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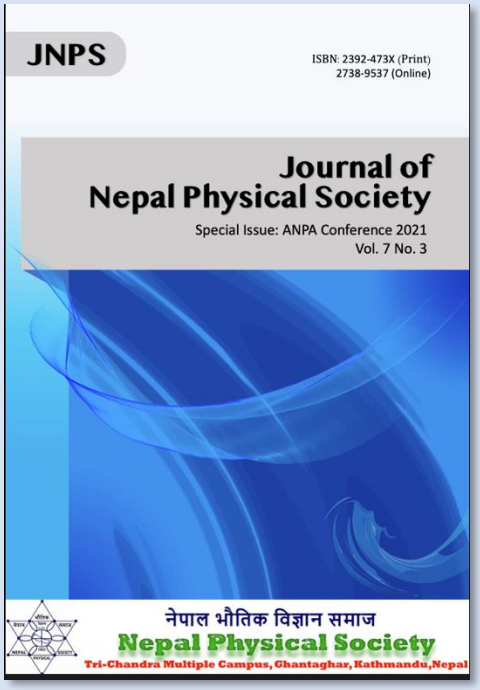

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Overview of μSR Study in Water and Ice

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Abstract. Muon spin rotation, relaxation and resonance (μSR) method has been used to understand the properties of materials and life. In order to apply the μSR method to life sciences, it is necessary to know the behavior of the muon and its species in different phases of water. In water, around 60% of incident muons found in the form of diagmetic muon, around 20% in the form of muonium and remaining fraction as a missing fraction however in ice, muon and muonium are found almost 50-50% of the incident muons. The missing fraction in water is attribute to radiolysis effect. In ice, the spin dipole interaction of muon with protons will help to understand μSR in water and in biosamples.

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INTRODUCTION

Water is an essential for functioning of life. Various life phenomena and some diseases are related to amount of water in the human body. It also plays important role for function of materials. Because of anomalous behavior of water with temperature and pressure, 17 polymorphs were reported experimentally [1]. So the behavior of water in materials varies with their phases. Even starting the study of water in materials from long ago, its various properties have not clearly understood yet.

Muon which is like a light proton acts as sensitive probe to materials in which it stops. It is available in both - positive and negative polarities in cosmic rays and accelerator facilities. Here discussion is focused on application of positive muon however the application of negative muon is out of scope of this paper. Because of fully spin polarized and asymmetric decay to positron, we can use it to understand local electronic and dynamic states of materials using muon spin rotation, relaxation and resonance (μSR) method [2]. μSR method has applied not only to materials sciences but also to life sciences like study of electron transfer in protein [3] and DNA [4], molecular dynamics, etc. The bound state of a muon and an electron is called as muonium (Mu = μ^+e^-). The Mu is considered as a light isotope of hydrogen and shows similar chemical behavior in materials. Both charge states - muon and Mu are helpful to provide information about the materials.

The detection of Mu in liquid was first reported by Percival et al in 1979 [5]. Then the μSR studies in biosamples – dilute aqueous solution of DNA [6], dried horse spleen ferritin [7], ferritin and apoferritin [8], cytochrome c [3], DNA [4, 9], hemoglobin [10], enzime [11], biosample from Alzehmer patient [12], biological aqueous solutions [13, 14] were reported. During these more than four decades, relatively slow progress of muon in life sciences with respect that in material science can be realized from the available literatures. For application of muon (using conventional and slow muon [15, 16, 17]) to life sciences, the interaction of muon and its charge states with water, and temperature and pressure dependent behavior is essentially important to separate the background signal.

In this article, an overview of μSR study in water and ice phases is presented.

μSR METHOD

Muon is a spin half elementary particle lies in the lepton family of second generation of the standard model of particles. The mass of a muon is about 207 times of an electron mass and 1/9 times of a proton mass. Its gyromagnetic ratio is around three times higher than that of proton (μ_μ = 3.18 μ_p) which makes it more sensitive to materials. Two special characteristics of muon – spin po-

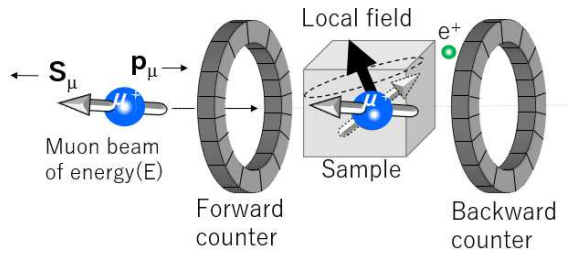

FIGURE 1. Schematic diagram of conventional μSR experimental set up. The decayed positrons from muons are collected from the forward and backward detectors placed around the sample.

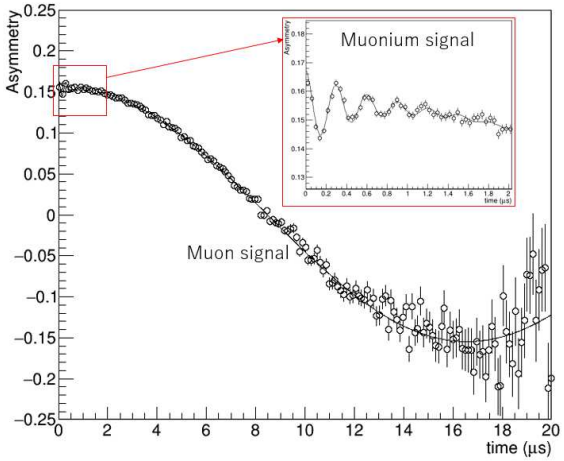

FIGURE 2. Time evolution of asymmetry in water at room temperature at transverse field 2.3 G. Muonium time spectra (inset) is superposed to muon spectra.

larized and asymmetric decay to positron (due to violation of parity in weak interaction) (life time 2.2 μs) make the muon as an exotic tool. It works as a sensitive magnetic (spin) probe in which it stops. μSR method provides the information about the local electronic and spin states of materials. Furthermore, it can apply without external perturbation to the system. Its time window ($10^{-11} - 10^{-5}$ s) is wider than the other techniques (NMR, neutron and Mossbaur). It stops interstitial sites near the high electron density. Its bound state with an electron known as Mu which is like a light isotope of hydrogen. It is an exotic atom made up of two lepton particles. The Mu can predict/mimic the behavior of H in the materials. For life science study, muon (μSR) can probe the dynamics of spin, electron, proton, ions and H [2]. It also probes the dynamics of reaction, catalytic processes, concentration of molecules, magnetic behaviors, etc. and phenomena based on these processes (like electron transfer in respiratory system, photosynthesis process, diagnosis of disease, clinical and medical fields).

μSR stands for muon spin rotation, relaxation, and resonance. The intention of the mnemonic acronym is to draw attention to the analogy with NMR and ESR. When muons are incident on material, decayed positrons are collected by detectors (forward and backward) around the sample as shown in Fig. 1. Time evolution of those positrons provide the information about the sample material. Suppose, F is positron events collected by forward counter and B is that by backward counter, then asymmetry = (F - αB) / (F + α B) = A_0 G(t), where α is alpha factor which depends on efficiency of detectors and sample positions, A_0 is initial asymmetry, and G(t) is polarization function [18]. Based on our need, we can apply external magnetic field along (longitudinal field or zero field measurement, ZF) or perpendicular (transverse field measurement, TF) to the direction of spin of the incident muon beam.

Since Mu is around 100 times more sensitive to magnetic field, Mu spectra is superposed to muon spectra. Figure 2 shows the time evolution of muon (slow rotation spectra) and Mu (fast rotational spectra) in water at TF 2.3 G at room temperature. The spectra were fitted with a function including muon and Mu sections in addition to time-independent background (Eq. 1). The fraction of muon and that of Mu formed in the sample, and corresponding relaxation rates can be extracted from the fitting of experimental μSR data.

$$\begin{aligned} f(t) = A_\mu exp(-\lambda_\mu t) cos(\omega_\mu t + \phi_\mu) \\ + A_{Mu} exp(-\lambda_{Mu} t) cos(\omega_{Mu} t + \phi_{Mu}) + B, \end{aligned} \quad (1)$$

where B is the time-independent background. The terms A_μ and A_{Mu} are the amplitudes of the spin precession corresponding to the polarization asymmetry for the μ^+ in diamagnetic states and Mu, respectively. The parameters λ_μ and λ_{Mu} are the muon and Mu relaxation rate, respectively. ω_μ and ω_{Mu} are the muon and Mu precession frequencies, respectively, and ϕ_μ and ϕ_{Mu} are the respective initial phases of their precessions. Under the transverse field of H(in G), the spins of μ^+ and Mu take precession with the angular velocities of ω_μ(in kHz) = $2\pi\times13.553\times$H and ω_{Mu} = $2\pi\times1390\times$H, respectively. Generally, the selection of fitting function depends on the nature of observed spectra, related phenomena, etc.

μSR STUDY IN WATER AND ICE

When muon beam incident into water, around 60% of incident muons remained in the diamagnetic muon form and around 20% in Mu in addition to remaining missing fraction (Fig. 3). However, in ice (freezed water), there is no such missing fraction [19]. As reported by Percival et al, interaction of Mu with transient paramagnetic

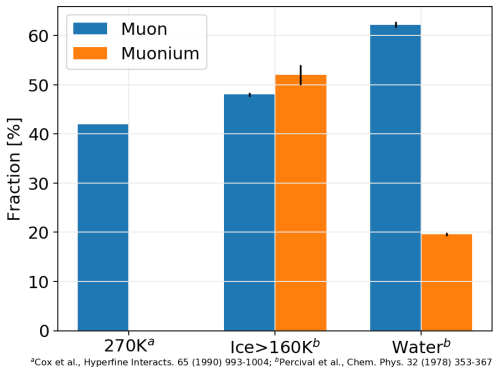

FIGURE 3. Fraction of muon and muonium in water and ice. The error bar is shown in black vertical line. The data are extracted from ref. [24] and ref. [19]

species like hydrated electron, hydroxyl radical and hydrogen atom (even small extent) formed by radiolysis of water within 100 ns is responsible for the missing fraction [20]. The intraspur reaction (muonium formation, direct generation of a fraction of the muons in diamagnetic molecules, the "missing" muon polarization) is explained based on two models - hot model and spur model [21].

Nagamine et al reported the long lived Mu in doubly distilled water [22]. However, in the presence of impurities like existence of molecular oxygen, there is relaxation of Mu due to spin exchange interaction of the Mu with paramagnetic oxygen molecules [13, 14, 23].

In addition, two steps process was reported by Percival et al and Cox et al when muon incident into water. First of all, the muon stops near the lone electron pair of oxygen and formed hydroxiom like ion (H_2MuO^+) (Eq. 2) which is similar to protonation process. Then the proton migration takes place and ultra light water (HMuO) is formed (Eq. 2).

$$\begin{aligned} H_2O + \mu^+ &\rightarrow H_2MuO^+ \\ H_2MuO^+ + H_2O &\rightarrow HMuO + H_3O^+ \end{aligned} \quad (2)$$

μSR study in ice (single crystal, hexagonal, polycrystalline) were reported by Percival et al [25, 26] and Cox et al [24, 27, 28]. The beating pattern in Mu signal obtained in ice was explained based on anisotropic diffusion of Mu in ice [29]. Llevel cross-resonance study in ice [24, 27, 28] with and without introducing defects were reported by Cox et al to understand the kinks/dips in the spectra. The stopping site and final state of muon as Mu in Bjerrum L-defect is expected however measurement in HF doped and NH_3 doped ice do not clear the image of expectation. Wang et al reported the study in various phases of ice (ice-II, ice-VI, ice-VIII and high density amorphous ice) [30] in temperature range from 5 K to 260 K. Based on the analysis of ZF μSR data using a single exponential function, they reported the relaxation rate from ZF is higher than that from TF measurement. The initial asymmetry dropped at around 140K for ice-II, ice-VI and ice-VIII except hexagonal ice (Ih). However, the reason of distinguished behavior Ih is not clearly understood.

Mu diffuses along c-axis in the crystal even at 8 K through the quantum tunneling [31, 32]. Theoretical calculation using ring polymer molecular dynamics method by Markland et al also reported the diffusion of Mu in water and Ih ice [33]. It is mentioned that Mu diffuses from one cavity to the next along the c-axis showing agreement with experiment. Furthermore, the Mu hyperfine frequency in water at STP is reported as 4422 $\pm$ 6 MHz [34] which is smaller than that in vacuum as 4463.4 MHz [35]. Its value in ice is larger than that in vacuum value.

MUON SITE AND INTERACTION WITH H_2O

So far, the most of the previous studies focused on muonium chemistry. To my best knowledge, the stopping sites of muon in water and ice is not clearly understood yet. In pure water, if muon stops nearby the protons then the spin-dipole interaction between the muon and protons will be appeared in the experimental signal. If the muon diffuses or hopes with temperature, the interaction will be changed which in turn change the nature of μSR spectra.

Ice follows the two ice rules [36] - (1) each oxygen atom is covalently bounded by two H and (2) one H atom along the O-O vertex making covalent bond with one O and hydrogen bond with another (Fig. 4). If ice violates one of the rules, then the defect created. Incident of muon may create the defect in ice. The stopping site of muon in ice (hexagonal ice) (Fig. 4) and its spin-dipole interaction with protons will help to understand the muon behavior in ice.

For application of muon to life science and even for hydrated materials samples, the effect of water should be appeared as background signal. To understand the targeted phenomena, the separation of spectra from water and sample (e.g., biosample) is necessary.

CONCLUSION

So far the muon and Mu fraction in water and ice were studied by several groups. In water, missing fraction and relaxation of Mu (based on purity of water) were understood. In ice, there is no missing fraction. It is important to know the stopping site and interaction of muon with nearby protons in water and ice which will help to separate the background signal from water in aqueous, biological and hydrated samples.

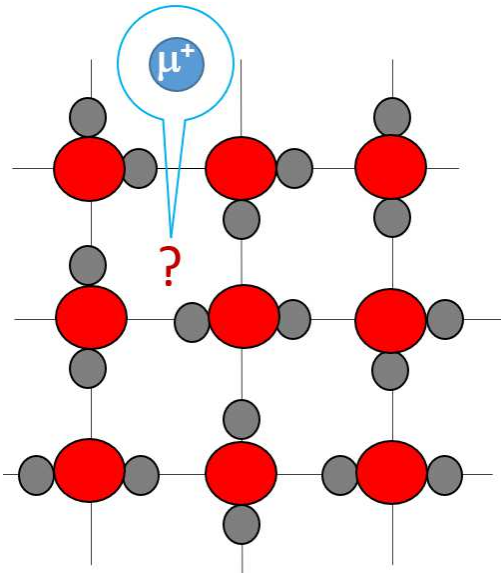

FIGURE 4. Schematic diagram (square ice) of ice following ice rules. Stopping site of muon is not understood in the system.

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