Determination of muon stopping sites and electronic structures in proteins

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1. Introduction

Complexity of biological molecules has prevented μSR studies in the life science field. Among the important biological phenomena, we targeted the electron-transfer process, which plays important roles in the photosynthesis and the respiratory chain (K. Nagamine et al., Physica B, 289-290 (2000) 631.; Y. Sugawara *et al*. JPS Conference Proceedings 2, 010310-1-5 (2014). etc.). In order to advance our investigation, determination of muon stopping sites in proteins is inevitable.

Recently level crossing resonance (LCR) under longitudinal field around 20 G was observed in the case of cytochrome *c* (Fig. 1 (a)). Cytochrome *c* is one of the members of the respiratory chain in mitochondria. LCR around 20 G had been observed also in the case of polyglycine (Fig. 1 (b)) (F. Pratt et al., private communication). Polyglycine (NH_2-CH_2-[CONH-CH_2]$_n$-COOH) is the simplest peptides made of aliphatic (-CH_2-) parts, peptide bonds (-CONH-) and terminal -COOH and -NH_2 groups. Under such a background, we carried out μSR measurements of glycine (NH_3^+-CH_2-COO^-) and glycylglycine (NH_3^+-CH_2-CONH-CH_2-COO^-) in June, 2017 (2017A0183). It was found that LCR around 20 G was observed only in the case of glycylglycine, and it was concluded that the LCR originate to muon or muonium stopped at peptide bonds (-CONH-). We speculate that the observed LCR would be quadrupole LCR (muon Zeeman splitting becomes equal to the nuclear quadrupole splitting), because the LCR was observed in the low magnetic field region (around 20 G) of LF. To confirm the proposed quadrupole LCR (QLCR), the comparative measurements of N-methylacetamide–^{14}N (I = 1, Q=0.16) and –^{15}N (I = –1/2, Q = 0) are important, because ^{15}N have no quadruple moment. By the way, μSR measurements of glycine–^{14}N and glycine–^{15}N had been carried out, and no LCR were observed around 20 G in both samples (2017A0183).

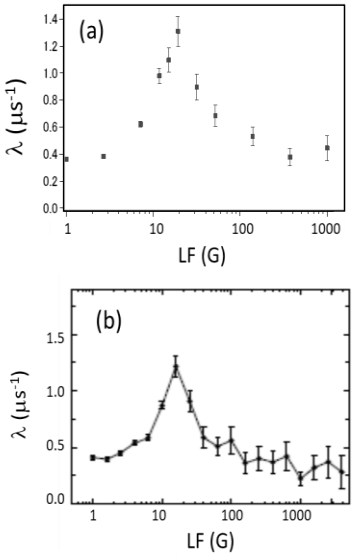

Fig. 1　Longitudinal field dependence of relaxation rate (λ) in dry cytochrome c (a) and polyglycine (F. Pratt et al., private communication (b) at 100K.

2. Experiment

1) Longitudinal μSR time spectra of N-methylacetamide (^{14}N and ^{15}N), triglycine, and L -histidyl-L-leucine were measured under the various longitudinal fields from 0 G to 3.5 kG and various temperatures from 300 K down to 10 K. For accurate and precise analysis of data, it is necessary to measure the spectra using the single pulse mode. However, the trouble of the kicker prevented use of the single pulse beam. Therefore, we measured the data using the double pulse mode except L -histidyl-L-leucine.

2) The relaxation rate (λ) for each μSR time spectrum was plotted against longitudinal field. An existence of muonic radicals was examined as an avoided level crossing resonance in the longitudinal field dependence data.

3. Results

As described the previous section, we could not use the single pulse mode because of trouble of the

kicker. We measured the data using the double pulse mode and carried out tentative analysis.

The relaxation spectra of ^{14}N species of N-methlyacetamide (NMAA; $CH_3CONHCH_3$), one of the simplest compound which contains a peptide bond (-CONH-), and triglycine at zero field at 15 K are shown in Fig. 2. The initial loss of asymmetry for NMAA was larger than that for triglycine. By the way, the full asymmetry estimated from the μSR data of silver was approximately 24%.

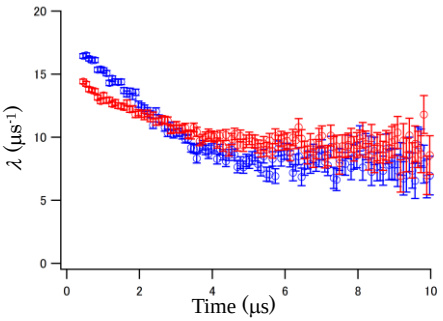

Fig. 2 μSR spectra of NMAA (red) and triglycine (blue) at ZF at 15K

Plots of the relaxation rate (λ) against longitudinal field (LF) are shown in Fig. 3. In both species of NMAA (^{14}N and ^{15}N), the local maximum of relaxation parameter λ was observed around 10G, although the maximum value of λ for NMAA-^{15}N was around half of that for -^{14}N. The result indicated that the origin of the peak would not be QLCR, although precise analysis of the data measured using the single pale beam is necessary for the final conclusion. By the way, the LF value of 10 G was a little lower than those of the other samples. The results of triglycine were consistent with those of glycine and glycylglycine (2017A0183).

We carried out also preliminary measurements of LSQ for L-histidyl-L-leucine (His-Leu) and the light illumination experiment of photosystem II. In the case of His-Leu, the local maximum of λ against LF was broad (Fig. 3(d)). It seemed that the relaxation process of muon stopped at a imidazole ring which is the side chain of histidine would exist around 20 ~ 30G region. Concerning the preliminary light illumination experiments of PSII, Mu (muonium) spin rotation in TF 2.3 G was observed.

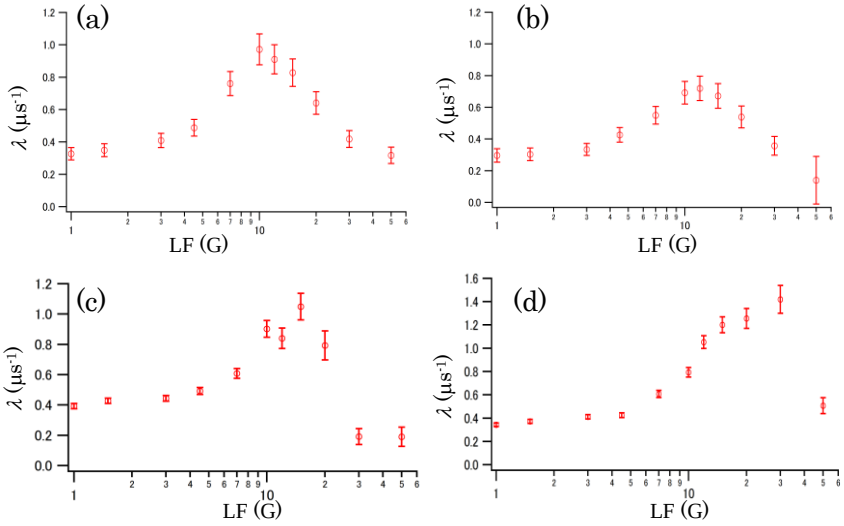

Fig. 3 Plot of the relaxation rate (λ) against longitudinal field (a) NMAA-^{14}N at 71 K (b) NMAA -^{15}N at 72 K (c) Triglycine at 99 K (d) His-Leu at 66 K

4. Conclusion

We examined LCR of NMAA-^{14}N and -^{15}N and triglycine in the low LF region. Unfortunately, we could not use the single pulse because of trouble of the kicker. Tentative analysis of NMAA-^{14}N and -^{15}N indicated that the LCR would not be QLCR. An important problem left is a precise quantitative analysis of the NMAA-^{14}N and -^{15}N data measured using the single pulse beam.