

Measurement of Hyperfine Field in Metal Complexes by Perturbed Angular Correlation of γ -rays

A. Yokoyama¹, I. Yamazaki¹, T. Hashimoto¹, K. Ihara¹, Y. Murakami², K. Takamiya³, W. Sato⁴, T. Saito⁵,
and Y. Ohkubo³

¹Graduate School of Natural Science and Technology, Kanazawa University

²Japan Atomic Energy Agency

³Research Reactor Institute, Kyoto University

⁴Graduate School of Science, Osaka University

⁵Radioisotope Research Center, Osaka University

Abstract – Several chelate complexes having similar structures around their metal sites to that of a protein have been investigated by using time-differential perturbed angular correlation (PAC) of γ -rays from the parent nuclei ¹¹⁷Cd ($T_{1/2} = 2.49$ h), ^{111m}Cd ($T_{1/2} = 48.5$ min), ¹¹¹In ($T_{1/2} = 2.81$ d), and ¹¹¹Ag ($T_{1/2} = 7.47$ d) in order to verify the effect of conformation of the ligands to the electric field gradients.

Keywords – Perturbed angular correlation of γ -rays, chelate complexes, electric field gradient

I. INTRODUCTION

Perturbed angular correlation of γ -rays (PAC) has an advantage in the measurement of the hyperfine field at a metal site of biological molecule in an aqueous solution as functioning in life. The electric field gradient (EFG) of the metal site of mavycyanin, a protein molecule with a single copper site was deduced by the method. It demonstrated that the site in a mutant-type mavycyanin, Thr15Ala-Mav, gives an EFG different from that in the wild-type mavycyanin does. The pH dependence of the EFG was also observed for both proteins[1]. The shift of gradient is considered to be due to some change of conformation of the ligand.

In order to verify the effect, several chelate complexes having similar structures around their metal sites to that of the protein have been investigated in the present study by using time-differential perturbed angular correlation (TDPAC) of γ -rays from the parent nuclei ¹¹⁷Cd ($T_{1/2} = 2.49$ h), ^{111m}Cd ($T_{1/2} = 48.5$ min), ¹¹¹In ($T_{1/2} = 2.81$ d), and ¹¹¹Ag ($T_{1/2} = 7.47$ d) as well.

The latter three nuclides decay to the same PAC probe, namely ¹¹¹Cd, but only ¹¹⁷Cd does to ¹¹⁷In.

II. EXPERIMENTS

The parent nuclei ¹¹⁷Cd and ^{111m}Cd were obtained by irradiating enriched ¹¹⁶CdO and ¹¹¹CdO powders, respectively, with thermal neutrons at Kyoto University Research Reactor. The ¹¹¹In sample was purchased from Nihon Medi-Physics Co. Ltd. Preparation of the tracer solutions was performed, but some

of the measured complex samples were subject to precipitation in solution.

The parent nuclei ¹¹¹Ag were obtained by irradiating a metal foil of Pd of natural abundance with thermal neutrons at JRR-3 or JRR-4 of Japan Atomic Energy Agency. The nuclei were produced via the ¹¹⁰Pd(n, γ)¹¹¹Pd reaction and the following β decay of ¹¹¹Pd ($T_{1/2} = 23.4$ min). Therefore the irradiated metal was let stand for 5 days for growth of the products of interest and disintegration of the by-products. Then, it was transported to Research Reactor Institute, Kyoto University and dissolved for preparation of the tracer solutions of ¹¹¹Ag through chemical separation with an ion exchange column or precipitation, then the complex samples were prepared and subject to PAC measurements there. The examples of ligands of the samples are ammine, o-phenanthroline, bismuthiol, cupferron and diethyldithiocarbamic acid (DDC) as listed with their coordinating atoms in Table 1.

III. RESULTS

Table 1 lists the EFG values $|V_{zz}|$ determined from the spectra and indicates that the EFG depends very much on the kind of donor atoms and very little on that of parent nuclei (¹¹¹Ag or ^{111m}Cd), although other parameters concerning the coordination (e.g., bond length and bond angle) are also involved in the electric field gradient. In order to extract detailed information on the structure around the probe, further study and discussion are needed.

Table 1. Hyperfine fields in metal complexes. The measurements were performed with ¹¹¹Ag parent nuclei but for the data with

Ligand	Donor atoms of ligand	$ V_{zz} $ / $10^{22}\text{V}\cdot\text{m}^{-2}$
ammine	N,N	2.83 ± 0.57
o-phenanthroline	N,N,N,N	2.90 ± 0.17
bismuthiol	S,S,S,S	1.00 ± 0.29
cupferron	O,O,O,O	$0.74 \pm 0.20^*$
DDC	S,S,S,S	$0.94 \pm 0.17^*$

asterisk using ^{111m}Cd parent nuclei.

REFERENCE

- [1] A. Yokoyama *et al*, Hyp. Int., in press (2008).