



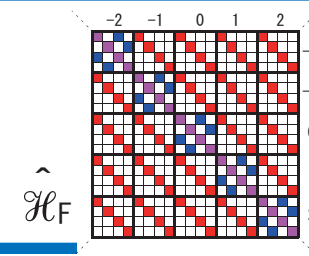
KYOTO UNIVERSITY
Global COE Program

INTEGRATED
MATERIALS SCIENCE

グローバルCOE講演会

Dr. Matthias Ernst

Physical Chemistry, ETH Zürich, Switzerland



Lectures on Advanced Solid-State NMR

2009.8.31 Mon. - 9.1 Tue

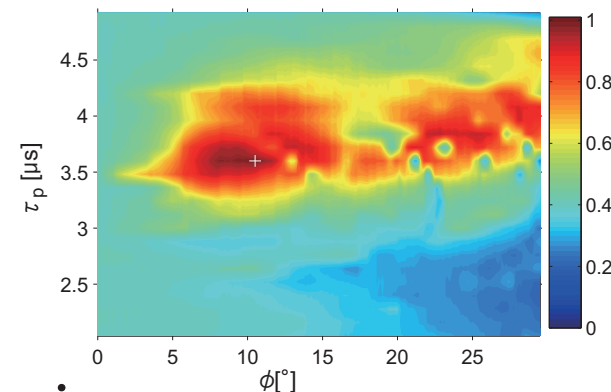
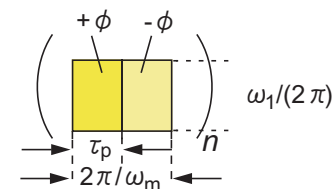
Faculty of Science Bldg. No. 6 Room 571

31 August 14:00-

1. Floquet Theory in Solid-State NMR: Introduction and Examples
2. Heteronuclear Spin Decoupling Under Magic-Angle Spinning
3. Spin Diffusion in MAS Solid-State NMR

1 September 10:00 - 12:00

4. Low RF Power and Fast Magic-Angle Spinning:
Challenges and New Opportunities
5. Echo-Phenomena in Solids:
Coherent Evolution and Spin Thermodynamics



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**TALK #1** *Floquet Theory in Solid-State NMR: Introduction and Examples*

The theoretical description of many experiments in solid-state NMR requires the treatment of multiple time dependencies in the Hamiltonian. The time dependencies originate from either macroscopic sample rotation (MAS, DOR, DAS) or from interaction-frame transformations if radio-frequency irradiations are involved. Treatment of time-dependent Hamiltonians is often done using Average Hamiltonian theory (AHT) [1] which is limited to a single cycle time. Treating Hamiltonians with multiple time dependencies using AHT requires approximations like a separation of time frames or the synchronization of frequencies.

This talk will give an introduction to Floquet theory [2] which will be illustrated using examples from solid-state NMR. Floquet theory has the advantage that it can describe multiple time dependencies in the Hamiltonian without making assumptions about the involved time scales of the characteristic frequencies. The emphasis will be on operator-based perturbation treatments where effective Hamiltonians can be derived in operator form [3-5] for problems of different dimensionality.

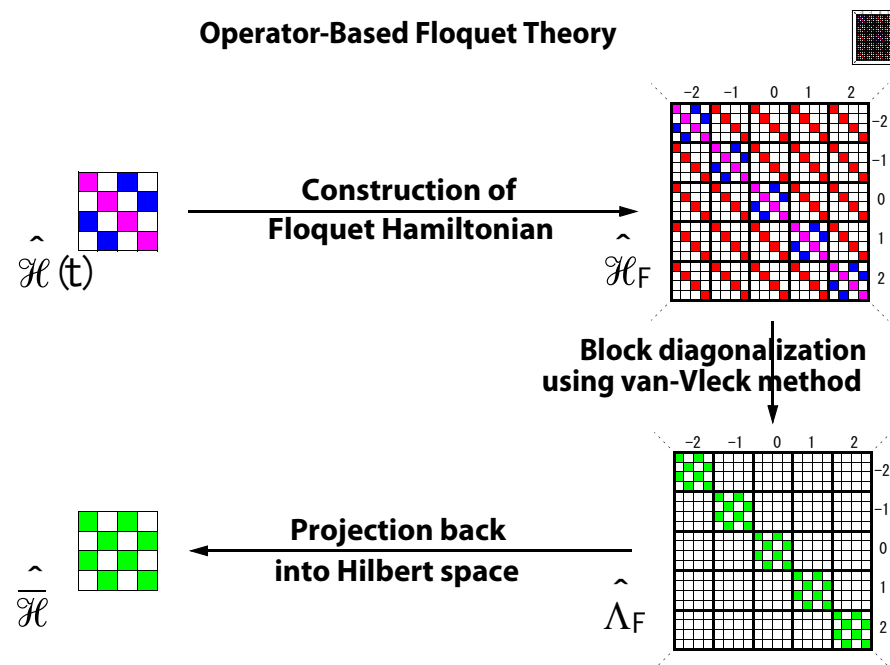
[1] Ulrich Haeberlen, "High Resolution NMR in Solids - Selective Averaging", Academic Press, New York (1976).

[2] J. H. Shirley, "Solution of the Schrödinger Equation with a Hamiltonian periodic in Time" Physical Review 138B, 979 (1965).

[3] Matthias Ernst, Ago Samoson, and Beat H. Meier, "Decoupling and Recoupling Using Continuous-Wave Irradiation in Magic-Angle-Spinning Solid-State NMR: A Unified Description Using Bimodal Floquet Theory.", The Journal of Chemical Physics 123, 064102-1-10 (2005).

[4] Matthias Ernst, Helen Geen, and Beat H. Meier, "Amplitude-Modulated Decoupling in Rotating Solids: A Bimodal Floquet Approach.", Solid-State Nuclear Magnetic Resonance 29, 2-21 (2006).

[5] Ingo Scholz, Paul Hodgkinson, Beat H. Meier, and Matthias Ernst, "Understanding two-pulse phase-modulated decoupling in solid-state NMR.", The Journal of Chemical Physics, 130, 114510 (2009).

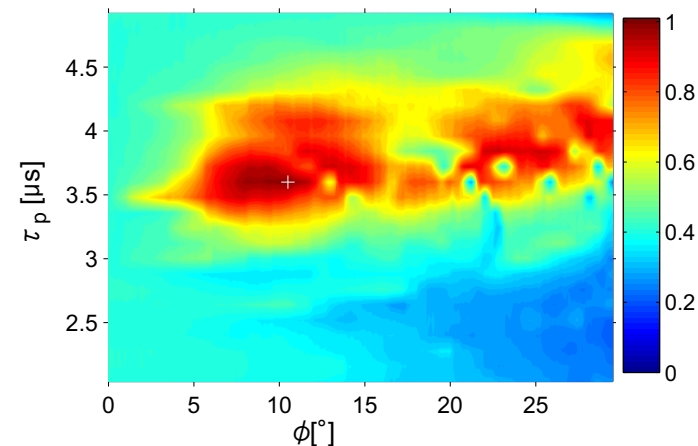




TALK #2 *Heteronuclear Spin Decoupling Under Magic-Angle Spinning*

Heteronuclear spin decoupling is an essential ingredient to obtain high-resolution spectra in solids under magic-angle spinning (MAS) conditions. [1] Initially high-power continuous-wave (cw) decoupling was used but it was observed that with increasing MAS frequencies the residual line width increases significantly. Therefore, multiple-pulse decoupling sequences have become very important at higher MAS frequencies.

A full analysis of decoupling sequences is only possible in an interaction frame where the rf Hamiltonian is transformed away. In such an interaction frame, the Hamiltonian is always time dependent with at least two frequencies: the MAS frequency and the basic frequency of the pulse sequence. Depending on the details of the decoupling sequence, additional frequencies can be present in the interaction frame. Time-dependent Hamiltonians with multiple frequencies can best be described using multi-mode Floquet theory [2] where incommensurate and commensurate frequencies can be treated. Using an operator-based perturbation treatment, one can obtain time-independent effective Hamiltonians. It is then possible to analyze the effective Hamiltonian in terms of the three effects discussed above. Using such an approach, one can understand the decoupling quality as a function of the experimental parameters like pulse length, rf-field amplitude and phase angles of commonly used decoupling sequences like cw decoupling, two-pulse phase-modulated (TPPM) decoupling [3], or XiX decoupling [4].



[1] Matthias Ernst, "Heteronuclear spin decoupling in solid-state NMR under magic-angle sample spinning", *J. Magn. Reson.* 162, 134 (2003).

[2] Matthias Ernst, Ago Samoson, and Beat H. Meier, "Decoupling and recoupling using continuous-wave irradiation in magic-angle-spinning solid-state NMR: A unified description using bimodal Floquet theory", *J. Phys. Chem.* 123, 064102 (2005).

[3] Andrew E. Bennett, Chad M. Rienstra, Michèle Auger, K. V. Lakshmi, Robert G. Griffin, "Heteronuclear decoupling in rotating solids", *J. Chem. Phys.* 103, 69516958 (1995).

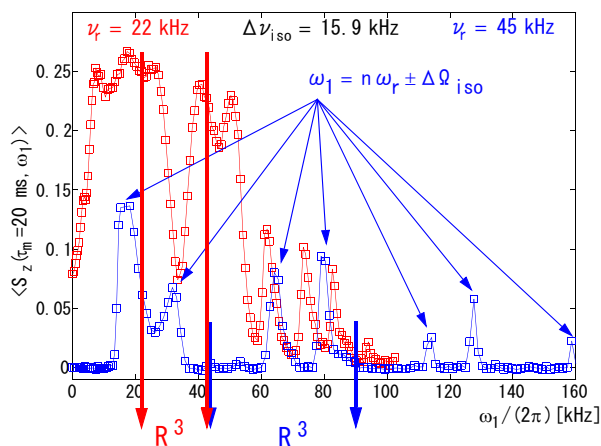
[4] Andreas Detken, Edme H. Hardy, Matthias Ernst, and Beat H. Meier, "Simple and efficient decoupling in magic-angle spinning solid-state NMR: the XiX scheme", *Chem. Phys. Lett.* 356, 298304 (2002).



TALK #3 Spin Diffusion in MAS Solid-State NMR

Proton-driven spin diffusion (PDSD) under magic-angle spinning (MAS) is one of the most important techniques in solid-state NMR to obtain distance constraints in uniformly or specifically labeled biomolecules. Advantages of PDSD over other pulse sequences are ease of implementation, low rf-field requirements, and reduced sensitivity to dipolar-truncation effects [1]. The latter is the reason that PDSD can also be used to obtain long-range distance constraints in uniformly labeled samples. At slower MAS frequencies, the residual line broadening by the heteronuclear dipolar couplings provides compensation for chemical-shift differences. At higher spinning frequencies, active recoupling of the heteronuclear dipolar couplings by cw irradiation of the protons at the $n=1$ rotary-resonance condition (DARR experiment [2],[3]) is used to broaden the lines and speed up the spin-diffusion process. The talk will emphasize three subjects related to the proton-driven spin-diffusion experiment:

- (i) Dipolar truncation. The PDSD experiment is one of the few experiments that allow the measurement of long-range distance constraints. This can be understood by analyzing the driving Hamiltonian of PDSD under MAS.
- (ii) Detailed investigation of the spin-diffusion process under cw irradiation of the proton. Using triple-mode Floquet theory [4], we explain why DARR is only effective in an intermediate spinning regime and not at fast MAS [5].
- (iii) Strong spinning-speed dependence of PDSD on the difference of the isotropic chemical shifts, spanning a range of 5-6 orders of magnitude. Its origin can be understood by using simple models for small spin systems.

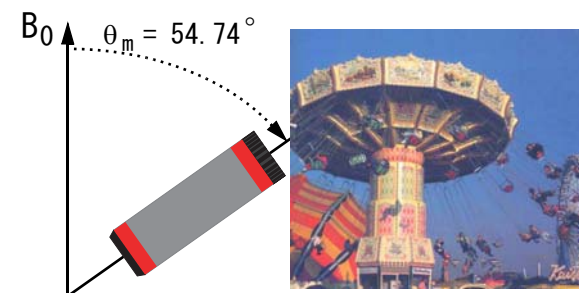


- [1] Andreas Grommek, Beat H. Meier, and Matthias Ernst, "Distance information from proton-driven spin diffusion under MAS", Chem. Phys. Lett. 427, 404-409 (2006).
- [2] K. Takegoshi, Shinji Nakamura, and Takehiko Terao, "¹³C-¹H dipolar-assisted rotational resonance in magic-angle spinning NMR", Chem. Phys. Lett. 344, 631-637 (2001).
- [3] K. Takegoshi, Shinji Nakamura, and Takehiko Terao, "¹³C-¹H dipolar-driven ¹³C-¹³C recoupling without ¹³C rf irradiation in nuclear magnetic resonance of rotating solids", J. Chem. Phys. 118, 2325-2341 (2003).
- [4] Ingo Scholz, Beat H. Meier, and Matthias Ernst, "Operator-Based Triple-Mode Floquet Theory in Solid-State NMR", J. Chem. Phys. 127 (2007).
- [5] Ingo Scholz, Theofanis Manolikas, Matthias Huber, Beat H. Meier, and Matthias Ernst, "MIRROR Recoupling And Its Application To Spin Diffusion Under Fast Magic-Angle Spinning", Chem. Phys. Lett. 460, 278-283 (2008).



TALK #4

Low RF Power and Fast Magic-Angle Spinning: Challenges and New Opportunities



Over the past years, magic-angle spinning (MAS) frequencies have been increasing up to 70 kHz that can be achieved with commercially available 1.3 mm MAS probes. Fast MAS is always connected to rotors of smaller diameter and, therefore, also smaller sample volume. The decreased sensitivity due to the reduced sample volume is only partially compensated by a larger filling factor (thinner rotor walls). There are several reasons why experiments under faster MAS are of interest. Firstly, the resolution of NMR spectra increases since rotational-resonance conditions can be avoided even at high static fields and decoupling performance increases with increasing MAS frequencies. Secondly, a new class of NMR experiments becomes accessible where rf-field amplitudes are lower than the MAS spinning frequencies [1-4]. Such low-power experiments reduce the sample heating induced by the electric field which is especially important for heat-sensitive samples. Thirdly, the implementation of adiabatic experiments that rely on resonance conditions involving the spinning frequency become more efficient.

In this talk I will discuss the advantages and disadvantages of low-power implementations of the various polarization-transfer and free-evolution time periods in typical NMR experiments, e.g., cross polarization, homonuclear polarization transfer, and decoupling during direct or indirect free evolution time.

[1] Matthias Ernst, Ago Samoson, and Beat H. Meier, "Low-Power Decoupling in Fast Magic-Angle Spinning NMR", *Chemical Physics Letters* 348, 293-302 (2001).

[2] Matthias Ernst, Andreas Detken, Anja Böckmann, and Beat H. Meier, "NMR Spectra of a Micro-Crystalline Protein at 30 kHz MAS.", *Journal of the American Chemical Society* 125, 15807-15810 (2003).

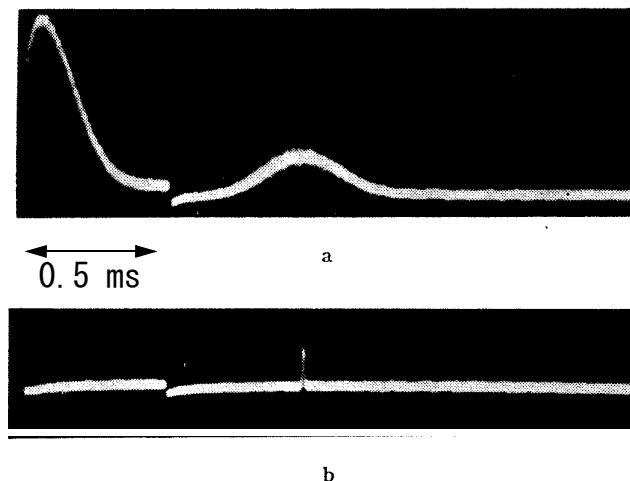
[3] Matthias Ernst, Marcel A. Meier, Ago Samoson, and Beat H. Meier, "Low-Power High-Resolution Solid-State NMR of Peptides and Proteins.", *Journal of the American Chemical Society* 126, 4764-4765 (2004).

[4] Adam Lange, Ingo Scholz, Theofanis Manolikas, Matthias Ernst, and Beat H. Meier, "Low-power cross polarization in fast magic-angle spinning NMR experiments.", *Chemical Physics Letters* 468, 100-105 (2009).



TALK #5 *Echo-Phenomena in Solids: Coherent Evolution and Spin Thermodynamics*

Since the first demonstration of spin echoes in 1950 by Erwin Hahn [1], they have attracted a lot of attention since they demonstrate the coherent time evolution of spin systems even if they appear to decay. This duality can be represented in the fact that on one hand we can describe many experiments in strongly-dipolar coupled spin systems using thermodynamic concepts where echo phenomena do not exist. But on the other hand, we can also describe them using the coherent time evolution of the spin system where we can induce echoes by inverting the sign of the Hamiltonian. The concepts and the limitations of the descriptions will be discussed based on spin-echo experiments in spin diffusion and in cross polarization under MAS.



E.L. Hahn, "Spin Echoes" Phys. Rev. 80, 580 (1950)

[1] Erwin L. Hahn, "Spin Echoes", Physical Review 80, 580 (1950).

[2] Susan M. De Paul, Marco Tomaselli, Alexander Pines, Matthias Ernst, and Beat H. Meier, "Reversal of Radio-Frequency Driven Spin Diffusion by Reorientation of the Sample Spinning Axis", The Journal of Chemical Physics 108, 826-829 (1998).

[3] Matthias Ernst, Beat H. Meier, Marco Tomaselli, and Alexander Pines, "Time Reversal of Cross Polarization in Solid-State NMR", Molecular Physics 95, 849-858 (1998).