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Achieving high resolution dipolar NMR information without fast sample spinning: Combining magic angle turning with dipolar based NMR methods

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ABSTRACT

In this article we present a new approach to high resolution NMR combining the concepts of magic angle hopping (MAH)/magic angle turning (MAT) and dipolar based NMR methods such as SEDOR, REDOR or cross polarization (CP). Employing aluminophosphates as model systems we demonstrate that No MAS needed (NOMAS) is capable of supplying high resolution dipolar information without the need of fast MAS.

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1. Introduction

Nuclear magnetic resonance (NMR) has evolved as one of the most powerful techniques for obtaining atomic scale information in a variety of materials. The applicability of NMR to solids was greatly enhanced by the advent of magic angle spinning (MAS), pioneered by Andrew and Lowe independent of each other. They proposed that spinning the sample at an angle $\theta = 54.7^\circ$, the so called magic angle, would average all first order interactions that scale as $3\cos^2\theta - 1$, where θ denotes the angle between the external magnetic field and the principal axis of the interaction [1,2] (second order interactions, such as quadrupolar interactions which scale as the fourth order Legendrian are not averaged by MAS [3]; here the static linewidth is merely reduced by a factor of 4). Thus, in most cases, magic angle spinning (MAS) in the solid state can be considered as mimicking the rapid time averaging of interactions in a liquid attributed to molecular motion leading to narrow lines, which significantly helps in improving resolution [4,5]. The spectral width of the various interactions (dipolar, chemical shift and quadrupolar interaction) typically covers a range of several to tens of kHz. Spinning speeds of up to 70 kHz are nowadays possible to average these interactions [6,7]. The resolution afforded by MAS has allowed significant structural insights into a variety of materials such as zeolites, minerals, glasses, ceramics, polymers and biomaterials among others.

Whereas the chemical shift interaction (in combination with an analysis of the quadrupolar interaction, where applicable) obtained under the high resolution conditions of fast MAS provides invaluable information about structural motifs on a length scale of 1–2 Å [4,8–18], information about structural details on an intermediate length scale (2–8 Å) becomes accessible by analyzing the magnetic dipolar coupling (D), which scales with the inverse cube of the internuclear distance r as $D \propto 1/r^3$, rendering it suitable to probe internuclear distances and molecular conformity [8]. A number of NMR sequences has been developed to reintroduce homo- and heteronuclear dipolar interactions such as Rotational Echo Double Resonance (REDOR), Transfer of Population in Double Resonance (TRAPDOR), Rotational Echo Adiabatic Passage Double Resonance (REAPDOR) and Hetero-Nuclear Correlation (HETCOR) for heteronuclear dipolar coupling and a variety of homo-nuclear techniques such as Radio Frequency Driven Recoupling (RFDR), Dipolar Recoupling with A Windowless Sequence (DRAWS), Double Quantum DRAWS (DQ-DRAWS) etc. [19–24], where the dipolar interaction is employed to obtain information about structural arrangement and topology. This is particularly important when samples are not amenable to diffraction techniques such as XRD, as is often the case with glasses and other amorphous materials or even proteins and biological materials that cannot be readily obtained in the crystalline state.

While MAS is a well-established method in solid state NMR, it may not always be possible, or indeed desirable, to perform high speed rotation on the sample. Such is the case with samples containing radioactive materials, which cannot be spun at high

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speeds [25]. In other samples, the rapid spinning may produce changes in the sample due to the high centrifugal acceleration associated with rapid spinning. Cases where the MAS process interacts, changes or in some way influences the physical or chemical process under study are unsuitable for study under MAS conditions. As an example, the centrifugal acceleration imposed by MAS indeed changes the crystallization kinetics in fragile heavy metal fluoride glasses [26]. Similarly, large intact tissue cannot be studied using MAS-NMR due to the potential tissue damage that may result from the high forces imposed on the sample under MAS [27,28]. Another limitation of MAS is the sealed rotors that are essential for experiments which make it difficult to pipe reactants into a rotor and pipe out products so that reactions can be studied in-situ. A protocol that will make such studies possible will be particularly attractive in the field of catalysis where in-situ NMR has been useful in revealing a variety of interesting reaction dynamics between the catalysts and the reactants, particularly the presence of transient species that do not survive long enough for ex-situ analysis [29].

Therefore, it would be highly desirable to have an NMR technique that affords high resolution while having the sample spinning at a relatively low speed (10–100 Hz).

Bax et al. presented an approach, in which the sample container, while being aligned with its principal axis at the magic angle, is advanced in discrete hops of 120°. The approach was coined magic angle hopping (MAH) [30,31]. As shown in Fig. 1, the experiment consists of evolution segments separated by discrete hops. During the hop, one component (sine or cosine) of the magnetization is "stored" in the z-direction. The MAH technique does not require continuous sample rotation but positioning the hops precisely can be difficult. As a result of MAH, a two dimensional spectrum results in which the indirect F1 dimension only contains the isotropic parts of the chemical shift, whereas the full chemical shift tensor (CSA) is retained in the F2-dimension. Gan showed that the same information could be obtained employing a continuous, but slow, sample rotation. This variation could be used without extended hardware modification on conventional MAS-NMR probes and is known as magic angle turning (MAT) NMR [32]. Many variations of the prototype MAT experiment have been developed including 5-π MAT, mixed amplitude and phase modulated MAT, sheared MAT, triple-echo MAT and a hybrid of the 5-π MAT and mixed amplitude and phase modulated MAT known as PHORMAT. The intrinsic details of these experiments are discussed in [33]; a variation combining MAT and MAH is presented in [34].

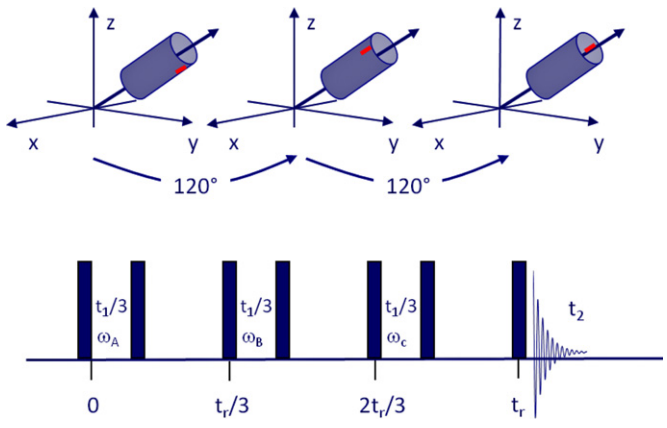

Fig. 1. Schematic representation of the working principle of the MAT (MAH) experiment. The evolution of the internal interactions at angles of 0°, 120° und 240° in the t_1-domain in combination with a suitable phase cycle entails isotropic signals in the indirect (F1) dimension, while retaining the full anisotropy of the interactions in the F2 domain.

The MAT/MAH approach therefore allows the characterization of structural motifs on a short length scale (1–2 Å) without the need for fast MAS. However, to our knowledge, no attempt has been made to extend this approach to obtain information on structural motifs on intermediate length scales via an analysis of the dipolar coupling in conjunction with MAH/MAT. By combining the MAT/MAH approach with dipolar based NMR techniques such as SEDOR, REDOR etc., such information will become accessible. In this contribution we present variations of the MAT/MAH approach enabling us to access the dipolar information.

Specifically, by employing alumina-phosphate glasses as model compounds, we present a study of spatial connectivity between ^{31}P and ^{27}Al by ^{27}Al→^{31}P CP spectral editing and ^{31}P{^{27}Al} MAT-REAPDOR NMR spectroscopy. The results clearly show that our NOMAS approach offers high resolution chemical shift information in combination with dipolar information without the need of fast MAS.

2. Experimental

2.1. Samples

The $60K_2O$–$40P_2O_5$ (mol%), $55K_2O$–$5Al_2O_3$–$40P_2O_5$ (mol%) and $26NaPO_3$–$74Al(PO_3)_3$ glasses were prepared by standard melt quenching techniques. $NaPO_3$, K_2CO_3, Al_2O_3 and $NH_4H_2PO_4$ precursors were mixed in the required stoichiometry in a Pt crucible and heated up to 800 °C for removal of NH_3 and CO_2, followed by melting at 900 °C in case of the binary glass and at 1100 °C in case of the aluminophosphate glass. The melt was then quenched between copper plates to obtain the glass. All the glasses prepared incorporated 0.1% Mn to reduce T_1. As a result, a repetition time (d_1) of around 10 s was suitable for all phosphate glass samples.

In order to demonstrate ^{27}Al→^{31}P CP spectral editing, a binary mixture comprising 50% by weight of a hydrated $NaPO_3$ glass and 50% by weight of $26NaPO_3$–$74Al(PO_3)_3$ glass (described in the previous paragraph) was prepared. The hydrated gels were obtained by dissolving 9.96 g $NaPO_3$ and 0.04 g $Mn(CH_3COO)_2$ in de-ionized water. After continuous stirring to ensure complete dissolution, the solution was placed in an oven at 90 °C for evaporation of water. The resulting $NaPO_3$ gel was not annealed subsequently. A repetition time (d_1) of around 5 s was found suitable for the hydrated gel. Since the $26NaPO_3$–$74Al(PO_3)_3$ glass requires a repetition time of 10 s, this was also used for the binary mixture.

2.2. NMR experiments

All NMR experiments reported have been carried out on a Bruker 300 MHz spectrometer, equipped with an Avance III console using standard 4 mm probes. The MAT spectra reported at low spinning speeds (15–30 Hz) were performed using a standard 4 mm probe and spinners with specialized rotor caps, employing the "NMR Rock Solid" equipment obtained from Bruker, which used pulses of air generated by a speaker to drive the rotor and achieved spin stabilization by aerodynamic effect rather than active feedback as is commonly used on the MAS controller. The ^{31}P MAS-NMR spectra presented have been referenced to the 0 ppm resonance of H_3PO_4.

3. Results and discussion

MAT uses a $\pi/2$ pulse to project magnetization into the xy plane and allows it to evolve during the evolution period followed by storage of one component in the z-direction. The other

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