Institut für Technische und Makromolekulare Chemie | RWTH AACHEN UNIVERSITY

MAX PLANCK INSTITUTE FOR CHEMICAL ENERGY CONVERSION

Accurate Homonuclear Distance Measurements Enabled by Fast Magic-Angle-Spinning Double-Quantum NMR Spectroscopy

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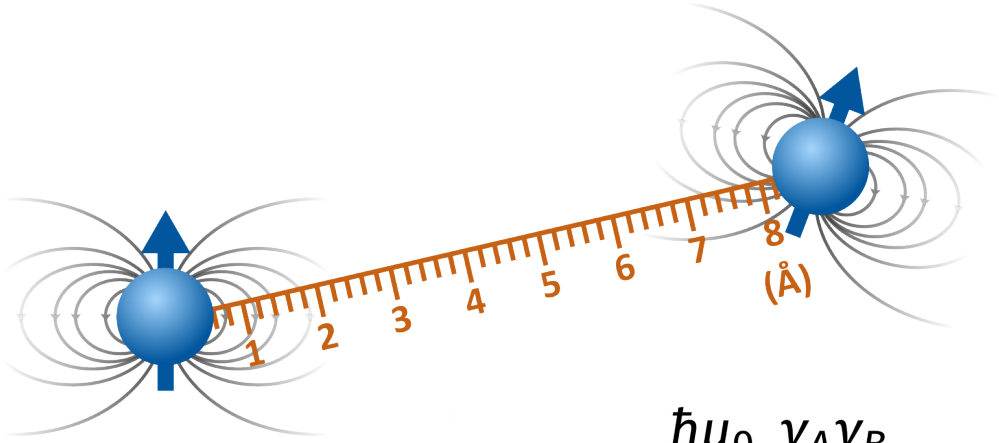
Group of Prof. Thomas Wiegand (MPI CEC / RWTH Aachen University)

August 24th, 2026
Davos, Switzerland

Solid-state NMR measurements of homonuclear distances



$$b_{AB} = -\frac{\hbar\mu_0}{4\pi}\frac{\gamma_A\gamma_B}{2\pi r_{AB}^3}$$

nuclear magnetic dipole-dipole interactions

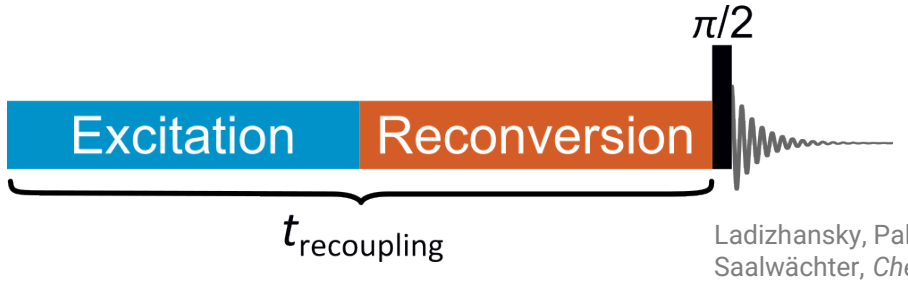
- *Distance restraints in disordered systems*
- *Structure & conformer determination*
- *Dynamics*
- …

- Heteronuclear distance measurements: classical REDOR approach …
- Homonuclear distance measurements with a high accuracy are challenging.

Shcherbakov, Medeiros-Silva, Tran, Gelenter, Hong, *Chem. Rev.* 2022, *122*, 9848-9879.
Hodgkinson, Emsley, *J. Magn. Reson.* 1999, *139*, 46-59.

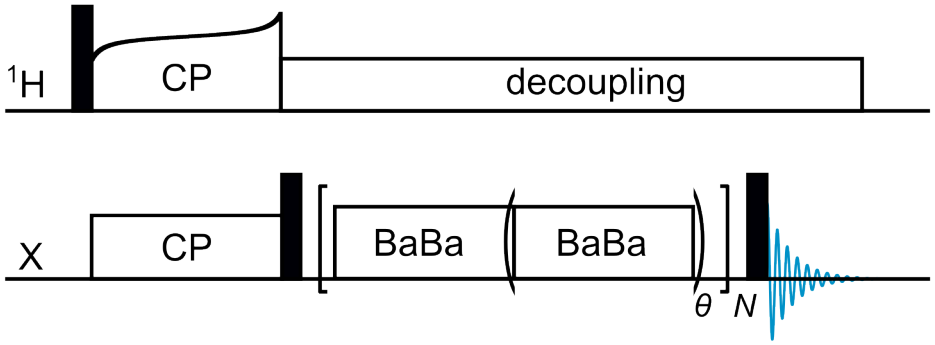
Solid-state NMR measurements of homonuclear distances

- Measure dipolar-coupling strength based on double-quantum (DQ) coherence excitation.



Ladizhansky, Palani, Mardini, Griffin, *Chem. Rev.* 2024, *124*, 12844-12917.
Saalwächter, *ChemPhysChem* 2013, *14*, 3000-3014.
Graf, Heuer, Spiess, Phys. Rev. Lett. 1998, *80*, 5738-5741.

- A robust experimental scheme:



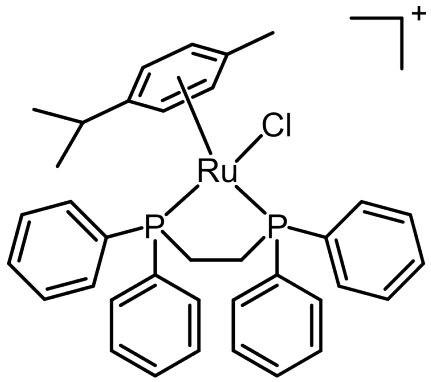
BaBa-xy16 recoupling: easy, efficient, and broadband

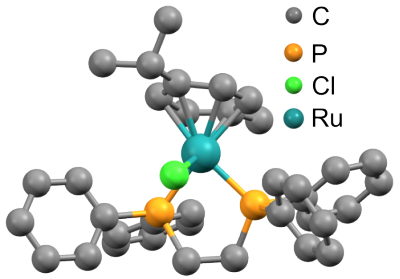
Constant-time Double-Quantum based Dipolar Recoupling Effects Nuclear Alignment Reduction (CT-DRENAR)

Experimental setup:
Ren, Eckert, *J. Magn. Reson.* 2015, 260, 46-53.
Ren, Eckert, *Solid State Nucl. Magn. Reson.* 2015, 71, 11-18.

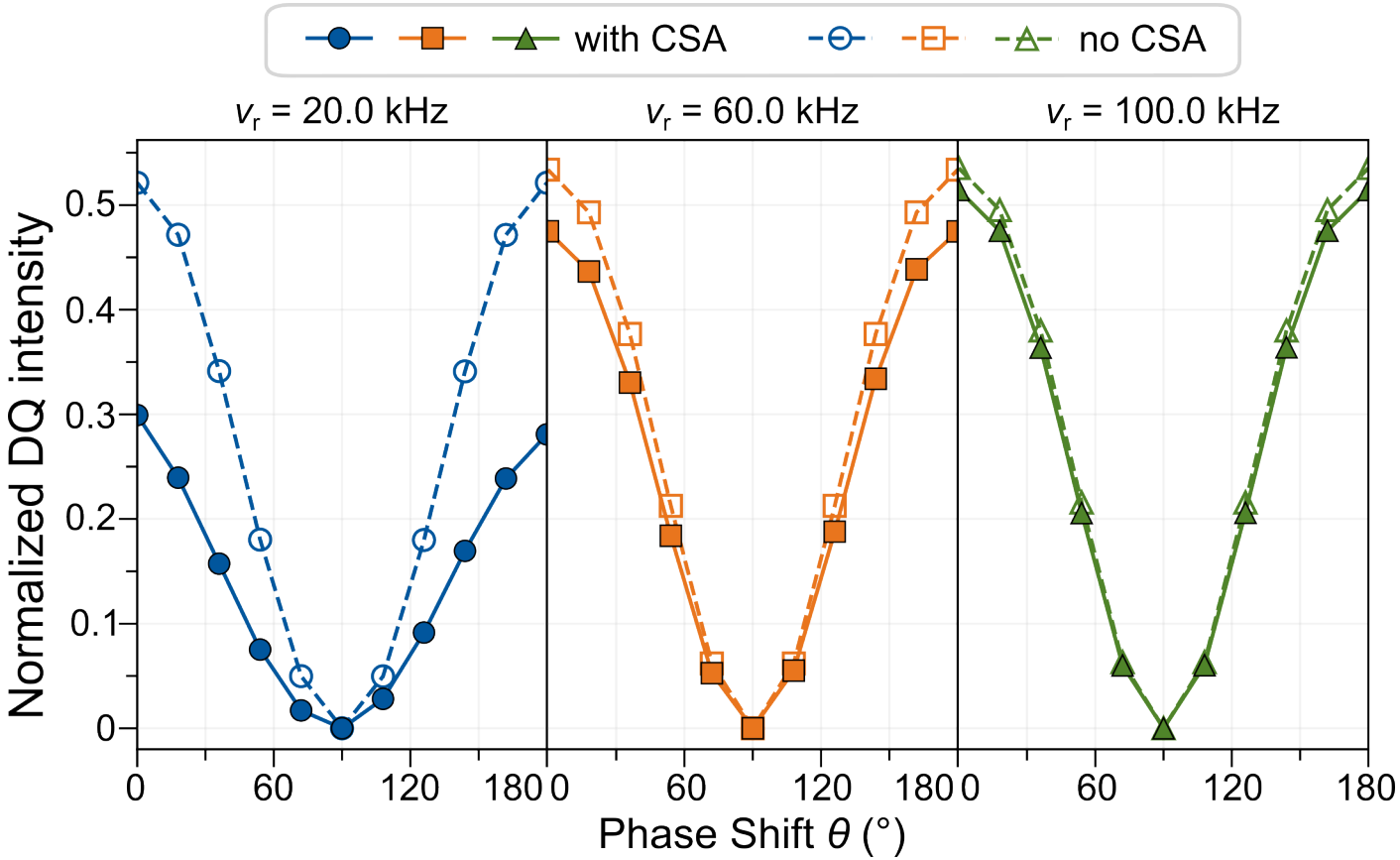
BaBa recoupling:
Saalwächter, Lange, Matyjaszewski, Huang, Graf, *J. Magn. Reson.* 2011, *212*, 204-215.
Feike, Demco, Graf, Gottwald, Hafner, Spiess, *J. Magn. Reson., Ser. A* 1996, *122*, 214-221.

Effect of chemical-shift anisotropy on DQ excitation





Ru-dppe

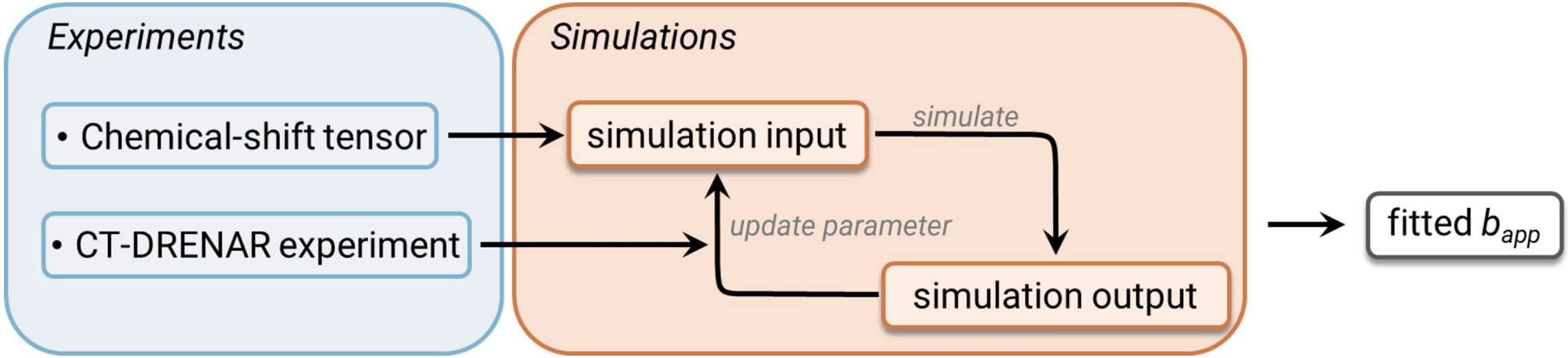


- Chemical shift anisotropy (CSA) leads to low DQ excitation efficiencies.
- Can be suppressed under fast MAS.

As mentioned in:
Saalwächter, Lange, Matyjaszewski, Huang, Graf, *J. Magn. Reson.* 2011, *212*, 204-215.
Kristiansen, Carravetta, van Beek, Lai, Levitt, *J. Chem. Phys.* 2006, *124*, 234510.
Gilchrist, Monde, Tomita, Iwashita, Nakanishi, McDermott, *J. Magn. Reson.* 2001, *152*, 1-6.

Fitting experimental data with numerical simulations

- We have established a numerical simulation approach to fit the experimental data and extract an apparent dipolar coupling constant (b_{app}).

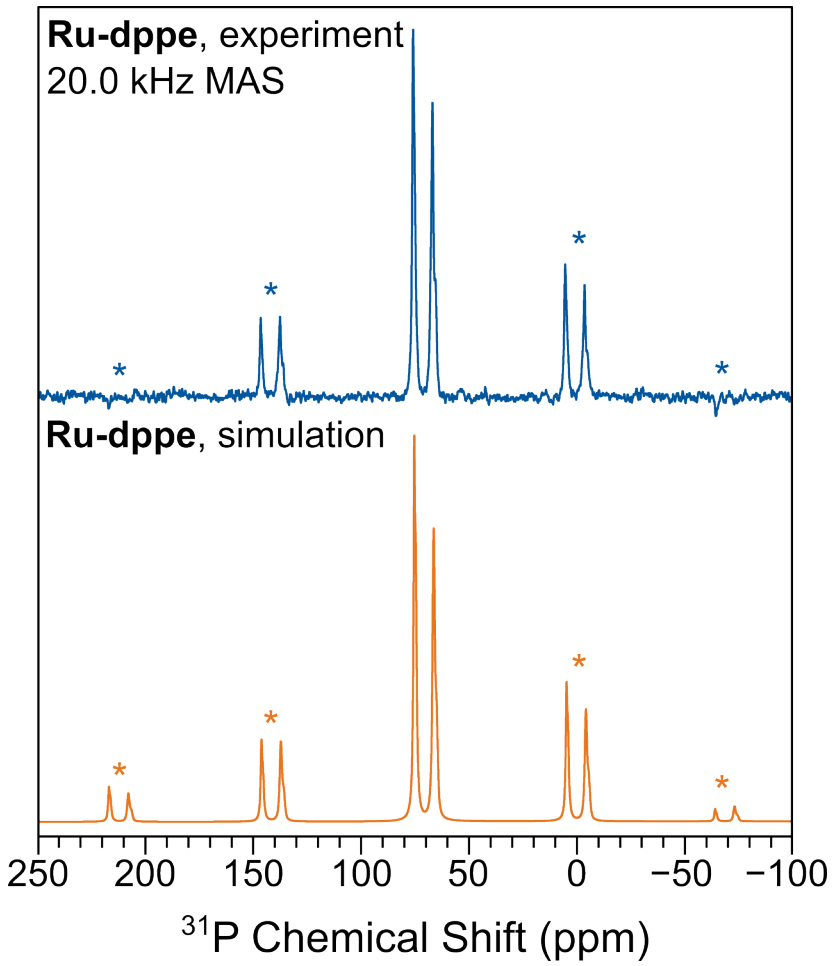


Chemical-shift tensor:

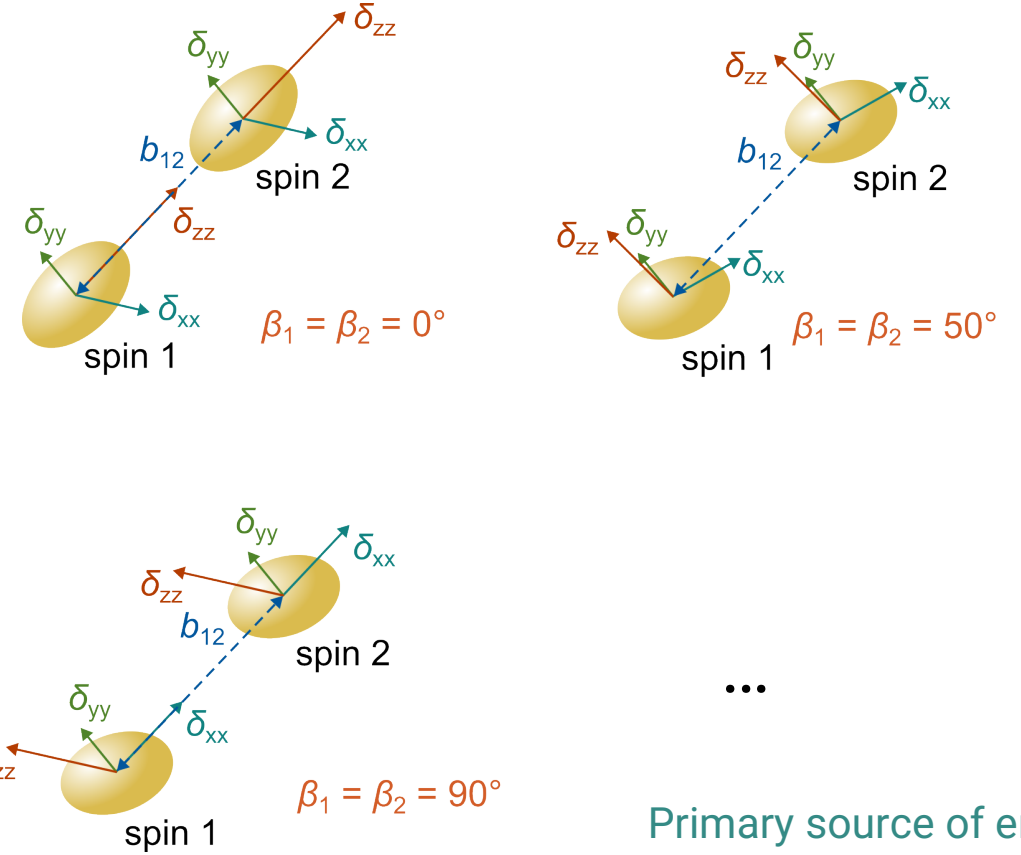
- Principal values: δ_{xx}, δ_{yy}, δ_{zz}
- Principal axis system (PAS) orientation: α, β, γ

Fitting experimental data with numerical simulations

Principal values: δ_{xx}, δ_{yy}, δ_{zz}



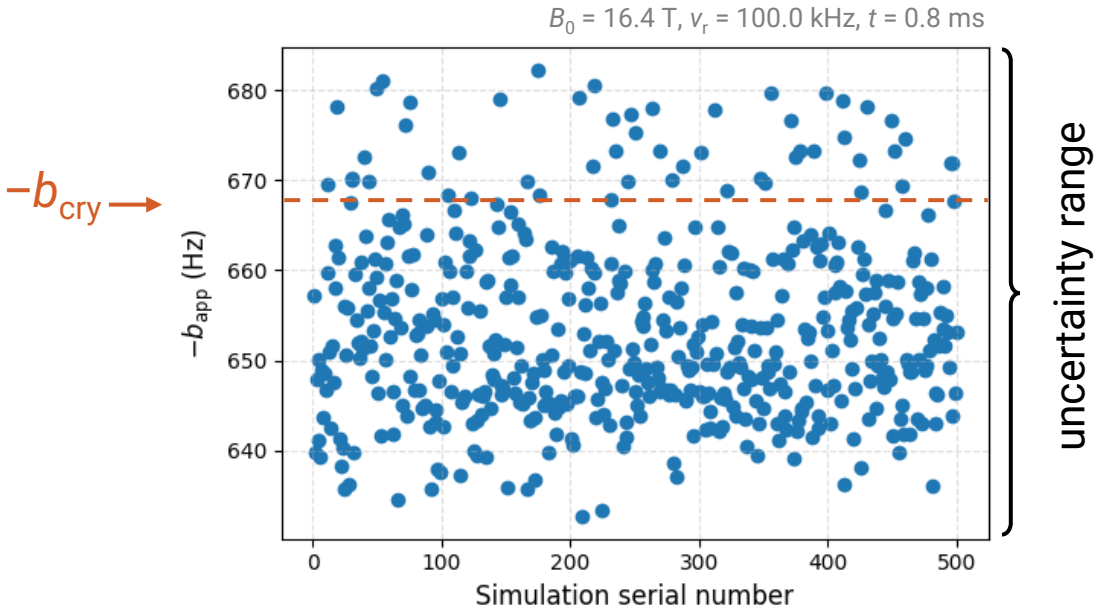
PAS orientation: α, β, γ

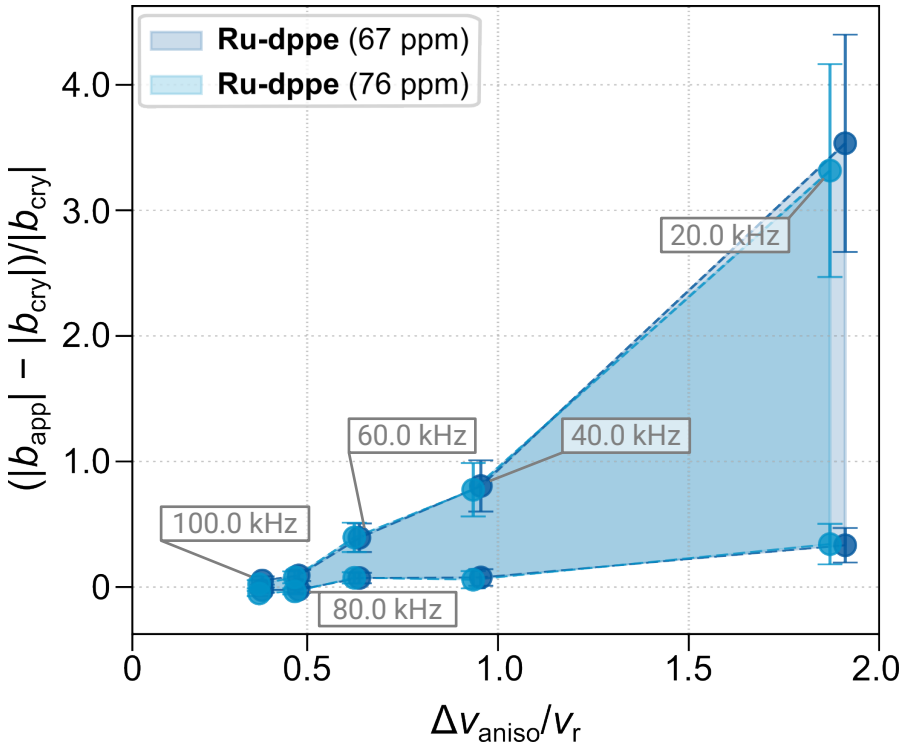


Primary source of error
(check the manuscript)

Improving accuracy with fast MAS

- Quantifying the uncertainty: Monte-Carlo sampling of tensor PAS orientations.



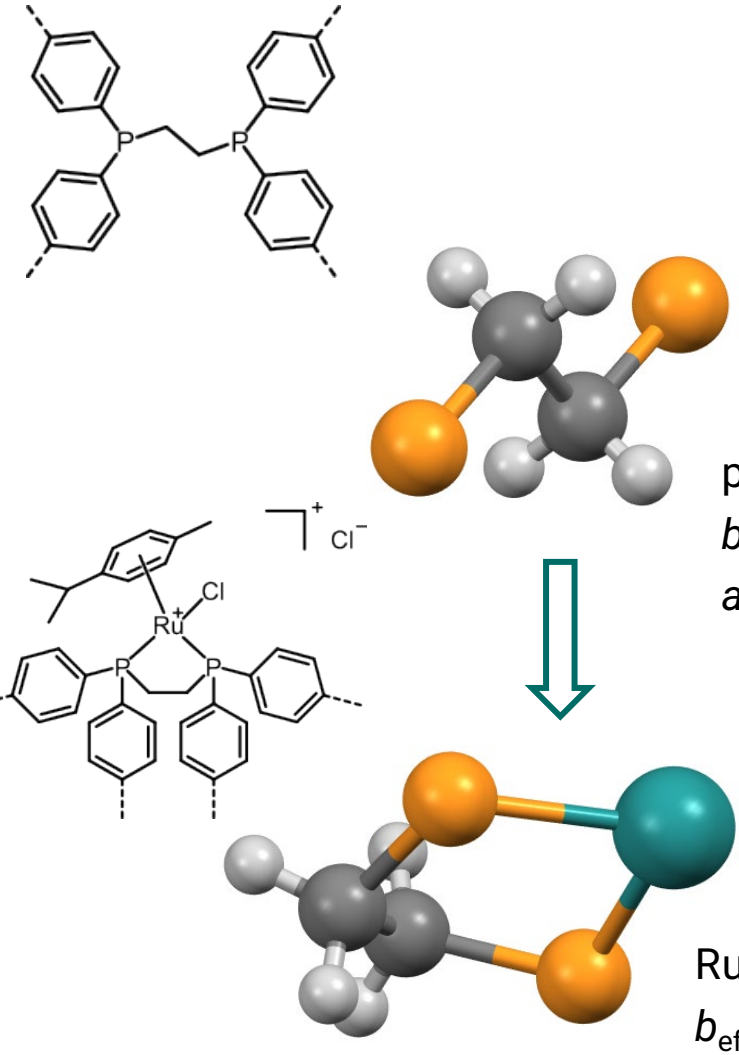


- Experimentally determined δ_{aniso} = 133 ppm, $\Delta\nu_{aniso}$ = 37.8 kHz (16.4 T)
- Measured r_{app} = [3.07 ± 0.02, 3.15 ± 0.01] Å compared to r_{cry} = 3.09 Å

Monte-Carlo sampling:
Gilchrist, Monde, Tomita, Iwashita, Nakanishi, McDermott, *J. Magn. Reson.* 2001, *152*, 1-6.

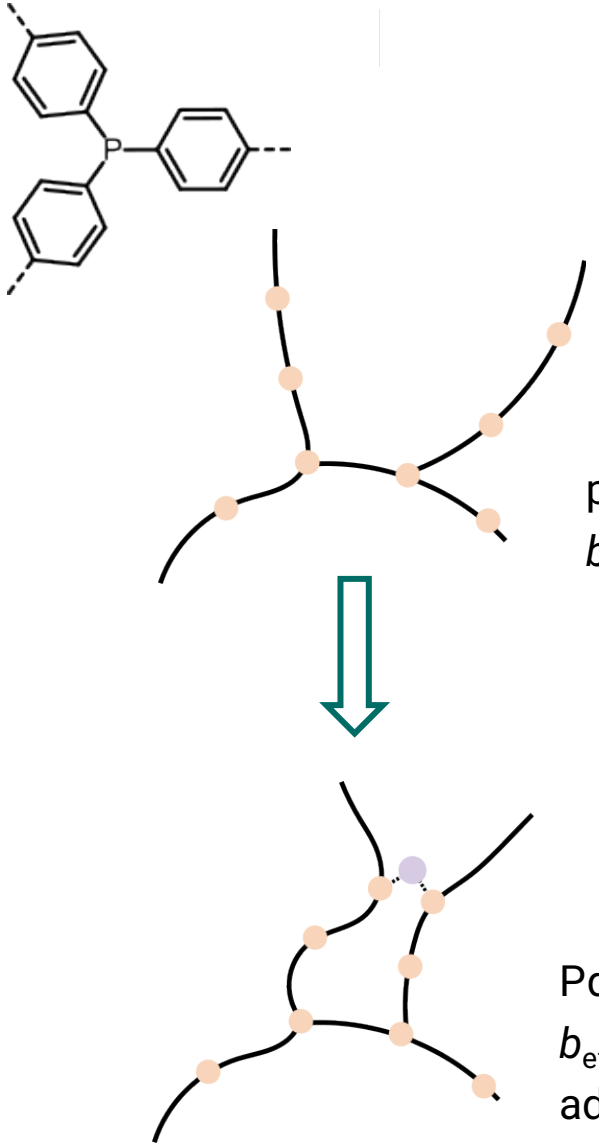
Conformational changes in heterogeneous catalysts

Janine Baums
Julia Nikodemus
Prof. Regina Palkovits
(RWTH Aachen)



pdppe polymer
b_{eff} = 286(4) ~ 303(4) Hz
anti-conformation

Ru@pdppe
b_{eff} = 626(22) ~ 674(32) Hz
nearly *gauche*-conformation

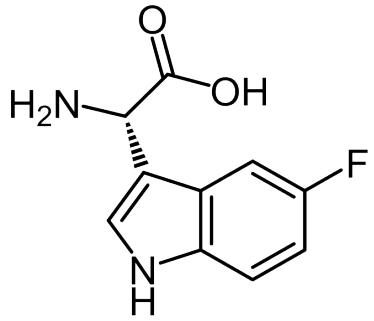


pTPP polymer
b_{eff} ≈ 105 Hz

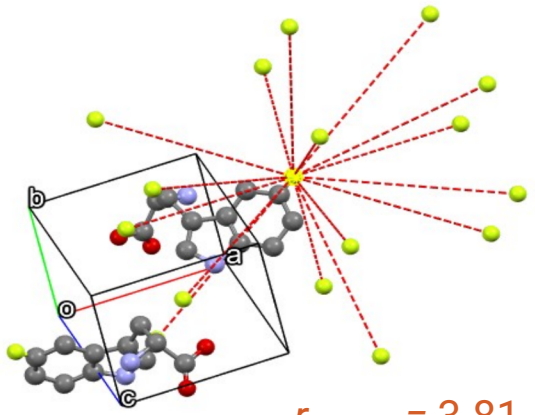
Pd@pTPP
b_{eff} ≈ 240 Hz
additional cross-linking

Baums, Kappel, Meise, Heggen, Weidenthaler, Hausoul, Palkovits, *ChemCatChem* 2025, *17*, e202402048.

Application to ^{19}F–^{19}F distance measurements



5-F-***L***-Tryptophan

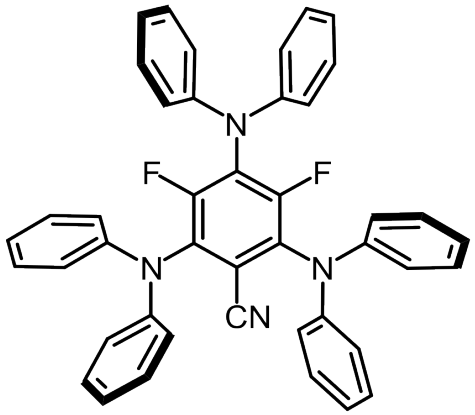


$r_{eff,\,cry}$ = 3.81 Å

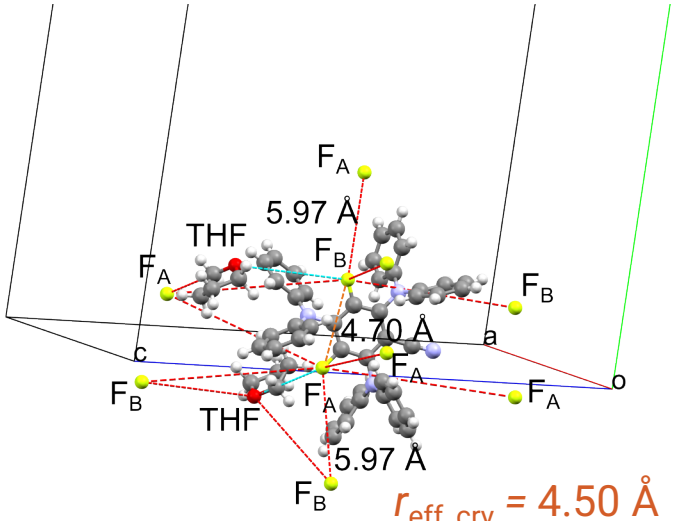
- $\Delta\nu_{aniso}$ = 35 kHz (16.4 T)

B_0 = 16.4 T, ν_r = 100.0 kHz, t = 0.16 ms

- Measured r_{app} = [3.72 ± 0.02, 3.81 ± 0.02] Å
- Error of 0.09 Å (2%)



3DPAFBN



$r_{eff,\,cry}$ = 4.50 Å

Tom Gabler
Prof. Kirsten Zeitler
(Leipzig University)

- $\Delta\nu_{aniso}$ = 70 kHz (16.4 T)

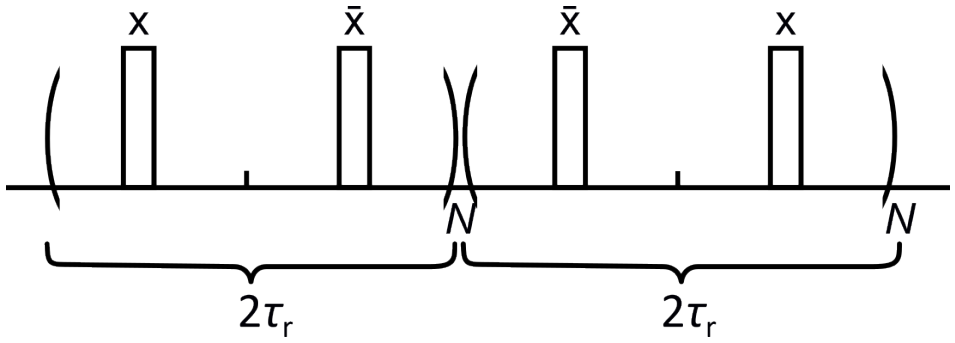
B_0 = 16.4 T, ν_r = 100.0 kHz, t = 0.48 ms

- Measured r_{app} = [4.34 ± 0.08, 4.82 ± 0.03] Å
- Error of 0.3 Å (7%)

Summary & outlook

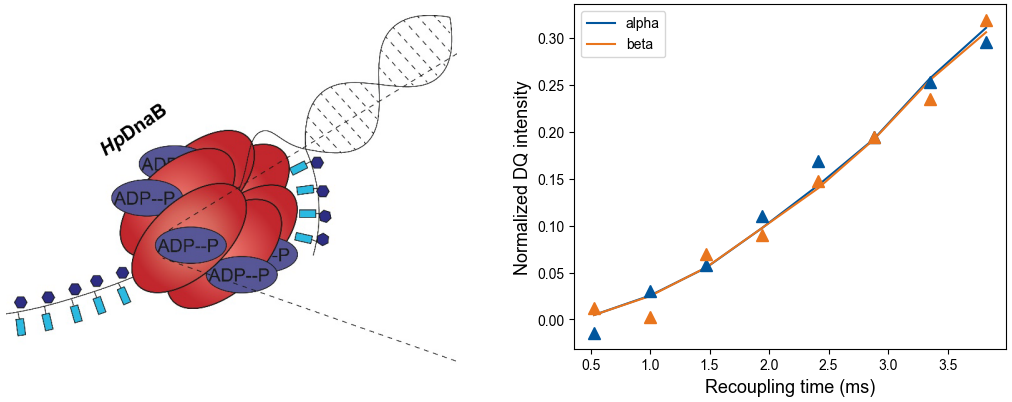
- Efficient DQ excitation: BaBa-xy16 & fast MAS.
- Quantified uncertainty: numerical simulation & Monte-Carlo sampling.
- ^{31}P and ^{19}F model systems: accuracy of 0.05 – 0.5 Å.

- *Alternative pulse sequence (e.g. $BR2_2^1$)*



Hu, Delevoye, Lafon, Trébosc, Amoureux, *J. Magn. Reson.* 2009, *200*, 178-188.
Zhang, Wang, Liu, Hu, Chen, Li, Amoureux, *Phys. Chem. Chem. Phys.* 2011, *13*, 5617-5620.

- *ADP-DNA binding in a DnaB helicase*



Wiegand, Böckmann, Meier *et al.*, *Nat. Commun.* 2019, *10*, 31.
Malär, Meier, Wiegand *et al.*, *Nat. Commun.* 2021, *12*, 5293.

Acknowledgements

Check the preprint:

Wu *et al.*, "Accuracy in Homonuclear Distance Determinations by Solid-State NMR Spectroscopy: The Benefits of Fast Magic-Angle Spinning up to 100 kHz", *ChemRxiv* (available soon …)

My webpage and GitHub account: https://yufewu.github.io/

- Python package for data simulation and analysis.
- Rotor-management system with a web-interface.

Thank you for your attention!

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Prof. Dr. Kirsten Zeitler (Leipzig University)