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Hardware modification of a 7 mm MAS NMR probe to a single-crystal goniometer

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Abstract

Tensorial terms of the Hamiltonian can be measured by solid-state single-crystal nuclear magnetic resonance (NMR) spectroscopy which requires a goniometer NMR probehead. Goniometer probes; however, are not standard parts of solid NMR spectrometers and are available only at a much higher price than magic-angle spinning (MAS) probeheads widely used in research. Due to requirements of MAS experiments, modern probeheads are designed for small ceramic rotors, which are 1–4 mm in diameter, to reach very high angular frequencies, so there are several older 7 mm MAS probeheads used rarely todays in NMR laboratories. In this paper, a simple method is presented how to rebuild step-by-step a 7 mm Bruker MAS probehead to be suitable for single-crystal spectroscopy. In the second part ^{31}P chemical shift tensors of $Na_4P_2O_7 \cdot 10H_2O$ are determined to demonstrate the functionality of the rebuilt probehead.

Keywords: NMR; Single crystal; MAS probe; ASICS; Goniometer; Sodium pyrophosphate; Home-built probehead; Nuclear magnetic resonance; 31-P NMR; Crystal orientation

1. Introduction

Several magnetic interactions are known in the nuclear magnetic resonance (NMR) spectroscopy, thus many tensorial terms appear in the Hamiltonian. Most important ones are chemical shielding, dipolar and quadrupolar coupling. In solid state, the intermolecular distances and orientations are fixed and NMR spectra become sensitive of crystal orientation. In single crystals, macroscopic orientation correlates directly with molecular orientation. This makes it possible to determine not only the isotropic average but all components of tensors. Knowing these values may give further details on microscopic structure, bonds in solid state, etc. Theoretical calculations also provide primarily tensorial components and they are averaged mathematically later in NMR spectra simulations. In testing the accuracy of mathematical methods comparing of tensorial elements directly is a better way than comparing simulated isotropic spectra.

As these NMR experiments require large single crystals that in many cases hardly available, other methods have been developed to determine anisotropy components. Principal values of chemical shielding and partial information on orientation can be obtained analyzing rotational sidebands in magic-angle spinning (MAS) experiments or using two-dimensional methods [1–4]. All techniques using powder samples; however, can supply only relative information on tensor orientations, i.e. orientation between shielding tensors of different nuclei. To determine orientation relative to the crystal lattice the most straightforward way is still to use solid-state single-crystal spectroscopy. In such an experiment, several NMR spectra need to be recorded of one single crystal, knowing the direction of the crystal axes in the laboratory frame for each spectrum. The experiment requires a goniometer NMR probehead for exact orientation of the crystal. Goniometer probes; however, are not standard parts of solid NMR spectrometers and are available only at a much higher price than MAS probeheads widely used in research today or they must be constructed at home [5–7]. In this technical paper, a simple method to rebuild a 7 mm Bruker MAS probehead to be suitable for single-crystal spectroscopy is presented.

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2. Hardware construction

To get high-resolution solid-state spectra similar to the ones recorded in liquid phase, MAS has been developed [8,9]. Under MAS conditions the sample is filled in a rotor and it is rotated about an axis inclined at 54.7° to the external magnetic field. Typical rotating frequencies are in the region of 5–27 kHz. As a side-effect there are rotational sidebands under MAS conditions. In order to decrease the disturbing effect of sidebands for observing isotropic lines, MAS NMR probeheads are designed to reach higher and higher spinning frequencies [10]. Probably, there are older 7 mm MAS probeheads used rarely todays in several NMR laboratories as modern MAS probes are designed for rotors 1–4 mm.

It was our basic principle not to degrade the original functionality of the probehead so the rebuilding was carried out in a completely reversible way. All extra parts were fixed by screws, pins or soldering. No extra hole was drilled in the original parts. Some other aspects had to be considered during the rebuilding process.

- No ferromagnetic or strong paramagnetic materials could be used. It would have been a security risk as very strong attractive forces inside the cryomagnet can even tear out small parts. These flying parts can damage electronics around the probe and it is extremely difficult to remove them from the cryomagnet bore. Plexi-glass proved to be an ideal material for our extra parts. It can be shaped easily.
- Bruker narrow bore magnets widely used all over the world have a bore of 54 mm. There is very small room in the probehead cylinder for our extra parts. In these spectrometers using a worm for positioning the crystal would require more space or disassembling the probehead in an irreversible way. In present case, instead of continuous positioning we used discrete steps. A ratchet wheel was designed to orientate the sample in the magnet. The sample was glued directly onto the wheel. This solution has some advantages: the same precision can be reached as if a worm and a stepper motor was applied, can be operated with a single cord, cheap, a number of identical gears may be built and store the samples glued for several experiments. On the other hand, there is no need to have more than 10–15 points to fit sine curves.
- Keeping the size of metallic parts as small as possible is important because all metallic parts influence the oscillator impedance adding extra capacity must be compensated by tuning the probe. They reduce the frequency range in which the probehead operates properly. Therefore, thin wires were used and unnecessary copper from printed circuit board (PCBs) was removed.

Respecting these considerations, 10 new parts were constructed. This 'rebuilding kit' can be seen in Fig. 1.

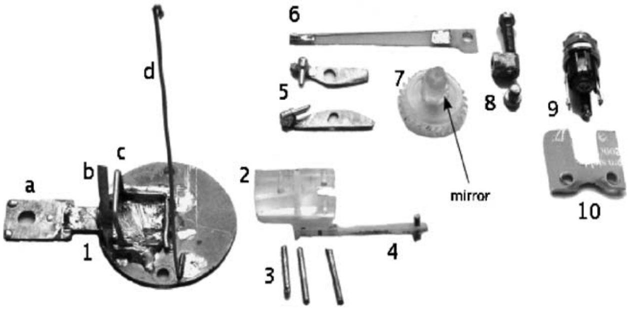

Fig. 1. Probehead rebuilding kit: (1) top PCB plate, (1a) hold-down-clip, (1b) signal contact, (1c) cord leader, (1d) signal contact wire, (2) bridge, (3) copper pins (1.50 mm in diameter), (4) board to keep pins in line, (5) RF contacts, (6) ratchet pawl (signal contact), (7) ratchet wheel (sample holder), (8) screws to hold the pawl and (9–10) signal connector and fixing plate.

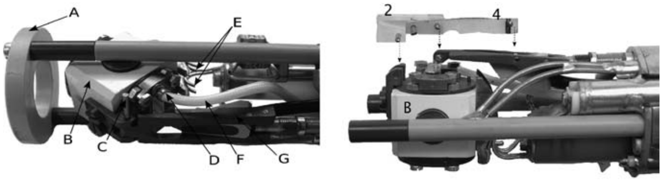

Fig. 2. Modifying the flipping angle of the stator. Left: original state of the stator. (A) top ring, (B) stator, (C) pin, (D) metal ring, (E) RF contacts, (F) air flow pipe for sample eject and (G) flipping rod. Right: inserting the bridge and the stiffening plate and fixing them by three pins indicated by vertical arrows.

At first, the metal ring (denoted by D in Fig. 2) fixing the air flow pipe (F) was moved away with ca. 8 mm along the pipe from the bottom of ceramic stator (B). After detaching of the pipe, the metal ring was removed from the pipe and kept in a safe place. Unfortunately, the probehead is designed originally to operate only in a small region around the magic angle. To change the flipping angle of the stator to be perpendicular to the external field requires constructing a plexi-glass 'bridge' (2 in Fig. 1) and a stiffening plate of PCB (4 in Fig. 1). The original copper pin (C) between the stator (B) and the flipping rod (G) was gently knocked out by a metal pin having smaller diameter. Such a reversible way all pins can be carefully removed and reinserted several times. The bridge is inserted between the stator and the flipping rod and fixed by pins. The stiffening plate (4) is fixed by the same two pins to the bridge (2) and a shorter one to the rod (G) to avoid extra freedom of movement and make adjustment possible both in push and pull directions by the micrometer screw. Details can be seen in Fig. 2 on the right. Calibration and fine adjustment of the flipping angle will be done by micrometer screw at bottom.

The gold-plated electric contacts (E) that connect the coil in the stator to the amplifier circuit are short, too. A new pair of copper contacts (5) (with 1 mm in diam. gold-plated copper pins) were assembled to the original contacts to