三次元磁場配向させた微結晶懸濁液の in situ 固体 NMR による化学シフト異方性解析

Analysis on Chemical Shift Anisotropy via *In situ* Solid-state NMR for Magnetically Oriented Microcrystal Suspension

京大院農[1]，京大院理[2]　○安井 颯[1]，小林 加代子[1]，和田 昌久[1]，武田 和行[2]，久住 亮介[1]
Kyoto Univ., ○Hayate Yasui, Kayoko Kobayashi, Masahisa Wada, Kazuyuki Takeda, Ryosuke Kusumi
E-mail: yasui.hayate.44s@st.kyoto-u.ac.jp

Solid-state NMR is a powerful spectroscopic tool, providing clues for structure and dynamics in solids. In addition, information about the electronic state can be extracted from chemical shift (CS). One traditional way toward full determination of the CS tensor, including its principal values and orientation, is to employ the single-crystal (SC) rotation method, where changes in the chemical shift is observed while the crystal is rotated over three different orthogonal axes using a goniometer whose axis is set normal to the static magnetic field B_0. This method requires a relatively large SC which is often hard to obtain. So far, we have succeeded in determining CS tensors for an assembly of magnetically aligned micrometer-sized crystals prepared in UV-curable viscous medium under rotating magnetic field with modulation[1]. We have also demonstrated *in-situ* NMR of a Magnetically Oriented Microcrystal Suspension (MOMS) in liquid medium without the irreversible UV-cure[2]. In MOMS, rotation of the aligned microcrystals can only be performed about one of the magnetic susceptibility axes, which, however, is insufficient for full determination of the CS tensor as long as the sample-rotation axis is normal to B_0. Even though one may be tempted to tilt the rotation axis, it would degrade the efficiency of three-dimensional alignment of the microcrystals.

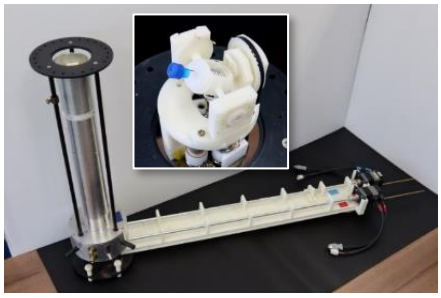

Fig. 1 Photographs of the whole and probehead of the developed probe.

In the present study, we developed a probe, as shown in Fig. 1, which enables temporal tilt of the axis of modulated-rotation only during the period of pulse application and NMR signal acquisition. This probe is connected to an OPENCORE NMR spectrometer[3] equipped with a power amplifier (JEOL CMX300 Infinity) and used in a 7.05-T (300 MHz) superconducting magnet. In this probe, the axes χ_1, χ_2, and χ_3 of the magnetic susceptibility tensor are aligned in a reference frame fixed in the modulatory rotating sample tube. With $0 > \chi_1 > \chi_2 > \chi_3$, the χ_1- and χ_3-axes are parallel to the initial direction of the B_0 and to the modulated-rotation axis, respectively. After modulated rotation has been implemented long enough for three-dimensional orientation, the axis of rotation is temporally tilted and then an NMR signal is acquired. By repeating measurements for different rotation angles θ, a SC rotation pattern around the tilted axis is obtained from the MOMS.

Figure 2 shows ^{13}C solid-state cross polarization (CP) NMR spectra obtained for magnetically-oriented L-alanine microcrystals (20–45 μm) in insoluble liquid with viscosity of 12 Pa · s. The intermittent rotation was applied at a rate of 15 rpm with a pause for 1 s every 180° rotation. The tilting angle was set to 30°. As demonstrated, changes in the peak positions and thereby in the chemical shift with the rotation angle θ, exhibited a clear SC rotation pattern, from which the CS tensors of ^{13}C in L-alanine can be completely characterized.

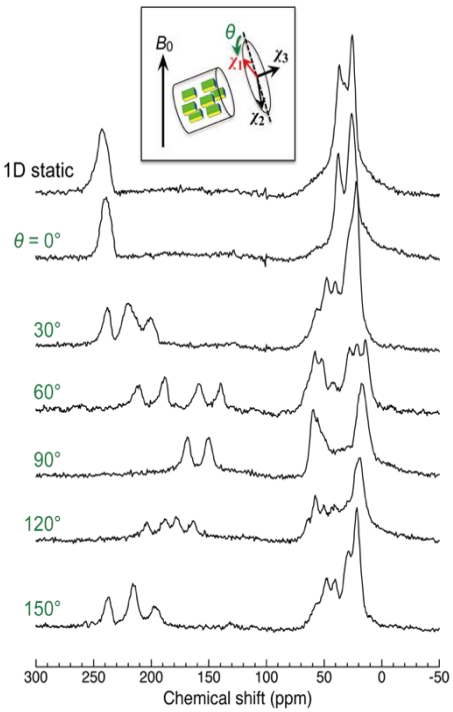

Fig. 2 ^{13}C solid-state CP spectra of L-alanine microcrystals suspended in insoluble liquid under intermittent rotation. θ indicates the direction of the χ_1-axis with respect to B_0 just before applying the temporal tilt by 30°.

References: 1), R. Kusumi et a., *J. Magn. Reson.*, **223**, 68 (2012); 2), R. Kusumi et al, *J,Magn. Reson.* **309**, 106618 (2019); 3), K. Takeda, *J. Magn. Reson.* **192**, 218 (2008).