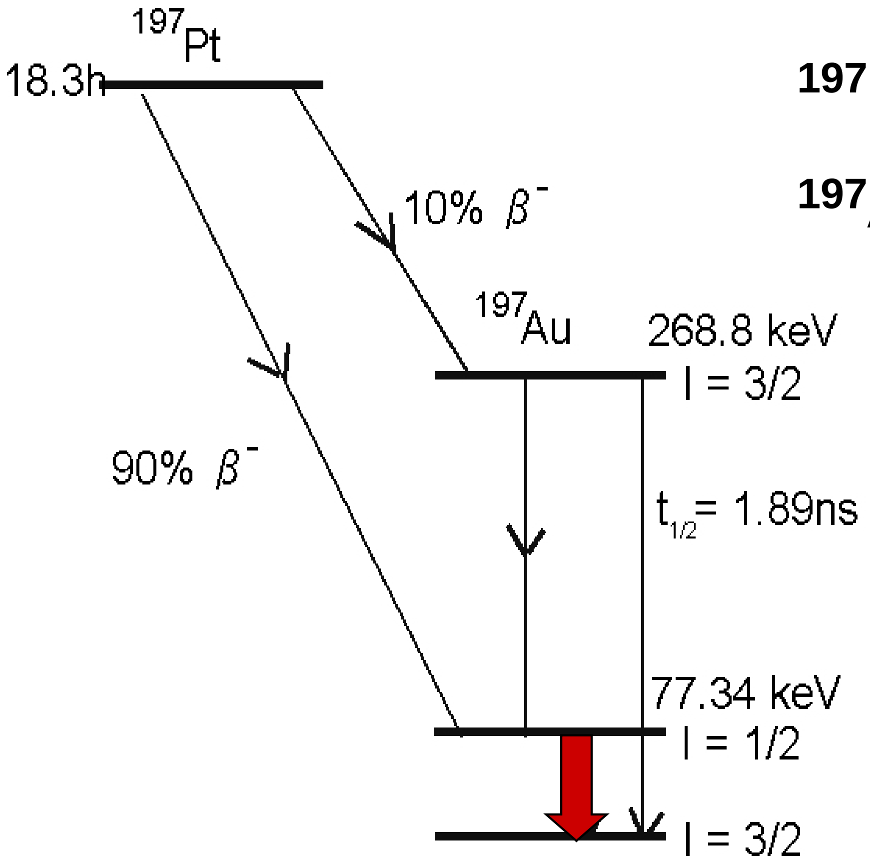
^{197}Auメスバウアー分光法とその応用:
金ナノ粒子の構造と電子状態

^{197}Au Mössbauer spectroscopy



^{196}Pt + n → ^{197}Pt +γ

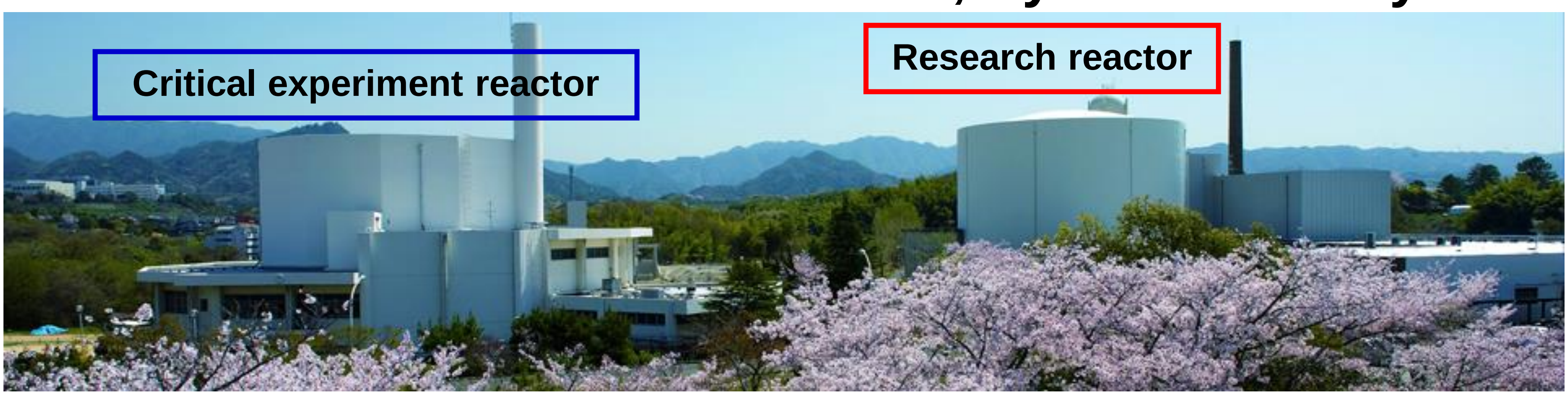
^{197}Pt → (18.3h) →

^{197}Au + β^- + $h\nu$(∼0.6MeV)

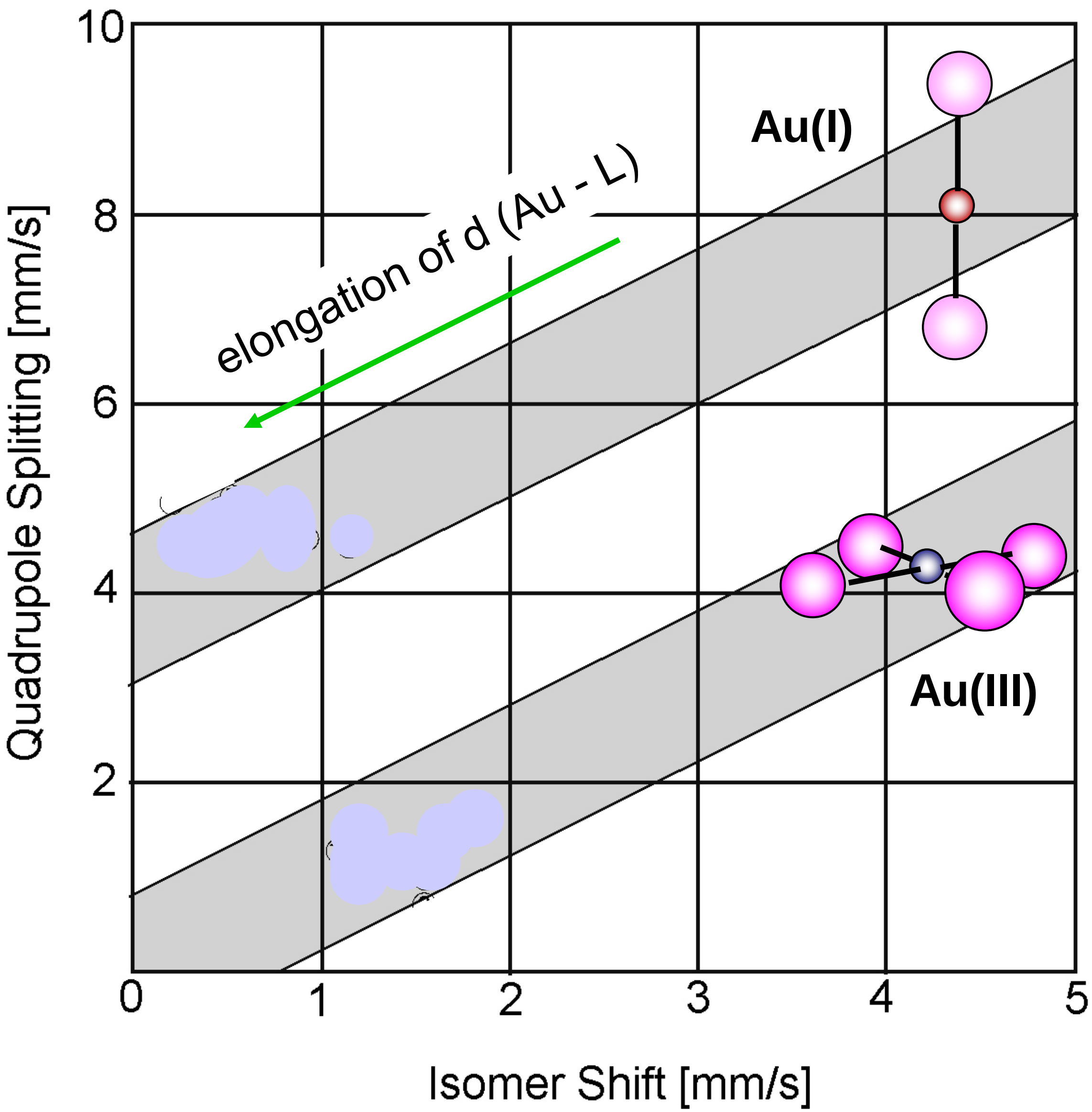
^{197}Au Mössbauer spectroscopy is one of the most powerful method to investigate the chemical bond and valence state of gold atoms

Research Reactor Institute, Kyoto University

Research Reactor Institute, Kyoto University



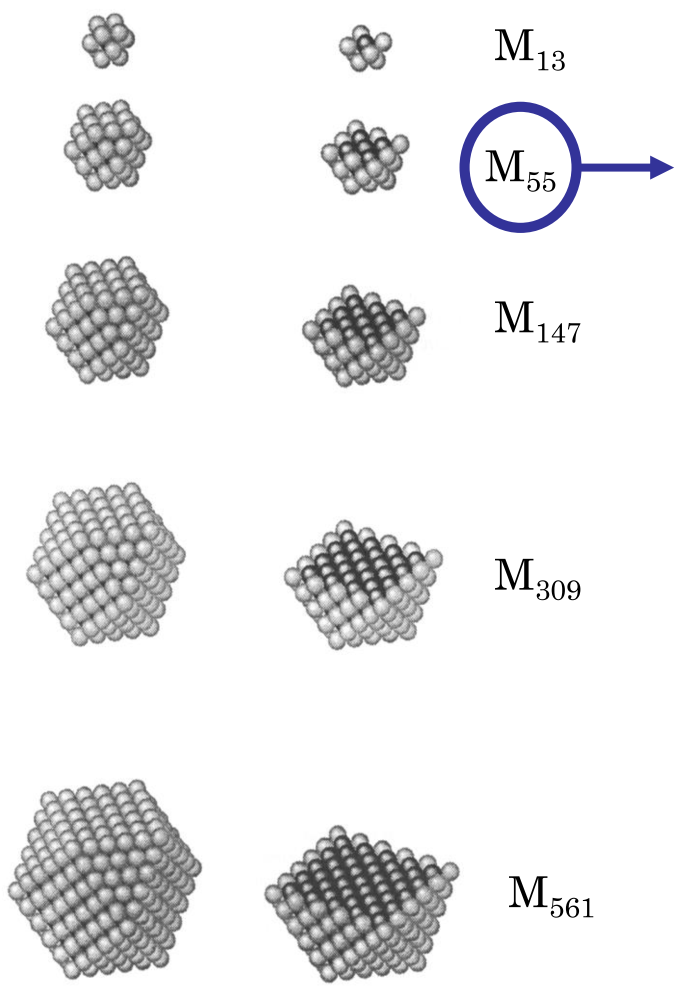
Relationship between isomer shift and quadrupole splitting for Au(I) and Au(III) compounds.

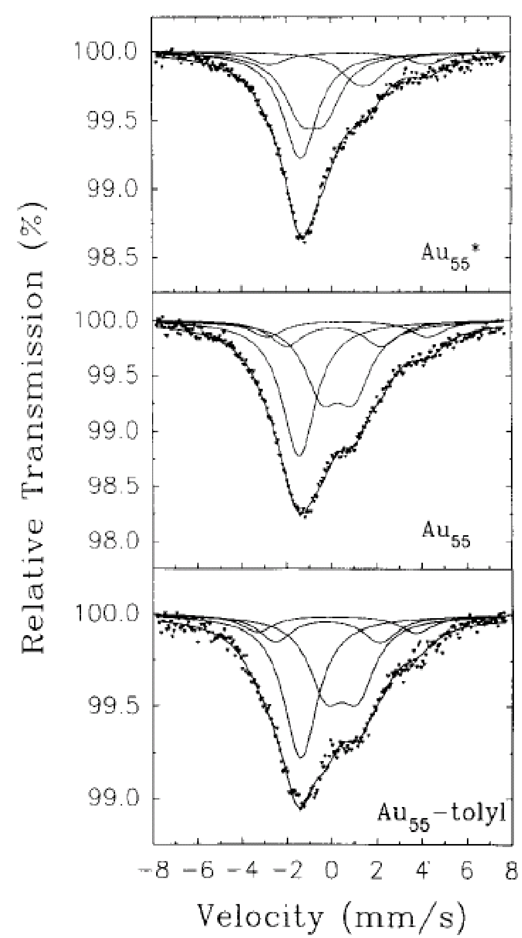


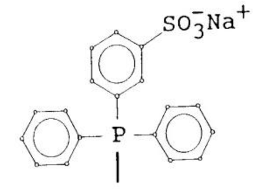
R.V. Parish

“Mössbauer Spectroscopy Applied to Inorganic Chemistry” ed. by G.J. Long, Plenum Press, 1984, Vol. 1, p. 577.

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

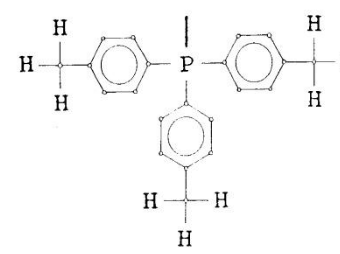






$Au_{55}(PPh_2(C_6H_4SO_3))_{12}Cl_6$

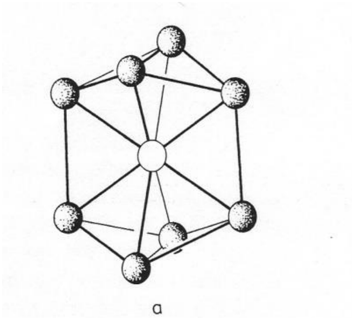
$Au_{55}(PPh)_{12}Cl_6$



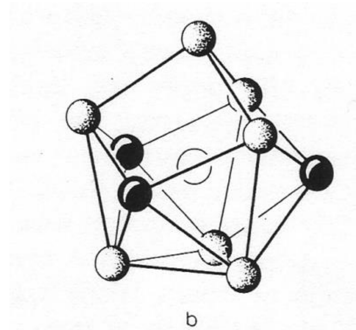
$Au_{55}(P(C_6H_4CH_3)_3)_{12}Cl_6$

D. A. van Leeuwen, Physics and Chemistry of Metal Cluster Compunds, L. J. de Jongh ed., KLUWER, 1999.

Relationship between structure and ^{197}Au Mössbauer spectra

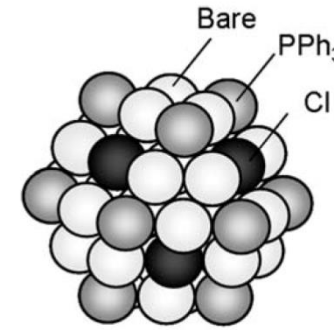


$[Au_9(PPh_3)_8](NO_3)_3$

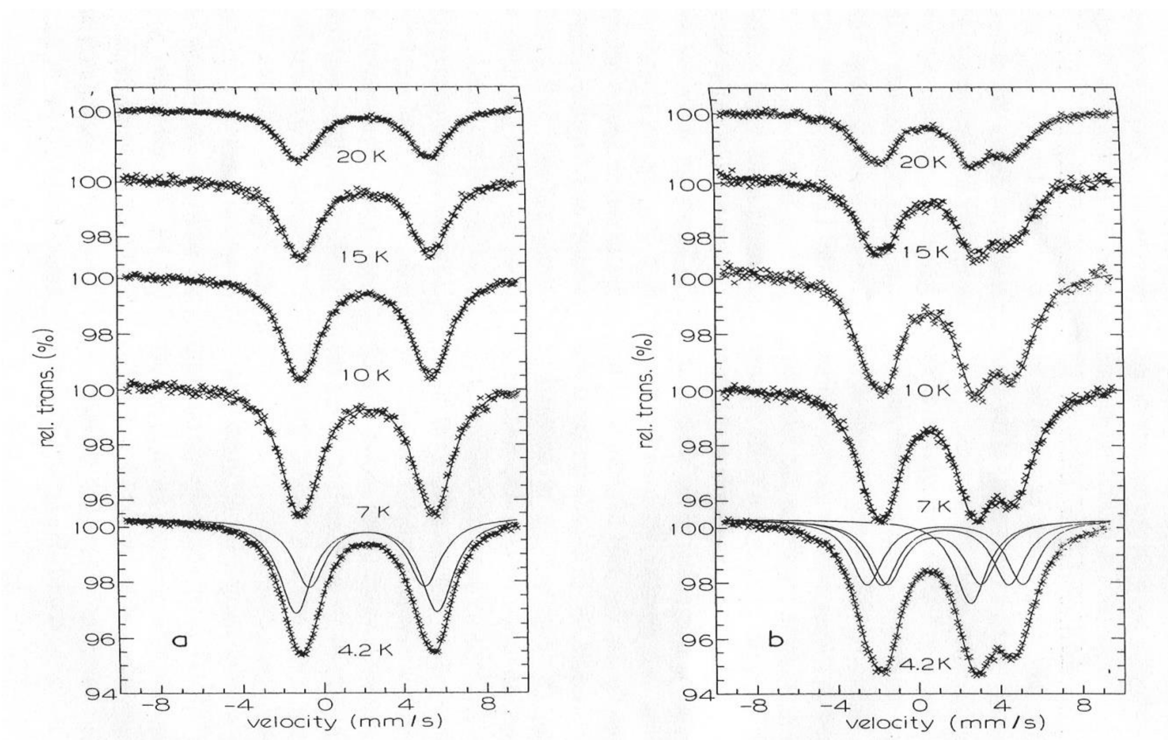


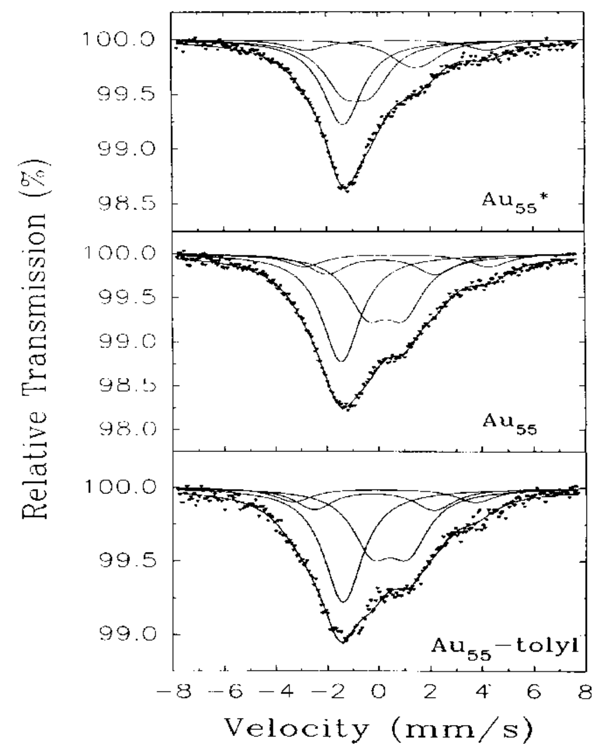
$Au_{11}(PPh_3)_7(SCN)_3$

← **Missing link** →



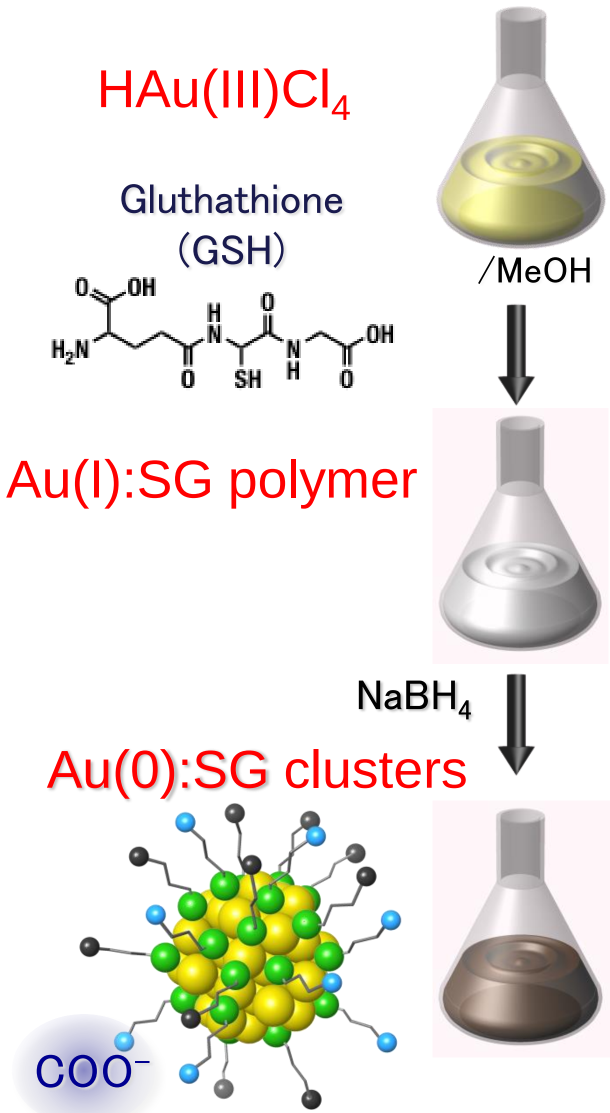
$Au_{\mathbf{55}}(PPh)_{\mathbf{12}}Cl_{\mathbf{6}}$





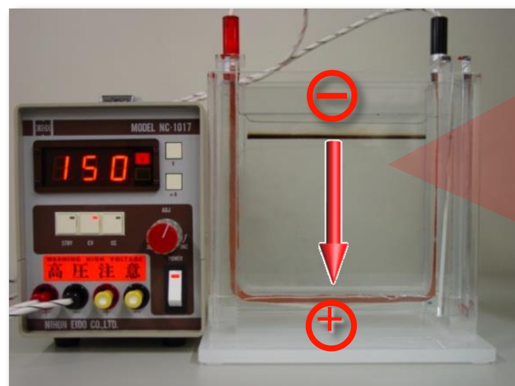
H.H.A. Smit, et al *Physica B* 153, 33 (1988), F. M. Mulder, et al., Nanostructured Materials, 7, 269 (1996).

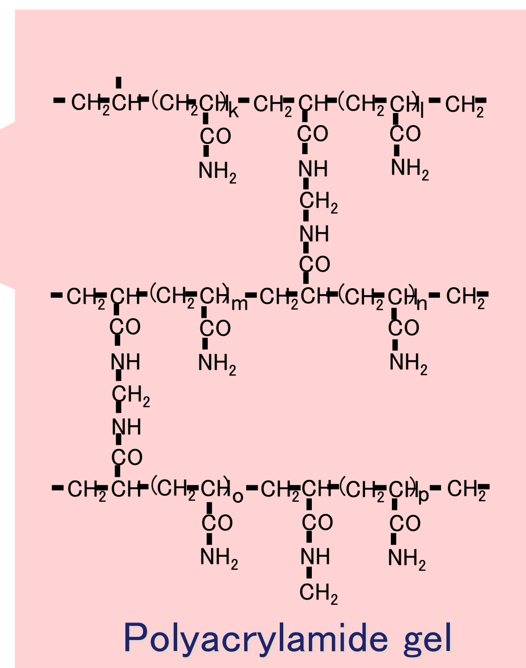
Isolation of Glutathione-Protected Gold Clusters, $Au_n(SG)_m$



Y. Negishi, T. Tsukuda, et al., *J. Am. Chem. Soc.*, **126**, 6518 (2004)..

Y, Negishi, T. Tsukuda, et al., *J. Am. Chem. Soc.*, **127**, 5261 (2005).

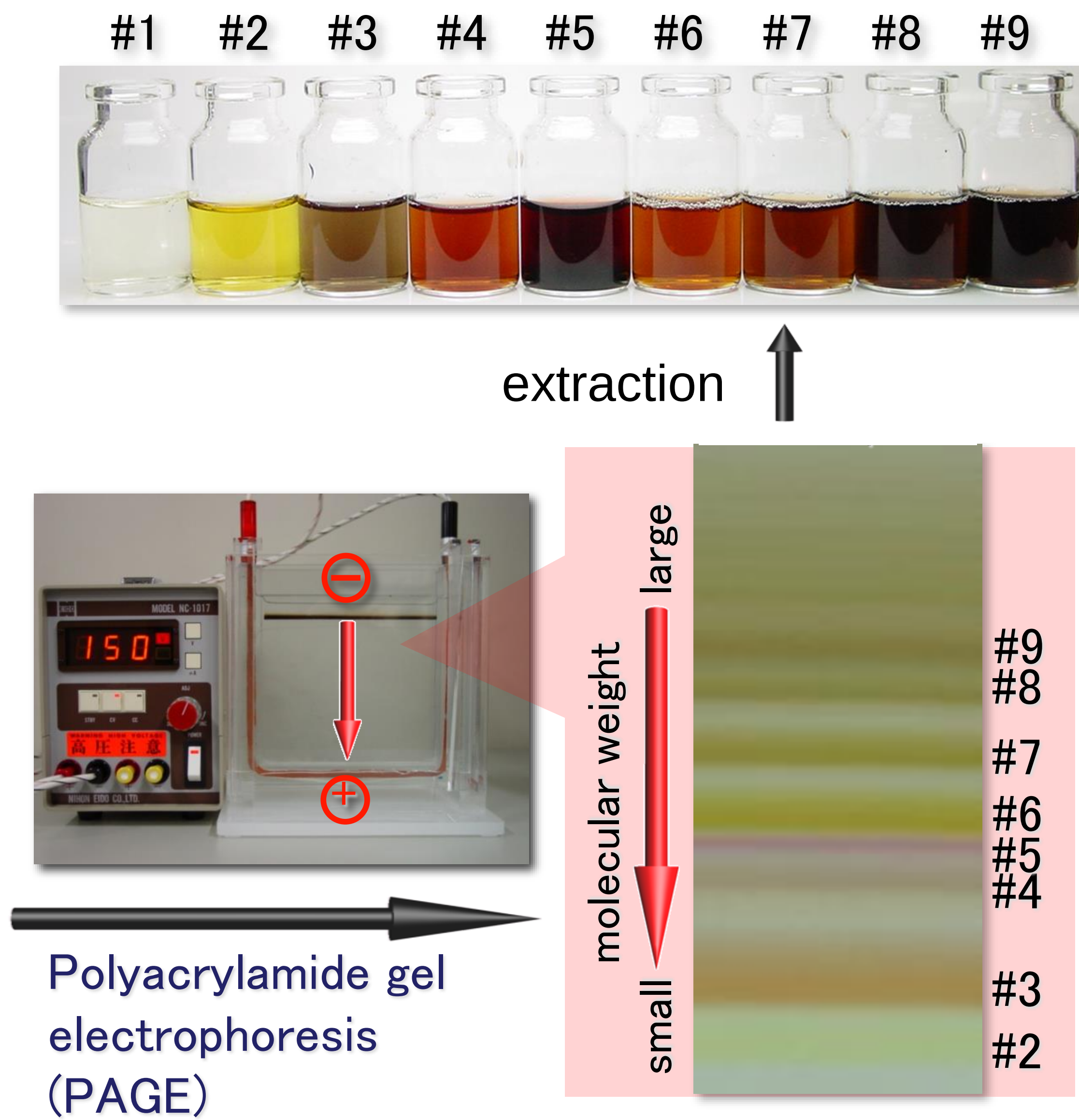




Polyacrylamide gel electrophoresis (PAGE)

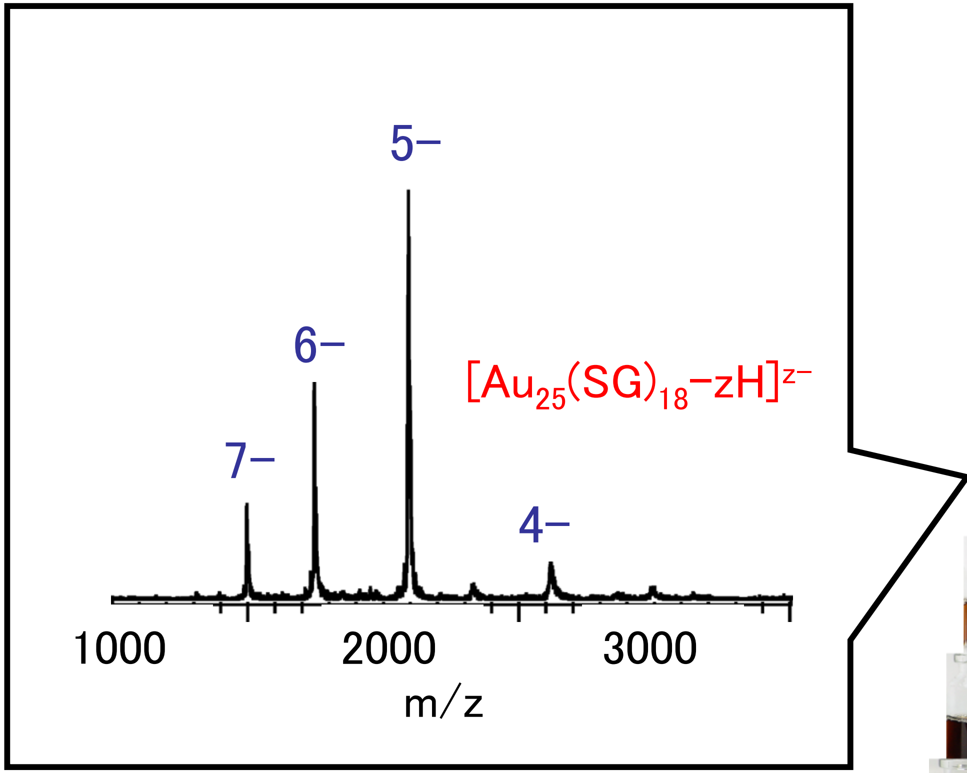
Isolation of Glutathione-Protected Gold Clusters, $Au_n(SG)_m$

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

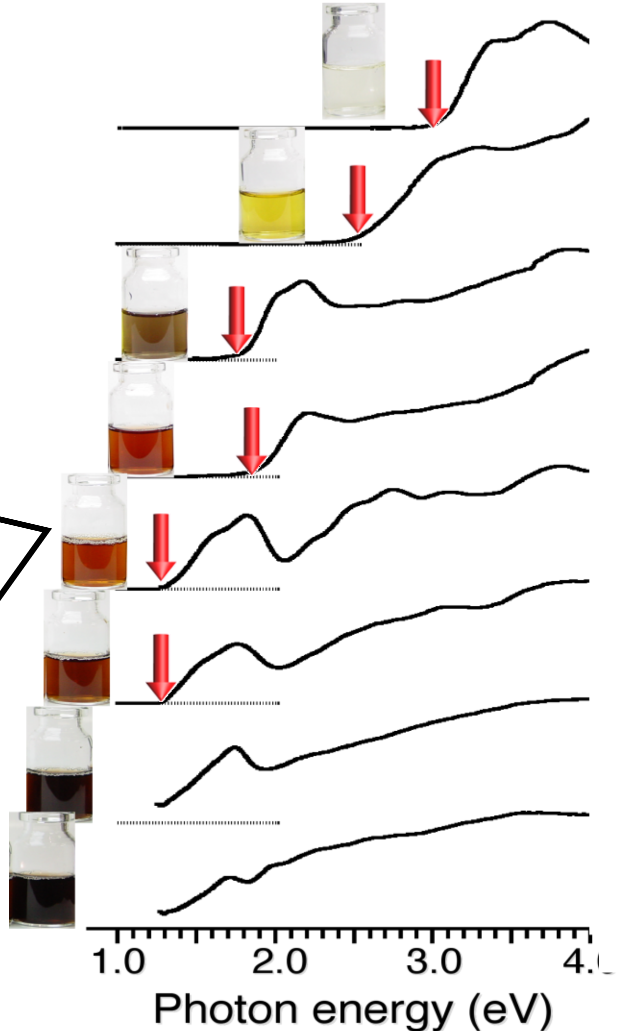


Systematic Isolation of Glutathione-Protected Gold clusters

ESI mass spectrum



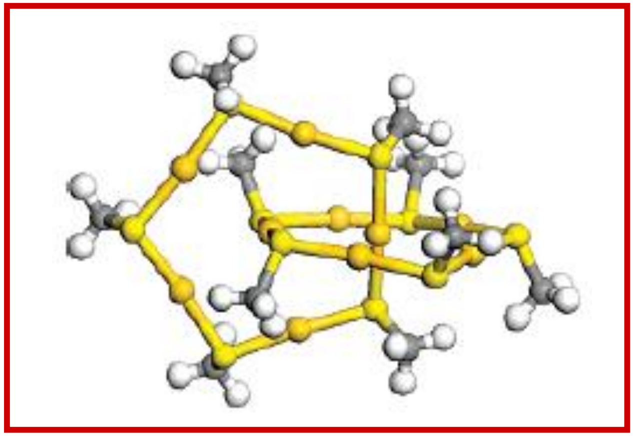
UV-vis absorption spectra



Singly-sized cluster is included

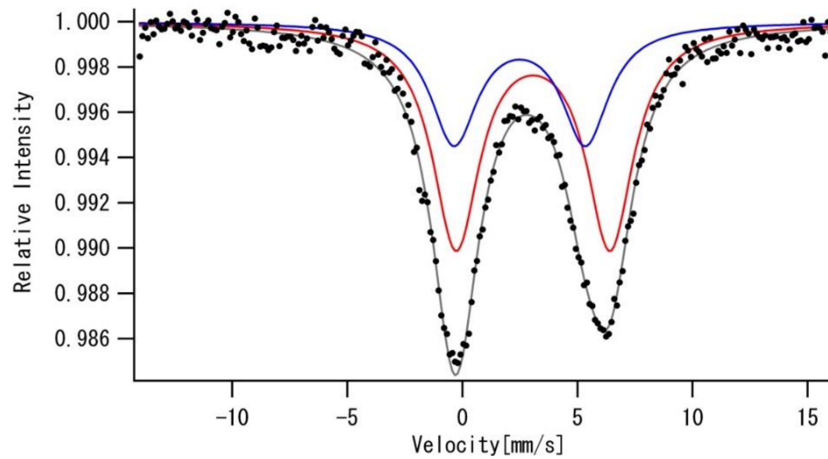
Y. Negishi, T. Tsukuda, et al., *J. Am. Chem. Soc.*, **126**, 6518 (2004)..
Y, Negishi, T. Tsukuda, et al., *J. Am. Chem. Soc.*, **127**, 5261 (2005).

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

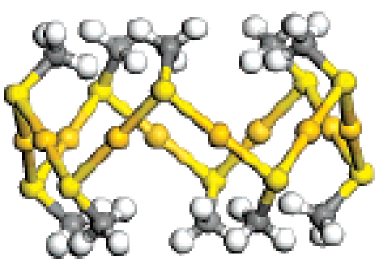


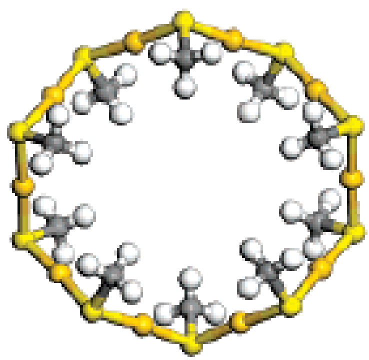
Two doublets of ^{197}Au Mössbauer spectra for $Au_{10}(SG)_{10}$ suggests the catenane structure.

Two kinds of Au-S bond length



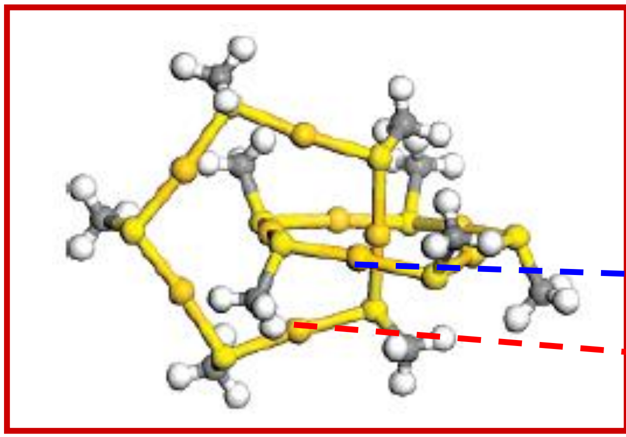
K. Ikeda, Y. Kobayashi, Y. Negishi, M. Seto, T. Tsukuda, N. Kojima, et al., *J. Am. Chem. Soc.*, **129**, 7230 (2007).



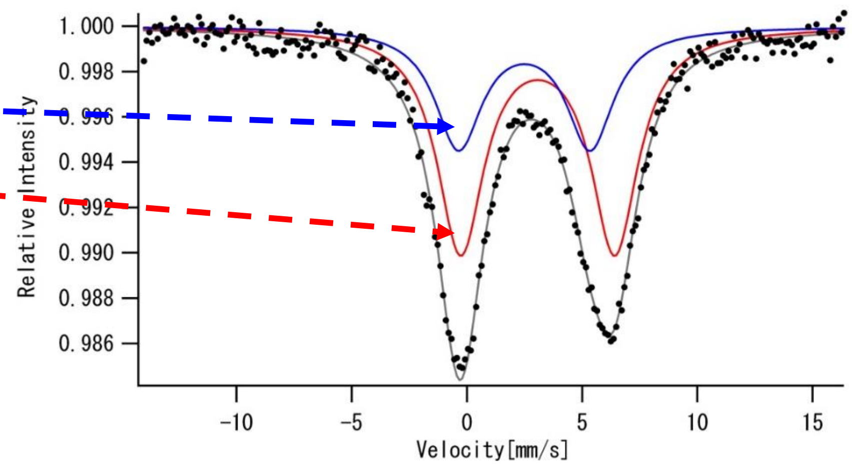


H. Gronbeck, M. Walter, and H. Häkkinen, "Theoretical characterization of cyclic thiolated gold clusters", *J. Am. Chem. Soc.*, **128**, 10268 (2012).

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

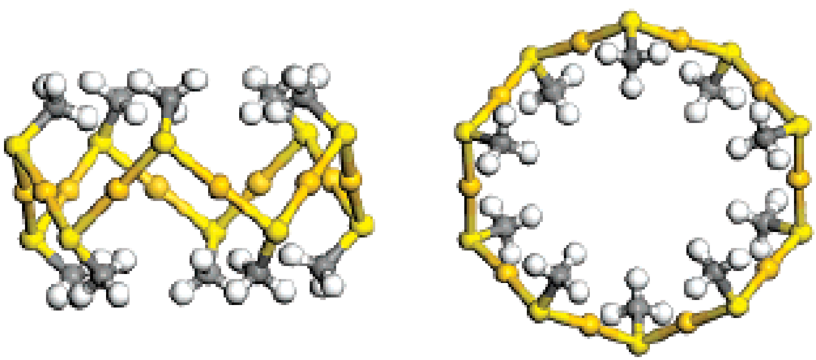


Two kinds of Au-S bond length



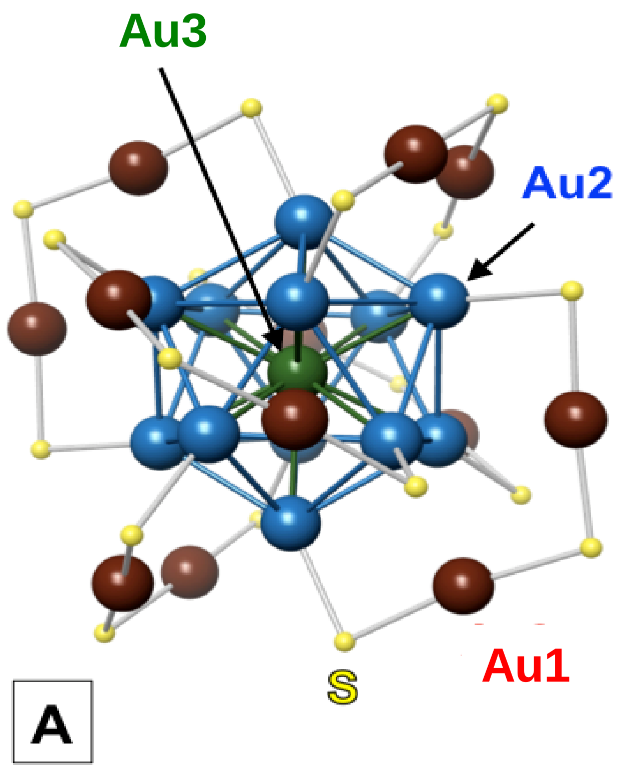
Two doublets of ^{197}Au Mössbauer spectra for $Au_{10}(SG)_{10}$ suggests the catenane structure.

K. Ikeda, Y. Kobayashi, Y. Negishi, M. Seto, T. Tsukuda, N. Kojima, et al., *J. Am. Chem. Soc.*, **129**, 7230 (2007).

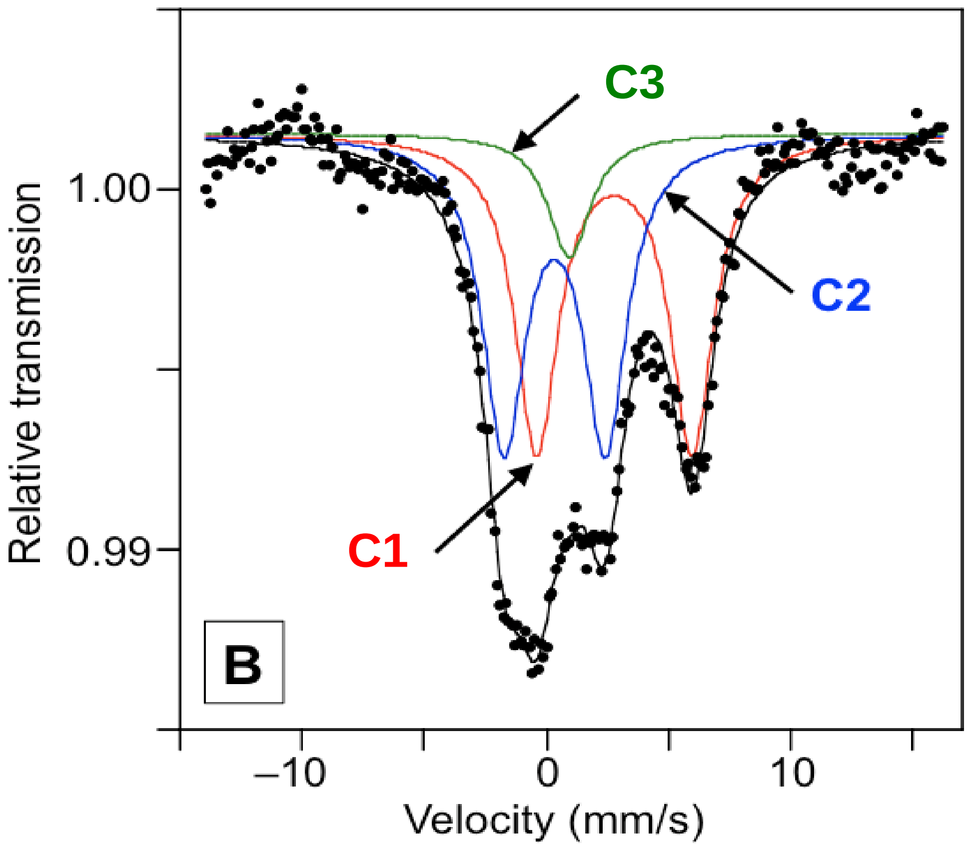


H. Gronbeck, M. Walter, and H. Häkkinen, "Theoretical characterization of cyclic thiolated gold clusters", *J. Am. Chem. Soc.*, **128**, 10268 (2012).

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



Structure of $Au_{25}(SC_2H_4Ph)_{18}$



T. Tsukuda, Y, Kobayashi, Y. Negishi, N. Kojima, *Chem. Lett*., **40**, 1292 (2011).

M. W. Heaven, et al., *J. Am. Chem. Soc*., **130**, 3754 (2008).

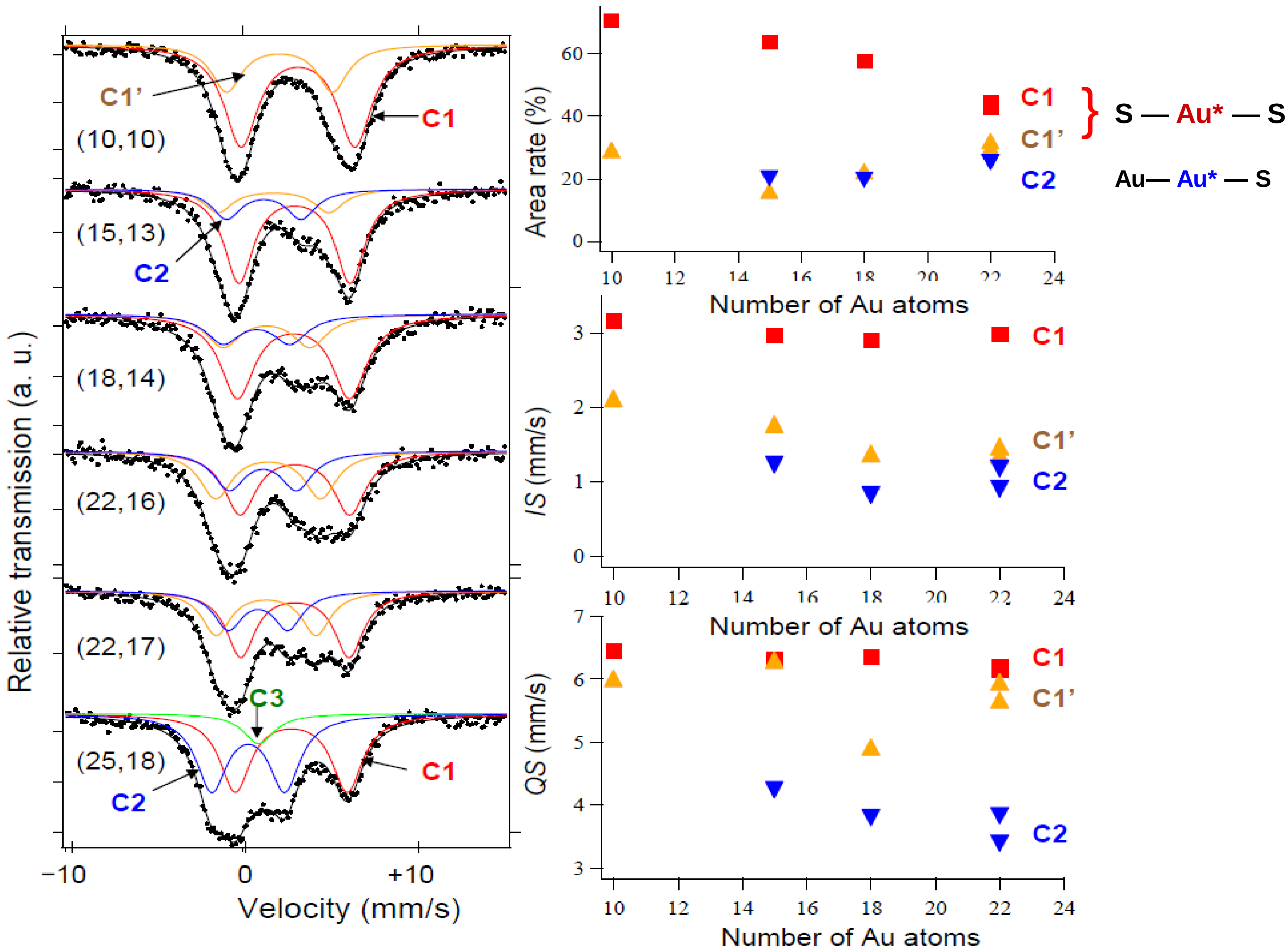
M. Zhu, E, Lanni, et al., *J. Am. Chem. Soc*., **130**, 1138 (2008).

J. Akola, H. Häkkinen, et al., *J. Am. Chem. Soc*., **130**, 3756 (2008).

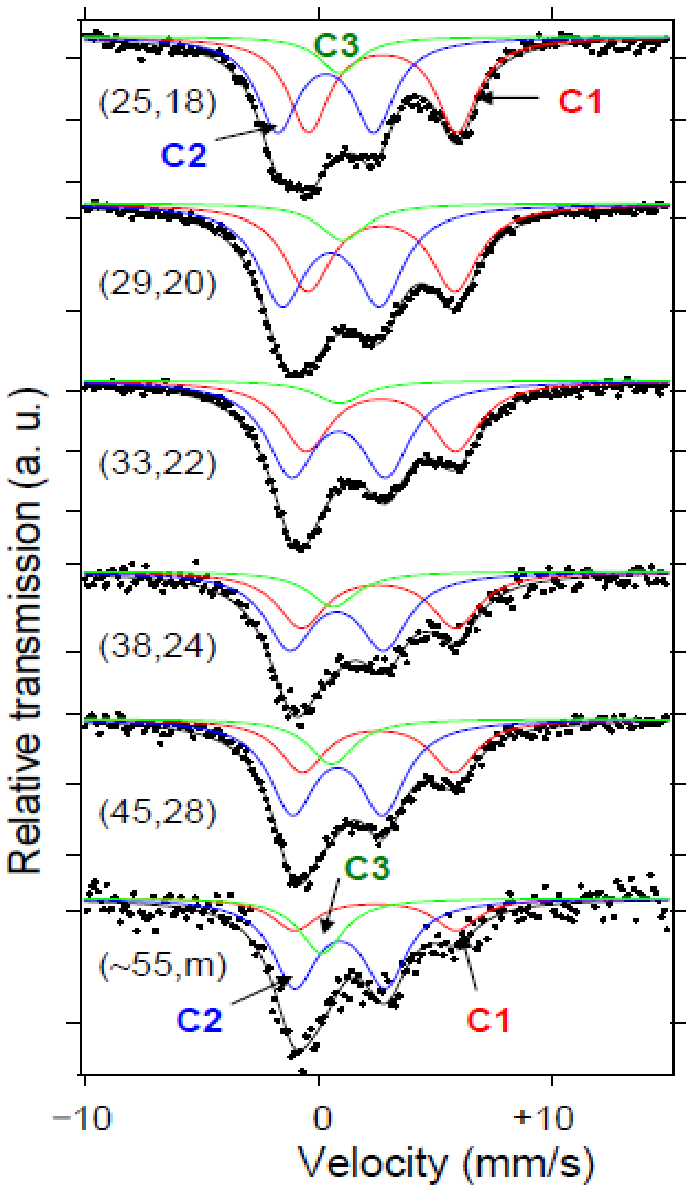
Relative recoil-free fraction

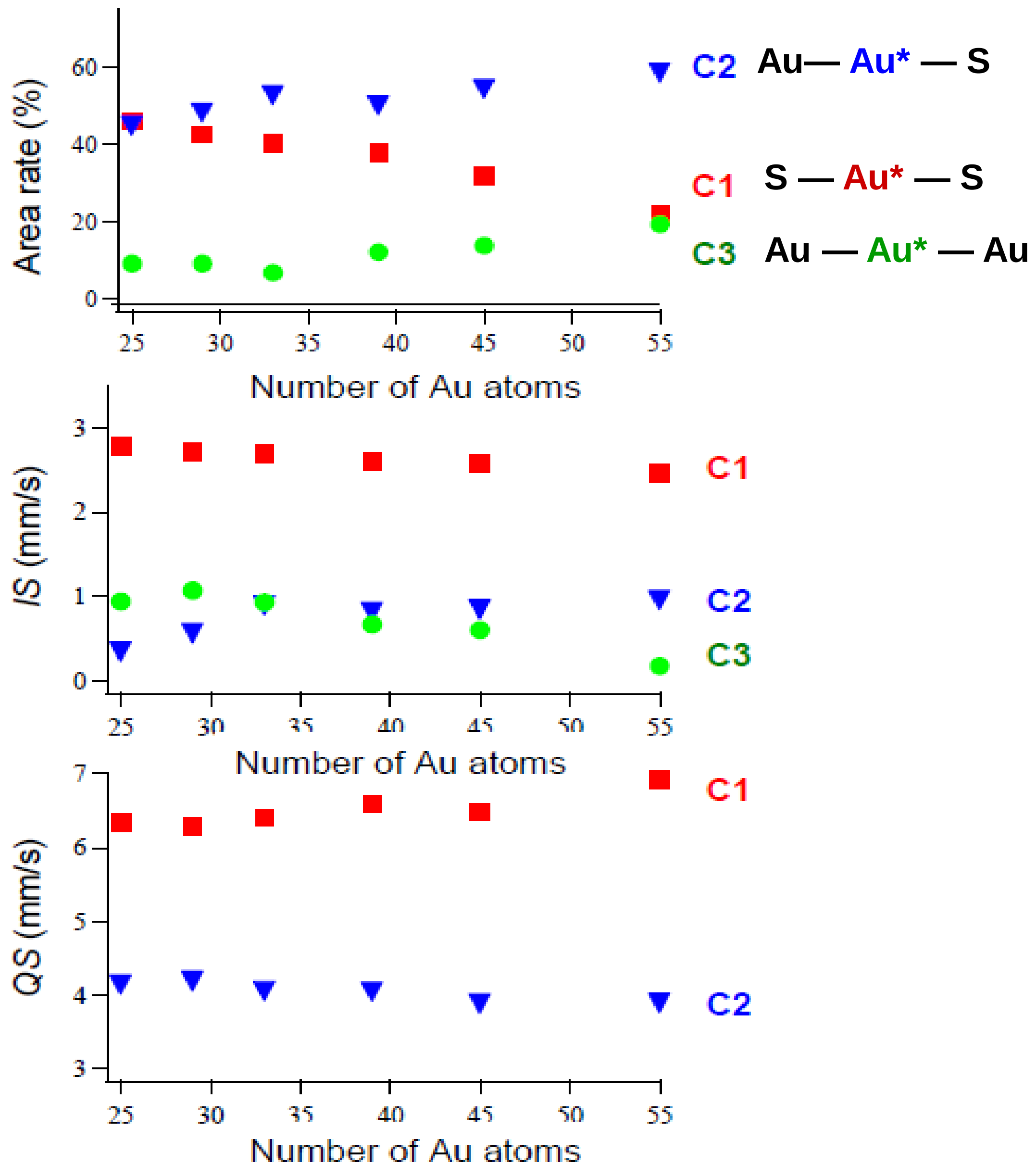
f(Au1): *f*(Au2): *f*(Au3) = 1.03 : 1.00 : 2.44

^{197}Au Mössbauer spectra of $Au_n(SG)_m$ (n = 10 – 25)

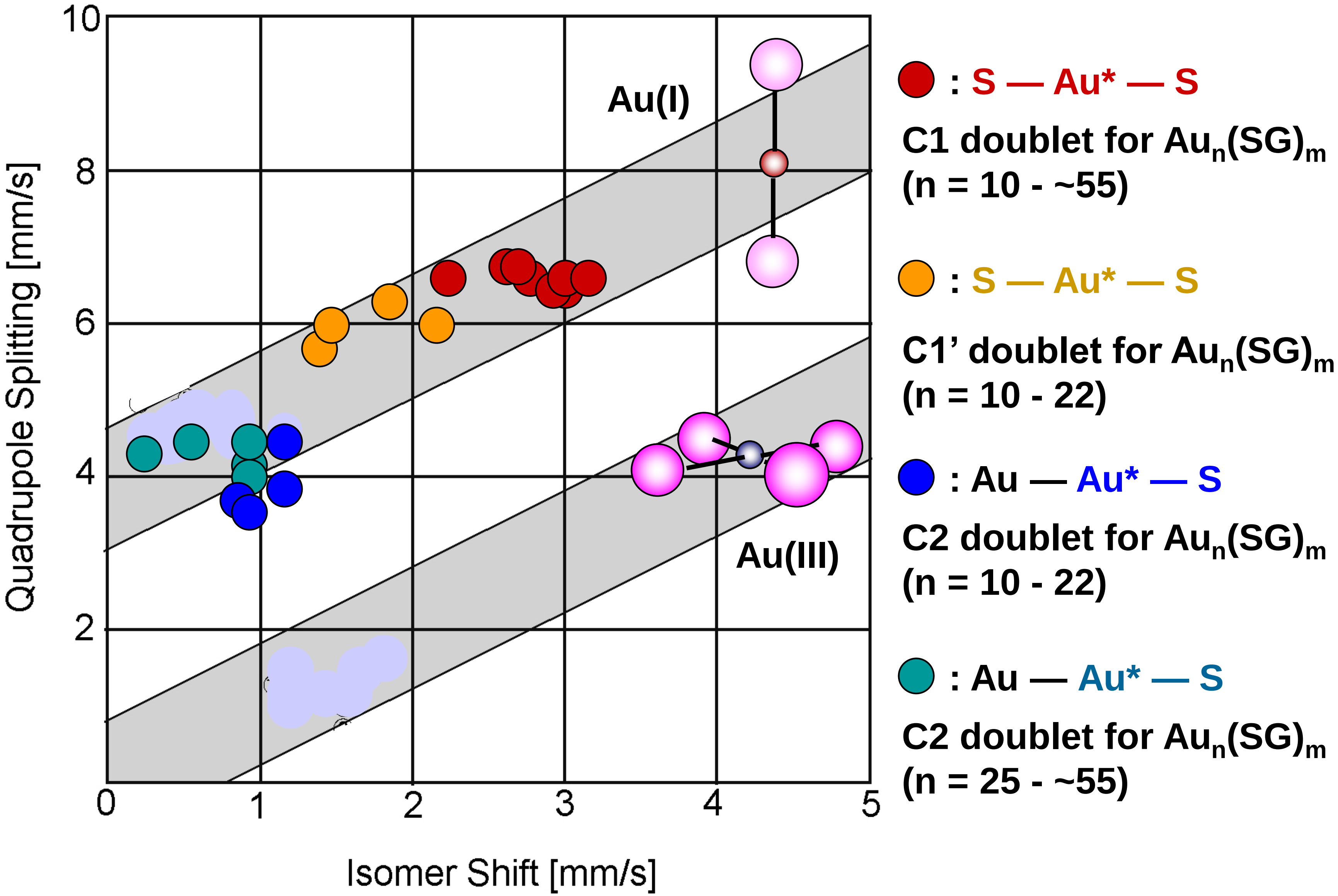


^{197}Au Mössbauer spectra of $Au_n(SG)_m$ (n = 25 – ~55)





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



Number of Au atoms in the three sites for $Au_n(SG)_m$

Recoil-free fraction of Au in $Au_{25}(SG)_{18}$ *f*(Au1): *f*(Au2): *f*(Au3) = 1.03 : 1.00 : 2.44

$Au_n(SG)_m$	**Number of Au1 site** (-S-Au*-S-)	**Number of Au2 site** (Au-Au*-S-)	**Number of Au3 site** (Au-Au*-Au)
(10, 10)	**10**	**0**	**0**
(15, 13)	12	3	0
(18, 14)	14	4	0
(22, 16)	17	5	0
(22, 17)	17	5	0
(25, 18)	**12**	**12**	**1**
(29, 20)	13	15	1
(33, 22)	14	18	1
(38, 24)	**15**	**21**	**2**
(45, 28)	15	27	3
(~55, m)	~13	~37	~5

N. Kojima, Y. Kobayashi, Y. Negishi, M. Seto, T. Tsukuda, *Hyperfine Interactions*, 217, 91-98 (2013).

Face-fused bi-icosahedral Au_{23} core

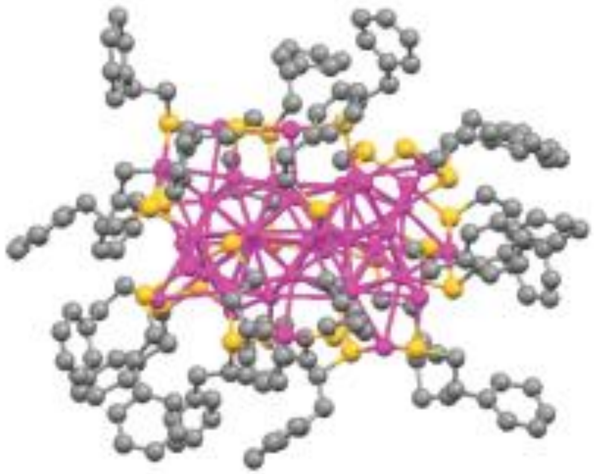


Figure 1. Total structure of $Au_{38}(SC_2H_4Ph)_{18}$ (L-isomer, color labels: magenta, Au; yellow, S; gray: C, H atoms are omitted).

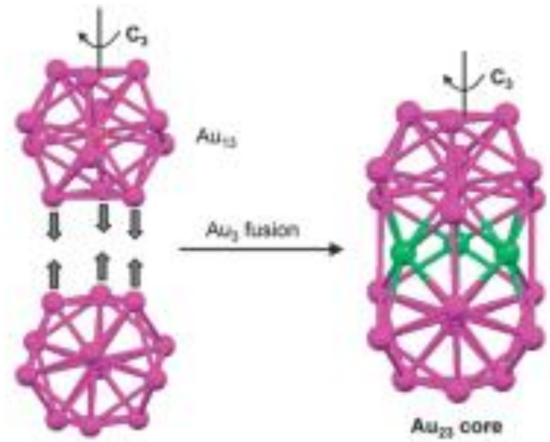
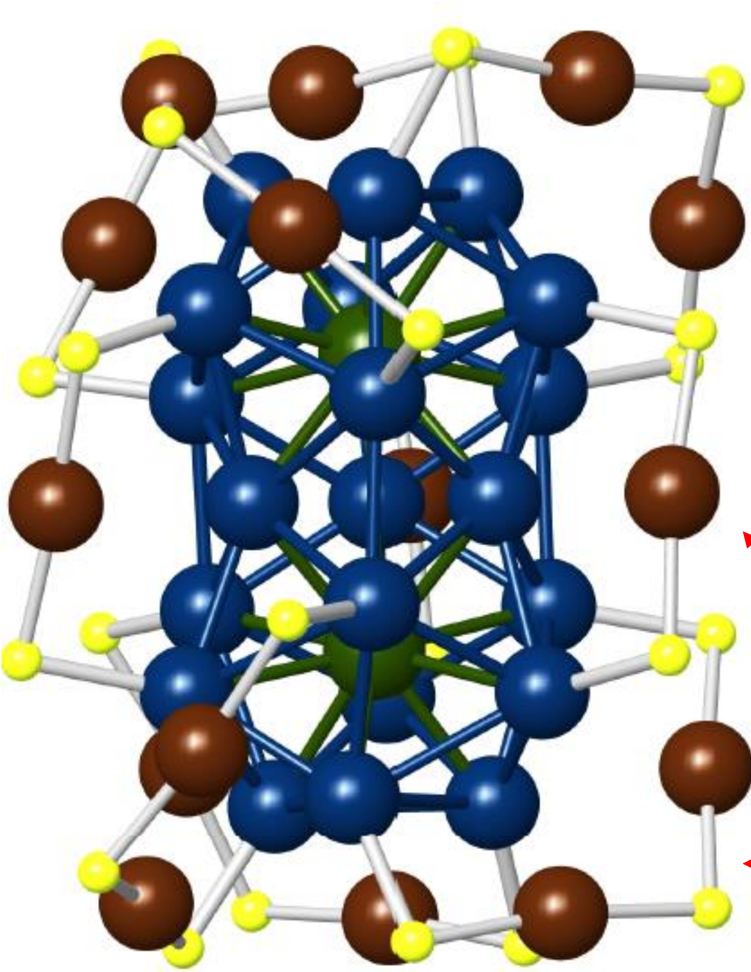


Figure 2. Anatomy of the Au_{23} core structure of $Au_{38}(SC_2H_4Ph)_{24}$.

Face-fused bi-icosahedral Au_{23} core with 9 staples for $Au_{38}(SC_2H_4Ph)_{24}$:
H. Qian, et al., *J. Am. Chem. Soc*., **132**, 8280 (2010).

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



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

Au1: 15   Au2: 21   Au3: 2

3 monomeric staple (-S(G)-Au-S(G)-)

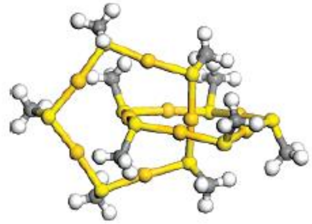
n(Au1) = 3 **X** 1 = 3, *m*(SG): 3 **X** 2 = 6

6 dimeric staple (-S(G)-[Au-S(G)-]$_2$)

n(Au1) = 6 **X** 2 = 12, *m*(SG): 6 **x** 3 = 18

Structure of $Au_n(SG)_m$ by the analysis of Mössbauer spectra

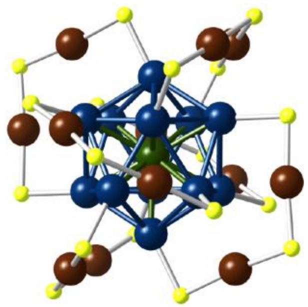
$Au_{10}(SG)_{10}$



Catenane structure with two interlocked pentamers

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

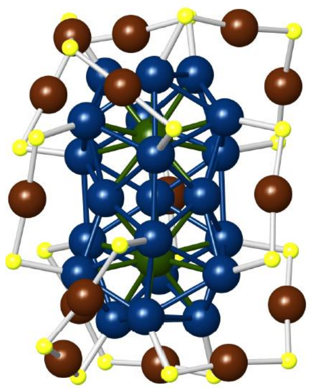
$Au_{25}(SG)_{18}$



Icosahedral Au_{13} core whose surface is protected by 6 dimeric staples (-S(G)-[Au-S(G)-]$_2$)

25 < n < 38 : Extended icosahedral Au_{13} core protected by staples

$Au_{38}(SG)_{24}$



Face-fused bi-icosahedral Au_{23} core whose surface is protected by 3 monomeric staples (-S(G)-Au-S(G)-) and 6 dimeric staples (-S(G)-[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 – ~55) 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).

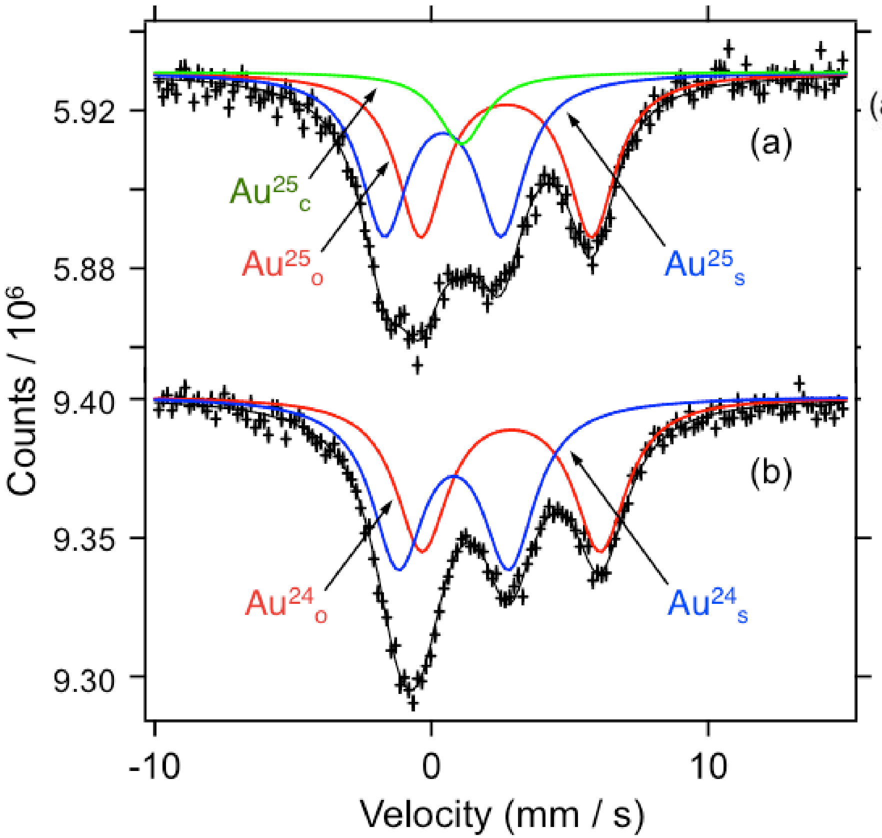
3) $Au_{25}(SG)_{18}$ – ~$Au_{55}(SG)_m$: S-Au-S bond (C1), Au-S bond (C2), and Au core atom free from SG (C3). The Au core atom appears at $Au_{25}(SG)_{18}$ for the first time on going from $Au_{15}(SG)_{13}$ to $Au_{25}(SG)_{18}$, then the line profile continuously changes from $Au_{25}(SG)_{18}$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

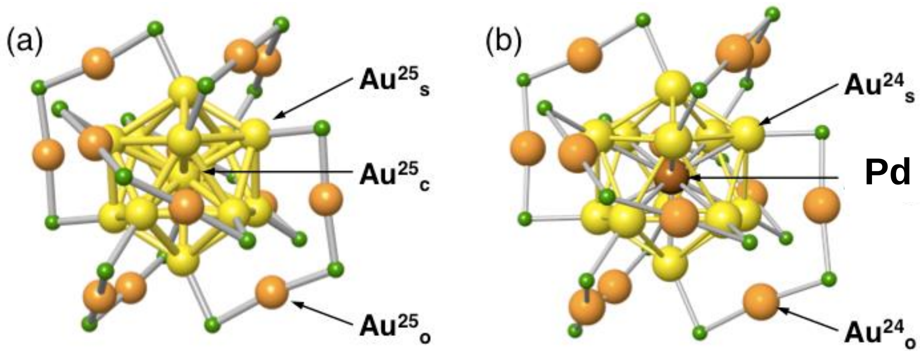
4) The valence state of Au atom coordinated by two S atoms or one S atom is Au(I).

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) $Au_{25}(SC_{12}H_{25})_{18}$

(b) $Au_{24}Pd\ (SC_{12}H_{25})_{18}$

Y. Negishi, Y. Kobayashi, N. Kojima, M. Seto, T. Tsukuda, *J. Phys. Chem. Lett*. (2013) in press.

Synthesis of Dodecanethiol-Protected Gold Clusters, $Au_n(SR)_m$

$$H[Au^{III}Cl_4] \xrightarrow{(n\text{-}C_8H_{17})_4N^+Br^-} (n\text{-}C_8H_{17})_4N^+[AuCl_4]^- \xrightarrow[NaBH_4]{C_{12}H_{25}SH} Au_n(SR)_m$$

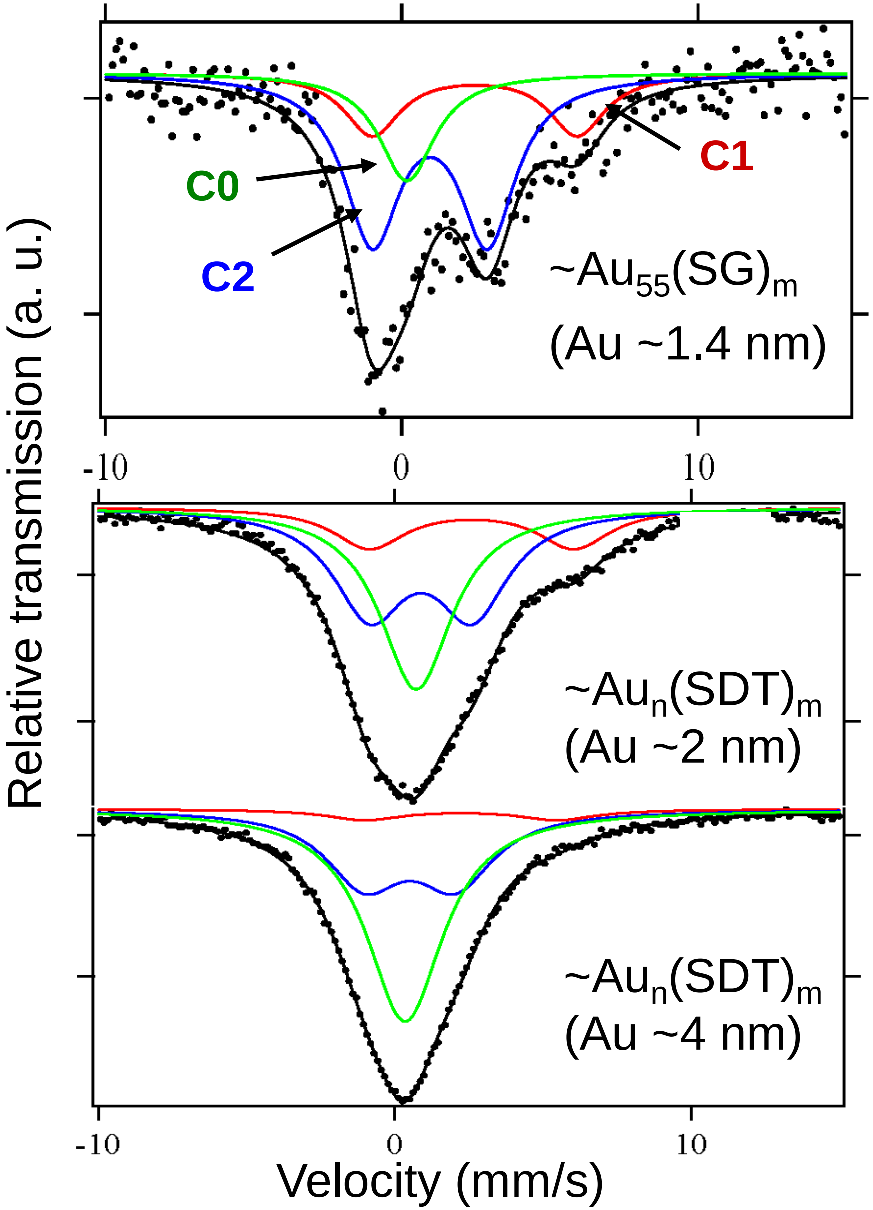
$(R = C_{12}H_{25})$

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.

N. Nagao, G. Harada, T. Sugawara, et al., *Jpn. J. Appl. Phys*., **43**, 7742 (2004).

^{197}Au Mössbauer spectra between ~$Au_{55}(SG)_m$ 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 %