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Journal of Magnetic Resonance 173 (2005) 84–89
JMR Journal of Magnetic Resonance
www.elsevier.com/locate/jmr

Practical aspects of shimming a high resolution magic angle spinning probe

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Received 7 October 2004; revised 16 November 2004
Available online 13 December 2004

Abstract

High resolution magic angle spinning (HRMAS) has become an extremely versatile tool to study heterogeneous systems. HRMAS relies on magic angle spinning of the sample to average out to zero magnetic susceptibility differences in the sample and to obtain resonance linewidths approaching those of liquid state NMR. Shimming such samples therefore becomes an important issue. By analyzing the different sources of magnetic field perturbations present in a sample under MAS conditions, we propose a simple protocol to obtain optimum shim settings in HRMAS. In the case of aqueous samples, we show that the lock level cannot be used as a reliable indicator of the quality of the shims at high spinning speeds. This effect is explained by the presence of temperature gradients imparted by the sample rotation.

Keywords: HRMAS; Shimming; Magnetic susceptibility differences; Temperature gradients

1. Introduction

High resolution magic angle spinning (HRMAS) has become a ubiquitous tool to study heterogeneous systems endowed with sufficient dynamics by NMR [1–9]. The domain of application of HRMAS is extremely diverse and includes the analysis of molecules issued from solid phase synthesis [10,11], molecules in membrane environment [12,13], swollen polymers, mesoporous materials [14], cells [15–18], and even biopsies [19–25]. While the dynamics of some of the molecules present in such system is comparable to molecules in solution [26,27], the inherent sample heterogeneity precludes the obtaining of high resolution NMR spectra under static conditions. The main role of magic angle spinning (MAS) is therefore to average out internal magnetic susceptibility differences present in such samples [28,29]. Concomitantly, MAS also averages out to zero residual dipolar interactions that might be present in the sample provided that their intensity is smaller than the spinning speed [30].

When using HRMAS to study highly dynamic systems such as metabolites in a biopsy or true liquids, proper shimming is of the uttermost importance to analyze the fine structure present in these spectra. The requirements become similar to what is expected of a regular high resolution liquid state probe. In this article, we analyze the different factors that affect the quality of shimming in a high resolution MAS probe. Using some theoretical considerations that are confirmed by experimental observations, we propose a simple protocol to obtain shims of optimum quality on different samples in different solvents.

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doi:10.1016/j.jmr.2004.11.022

2. Hardware considerations

The following description pertains mainly to Bruker HRMAS probes, however, many of the general features presented below also apply to other manufacturer's probes. HRMAS experiments are usually performed on standard liquid-state NMR spectrometers equipped with a dedicated probe that allows to spin the sample at the magic angle. The radio-frequency circuits of these probes are designed to withstand only the power classically available on liquid-state NMR spectrometers. Therefore, they cannot be used to perform typical solid-state type experiments like cross-polarization. They are usually fitted with a gradient coil generating a linear field gradient along the magic angle axis that allows to perform coherence selection experiments [1]. A HRMAS probe is designed to minimize the different sources of magnetic field perturbations in close proximity to the sample in order to obtain resonance linewidths similar to those obtained on a standard liquid-state high resolution probe. The sample is contained in a 4 mm ZrO_2 rotor that is able to withstand the strong centrifugal forces created by high spinning speeds. To optimize the sensitivity of the probe, the rotor is fitted with Teflon inserts to define a 50 μl volume that matches exactly the detection volume of the solenoidal coil. This experimental set-up allows to detect all the material contained in the rotor which means that the whole sample contributes to the detected signal, a situation which is in contrast to classical high resolution probes where typically only half of the sample is detected. Despite the presence of several sample/rotor interfaces in the coil detection volume, the NMR lineshape is not affected by these magnetic perturbations provided the sample is rotated at the magic angle (see detailed explanations below).

3. Shimming the residual field distortions in a HRMAS probe

When placed in a homogeneous B_0 magnetic field, even a well designed HRMAS probe will disturb the magnetic field lines. Like in high resolution liquid state NMR, the resultant field distortions have to be corrected using the shim system of the spectrometer. The shimming procedure differs however by the fact that the correction gradients have to be applied along the MAS axis [31]. A linear combination of the usual shims found on a high resolution NMR instrument must therefore be used. For a HRMAS probe with a stator positioned in the (x,z) plane of the laboratory frame, inhomogeneities of the B_0 field along the rotation axis can be corrected up to the third order by using the zonal shims $\boldsymbol{B}_{Z^1}^{\mathrm{MAS}}$, $\boldsymbol{B}_{Z^2}^{\mathrm{MAS}}$ and $\boldsymbol{B}_{Z^3}^{\mathrm{MAS}}$. The radial inhomogeneities do not require any corrections since they are averaged out by the rotation. This averaging process is similar to what is found in a classical high resolution sample where slow sample spinning leads to an improvement of the linewidth. The zonal shims of the MAS frame are related to the classical laboratory frame shims by the following relations [31]:

$$\begin{aligned}
\boldsymbol{B}_{Z^1}^{\mathrm{MAS}} &= \frac{1}{\sqrt{3}}\boldsymbol{B}_{Z^1}^{\mathrm{LAB}} - \frac{\sqrt{2}}{\sqrt{3}}\boldsymbol{B}_{X}^{\mathrm{LAB}},\\
\boldsymbol{B}_{Z^2}^{\mathrm{MAS}} &= \boldsymbol{B}_{(X^2-Y^2)}^{\mathrm{LAB}} - 2\sqrt{2}\boldsymbol{B}_{ZX}^{\mathrm{LAB}},\\
\boldsymbol{B}_{Z^3}^{\mathrm{MAS}} &= -\frac{2}{3\sqrt{3}}\boldsymbol{B}_{Z^3}^{\mathrm{LAB}} - \frac{1}{\sqrt{6}}\boldsymbol{B}_{Z^2X}^{\mathrm{LAB}} + \frac{5}{\sqrt{3}}\boldsymbol{B}_{Z(X^2-Y^2)}^{\mathrm{LAB}} - \frac{5}{3\sqrt{6}}\boldsymbol{B}_{X^3}^{\mathrm{LAB}}.
\end{aligned} \tag{1}$$

Considering the small volume occupied by a HRMAS sample, the set of shims described in Eq. (1) is sufficient to shim a sample spinning at the magic angle in a correctly designed HRMAS probe. For a static sample, tesseral shims in the MAS frame have to be considered as well [31]. From a practical point of view, the correct setting of the shims $\boldsymbol{B}_{(X^2-Y^2)}^{\mathrm{LAB}}$, $\boldsymbol{B}_{Z^3}^{\mathrm{LAB}}$, and $\boldsymbol{B}_{Z(X^2-Y^2)}^{\mathrm{LAB}}$ is crucial to obtain a correct lineshape.

This section introduces some important concepts that are essential to shim a sample in rotation at the magic angle. We now turn to a more practical aspect and try to answer the following basic question: How different is the optimum shimming between two different samples? To answer this question, we need to examine in details the averaging process of magnetic susceptibilities by MAS.

4. General considerations on the averaging on magnetic susceptibilities differences under MAS in a heterogenous sample

The averaging of magnetic susceptibility differences present in a heterogeneous sample by MAS is an essential aspect of HRMAS spectroscopy. The additional magnetic fields created by volume elements of different magnetic susceptibilities can be treated as dipolar fields [26,32,33] that vanish when the sample is rotated at the magic angle. Strictly speaking, this averaging to zero by MAS is only true if the differences in magnetic susceptibilities are reasonably small and if the magnetic susceptibilities are isotropic. These two conditions are usually fulfilled in HRMAS samples. Consequently, the contribution of volume elements of different magnetic susceptibilities to the width of the NMR resonance vanishes and only spinning sidebands, at frequencies multiple of the spinning frequency, remain in the spectrum. The fact that inhomogeneous bulk magnetic susceptibility can be efficiently removed by MAS was demonstrated both experimentally and theoretically by Doskocilova et al. [28], VanderHart [34], and Garroway [29] in the case