$^{197}$Auメスバウアー一分光法とその応用：
金ナノ粒子の構造と電子状態
$^{197}$Au Mössbauer spectroscopy

$^{196}$Pt + n → $^{197}$Pt + $\gamma$

$^{197}$Pt → (18.3h) → $^{197}$Au + $\beta^-$ + hν($\sim$0.6MeV)

$^{197}$Au Mössbauer spectroscopy is one of the most powerful method to investigate the chemical bond and valence state of gold atoms

Research Reactor Institute, Kyoto University
Research Reactor Institute, Kyoto University

Critical experiment reactor

Research reactor
Relationship between isomer shift and quadrupole splitting for Au(I) and Au(III) compounds.

R.V. Parish

Gold nano-clusters with magic number and $^{197}$Au Mössbauer spectra

Relationship between structure and \textsuperscript{197}Au Mössbauer spectra

\[ \text{[Au}_9\text{(PPh}_3\text{)}_8\text{]}\text{(NO}_3\text{)}_3 \]

\[ \text{Au}_{11}\text{(PPh}_3\text{)}_7\text{(SCN)}_3 \]

\[ \text{Au}_{55}\text{(PPh)}_{12}\text{Cl}_6 \]

Isolation of Glutathione-Protected Gold Clusters, $\text{Au}_n(\text{SG})_m$


Isolation of Glutathione-Protected Gold Clusters, $\text{Au}_n(\text{SG})_m$

$\text{Au}_n(\text{SG})_m$

- $#9 = (39, 24)$
- $#8 = (33, 22)$
- $#7 = (29, 20)$
- $#6 = (25, 18)$
- $#5 = (22, 17)$
- $#4 = (22, 16)$
- $#3 = (18, 14)$
- $#2 = (15, 13)$

Polyacrylamide gel electrophoresis (PAGE)

Extraction

Molecular weight

Small

Large
Systematic Isolation of Glutathione-Protected Gold clusters

ESI mass spectrum

UV-vis absorption spectra

[S$_{25}(SG)_{18}^{-z}H]^{z-}$

1000 2000 3000

$[Au_{25}(SG)_{18}^{-2}H]^{2-}$

Singly-sized cluster is included

Possible structures of $\text{Au}_{10}(\text{SR})_{10}$ and $^{197}\text{Au}$ Mössbauer spectra of $\text{Au}_{10}(\text{SG})_{10}$

Two doublets of $^{197}\text{Au}$ Mössbauer spectra for $\text{Au}_{10}(\text{SG})_{10}$ suggests the catenane structure.


Possible structures of $\text{Au}_{10}(\text{SR})_{10}$ and $^{197}\text{Au}$ Mössbauer spectra of $\text{Au}_{10}(\text{SG})_{10}$

Two kinds of Au-S bond length

Two doublets of $^{197}\text{Au}$ Mössbauer spectra for $\text{Au}_{10}(\text{SG})_{10}$ suggests the catenane structure.


Molecular structure of $\text{Au}_{25}(\text{SR})_{18}$ and $^{197}\text{Au}$ Mössbauer spectra of $\text{Au}_{25}(\text{SG})_{18}$

Structure of $\text{Au}_{25}(\text{SC}_{2}\text{H}_{4}\text{Ph})_{18}$


Relative recoil-free fraction

$f(\text{Au1}) : f(\text{Au2}) : f(\text{Au3}) = 1.03 : 1.00 : 2.44$

$^{197}$Au Mössbauer spectra of $\text{Au}_n(\text{SG})_m \ (n = 10 - 25)$

![Graphical representation of Mössbauer spectra and related data analysis.](image-url)
$^{197}$Au Mössbauer spectra of $\text{Au}_n(SG)_m$ ($n = 25 - \sim 55$)

- C1: Au–Au*–S
- C2: S–Au*–S
- C3: Au–Au*–Au

Graphs showing relative transmission and area rate as a function of the number of Au atoms.

- Velocity (mm/s)
- Relative transmission (a. u.)
- Area rate (%)
- S / $S$ (mm/s)
- QS (mm/s)
Relationship between isomer shift and quadrupole splitting for Au(I) and Au(III) compounds.

- Au(I) C1 doublet for $\text{Au}_{n}^{(SG)}_{m}$ ($n = 10 - \sim 55$)
- Au(I) C1' doublet for $\text{Au}_{n}^{(SG)}_{m}$ ($n = 10 - 22$)
- Au(III) C2 doublet for $\text{Au}_{n}^{(SG)}_{m}$ ($n = 25 - \sim 55$)

- Red circle: S — Au* — S
- Orange circle: S — Au* — S
- Blue circle: Au — Au* — S
- Teal circle: Au — Au* — S
### Number of Au atoms in the three sites for \( \text{Au}_n(\text{SG})_m \)

Recoil-free fraction of Au in \( \text{Au}_{25}(\text{SG})_{18} \)  
\[ f(\text{Au1}): f(\text{Au2}): f(\text{Au3}) = 1.03 : 1.00 : 2.44 \]

<table>
<thead>
<tr>
<th>( \text{Au}_n(\text{SG})_m )</th>
<th>Number of Au1 site (-S-Au*-S-)</th>
<th>Number of Au2 site (Au-Au*-S-)</th>
<th>Number of Au3 site (Au-Au*-Au)</th>
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<td>2</td>
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<td>(45, 28)</td>
<td>15</td>
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<tr>
<td>(~55, m)</td>
<td>~13</td>
<td>~37</td>
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Face-fused bi-icosahedral Au$_{23}$ core

Geometrical structure of $\text{Au}_{38}(SG)_{24}$

Face-fused bi-icosahedral $\text{Au}_{23}$ core whose surface is protected by 3 monomeric staples (-S(G)-$\text{Au}$-S(G)-) and 6 dimeric staples (-S(G)-[$\text{Au}$-S(G)-]$_2$)

- **Au1**: 15
- **Au2**: 21
- **Au3**: 2

3 monomeric staple (-S(G)-$\text{Au}$-S(G)-)

$n(\text{Au1}) = 3 \times 1 = 3, \quad m(\text{SG}): 3 \times 2 = 6$

6 dimeric staple (-S(G)-[$\text{Au}$-S(G)-]$_2$)

$n(\text{Au1}) = 6 \times 2 = 12, \quad m(\text{SG}): 6 \times 3 = 18$
Structure of $\text{Au}_n(\text{SG})_m$ by the analysis of Mössbauer spectra

$\text{Au}_{10}(\text{SG})_{10}$  Catenane structure with two interlocked pentamers

$10 < n < 25$ : Formation of assembled Au atoms with only surface

$\text{Au}_{25}(\text{SG})_{18}$  Icosahedral $\text{Au}_{13}$ core whose surface is protected by 6 dimeric staples ($-\text{S(G)}-[\text{Au}-\text{S(G)}-]_2$)

$25 < n < 38$ : Extended icosahedral $\text{Au}_{13}$ core protected by staples

$\text{Au}_{38}(\text{SG})_{24}$  Face-fused bi-icosahedral $\text{Au}_{23}$ core whose surface is protected by 3 monomeric staples ($-\text{S(G)}-\text{Au-S(G)}-$) and 6 dimeric staples ($-\text{S(G)}-[\text{Au-S(G)}-]_2$)

$38 < n$ : Molecular structure becomes to be extended towards to close-packed structure
Conclusion

$^{197}$Au Mössbauer spectra of glutathione-protected Au clusters, $Au_n(SG)_m$ ($n = 10 - \sim55$) were successfully analyzed based on the structure of $Au_{25}(SG)_{18}$.

1) $Au_{10}(SG)_{10}$: two kinds of S-Au-S bond (two doublets of C1 and C1').

2) $Au_{15}(SG)_{13} - Au_{22}(SG)_{17}$: two kinds of S-Au-S bond (C1 and C1'), and Au-S bond (C2).

3) $Au_{25}(SG)_{18} - \sim Au_{55}(SG)_m$: S-Au-S bond (C1), Au-S bond (C2), and Au core atom free from SG (C3). The Au core atom appears at $Au_{25}(SG)_{18}$ for the first time on going from $Au_{15}(SG)_{13}$ to $Au_{25}(SG)_{18}$, then the line profile continuously changes from $Au_{25}(SG)_{18}$ to $\sim Au_{55}(SG)_m$.

4) The valence state of Au atom coordinated by two S atoms or one S atom is Au(I).

5) The valence states of Au atoms on the surface of Au skeleton are Au(I), while those of the core Au atoms in Au skeleton are Au(0).

6) The geometrical structures of $Au_{10}(SR)_{10}$, $Au_{25}(SR)_{18}$, and $Au_{38}(SR)_{24}$ are consistent with the analysis of the $^{197}$Au Mössbauer spectra of $Au_{10}(SG)_{10}$, $Au_{25}(SG)_{18}$, and $Au_{38}(SG)_{24}$. 
$^{197}$Au Mössbauer spectroscopy is the most powerful probe to investigate the structure and electronic state of gold nanoparticles.

(a) $\text{Au}_{25} (\text{SC}_{12}\text{H}_{25})_{18}$

(b) $\text{Au}_{24}\text{Pd} (\text{SC}_{12}\text{H}_{25})_{18}$

The average diameter of dodecanethiol-chemisorbed cluster prepared by the direct chemisorption method was 1.9 nm, and the averaged diameter of cluster prepared by the ligand-exchange method was 4.0 nm.

The average cluster sizes of 1.9 nm and 4 nm were determined by transmission electron microscopy (TEM) and wide-angle X-ray diffraction analysis.

$^{197}$Au Mössbauer spectra between $\sim$Au$_{55}$(SG)$_m$ and Au$_n$(SDT)$_m$ ($DT = C_{12}H_{25}$)

Area (C1): 22.1 %
Area (C2): 58.6 %
Area (C0): 19.3 %

Area (C1): 17.3 %
Area (C2): 43.7 %
Area (C0): 39.0 %

Area (C1): 5.6 %
Area (C2): 37.7 %
Area (C0): 56.8 %