Solid-State NMR for Molecular Science

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1994 B.S. Himeji Institute of Technology (University of Hyogo)
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Professional Employment
1999 Postdoctoral Fellow, National High Magnetic Field Laboratory, Florida State University
2001 Assistant Professor, Yokohama National University
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2002 The Young Scientist Poster Award, The Nuclear Magnetic Resonance Society of Japan

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In order to elucidate functions of molecules, characterization of the molecule is the first step. There is a variety of important molecules, which are insoluble in any solvents and functional at amorphous state. Solid-state NMR enables us to obtain a variety of information at atomic resolution without damage to molecules and significant restrictions. Thus, solid-state NMR is one of the essential tools for the characterizations of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their application to structural biology and materials science. We study characterizations of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

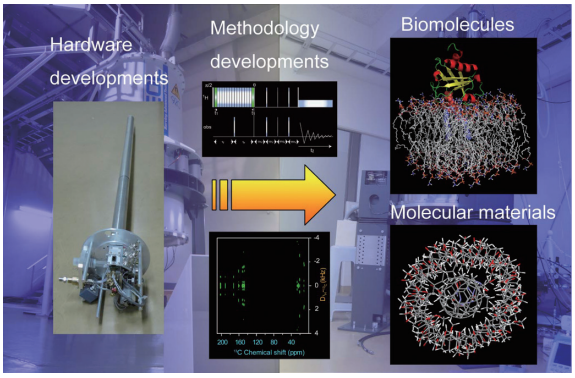

Figure 1. Outline of our studies.

Selected Publications

- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
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- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).
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- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "'Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).
- M. Yagi-Utsumi, S. G. Itoh, H. Okumura, K. Yanagisawa, K. Kato and K. Nishimura, "The Double-Layered Structure of Amyloid-β Assemblage on GM1-Containing Membranes Catalytically Promotes Fibrillization," *ACS Chem. Neurosci.* **14**, 2648–2657 (2023).

1. Developments of Solid-State-NMR Techniques

Unlike solution NMR, it is not easy to achieve high resolution ^{1}H NMR spectra in solid-state NMR, since ^{1}H homonuclear dipolar couplings broaden the signals in rigid organic solids. In order to achieve ^{1}H high resolution spectra, ^{1}H homonuclear dipolar couplings must be removed by application of either sufficiently high magic angle spinning (MAS) or combination of MAS at moderate speed with multiple pulse (MP). Recent developments of fast MAS techniques enabled to remove ^{1}H homonuclear dipolar couplings efficiently with expense of sensitivity reduction. In the conventional latter approach, the MP average spin part of ^{1}H homonuclear dipolar coupling Hamiltonian at time scale shorter than MAS period. Using a high power radio frequency field, it is possible to achieve short cycle time for MP and enable combination of fast MAS without interferences between spin and spatial parts.

We have developed new MP sequences enabling us to achieve efficient ^{1}H homonuclear dipolar decoupling by removing high order correction terms. Those performances are theoretically evaluated and partly tested experimentally. The project is on the way.

In addition, we have developed new spectral editing pulse sequences which enable the selection of ^{13}C signals depending on the number of directly attached ^{1}H. The techniques are evaluated theoretically. This project is also on the way.

2. Developments of Core Technologies for Solid-State NMR Probes

We have been working on developments of totally original solid-state NMR probes for a couple of years. The probe had been successfully built using originally designed parts except for a spinning module for 400MHz NMR. Then, we have been working on developments of original sample spinning modules for MAS solid-state NMR probes which are fully compatible with Bruker spectrometers and commercial sample tubes. We started the design of a spinning module for a standard 4.0 mm sample tube for Bruker. After 3 times of version up, our original spinning module exceeded the spinning performance of the commercial one from Bruker.

In order to achieve further improvements for our original spinning module, further developments are currently underway together with the development of original sample tubes. The spinning module is under designed in order to realize installation of the module to a narrow bore solid-state NMR probe with outer sleeve diameter of 38 mm.

We have also started the development of the original spinning module for a 2.5 mm sample tube.

3. Characterization of Synthetic Molecules by Solid-State NMR

Solid-state NMR is one of the efficient techniques to characterize amorphous samples such as synthetic molecules. We are working on the characterization of new synthetic molecules categorized to covalent organic frameworks (COFs) which are designed by Associate Prof. Segawa group in IMS. Tentative ^{13}C solid-state NMR signal assignments had been successfully achieved. The obtained results sufficiently prove the achievement of the aimed molecular form of COFs for the sample. This project is also on the way.