Possible muonic radical formation in cytochrome c


The electron-transfer process plays important roles in the photosynthetic electron transfer chain in chlorophylls and the respiratory chain in mitochondria. Two of the authors of this work (KN and ET) have previously successfully measured μSR spectra of hemoprotein of cytochrome c and DNA. The major parts of μSR spectra were found to follow the Risch-Kehr (R-K) function, \( G(t) = \exp(\Gamma t) \text{erfc}(\Gamma t)^{1/2} \), where \( \Gamma \) is the relaxation parameter. Longitudinal magnetic field dependence of \( \Gamma \) reflects the behavior of the electron brought by the muon. Motivated by these situations, we have been examining μSR spectra of cytochrome c, which is one of the members of the respiratory chain in mitochondria.

It was found that some fractions of the μSR amplitude can be attributed to the muonic radical formation on the basis of an avoided level crossing resonance in the longitudinal field dependence data, the results of which are reported herein.

The μSR measurements of oxidized cytochrome c of horse heart (water content was less than 5 % w/w) were carried out at RIKEN-RAL and J-PARC MUSE. The \( B_{\text{ext}} \) dependence of the relaxation data were analyzed by Lorentzian function.

The longitudinal field dependence of the initial and the baseline asymmetries and relaxation rates (\( \lambda \)) values are shown in Fig. 1a. The \( \lambda \) became large at around 10 ~ 20 G. Some fractions of the μSR amplitude could be attributed to the muonic radical formation on the basis of an avoided level crossing resonance.

Similar experimental results had been obtained in the case of polyglycine. Judging from the structural analogy (Fig. 1b), the muonic radical would be formed at a carbonyl moiety of polypeptide bonds, which form the main chain of cytochrome c. We should pay attention to the following classification to consider the muon stopping sites and behavior of electrons brought by muons.

1. peptide bonds (-CO-NH-) and side chains of Gln and Asn (-CONH2)
2. side chains of Glu and Asp (-COO-)
3. aromatic side chains i.e. phenylalanine, tryptophan, tyrosine, and histidine
4. the porphyrin ring of the heme part.

When a part of the muons stopped at the moieties classified to 1 and 2, muonium radicals would be formed. On the other hand, when muons stopping at the moieties classified to 3 and 4, electrons which were brought by muons would delocalized and diffuse in proteins. Due to the latter contribution, the other fractions of μSR spectra would follow the R-K function.

Improved studies, both experimental and theoretical are in progress.

References
5) F.L. Pratt et al., (private communication).