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Pulsed Field Gradient NMR in Combination with Magic Angle Spinning - New Possibilities for Studying Diffusion in Lipid Membranes and Heterogeneous Materials

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1. Introduction

The **combination of MAS NMR spectroscopy with Pulsed Field Gradient (PFG) NMR** opens novel possibilities **for investigating diffusion processes of heterogeneous, non-liquid samples**. The advantages are based on the effect of line narrowing and concern (i) a prolongation of the intervals during which the magnetic field gradients may be applied and a corresponding enhancement in the sensitivity towards small molecular displacements as well as higher spatial resolution, and (ii) an enhanced resolution in the chemical shift scale. MAS PFG NMR facilitates investigations of materials that were hardly accessible by conventional PFG NMR-based techniques so far.
In this contribution, recent progress and novel technical possibilities in this field are demonstrated using examples from biophysical research and material sciences.

2. MAS PFG using strong gradient pulses

In lipid membranes, or other semi-solid systems, signals are broadened by several anisotropic interactions in the NMR Hamiltonian like magnetic susceptibility, chemical shift anisotropy or even dipolar coupling. [1] Those interactions have to be suppressed by spectroscopic techniques or by using solid-supported membranes oriented at the magic angle in order to observe resolved spectra and to apply echo sequences that use pulsed field gradients. The most effective technique to get rid of the unwanted broadening mechanisms and to produce highly resolved spectra with high sensitivity, is the application of magic angle sample spinning (MAS). [1]
Modern MAS probes for high-resolution MAS NMR (HR-MAS) are usually equipped with coils to produce pulsed field gradients.[2, 3] It has been shown that lateral diffusion can be nicely studied by using a combination of PFG and MAS. The technique has been successfully applied to study the lateral diffusion of molecules embedded in cubic liquid-crystalline phase and in lipid bilayers. [4-7]
It is highly desirable to develop MAS probes with PFG capabilities that allow the application of very strong gradient pulses. However, there are disadvantages if MAS stators are equipped with gradient coils - the Q factor of the resonance circuits may decrease which negatively affects the performance with respect to efficiency (short pulses and high sensitivity) and, due to the forces caused by the strong currents in the magnetic field, the mechanical stability might become an issue.
In this report we explore another setup, namely the use of a conventional narrow-bore MAS probe that is inserted into a micro-imaging system. This technique has some

important advantages compared to the construction of an MAS probe whose stator is wrapped by a gradient coil: i) The gradient coils are separated from the radio-frequency parts of the probe thus minimizing any impact of the gradient coils onto the radio-frequency properties of the probes circuits. ii) An external cooling of the gradient coils can be used, thus enabling high currents, high gradient strengths, and high linearity. iii) There is no torque acting on the stator caused by high currents in the gradient coils, which otherwise could compromise the mechanical stability and could disorient the sample, thus leading to distorted NMR results.

A remarkable increase in gradient strength available is achieved – strong, pulsed field gradients up to 2.6 T/m along the magic angle can be created with extremely high accuracy and stability. The micro-imaging device does not influence the performance of the probe and is not inducing forces on the sample. It is shown that PFG NMR-experiments using stimulated echo sequences can be performed on this system with great accuracy. [7]

In order to demonstrate the functioning of the described setup we have chosen a sample composed of the lipid 1-monooleoly-rac-glycerol (Monooleoin, MO) and deuterated water, which forms a bicontinuous cubic liquid-crystalline phase, a good model for biological membranes. The lateral diffusion coefficient of lipids and water could be measured with high precision.

Besides investigations of biological samples, MAS PFG NMR is demonstrated to have remarkable advantages in comparison with conventional PFG NMR, if applied to diffusion measurements in beds of nanoporous particles, notably zeolites. The strong gradients in combination with high spectral resolution allow the investigation of mixtures of molecules containing very fast and very slow diffusing molecules. This is demonstrated measuring the diffusion coefficients of water, benzene, ethene, and ethane simultaneously sorbed in NaX zeolite.

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