Research Overview

Yoko Sugawara

The author's research field is biophysics by means of vibrational spectroscopy and crystallography. The author joins the muon group since 2011 and is working to establish μSR experiments as a new biophysical method.

1. Pre-resonance Raman spectroscopy and *ab initio* calculations of intramolecular force fields of amide compounds (1975 ~ 1984).

The author had started research in the field of vibrational spectroscopy. The first theme was pre-resonance Raman spectra of amide compounds. It was shown that Raman intensities of the amide bonds such as amid I, II and III were specifically enhanced when ultraviolet lasers were used (Fig. 1). The amide bands which reflect the second-order structure of proteins would be selectively measured in pre-resonance/resonance Raman spectra of proteins.

Ab initio calculations of force fields of amide compounds were examined and it was revealed that the calculations offer valuable information on the off-diagonal elements of the force fields which were often difficult to be determined only by the empirical method.

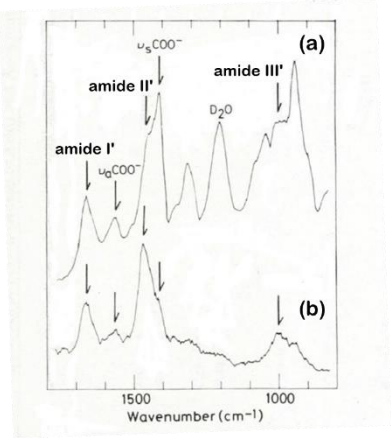

Fig. 1 Raman spectra of poly(L-glutamic acid) in D_2O exited by the 488.0 (a) and 257.3 nm (b) lase lines

2. Crystallographic analysis of temperature and/or humidity induced phase transitions among pseudopolymorphs of nucleotides (1982 ~)

Humidity- and temperatur-induced structural transitions occur in the cases of many hydrate crystals. Loss of water molecules in crystals lower the crystallinity in general. However, single crystal–single crystal transitions were found to proceed in the case of nucleotide or nucleoside hydrates due to flexibility of the structure, e.g., conformational changes and reconstruction of hydrogen bonding networks (Fig.2).

The transitions usually accompany large hysteresis, and metastable states easily appear. There were peculiar transitions in which the intermediate phase observed in the absorption was different from that observed in the desorption processe (a cyclic transition), and two different dehydrated crystal structures appeared depending on the temperature conditions (a bifurcate transition) (Fig. 3). These characteristics cause attention from a view point of physical properties. Recently, we revealed the mechanism of the transition on the basis of the crystal structures of the intermediate phases where the double or the triple periodic structure appeared. The analysis was carried out by not only X-ray crystallographic method but also neutron diffraction, Raman spectroscopy and molecular dynamics calculations to reveal the

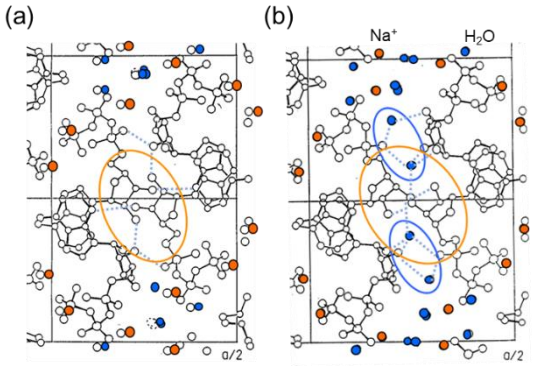

Fig. 2 Humidity induced phase transition of disodium adenosine 5'-triphsphate. Crystal structures of the dehydrate (a) and the trihydrate (b)
Blue circle, water molecules lost in the dihydrate; orange circle, moiety where conformational changes were

mechanism of phase transitions.

Similar phenomenon occurs in protein crystals. Decrease of water contents induces single crystal-single crystal transitions in the cases of xylose isomerase, thaumatin etc.. Crystal structure analysis and theoretical calculation to evaluate interactions have been carried out paying attention to a role of solvents in crystal formation.

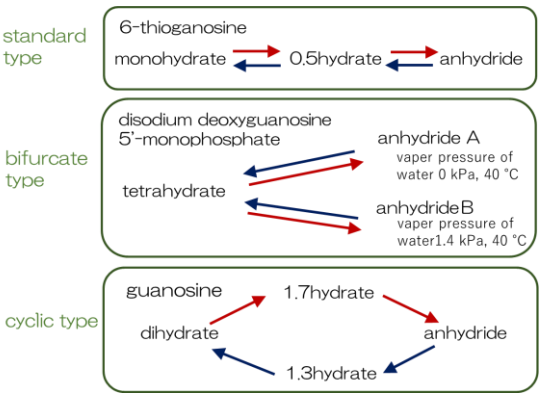

Fig. 3 Three types of phase transitions of nucleoside/nucleotide hydrates
Red and blue arrows indicate desorption and absorption process, respectively.

3. μSR studies of biomacromolecules (2011~)

At the start of Grant-in-Aid for Scientific Research on Innovative Areas "Frontier of Materials, Life and Elementary Particles Science explored by Ultra Slow Muon Microscope", the author joined the group to apply μSR to biophysical research. The research is connected with the proposal at Toyota Physical and Chemical Research Institute as a visiting fellow.

The muon (μ) is an elementary particle with a positive or a negative electric charge ($\pm e$) and a spin of 1/2. When a positively charged muon (μ^+) is implanted into materials, it captures an electron and a muonium (Mu) which is a hydrogen-like exotic atom is formed. It attacks an unsaturated bond of compounds and a radical, conventionally called as a muonium radical, is formed. The spin states of a muon or a muonium reflect the local magnetic field around the stopping sites and are monitored through the direction of a positron which is emitted when the muon or the muonium decays with a mean lifetime of 2.2 μs (Fig. 4).

Nagamine and his collaborators applied μSR to monitor electron transfer process in cytochrome *c* which is a member of a respiratory chain in mitochondria. They used "the labelled electron method" developed in the research of electron movement along *trans*-polyacethylene (Nagamnieet al., Phys. Rev. Lett. 53 (1984)1763.). The values of the relaxation parameter were found to depend on water contents and temperature. The information on muon stopping sites in proteins is inevitable to deepen understanding of the results. Experimental and theoretical approach to determine muon stopping sites on the basis of μSR data of basic components of biomacromolecules is in progress (Fig. 5).

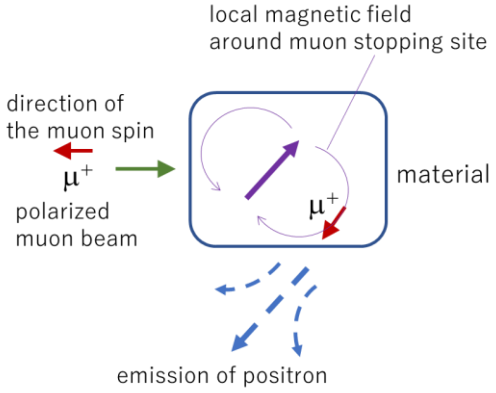

Fig. 4 Schematic diagram of the μSR experiment

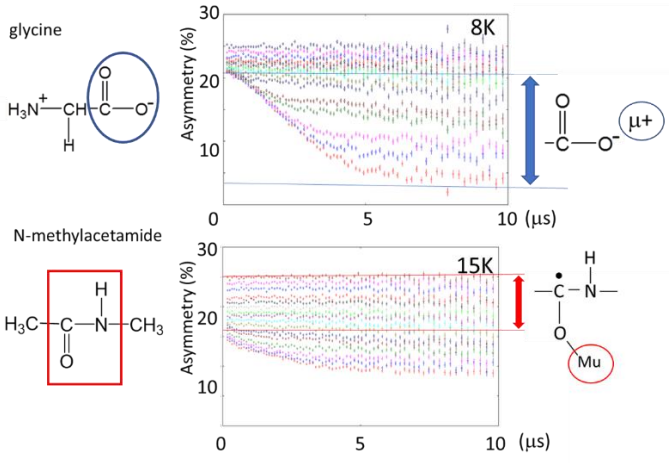

Fig. 5 μSR spectra of glycine (a) and N-methylacetamide (b)
Muon (μ+) and muonium (Mu) radical are the main components, respectively.

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(Book chapter)

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