

STUDY ON THE STRUCTURE AND ELECTRONIC STATE OF THIOLATE-PROTECTED GOLD CLUSTERS BY MEANS OF ^{197}Au MOSSBAUER SPECTROSCOPY

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In the last decade, small Au clusters composed of less than 100 atoms protected by organic ligands have attracted much attention as a prototypical system for fundamental studies on quantum size and as a building block of nano-scale devices [1]. Among small Au clusters, the Au-thiolate compound composed of 25 Au atoms and 18 thiolates ($\text{Au}_{25}(\text{SR})_{18}$) has been studied most extensively as a prototype system of stable $\text{Au}_n(\text{SR})_m$ clusters [2]. According to the structural analysis, $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ is composed of an icosahedral Au_{13} core whose surface is protected by six staples, $-\text{S}(\text{R})-\text{Au}-\text{S}(\text{R})-$, which is shown in Fig. 1 [3]. Based on the geometrical structure of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$, we have successfully analyzed the ^{197}Au Mössbauer spectra of $\text{Au}_n(\text{SG})_m$ ($n = 10 - \sim 55$) and dodecanethiolate-protected Au clusters with the average diameters of 2 - 4 nm [4].

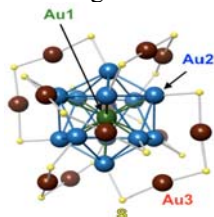


Figure 1. Core structure of $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ [3].

The $\text{Au}_n(\text{SG})_m$ samples with $(n, m) = (10, 10) - (\sim 55, m)$ were fractionated using polyacrylamide gel electrophoresis (PAGE) [5]. In order to obtain the ^{197}Au Mössbauer spectra with sufficient S/N ratio, each cluster was accumulated up to 50 - 100 mg by repeating the elaborative PAGE procedure [6]. The dodecanethiolate-protected Au clusters with the average diameters of 2 nm and 4 nm were prepared by the direct chemisorption method and the ligand-exchange method, respectively [7].

^{197}Au Mössbauer measurement was carried out at Research Reactor Institute of Kyoto University. The γ -ray source (77.3 keV), ^{197}Pt , was generated by the neutron irradiation to 98 % - enriched ^{196}Pt metal foil. The γ -ray source and samples were cooled down to 16 K. The isomer shift of Au foil was referenced to 0 mm/s.

The ^{197}Au Mössbauer spectra of $\text{Au}_n(\text{SG})_m$ are shown in Fig. 2. These spectra were analyzed based on the structure of $\text{Au}_{25}(\text{SR})_{18}$ ($\text{SR} = \text{SC}_2\text{H}_4\text{Ph}$). The Mössbauer spectra of a series of $\text{Au}_n(\text{SG})_m$ evolve drastically as a function of the core size. Asymmetric doublet profile of the $\text{Au}_{10}(\text{SG})_{10}$ spectrum can be fitted by a superposition of two sets of doublets, which correspond to the Au(I) atoms directly coordinated by two SG ligands.

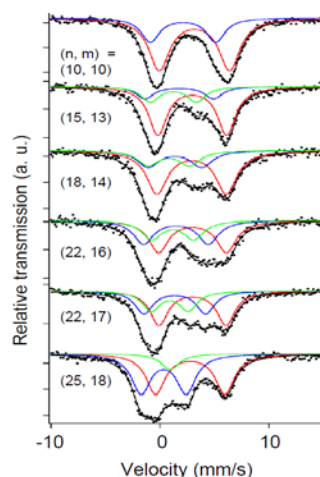


Figure 2. ^{197}Au Mössbauer spectra of $\text{Au}_n(\text{SG})_m$ ($n = 10 - 25$) [4].

The spectra of $\text{Au}_n(\text{SG})_m$ ($15 \leq n \leq 22$) can be fitted by three sets of doublets. Two components are assigned to the Au(I) atoms coordinated by two SG ligands since the IS and QS values are smoothly correlated to those of $\text{Au}_{10}(\text{SG})_{10}$. The third component having the smallest IS and QS values is assigned to the Au(I) atoms coordinated by single SG ligand which is smoothly correlated to those of the Au(I) atoms coordinated by single SG ligand in $\text{Au}_{25}(\text{SR})_{18}$. The spectral profile abruptly changes on going from $\text{Au}_{22}(\text{SG})_{16}$ to $\text{Au}_{25}(\text{SG})_{18}$, where a core Au atom free from SG appears for the first time, then it smoothly changes to that of $\text{Au}_{\sim 55}(\text{SG})_m$.

In this paper, we will review the molecular structures and the Au electronic states of small Au clusters composed of less than 100 Au atoms protected by organic ligands by means of ^{197}Au Mössbauer spectroscopy.

- [1] M.-C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293.
- [2] (a) T. G. Schaff, R. L. Whetten, J. Phys. Chem. B104 (2009) 2630, (b) R. C. Price, R. L. Whetten, J. Am. Chem. Soc., 127 (2005) 13750, (c) H. Tsunoyama, Y. Negishi, T. Tsukuda, J. Am. Chem. Soc., 128 (2006) 6036.
- [3] (a) M. W. Heaven, A. Dass, P. S. White, K. M. Holt, R. W. Murray, J. Am. Chem. Soc., 130 (2008) 3754, (b) M. Zhu, E. Lanni, N. Garg, M. E. Bier, R. Jin, J. Am. Chem. Soc., 130 (2008) 1138.
- [4] N. Kojima, K. Ikeda, Y. Kobayashi, T. Tsukuda, Y. Negishi, G. Harada, T. Sugawara, M. Seto, Hyperfine Interactions, (2012) in press.
- [5] Y. Negishi, K. Nobusada, T. Tsukuda, J. Am. Chem. Soc. 127 (2005) 5261.
- [6] K. Ikeda, Y. Kobayashi, Y. Negishi, M. Seto, T. Iwasa, K. Nobusada, T. Tsukuda, N. Kojima, J. Am. Chem. Soc., 129 (2007) 7230.
- [7] O. Nagao, G. Harada, T. Sugawara, A. Sasaki, Y. Ito, Jpn. J. Appl. Phys., 43 (2004) 7742.