Solid State NMR

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Solid-state NMR spectroscopy is capable of providing valuable and detailed insight into the structure and the dynamics of a wide range of systems from classical polymers and liquid-crystalline materials to complex supramolecular architectures. In particular hydrogen bonds, intermolecular packing arrangements and dynamics of molecular segments can be investigated in great detail - in most cases without the need for special sample preparation. As an example, Figure 1 shows nanoscopic supramolecular columns with high charge carrier capabilities, formed by self-assembly of dendritic molecules, which has been elucidated by a combination of $^1$H solid-state NMR (spectra shown) and X-ray diffraction. In order to access and exploit the rich variety of information inherent to NMR spectra, the solid-state NMR group devotes considerable efforts to the development of new advanced methods and their application to systems of current interest.

The NMR methods currently developed and applied are all based on the technique of fast magic-angle spinning (MAS) which, at high spinning frequencies of up to 30 kHz, allows for an efficient suppression of typical interactions present in the solid state, such as chemical shielding anisotropies or dipole-dipole couplings which broaden the resonance lines and hamper the spectral resolution. Under fast MAS conditions, however, individual resonances of molecular segments can be resolved and, in this way, site-specific information becomes accessible. The basic experimental strategy for obtaining highly specific information is the combination of two or more spectral dimensions. During certain periods of the experiments, interactions averaged by MAS can be selectively recoupled and, thus, be used to access information on molecular structure and dynamics.

**Keywords:**
- Supramolecular Architectures
- Hydrogen Bonds
- Molecular Structure and Dynamics

**Cross-links to other projects:**
- EPR spectroscopy
- High Resolution NMR Spectroscopy
- Hydrogen-bonded Aggregates
- Microscopic Structure from Ab-initio Calculations
- Magnetic Resonance at Surfaces
- Proton-conductive Polymers
- Functional Materials from Discotic Mesophases
- Biology-inspired Materials
- Dynamic Nanostructures in Amorphous Materials

**Hardware:**
- Bruker DRX 700, 500 and 300 Spectrometers
- Tecmag 300 Spectrometer

*NMR investigations of a nanoscopic supramolecular column formed through self-assembly of dendritic molecules. On the left: $^1$H NMR spectra of the solution, the isotropic melt, the hexagonal-columnar liquid-crystalline state and the glassy state. $^1$H shift effects caused by adjacent $\pi$-electron systems are indicated by arrows. On the right: Sandwich-type stacking of the nitro-fluorenone moieties with proton-proton distances of 3.5 Å, as determined by $^1$H-$^1$H DQ NMR spectroscopy; structure of the supramolecular cylinders with stacks of fluorenone sandwiches in the centre, as derived from NMR and X-ray studies.*
From two-dimensional double-quantum (DQ) NMR experiments, dipole-dipole coupling constants can be determined, for example between two $^1\text{H}$ nuclear spins. In this way, distances between coupled spins can be measured in rigid samples, while in mobile systems the anisotropy of the molecular dynamics, as described by a dynamic local order parameter, is probed. The simple and robust $^1\text{H}-^1\text{H}$ DQ experiment is particularly useful for studying hydrogen-bonded systems or dynamics of polymers or liquid crystals.

However, even at very high static magnetic fields of up to 16.4 Tesla (corresponding to a $^1\text{H}$ Larmor frequency of 700 MHz) and fastest MAS, solid-state $^1\text{H}$ NMR spectra are still limited with respect to the spectral resolution achievable. Taking advantage of the larger spread of chemical shifts of rare nuclei such as $^{13}\text{C}$ or $^{15}\text{N}$, heteronuclear multiple-quantum NMR methods have been developed. Based on the resolution of $^{13}\text{C}$ NMR spectra, $^1\text{H}-^{13}\text{C}$ recoupling experiments have been designed which allow the segmental dynamics of $\text{CH}_n$ groups to be individually measured. These new experiments bear the potential to replace established $^2\text{H}$ (deuteron) NMR methods – making selective isotopic enrichment dispensable and multiple sites accessible by a single experiment on a single sample. When using rare nuclei such as $^{13}\text{C}$ or $^{15}\text{N}$, however, NMR signal sensitivity becomes a major issue, which we have addressed by adapting so-called inverse-detection schemes from solution-state NMR to solid-state conditions. The larger sensitivity of $^1\text{H}$ detection presently allows for sensitivity gains of about a factor 10 in heteronuclear $^1\text{H}-^{15}\text{N}$ correlation spectra in the solid-state, which means that measurement time requirements can be reduced by factors of up to 100.

**REFERENCES:**
