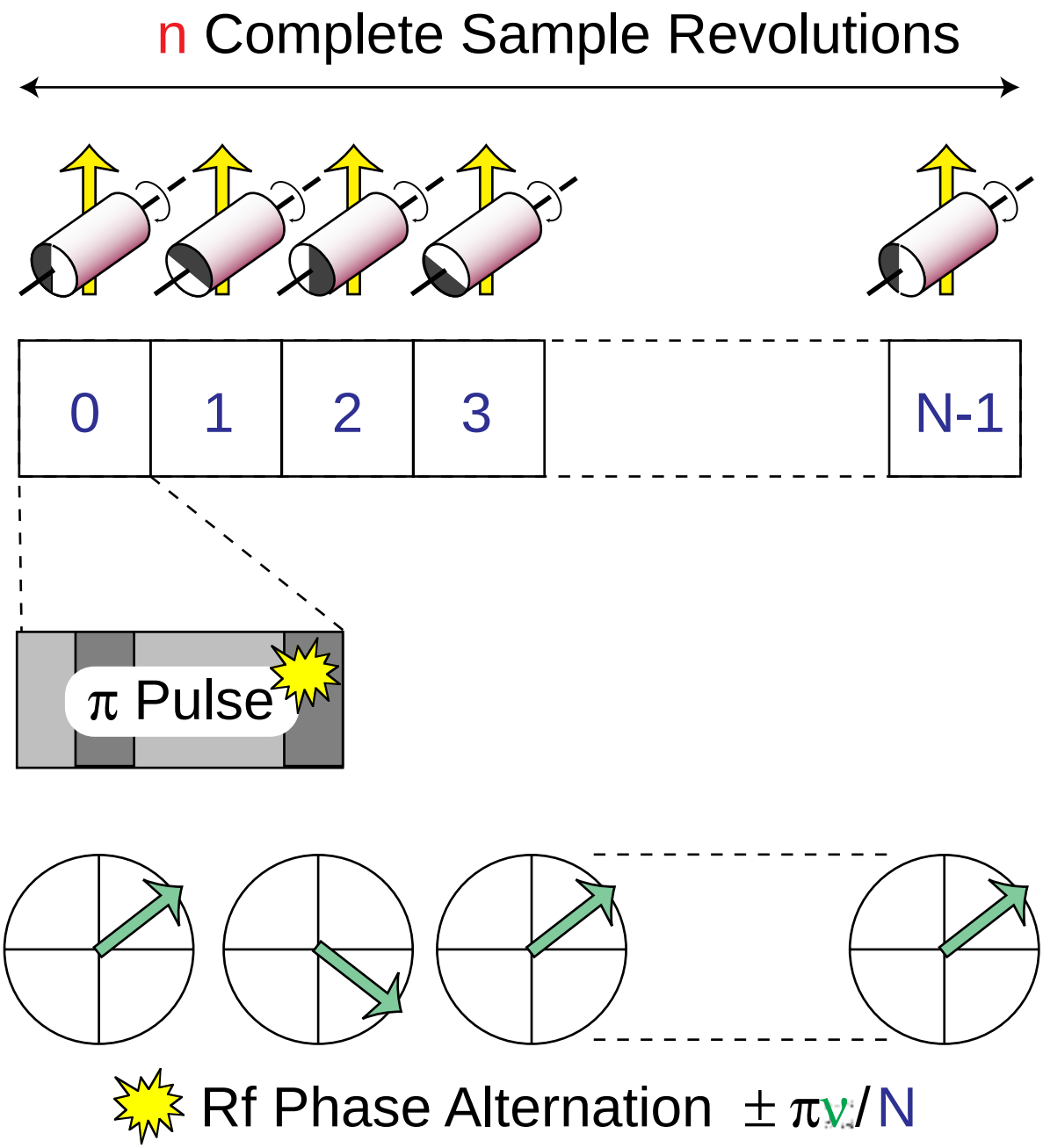
For $\mathbb{C}N_n^{\nu}$:

$$\bar{H}^{(1)}_{lm\lambda\mu} = 0 \quad \text{if} \quad mn - \mu\nu \neq N \times \text{integer}$$

Selection Rules for $C7_2^1$



Structure of $\mathbb{R}N_n^{\nu}$ Sequences



Average Hamiltonian Selection Rules

For $\mathbb{R}N_n^{\nu}$:

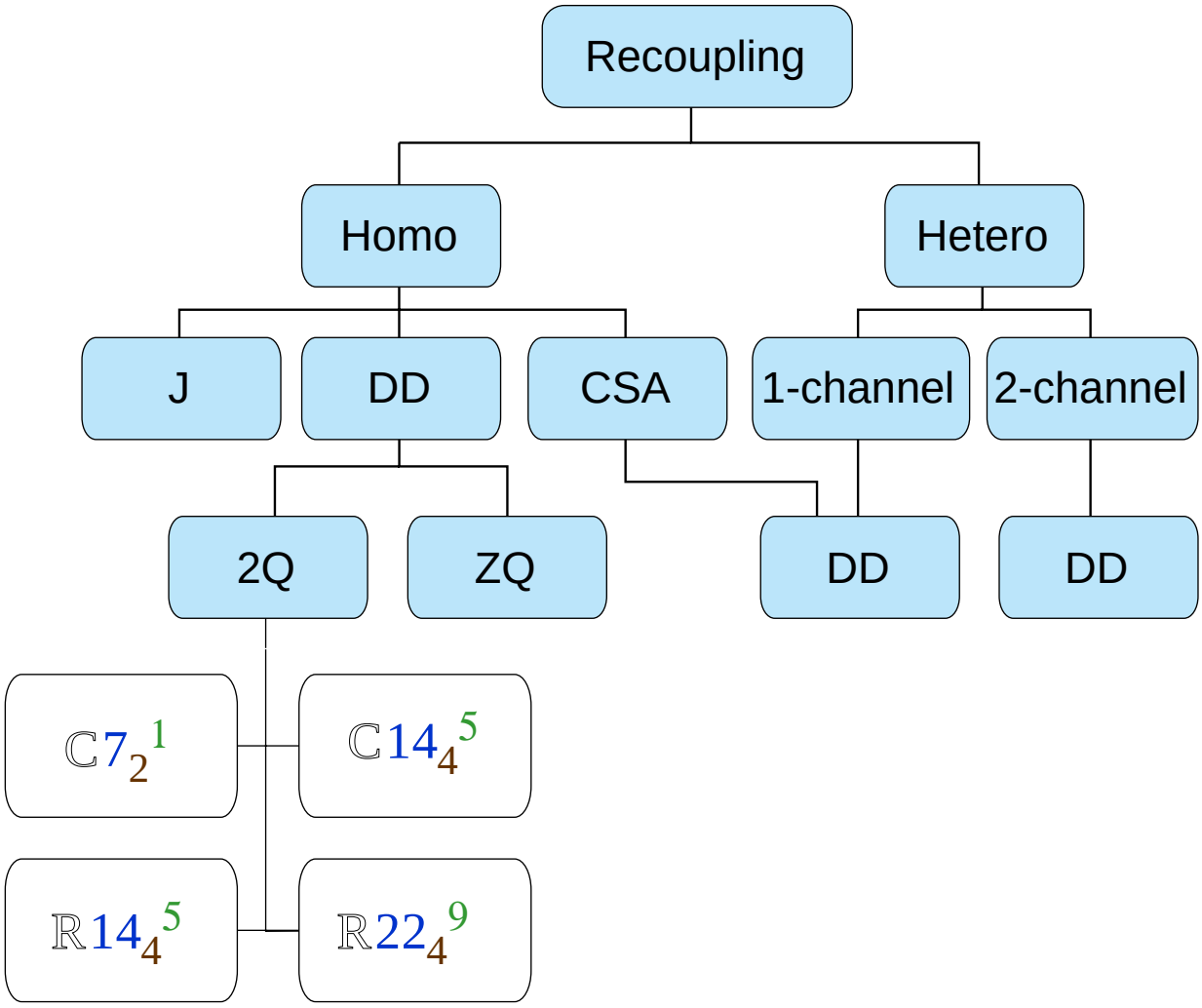
If λ = odd:

$$\bar{H}^{(1)}_{lm\lambda\mu} = 0 \quad \text{if} \quad mn - \mu\nu \neq N/2 \times \text{odd integer}$$

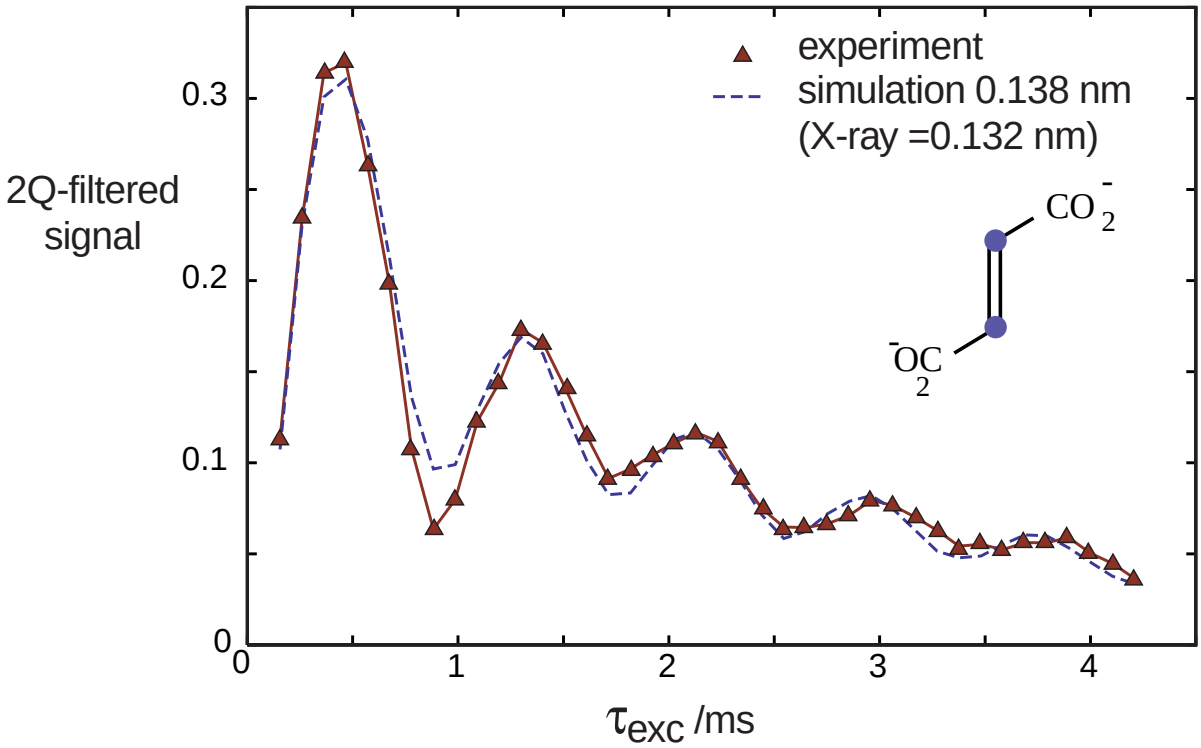
If λ = even:

$$\bar{H}^{(1)}_{lm\lambda\mu} = 0 \quad \text{if} \quad mn - \mu\nu \neq N/2 \times \text{even integer}$$

Symmetry Solutions for 2Q Recoupling



Measurement of a ^{13}C–^{13}C distance with $\mathbb{R}26_8^9$

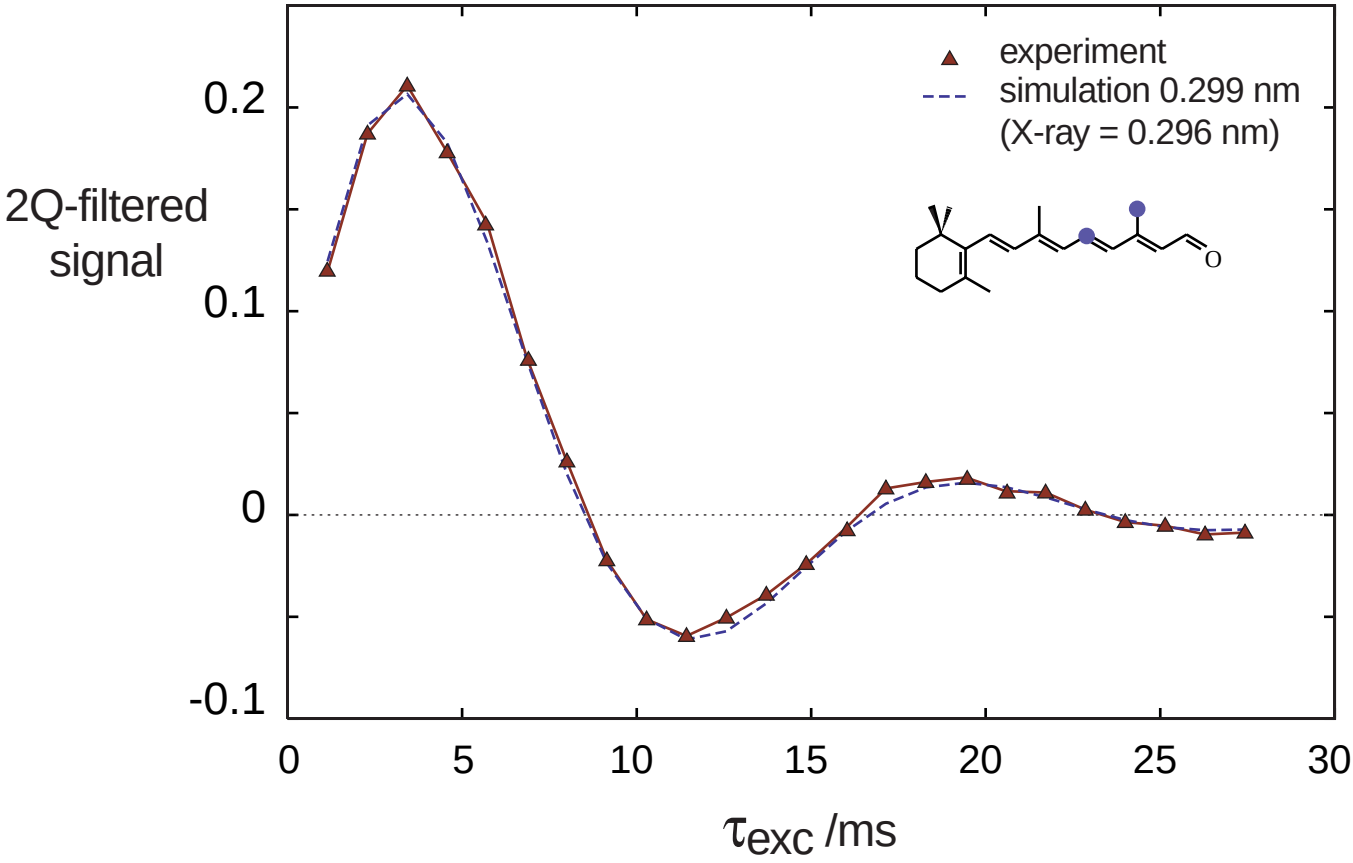


spinning frequency = 11.850 kHz
field = 4.7 T

Marina Carravetta
Mattias Edén

Measurement of a ^{13}C–^{13}C distance with

$$\mathbb{R}22_4^9$$



spinning frequency = 7.000 kHz
field = 9.4 T

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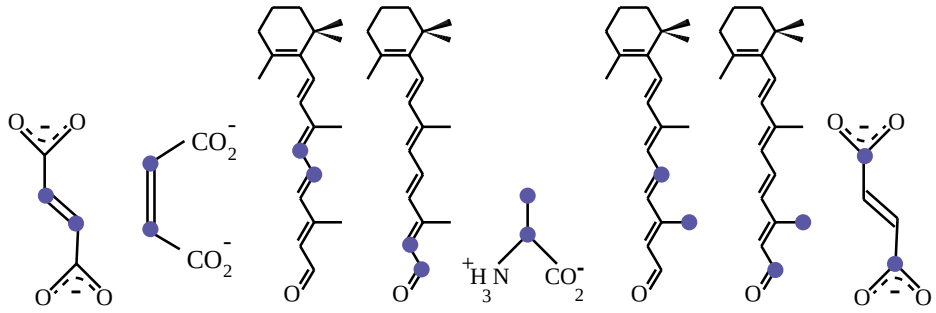
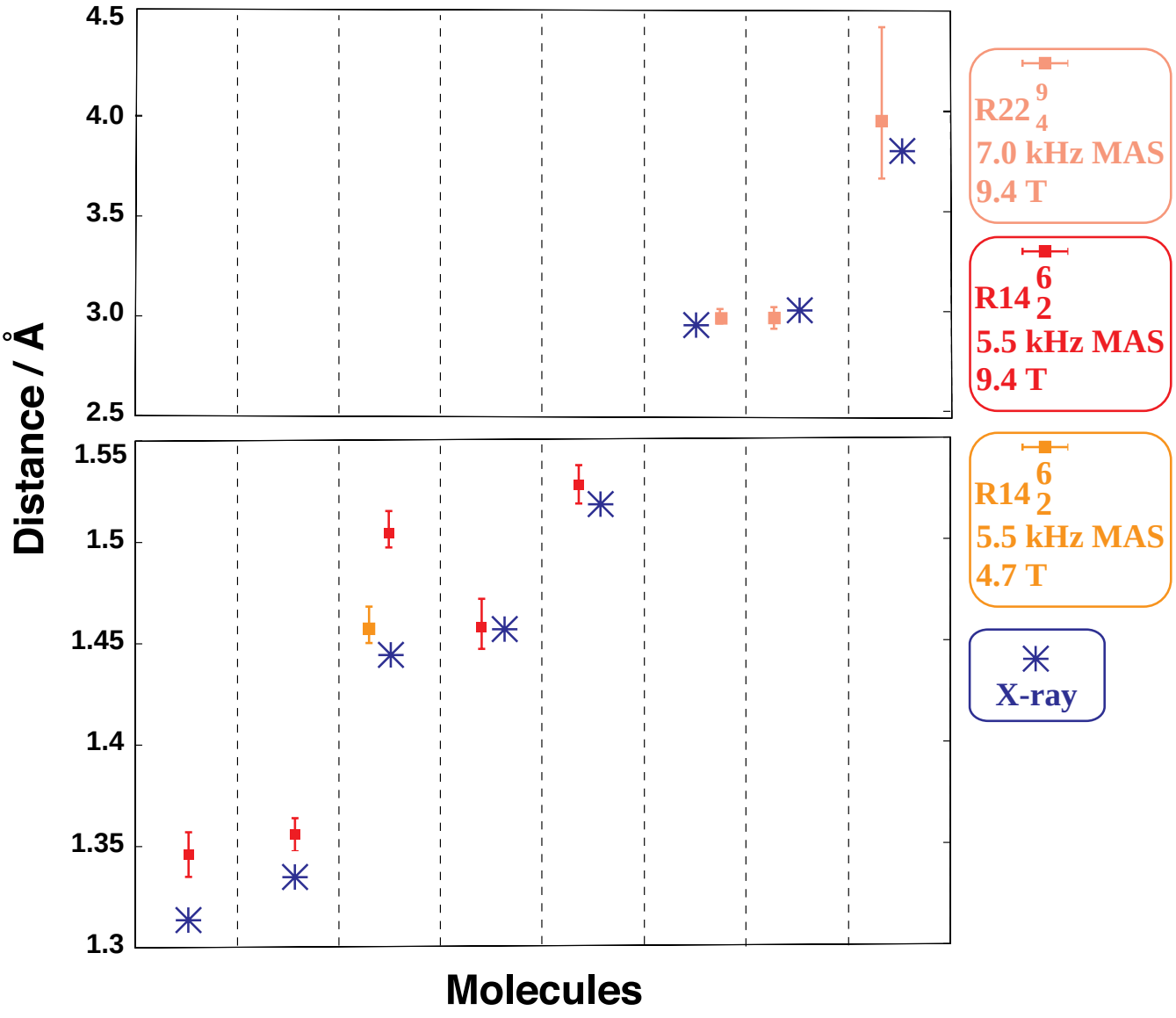
Mattias Edén

Measurement of ^{13}C- ^{13}C distances





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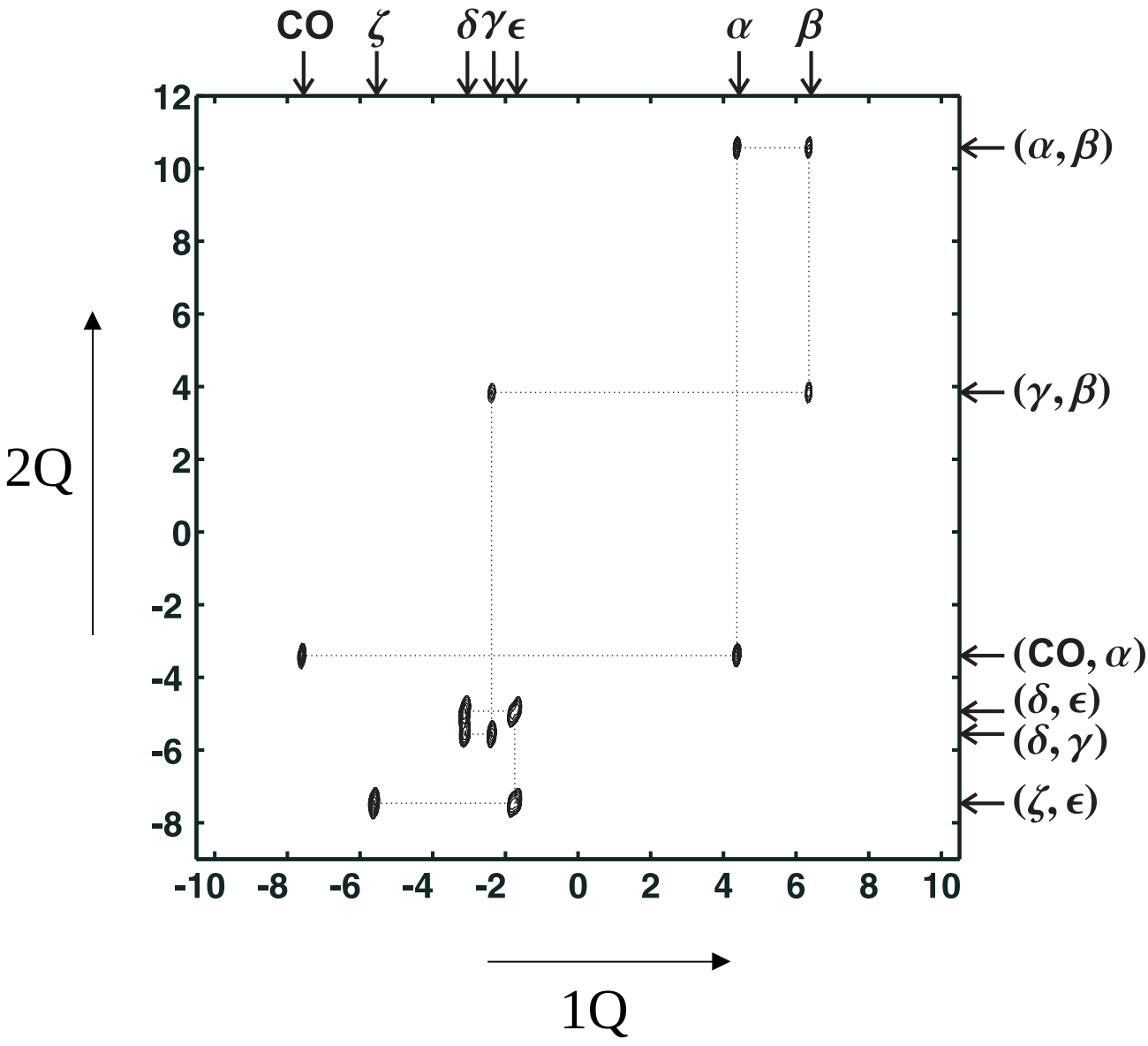
2Q ^{13}C Spectrum with

$\mathbb{C}14_4^5$

$\mathbb{C} = 360_0$

[U-^{13}C]-tyrosine
spinning frequency = 20 kHz; field = 9.4 T



Andreas Brinkmann

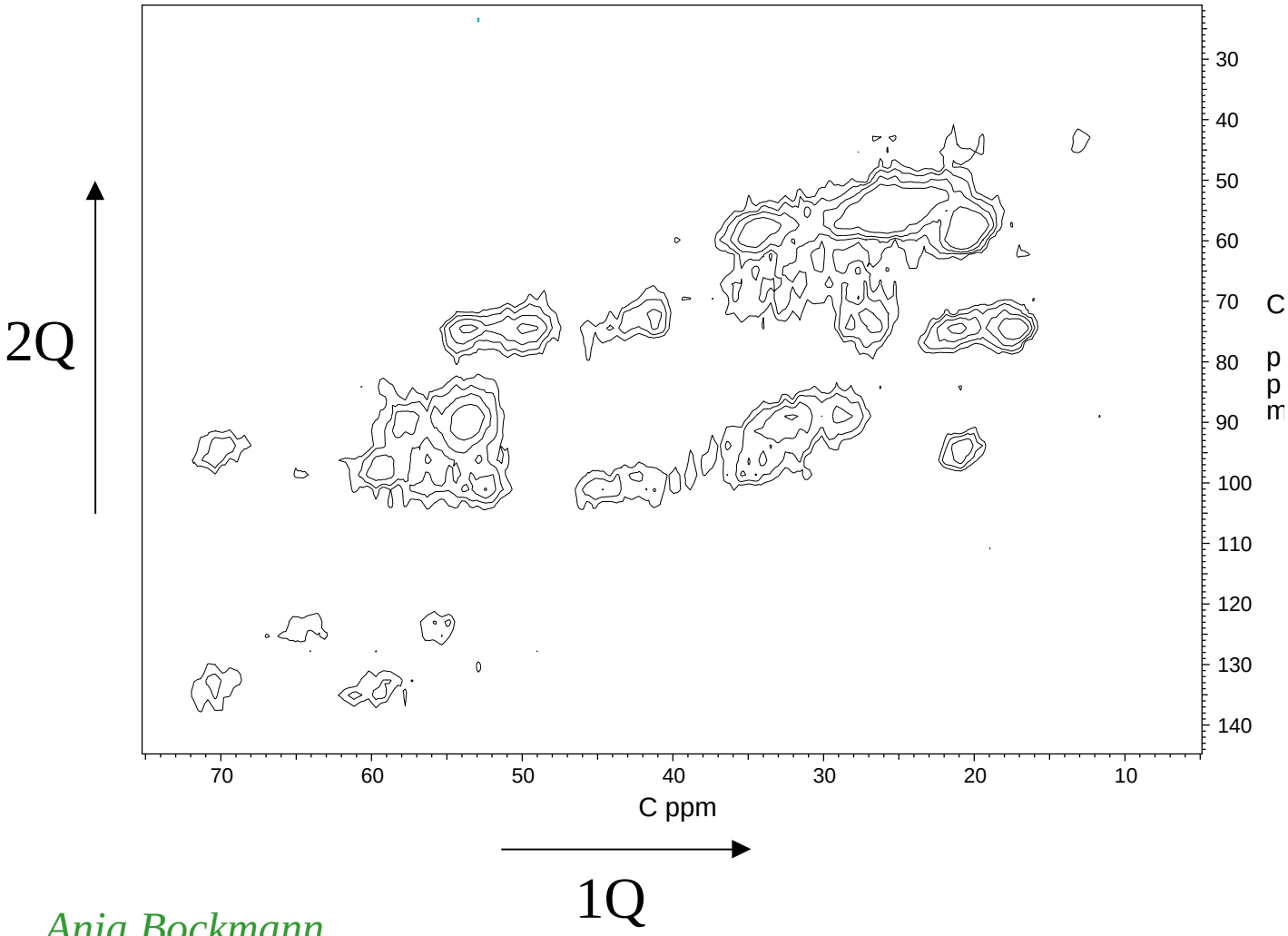
2Q ^{13}C Spectrum with

$\mathbb{C}14_4^5$

$\mathbb{C} = 360_0$

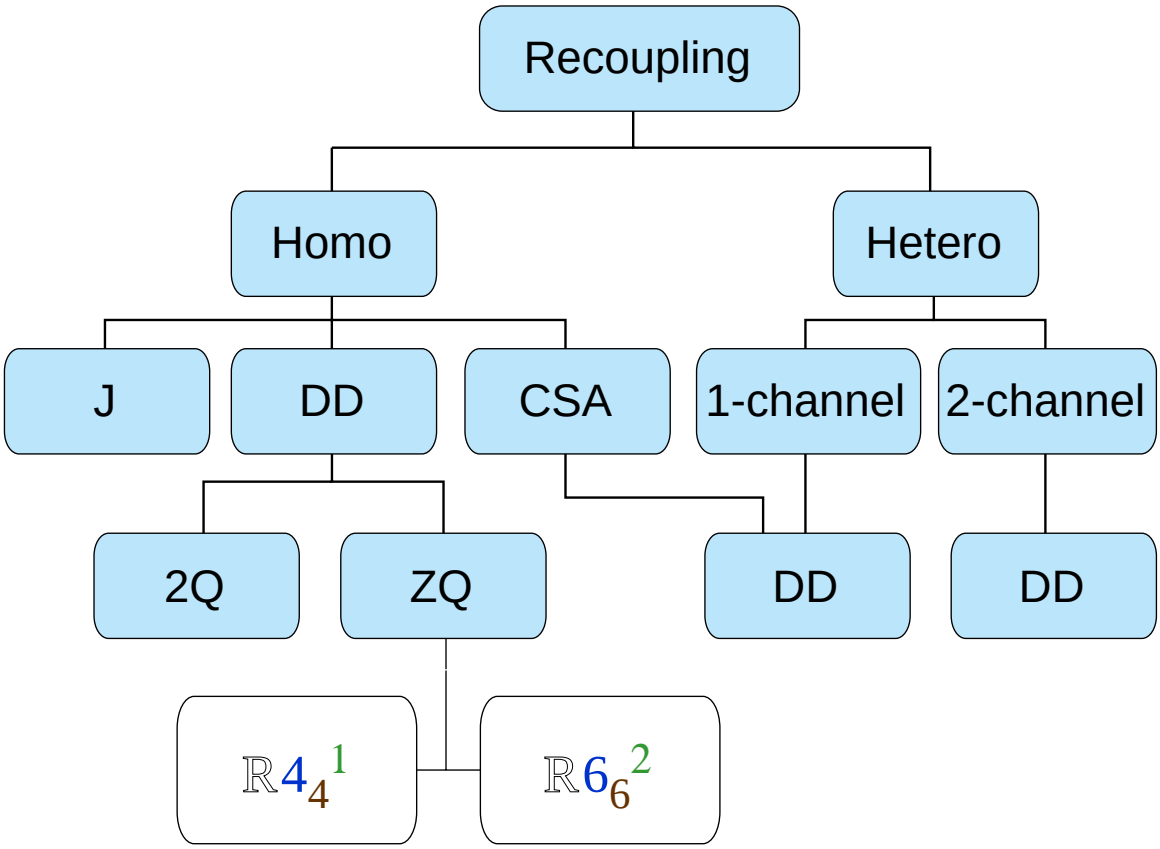
[U-^{13}C]-catabolite repression HPr (11 kDa), aliphatic region
spinning frequency = 14 kHz; field = 9.4 T

SC14 spectrum of CRH - aliphatic resonances



Anja Bockmann,
François Penin
Andreas Brinkmann

Symmetry Solutions for ZQ Recoupling

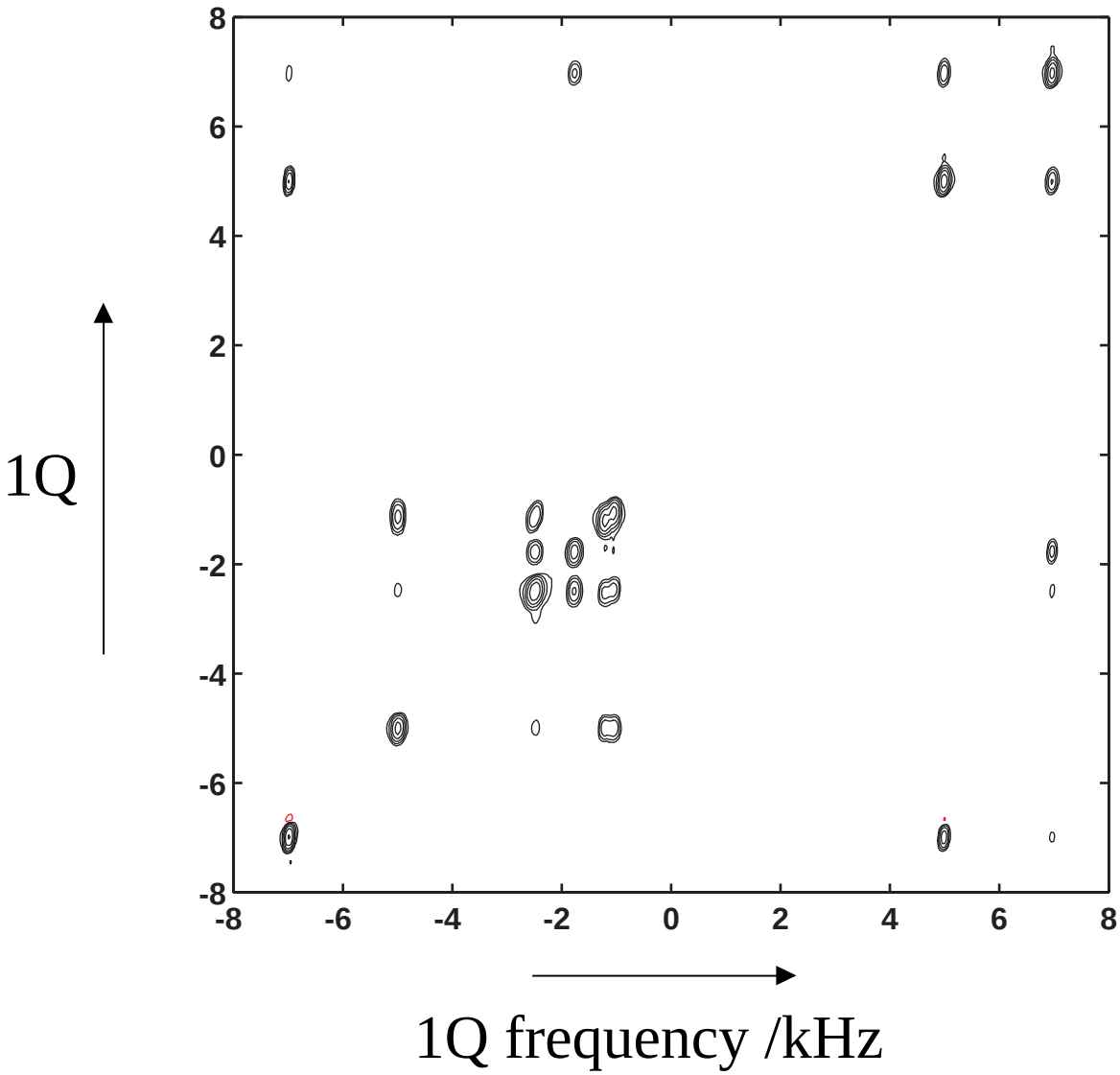


^{13}C-^{13}C correlation with

$$\mathbb{R}6_6^2$$

$$\mathbb{R} = 90_{180}\,270_0$$

[U-^{13}C]-tyrosine; spinning frequency = 28 kHz; mixing interval = 1 ms; field = 9.4 T



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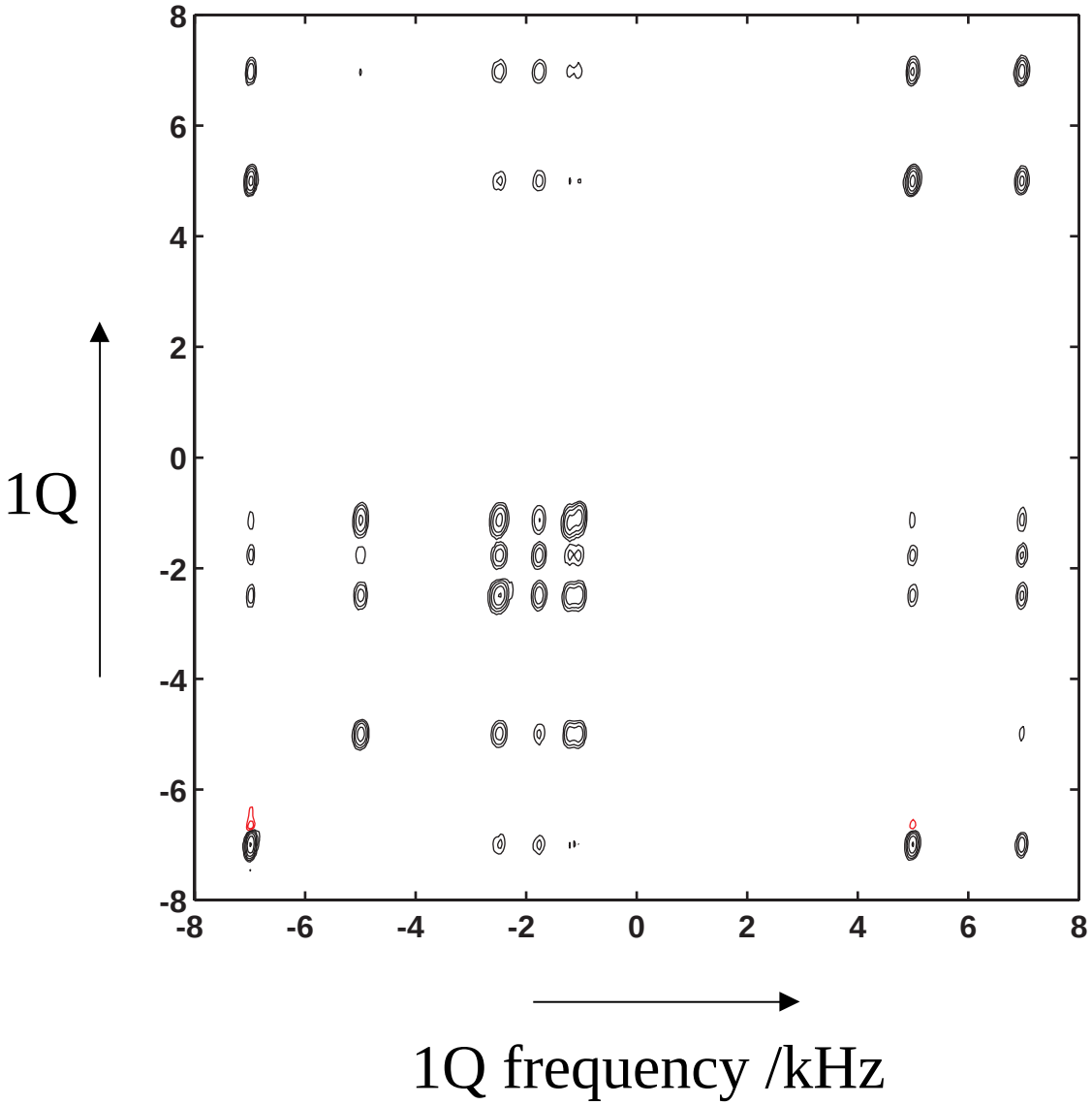
Jörn Schmedt auf der Günne

^{13}C-^{13}C correlation with

$$\mathbb{R}6_6^2$$

$$\mathbb{R} = 90_{180}\,270_0$$

[U-^{13}C]-tyrosine; spinning frequency = 28 kHz; mixing interval = 10 ms; field = 9.4 T



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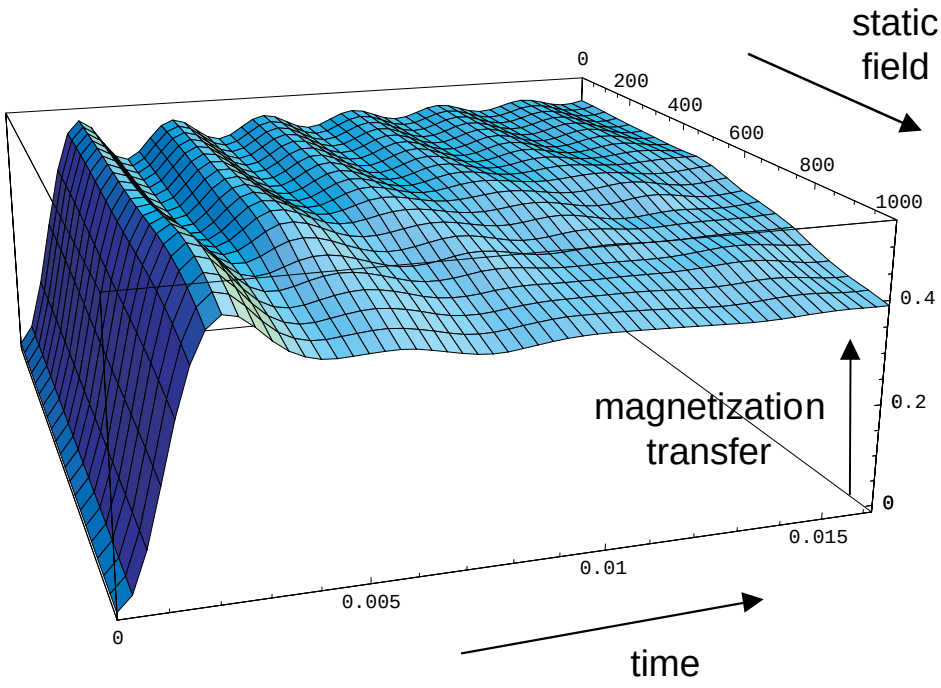
Simulations at 38 kHz MAS

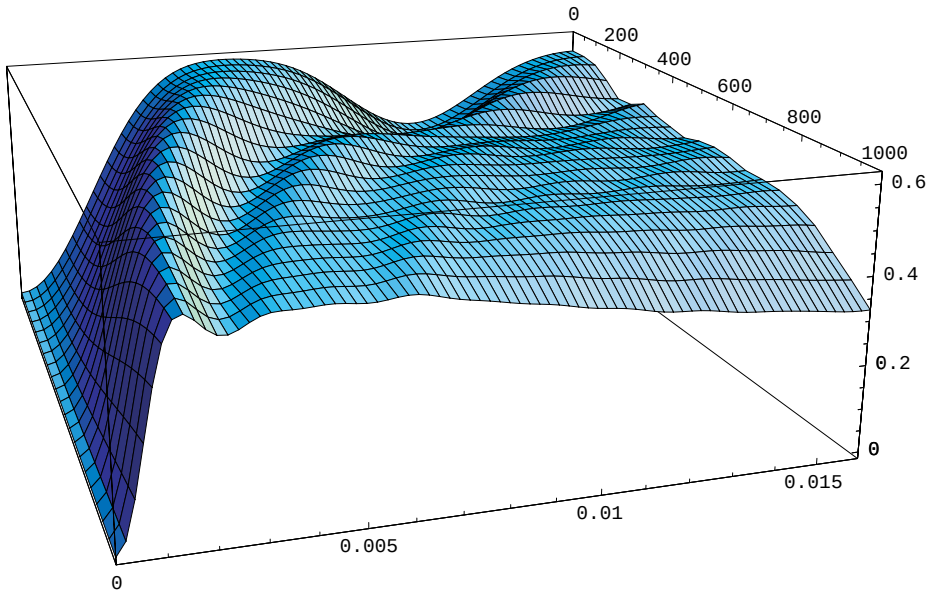
$\mathbb{R}6_6^2$

(with 38 kHz rf field)



RFDR

(with 150 kHz rf field)



38kHz spinning;
$^{13}C_2$-glycine parameters

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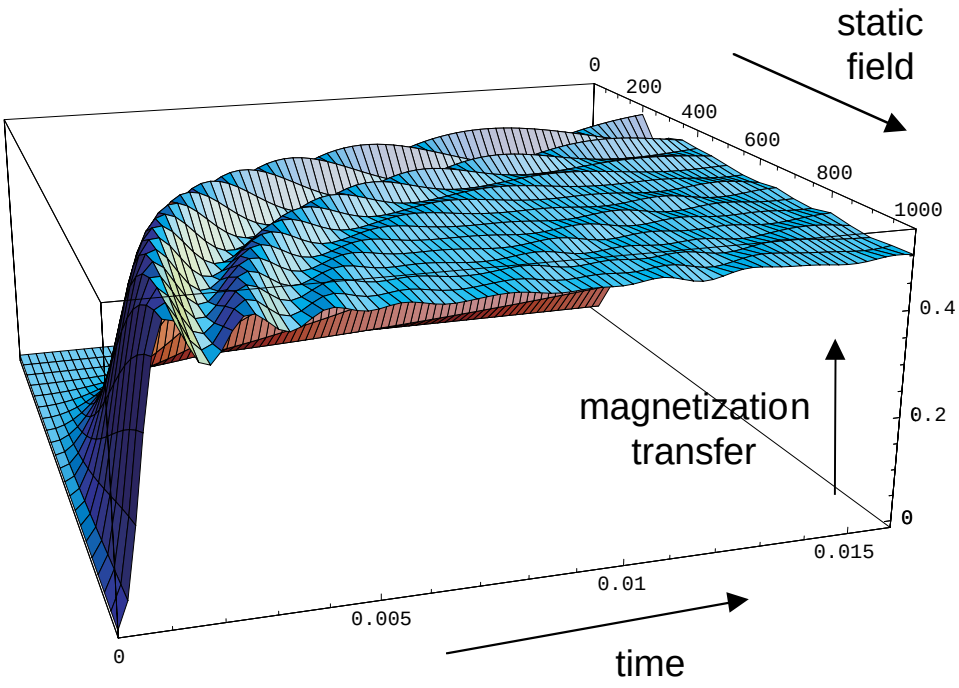
RFDR / RIL comparison

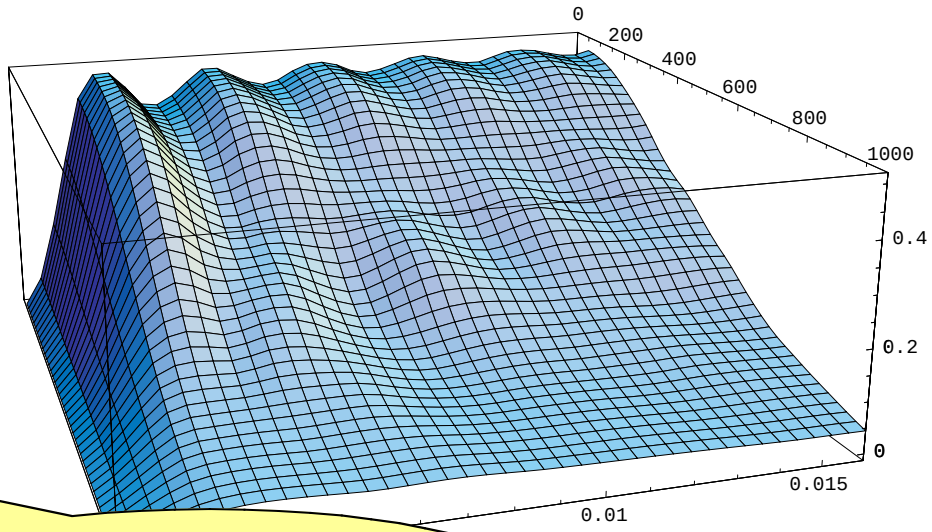
RFDR

(38 kHz MAS, infinite rf field)



RIL

(5 kHz MAS, 50 kHz CW rf + infinitely strong π pulses)



RIL can't be implemented at high MAS freq

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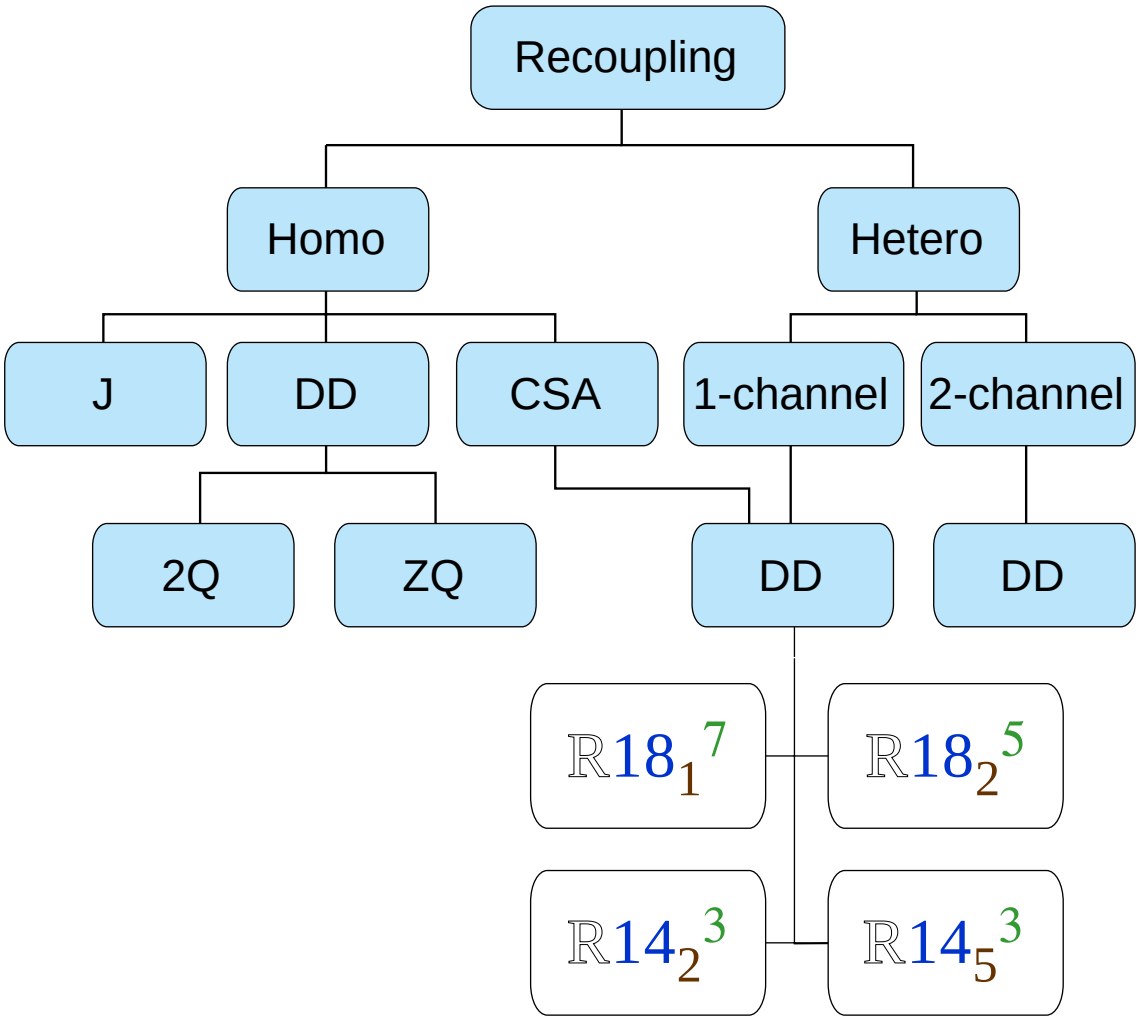
$^{13}C_2$-glycine parameters

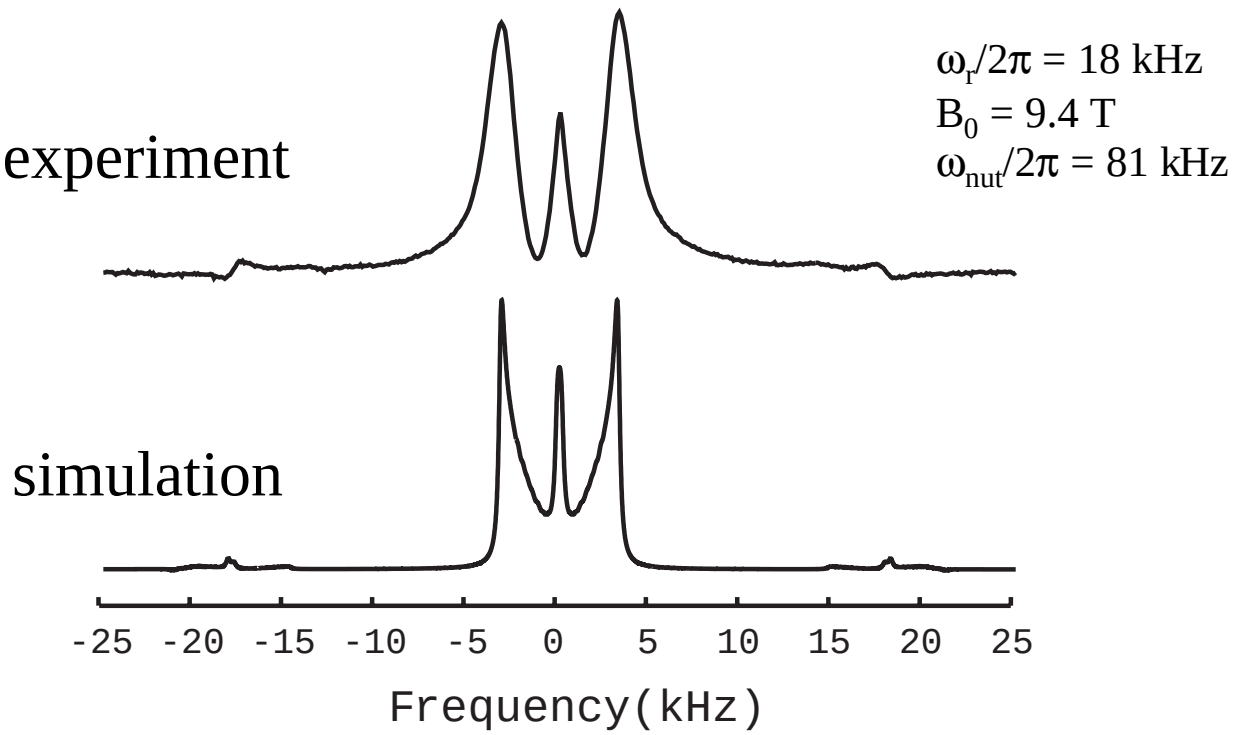
Heteronuclear DD & CSA Recoupling



Heteronuclear Recoupling by $\mathbb{R}18_2^5$: CH case

$\mathbb{R} = 180_0$

^{13}C spectrum of [^{15}N, 2-^{13}C]-alanine, with $\mathbb{R}18_2^5$ applied to the protons



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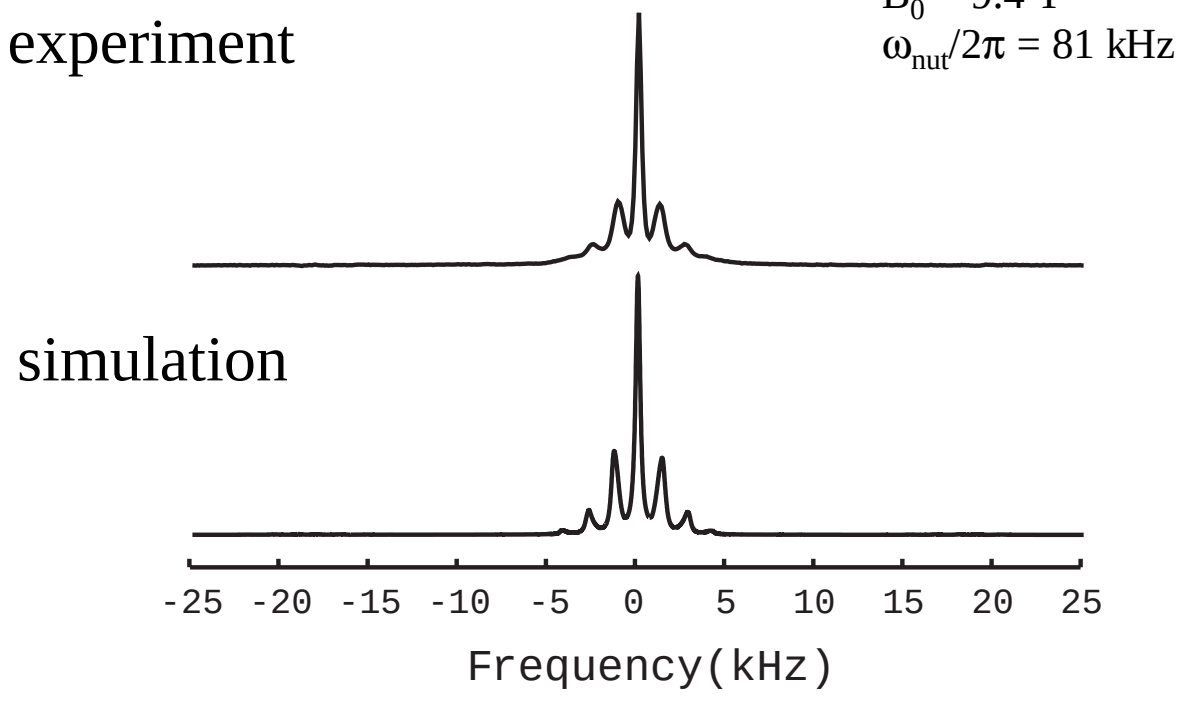
Heteronuclear Recoupling by $\mathbb{R}18_2^5$: CH_3 case

$\mathbb{R} = 180_0$

^{13}C spectrum of [3-^{13}C]-alanine,
with $\mathbb{R}18_2^5$ applied to the protons

$\omega_r/2\pi$ = 18 kHz
B_0 = 9.4 T
$\omega_{nut}/2\pi$ = 81 kHz



Xin Zhao, Mattias Edén

Conclusions

- Symmetry solutions exist for a wide range of decoupling/recoupling tasks in MAS NMR
- Capable of good performance at high spinning frequencies/high fields
- Quantitative spin dynamics -- detailed structural information

Coworkers

Stockholm

- Marina Carravetta
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