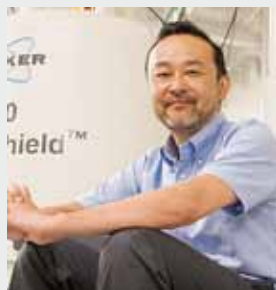


Solid State NMR for Molecular Science

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Professional Employment

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Keywords Solid State NMR, Biomolecules, Developments

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

We have been working on the methodology and hardware developments of solid state NMR and their applications such as structural biology and material science. We study for characterization of biomolecules such as peripheral membrane proteins and organic molecules such as natural products and synthetic polymers. Characterizations of several molecular materials in addition to biomolecules are under investigations with several corroborators using solid state NMR.

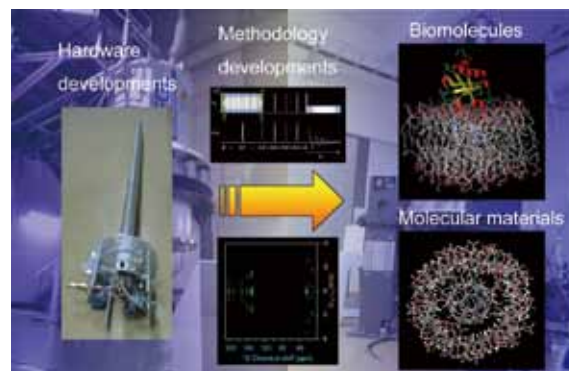


Figure 1. Outline of our studies.

Selected Publications

- J. Hu, R. Fu, K. Nishimura, L. Zhang, H. X. Zhou, D. D. Busath, V. Vijayvergiya and T. A. Cross, "Histidines, Heart of the Hydrogen Ion Channel from Influenza A Virus: Toward an Understanding of Conductance and Proton Selectivity," *Proc. Natl. Acad. Sci. U.S.A.* **103**, 6865–6870 (2006).
- K. Nishimura and A. Naito, "Remarkable Reduction of RF Power by ATANSEMA and DATANSEMA Separated Local Field in Solid-State NMR Spectroscopy," *Chem. Phys. Lett.* **419**, 120–124 (2006).
- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C- $\delta 1$," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, " ^2H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^1H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β -Sheet Structures by High Resolution ^1H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C- $\delta 1$ Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).

1. Molecular Proximity Revealed by Solid State NMR

Molecular proximity is one of the important information to characterize structure and functions of various molecules. However, the isotope enrichments of those samples are difficult or limited. Thus, low sensitivity natural abundant isotopes must be observed. Furthermore, so far many of developed solid state NMR techniques have been designed for the study of isotope enriched sample. Thus methodology developments and analysis optimized for natural abundant samples are quite important.

We have been exploring to reveal molecular proximity of biomolecules and synthetic polymers without isotope enrichment based on different approaches.

^1H detection is one of the possibilities in order to overcome sensitivity issue for the observation of natural abundant samples. However, solid organic samples possess ^1H homonuclear dipolar coupling which results in significant broadening of spectra. Thus unlike solution NMR, it has been difficult to observe ^1H high resolution spectra for organic solids. However, high speed MAS technique has made a remarkable progress in the past decade. It enables to observe high resolution ^1H spectra only by using MAS and gives reliable isotropic chemical shifts.

We have attempted to reveal molecular proximity by observing high resolution ^1H spectra using ultra high speed MAS under ultra high field. With collaborators, we have successfully revealed molecular packing in silk fibroin based on accurately determined ^1H position in model peptide which obtained from the analysis of cross peak growing for ^1H -homonuclear double quantum-single quantum correlation spectra^{1,2)} at various mixing time.

As an alternative approach, so far CRAMPS technique which utilize multiple pulse (MP) ^1H homonuclear dipolar decoupling under magic angle spinning has been used to observed high resolution ^1H spectra under magic angle spinning. In this technique, averaging cycle of ^1H homonuclear dipolar interaction based on MP must be short enough compare to the MAS rotation period in order to avoid interference between spin and sample rotations. Thus high power RF field is required for ^1H to satisfy above requirements. Furthermore, MP also scales down isotropic chemical shifts of ^1H simultaneously. Thus careful calibrations of experimental parameters are essential in order to observe correct isotropic chemical shifts. Using CRAMPS approach for ^1H dimension, it is possible to obtain high resolution ^1H - ^{13}C heteronuclear correlation spectra under moderate speed MAS.

We are currently investigating intermolecular proximity of cage molecules with collaborator. By using ^1H - ^{13}C heteronuclear correlation experiments under high field, it enables to detect intermolecular ^1H - ^{13}C heteronuclear correlation based on heteronuclear dipolar couplings. Compared to ^1H -intermolecular correlation approach mentioned above, detectable distance range are limited and sensitivity is lower, however ^{13}C detection enables well resolved sharp signals.

2. Proton Localization in ZnO Nanorods Revealed by In-Situ ^1H -Magic Angle Spinning Solid State NMR Spectroscopy³⁾

ZnO nanorods can be grown using aqueous solution. Unique shape of ZnO nanorods are studied for various applications such as biosensors, piezoelectric generators, dye-sensitized solar cells. Aqueous-grown ZnO nanorods might contain various kinds of impurities from source materials. Considering aqueous-growth of ZnO nanorods, we pay attention on incorporated hydrogen atoms, which can act as shallow donors.

In this study, local environments of protons incorporated in aqueous grown ZnO nanorods at different temperatures and approaches were studied prepared by collaborator by in-situ ^1H -magic angle spinning solid state NMR spectroscopy. We found out that the amount of protons incorporated in ZnO nanorods were increased toward increase of temperature of hydrothermal synthesis. However those for annealed samples at 500 °C after thermal synthesis release protons toward increase of temperature of hydrothermal synthesis. Furthermore, protons incorporated in ZnO nanorods prepared by either hydrothermal synthesis using autoclave or microwave irradiations exhibited different proton concentrations and adsorptive activities. Those results indicate that adsorptive activity of protons incorporated in ZnO nanorods may vary depending on the preparation procedures.

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- 2) T. Asakura, K. Yazawa, K. Horiguchi, F. Suzuki, Y. Nishiyama, K. Nishimura and H. Kaji, *Biopolymers* **101**, 13–20 (2014).
- 3) K. Ogata, S. Sasa, M. Inoue, M. Yano and K. Nishimura, to be submitted.

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