

Chapter 2

Liganded Silver and Gold Quantum Clusters: Background of Their Structural, Electronic, and Optical Properties

2.1 Introduction

The purpose of this chapter is first to introduce physical background allowing one to gain understanding about the connection between electronic energy quantization in metal nanoclusters and their optical properties. The optical response, in terms of electronic transitions whose positions and intensities are predicted by sophisticated quantum mechanical calculations, will be described. The concept of ligand-protected metal clusters will be introduced, and we then will summarize briefly the synthetic work on liganded quantum clusters of gold and silver and their characterization. Finally, we will discuss the link between their structural, electronic, and optical properties.

2.2 Basics: From Free Electron Model to Electronic Energy Quantization in Metal Nanoclusters

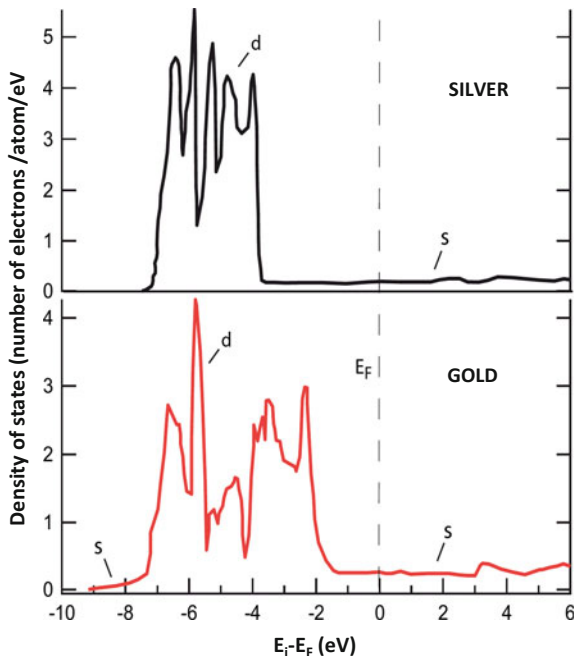
Along the atomic to bulk scale of noble metal systems, different properties and material behavior can be found. According to the number of metal atoms, classification into three size domains, corresponding to three different characteristic length scales, can be made: large nanoparticles, small nanoparticles, and clusters (or nanoclusters). The wavelength of light is the first characteristic length scale encountered for these three size domains. For large metal nanoparticles (where their size is in the range of the wavelength of light), the optical properties can be quantitatively described with Mie theory for small metal spheres [1]. Applying Maxwell's equations with appropriate boundary conditions in spherical coordinates, optical absorption, light scattering, and extinction of a metal sphere depend on its volume

and bulk dielectric functions. When particle size approaches the second characteristic length (where their size is much smaller than the wavelength of light), electron mean free path (the average distance an electron travels between two adjacent collisions), is ~ 50 nm for gold and silver. The dielectric function, and refractive indices become size dependent. As a result, the optical responses such as plasmon absorptions of medium size metal nanoparticles have different size dependences compared with large nanoparticles. Mie theory still can be extended into this quasi-static regime. In the third characteristic length, optical, electronic, and chemical properties of metal clusters are dramatically different from the other two size regimes. In this smallest size regime, metal clusters become “molecular-like species,” and discrete states with strong fluorescence can be observed. Recent progress in theory, in particular time-dependent density functional theory (TDDFT), allows for investigation of optical properties to be extended to more than 100 atoms for the simplest noble metal systems. This is size regime of small metal clusters with molecular-like properties that is the primary topic of this book.

Optical response of metal nanoparticles is strongly dependent on dielectric function of metal and the embedded medium. Metal band structure is only weakly size dependent. Bulk metals have continuous band structures, and the conduction bands are occupied with free electrons.

In Fig. 2.1, the densities of states calculated for the silver and gold noble metals are compared [2, 3]. The d-type contributions dominate in contrast to the densities

Fig. 2.1 Density of states (DOS) calculated for the noble metals Ag and Au. (Reproduced with permission from Refs. [2, 3]. Copyright 1972 John Wiley and Sons)



of states related to s-type electrons with lower intensities and smooth behavior which are located at left and right sides of the d-states. However, in the case of gold, the electronic states of d-character are around 2 eV below the Fermi level (E_F), while in the case of silver they are located approximately 4 eV below E_F . In addition, it is noteworthy that the band in gold is substantially broader than for silver and appears divided into two regions. Indeed, the relativistic effects such as spin–orbit coupling are particularly important in the case of gold, and separation of angular momentum $j = 3/2$ and $j = 5/2$ is visible in the density of states [3]. Such band structure is also observed for metal nanoparticles larger than 2 nm, in which the density of states is large enough and energy level spacing between adjacent quantum states is much smaller than thermal energy. Thus, these delocalized free electrons coherently oscillate and give rise to the well-known surface plasmon absorption. Differences in size-dependent optical response are mainly due to the change caption of Fig. 2.2 Fe.

In order to understand the fundamental properties of metal nanoparticles, the free-electron theory represents a model which provides intuitive insight into the electronic properties of metal nanoparticles, in spite of severe approximations such as neglect of electron–electron or electron–ion lattice interactions (both aspects are indeed fundamentally important). Nevertheless, the free electron model is suitable for the first-order approximation, and therefore we use this simple model to acquire some quantitative estimation of electronic energy quantization in noble metal nanoclusters.

The free electron model is neglecting the interactions between electrons. This approach of the electron gas without interaction allows the dispersion relation between energy/wave vector of electrons to be introduced and the concept of Fermi sphere. To determine the spectrum of permitted values of the electronic wave vector, one has to consider a three-dimensional cubical box that has a side length a . The surfaces of constant energy are spheres with radius $k = \sqrt{2mE}/\hbar$. System with N electrons is occupied according to the Pauli principle at $T = 0$, and all states within the “Fermi sphere” with radius k_F and volume $\frac{4}{3\pi k_F^3}$ are occupied. This defines the Fermi surface with the Fermi energy $E_F = \frac{\hbar^2 k_F^2}{2m}$ and the Fermi wave vector k_F . The Fermi energy is approximately 5.5 eV for gold and silver.

For small systems, the number of atoms is finite; thus, the spacing δ becomes noticeable and increases with decreasing cluster size. If we use the thermal energy ($k_B T$) at room temperature as a criterion, using $\delta = \frac{4\pi^2}{a^3} \left(\frac{\hbar^2}{2m} \right)^{\frac{3}{2}} E^{-\frac{1}{2}}$, we can estimate at what size electronic energy quantization will be comparable with thermal energy, that is, $\delta = k_B T$. By substituting all the constants (SI units) and the highest occupied energy level of gold (i.e., the Fermi level, $E_F \sim 5.5$ eV), the corresponding particle volume (a^3) is $\sim 5 \times 10^{-27} \text{ m}^3$ (thus an equivalent particle size ~ 1.7 nm). The number of valence electrons in the system is estimated to be about 280 [4]. Thus, one would expect electronic energy quantization to occur when the number of 6s valence electrons in a cluster drops to about 200–300.

2.3 Metal Optical Responses at Different Size Scales

The optical response of free-electron metals in the bulk state is well described by Drude-Lorentz-Sommerfeld/free electron model [5]. Based on this model, the macroscopic optical response of metals follows by summing the single electron response over the total number of the free electrons. Thus, according to this model, all the free electrons in a metal react in phase with the electrical field. In reality, due to the large electron density and delocalization, all the free electrons indeed coherently oscillate under a time-dependent electrical field, which gives the well-known bulk plasmon absorption.

Fig. 2.2 Optically allowed transitions T_e in eV and oscillator strengths f_e obtained from EOM-CCSD and STEOM-CCSD calculations using 11e-RECP with associated AO basis for the lowest energy structures of Ag_{5-8} . Most stable structure of Ag_9 cluster obtained from the RPA method. The *lines* have been broadened using Lorentzian function with the width of 0.15 eV. (Reproduced with permission from Ref. [6]. Copyright 2001 AIP Publishing)

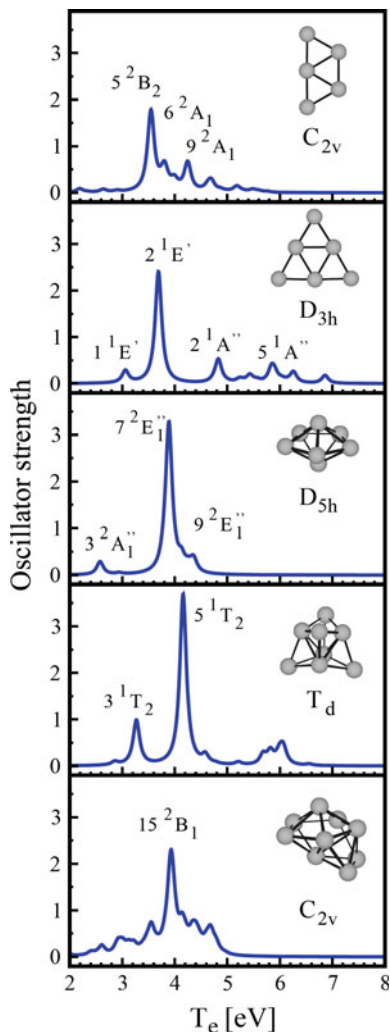
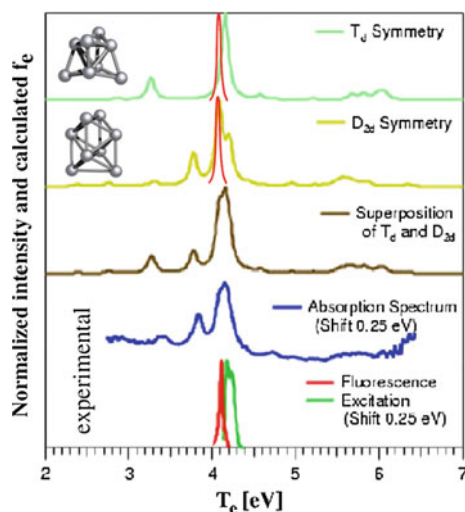


Fig. 2.3 Calculated absorption spectra and the position of the fluorescence for different isomers for Ag_8 with the measured excitation spectra shifted by 0.25 eV to account for the matrix shift. (Reproduced with permission from Ref. [7]. Copyright 2005 Springer)



In general, when the particle size decreases, the dielectric function begins to strongly depend on R . For small clusters of less than 10 nm size, Mie-Drude model is no longer appropriate to discuss absorption spectra. The geometry of the clusters must be determined by quantum chemical methods that often use group theory, and the optical response is described in terms of electronic transitions whose positions and intensities are predicted by sophisticated quantum mechanical calculations. As an illustration, the absorption spectra obtained with the ab initio EOM-CCSD and STEOM-CCSD methods accounting for electron calculation for the most stable structures of Ag_{5-8} are given in Fig. 2.2 [6]. This pioneering work is a nice illustration of the molecular-like behavior of nanoclusters leading to an electronic energy quantization and the changes in the leading features of the patterns as a function of the cluster size and corresponding structure.

Comparison of the theoretically obtained absorption spectra for different isomers of Ag_8 cluster using less accurate method such as random phase approximation (RPA) with experimental measurements in argon matrix allowed assignment of the isomeric structures to the measured features as shown in Fig. 2.3 [7]. This is encouraging for use of TDDFT approach for calculation of absorption properties of quantum-ligated clusters.

2.4 Time-Dependent Density Functional Theory (TDDFT)

Recent progress in computation methods, in particular within TDDFT approach, allows the investigation of optical properties of simplest noble metal systems to be extended to more than 100 atoms. TDDFT can be viewed as an exact reformulation of time-dependent quantum mechanics, where the fundamental variable is no longer

the many-body wave function but the density. This time-dependent density is determined by solving an auxiliary set of the Kohn-Sham equations. The important part of the many-body interaction is included in the so-called exchange-correlation potential, for which adequate approximations have been developed. If the external time-dependent potential is “small,” complete numerical solution of the time-dependent Kohn-Sham equations can be replaced by the linear response theory allowing to calculate photoabsorption spectra of relatively large systems.

In spite of the well-known approximations for electronic correlations within TDDFT and inclusion of only single excitations as well as the influence of the choice of the functionals on the accuracy, theoretical results for absorption spectra are in acceptable agreement with the available experimental findings, as shown in Ref. [8] on examples of ligated silver quantum clusters.

2.5 Optical Response from Noble Metal Clusters

2.5.1 *Absorption and Emission of Bare Gold Clusters*

In 1987, Markus and Schwentner first observed that gold dimers in rare gas matrices yield 450, 545, and 580 nm emission [9]. Harbich et al. also used a similar method to prepare Au_2 and Au_3 embedded in argon matrices and studied their optical response at low temperature [10, 11]. Absorptions centered on 235, 263, 285, 310, and ~ 345 nm are clearly distinguishable, and two emission regions centered on ~ 453 and 510 nm were observed from Au_3 [10]. Collings et al. also investigated the gas phase absorption spectra of gold clusters Au_n ($n = 7, 9, 11, 13$) and their cations using photodepletion spectroscopy [12]. Sharp lines between 1.9 and 5.6 eV in absorption bands were observed.

2.5.2 *Absorption and Emission of Bare Silver Clusters*

Kreibig studied the evolution of optical absorption of silver along the size scale from atoms over clusters to bulk. Discrete electronic transitions instead of a collective plasmon were observed for very small Ag_n clusters at low temperature, while the common metal properties were present in the case of silver systems embedded in glass which contain more than about 400 atoms [13]. In 1978, Ozin and Huber used cryo-photoclustering technique to prepare small silver clusters Ag_n (where $n = 2-5$) within Ar matrices at 10–20 K. Discrete absorption bands between 3.1 and 4.1 eV were observed from few atom silver clusters at low temperature. Later, using “soft landing” mass spectrometry [14], Harbich and coworkers were able to prepare size-selected silver dimers and trimers in solid Ar matrices, and investigated their absorptions and fluorescence. Ag_3 clearly shows absorptions at

318, 386, and 495 nm and had discrete emissions at 374, 616, and 705 nm. Notice that in the case of size-selected clusters such as Ag_8 and Ag_9 , different isomeric structures close in energy are presented, and their contribution has to be taken into account for interpretation of measured absorption spectra of these species [15]. Complementary to the studies on isolated silver clusters, Chen and coworkers [16] used zeolites to prepare fluorescent silver clusters at room temperature and Dickson and coworkers [17] produced, by photoreducing silver oxide films, fluorescent silver clusters. Solid Kr matrices, zeolites, or silver oxides increase cross section of irradiative decay and prevent dissociation of silver clusters, even though the excitation energies are comparable to the photodissociation energies of naked silver clusters. Indeed, Ag and Ag_2 loss is a general phenomenon for photodissociation of Ag_n clusters. Hild and coworkers [18] found that after excitation by photons with energies $1.5 \sim 4$ eV, silver clusters decay by emission of neutral atoms or dimers with lifetimes in the range 100 μs to 15 ms.

2.6 Role of Ligand Protection. Atomically Precise Clusters of Gold and Silver

The use of solid gas or inorganic matrices permits to protect gold or silver clusters from photodissociation. The large charge separation in excited states is also a possible process in the photophysics of ligated metal clusters composed by few atoms. Organic scaffolds allow the formation and stabilization of metal clusters in solution. The use of organic scaffolds for fluorescent metal nanoclusters is relatively new, first reported by the group of Dickson in 2002 for silver nanoclusters [19]. These organic scaffolds have tremendous potentials, as the interaction between the ligands and metal clusters can be adjusted leading to tunability in their spectroscopic properties. For example, by using DNA oligomers as organic scaffolds and by playing with the nucleotide sequence of DNA oligomers, it is possible to synthesize silver nanoclusters that emit from the blue to near-infrared region [20].

Ligands play very important roles in the formation of NCs as protective agents, which can prevent the metal clusters from aggregation and then keep the size-dependent fluorescence property. The formation and stabilization of gold or silver nanoclusters in solution have been accomplished in various ways (see Fig. 2.4). The proper choice of parameters for the reaction, including the temperature, the reducing method, the stabilizers, and the initial ratio of metal salt to stabilizer, plays a crucial role for the successful synthesis of nanoclusters and to limit the size to few atoms nanoclusters. In addition to the ultrasmall size, the ligands used for NCs preparation also have impacts on their fluorescence properties. Jin and coworkers [21] demonstrated that for gold NCs, the surface ligands of NCs not only can be used as capping agent but also largely affect the fluorescence of NCs through charge transfer from surface ligand to the gold core. If the surface ligands are strong electron donors, the fluorescence can be enhanced. In fact, the

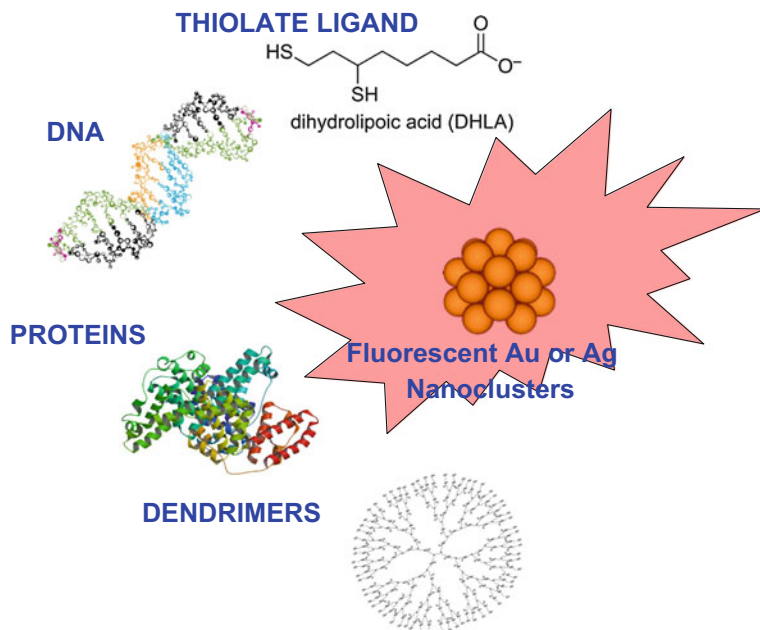


Fig. 2.4 Protected metal nanoclusters with possible scaffolds

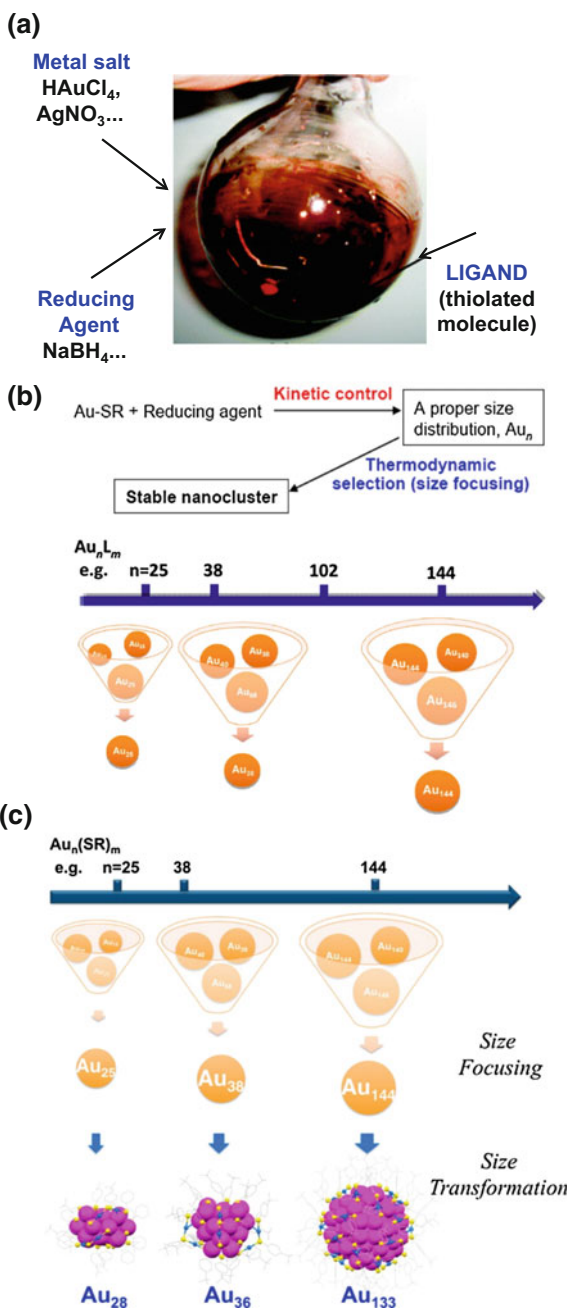
ligands with electron-rich atoms or groups have been found to be an effective choice of surface ligands to enhance the fluorescence of NCs.

2.6.1 Synthetic Routes

The production of silver and gold nanoclusters can be performed following several routes. The metal ions from dissolved metal salts can be reduced, either by a chemical reductant (e.g., sodium borohydride), (see Fig. 2.5a) by light (photoreduction with near-ultraviolet light) or by γ -rays (by radiolysis of water). The chemical reduction and the photoreduction are the most commonly used methods [22]. The specific properties of metal nanoclusters, such as the composition, stability, and fluorescence quantum yield, depend largely on the scaffold used during reduction.

Thiols are frequently used on noble metal substrates because of the strong affinity of sulfur for these metals. Also, thiolated ligands ($-SR$) have appeared to be extremely good candidates to produce ultrasmall nanocluster sizes, in particular for gold [4]. Following the pioneering work of Brust et al. [23] based on the reduction of the metal precursors and the formation of metal core, thiol-containing small molecules were extensively used to stabilize gold nanoclusters in the aqueous

Fig. 2.5 **a** General route to produce thiolate-protected nanoclusters by a chemical reductant. Schematic diagrams of **b** size focusing Methodology and **c** ligand exchange to induce size and structure transformation. Adapted with permission from Ref. [27]. Copyright (2015) American Chemical Society. Adapted with permission from [28]. Copyright (2010) American Chemical Society



solution. The use of thiol-containing small molecules as stabilizers permits to better control of production of AuNCs than phosphine-capped ones, due to the stronger Au-S covalent bonding. Generally, the method of synthesizing thiolate-capped AuNCs has processes as follows: Gold salts $[\text{AuCl}_4]^-$ are dissolved in water and then transferred to an organic solvent by phase transfer agent; the thiols are added to the mixture inducing reduction of Au^{3+} ions into Au^+ ions and form $\text{Au}^+\text{-SR}$ complexes or polymers; then, the Au^+ polymers are reduced by adding the reducing agent and lead to thiolate-protective gold nanoclusters.

Glutathione (GSH), a ubiquitous low-molecular weight thiol, played a significant role in producing gold NCs which showed good water solubility, bioactive surface, and high stability. It has been widely investigated for protecting the Au^{3+} ions when they were being reduced by sodium borohydride (NaBH_4) [24–26]. Whetten and coworkers have proposed an unprecedented thiol-protective AuNC route by using the GSH (N- γ -glutamyl-cysteinyl-glycine) as the stabilizer [26]. Tsukuda and colleagues have also reported the characterization of fractionated AuNCs protected by GSH monolayers. The as-prepared AuNCs were isolated into single-sized $\text{Au}_n(\text{SR})_m$ clusters by the polyacrylamide gel electrophoresis (PAGE) method and characterized using electrospray mass spectrometry [24, 25].

While the routes for producing metal NCs lead to a mixture of $\text{Au}_n(\text{SR})_m$ cluster sizes, achieving atomic precision and molecular purity is challenging because the nanocluster growth is extremely complicated and remains poorly understood. Nevertheless, a systematic methodology called “size focusing” (see Fig. 2.5b), for achieving size-specific gold and silver clusters with molecular purity, has been proposed. This methodology consists of two primary steps: (i) kinetically controlled synthesis of an $\text{M}_n(\text{SR})_m$ mixture with a properly controlled size range, and (ii) thermodynamically dictated size focusing on the mixture to single-sized nanoclusters. In parallel, a new approach, which is to utilize ligand exchange to induce size and structure transformation and, hence, to attain new $\text{M}_n(\text{SR})_m$ nanoclusters, was also proposed (see Fig. 2.5c) [27].

2.6.2 Characterization, Structural, Electronic, and Optical Properties

Concerning the characterization of the ultrasmall NCs, UV–Vis absorption spectroscopy, Fourier transform infrared spectroscopy (FTIR), circular dichroism (CD), and X-ray photoelectron spectrometry (XPS) are frequently utilized techniques. FTIR can be used to examine the structures of ligands and NCs, through the loss of S–H stretching vibration. These results inferred that the metal–S bond was formed, and that the NCs embedded in the template would not affect the surface structure of the template. The oxidation state of the metal atoms of the core can be examined by XPS. For gold the peaks measured at 84.0 and 84.9–85.3 eV corresponding to the binding energy of Au(0) and Au(I) are usually observed, which indicate that Au(III)

has been reduced by the capping agents. In UV–Vis absorption spectroscopy, the disappearance of the plasmon-absorption band is an indication of the formation of nanoclusters. The absorption bands of NCs are related to ligand and core size. The optical spectra of well-defined $\text{Au}_n(\text{SR})_m$ nanocluster are particularly useful in the routine syntheses, as the spectra provide a quick diagnosis of the crude product prior to mass spectrometric analysis [29].

Mass spectrometry-based methods, e.g., MALDI-TOF-MS and ESI-MS, were carried out to analyze the molecular weight of the ultrasmall NCs [30]. The use of traditional weak organic acid MALDI matrices has provided a means to measure the mass of the core of ligand-protected NCs; however, these matrices do not prevent extensive ligand fragmentation. The first MALDI spectra of intact $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ using various matrices were published by Dass et al. [31]. The use of glutathione as a ligand and its water solubility provides an opportunity to purify the cluster by running it through polyacrylamide gel electrophoresis (PAGE). The PAGE purification enabled the isolation of intact clusters, as demonstrated by Tsukuda et al. [24] for gold NCs and Bigioni et al. [32] for silver NCs.

However, due to a large amount of chemical noise and/or unresolved isotopic pattern and limited mass accuracy of MS instruments, alternate molecular formula with a very similar mass can lead to misleading formula. This underscores two challenges of peak identification from intact NCs, namely that multiple molecular formulae can be nearly isobaric, and that impurities or ligand fragmentation can generate a large amount of chemical noise which frustrates the assignment of atomic information. Clean samples and instrumentation with very high resolving power decrease the uncertainty of molecular formula assignments, since the number of indistinguishable, nearly isobaric, permutations is decreased. Our experimental group has pushed forward the isotope-resolved mass spectrometry to solve the molecular formula of ultrasmall NCs [33]. Examples of experimental and calculated isotopic distributions for gold–glutathione Au_nSG_m clusters are displayed in Fig. 2.6. The observed charge z of a gold–glutathione complex in the mass spectrum is the sum of the net charge q of the complex and the charge due to deprotonation of glutathione side chains. The observed charge of the complex and the number of deprotonation are both determined from the isotope-resolved mass spectrum resulting in a direct determination of the net charge q . Note that mass spectrometric identification of precise formulas of silver nanoclusters is still nontrivial because of the limited stability of $\text{Ag}_n(\text{SR})_m$ nanoclusters and the rich isotopic pattern that significantly broadens mass peaks caused by silver isotopes.

X-ray crystallography is the “holy-grail” technique to solve the crystal structure of nanoclusters and reveals the nature of bonding and the packing of atoms. The first breakthrough was achieved by Kornberg and coworkers when they reported the synthesis and total structure determination of Au NCs comprising 102 gold atoms and 44 p-mercapto-benzoic acid [34]. Since then, determination of more structures has been achieved. A summary of the reported $\text{Au}_n(\text{SR})_m$ structures is given in the excellent recent review of Jin [28]. Here are selected $\text{Au}_n(\text{SR})_m$ nanoclusters that have been synthesized in high purity and adequately characterized: $\text{Au}_{15}(\text{SR})_{13}$,

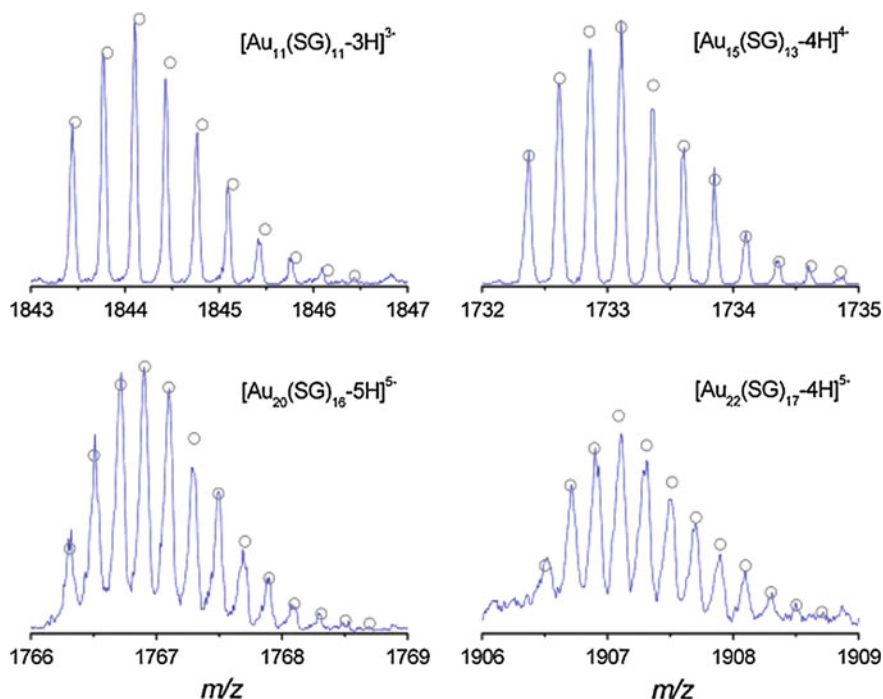


Fig. 2.6 Experimental isotopic distribution recorded for $\text{Au}_{11}(\text{SG})_{11}$ (charge state 3 $^-$), $\text{Au}_{15}(\text{SG})_{13}$ (charge state 4 $^-$), $\text{Au}_{20}(\text{SG})_{16}$ (charge state 5 $^-$), and $\text{Au}_{22}(\text{SG})_{17}$ (charge state 5 $^-$). Circles show the theoretical isotopic distributions. Reproduced with permission from Ref. [33]. Copyright © 2012 Elsevier B.V.

$\text{Au}_{18}(\text{SR})_{14}$, $\text{Au}_{20}(\text{SR})_{16}$, $\text{Au}_{22}(\text{SR})_{16,17,18}$, $\text{Au}_{23}(\text{SR})_{16}$, $\text{Au}_{24}(\text{SR})_{20}$, $\text{Au}_{24}(\text{SR})_{16}$, $\text{Au}_{25}(\text{SR})_q^8$ ($q = -1, 0, +1$), $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{30}\text{S}(\text{SR})_{18}$, $\text{Au}_{36}(\text{SR})_{24}$, $\text{Au}_{38}(\text{SR})_{24}$, $\text{Au}_{38}\text{S}_2(\text{SR})_{20}$, $\text{Au}_{40}(\text{SR})_{24}$, $\text{Au}_{44}(\text{SR})_{28}$, $\text{Au}_{52}(\text{SR})_{32}$, $\text{Au}_{55}(\text{SR})_{31}$, $\text{Au}_{64}(\text{SR})_{32}$, $\text{Au}_{67}(\text{SR})_{35}$, $\text{Au}_{99}(\text{SR})_{42}$, $\text{Au}_{102}(\text{SR})_{44}$, $\text{Au}_{104}(\text{SR})_{41}$, $\text{Au}_{130}(\text{SR})_{50}$, $\text{Au}_{133}(\text{SR})_{52}$, $\text{Au}_{137}(\text{SR})_{56}$, and $\text{Au}_{144}(\text{SR})_{60}$ [28]. On the other hand, here are some selected Ag nanoclusters protected by thiolates: $\text{Ag}_{11}(\text{SR})_7$, $\text{Ag}_{15}(\text{SR})_{11}$, $[\text{Ag}_{17}(\text{SR})_{12}]^{3-}$, $[\text{Ag}_{25}(\text{SR})_{18}]^-$, $\text{Ag}_{29}(\text{SSR})_{12}$, $\text{Ag}_{30}(\text{SR})_{18}$, $\text{Ag}_{31}(\text{SR})_{19}$, $[\text{Ag}_{32}(\text{SR})_{19}]^0$, $[\text{Ag}_{35}(\text{SR})_{18}]$, and $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$ [28]. Note that some bimetal nanoclusters (AuAg , AuCu , AuPt , ...) and other gold nanoclusters protected by various types of ligands (phosphine; diphosphine; selenolate; alkynyl) with crystal structures were solved by X-ray crystallography [28]. However, the extensive application of X-ray crystallography as a characterization technique is limited, because it is often challenging to produce sufficiently high-quality crystals for a solvent. Indeed, the stability of water soluble glutathione monolayer-protected gold and silver clusters has always been ambiguous at high temperature. The hydrolysis of glutathione (GSH) to pyroglutamic acid has always been observed in the ESI mass spectrometry of these clusters. The fragile nature of these clusters has been a concern not limited to mass spectrometric studies. The stability of water soluble glutathione monolayer-

nature of these clusters has been a concern not limited to mass spectrometric studies. The stability of water soluble glutathione monolayer-protected gold and silver clusters has prevented it from any type of crystallization studies. Although the metal core system is stable, the nature of glutathione ligand plays an important role in its stability. Glutathione (GSH) is a tripeptide (γ -Glu-Cys-Gly). It exists as disulfide GSSG. The bulky size of this ligand, easily hydrolysable amide bond, and stability restricted to lower temperatures makes it vulnerable to different degradation process. The difficulty to extract quantitative information from the diffraction patterns of nanosized and poorly crystallized compounds is the reason why X-ray powder diffraction (XRPD) techniques were mostly used to support the structural and microstructural features obtained by other techniques such as electron microscopy.

Also, NMR can be an important and indispensable tool for gaining insight into the structure of gold clusters. Jin and coworkers have demonstrated that the complicated 1D ^1H NMR spectrum of $\text{Au}_{25}(\text{SG})_{18}$ clusters, with the aid of 2D NMR experiments (COSY and HSQC), can provide a wealth of information and facilitate identification of the structure of $\text{Au}_{25}(\text{SG})_{18}$ clusters when combined with mass spectrometry and optical spectroscopy [35].

The X-ray structures of nanoclusters reveal that the surface thiolate ligands ($-\text{SR}$) do not simply passivate the gold core, instead, they form unique oligomeric units such as $\text{Au}(\text{SR})_2$ ($-\text{RS}-\text{Au}-\text{RS}-$) and $\text{Au}_2(\text{SR})_3$ ($-\text{RS}-\text{Au}-\text{S}(\text{R})-\text{Au}-\text{SR}-$) (called staples or semi-rings), which bind to the surface (i.e., core surface) gold atoms for protection; in other words, the staple units are anchored to the core by sulfur in atop positions. Interestingly, the Ag_{44} structure was found to be quite different from that of the same size Au_{44} nanocluster; thus, it was thought that Ag nanoclusters might follow quite different structural rules than gold nanoclusters. Silver nanoclusters exhibit more complex surface structures than gold; in particular, Ag and SR can assemble into three-dimensional structures.

Finally, concerning optical properties, strongly emissive nanoclusters are highly desirable. Strategies such as aggregation-induced fluorescence, silver doping, and ligand shell rigidification for increasing the PL quantum yield and tuning the PL colors of nanoclusters have been proposed. However, the origins of PL in nanoclusters are still not fully understood. The ligand molecules along with the geometric and electronic structures of the metal core play a major role in enhancing emissive properties. Such nanoclusters can be viewed as a “multi-shell system” (see Fig. 2.7) composed by (1) a metal core, (2) a metal–ligand interface, in particular with staple motifs leading to metal–sulfur bonds, and (3) the surface ligand molecules. These three shells may communicate in two different ways: charge transfer from ligand to metal core (analogy with ligand-to-metal charge transfer (LMCT)) or ligand-to-metal–metal charge transfer ((LMMCT) observed in metal complexes) and through direct bonding or direct donation of delocalized electrons of electron-rich groups of the ligands [21].

In the last 10 years, some general trends have been figured out concerning the de-excitation pathways following a visible or near-UV absorption. The following experimental and theoretical findings were assembled from the present work and literature to derive the energy diagram in Fig. 2.7.

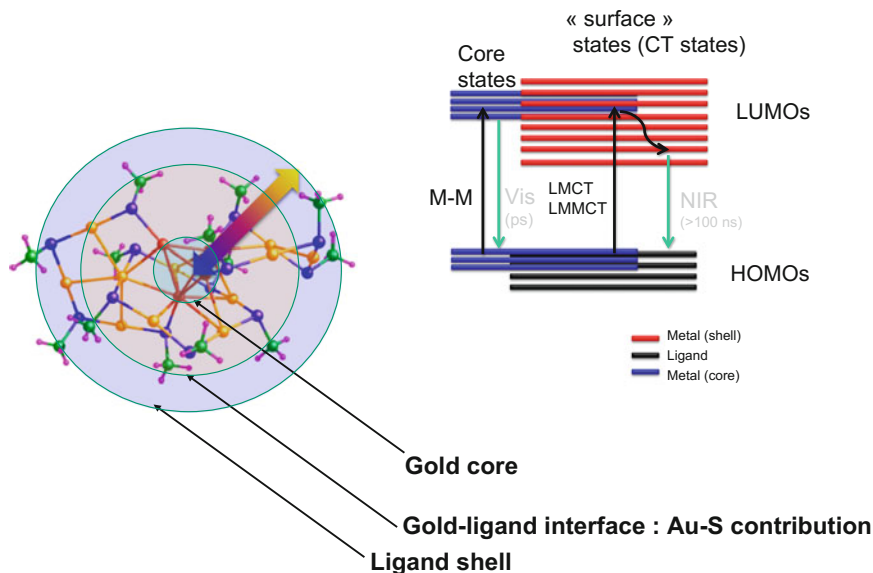


Fig. 2.7 Cartoon diagram showing the relaxation pathways in *gold nanoclusters*. Such nanoclusters can be viewed as a “multi-shell system” exemplified with $\text{Au}_{15}\text{SR}_{13}$ clusters (*left*)

Near-ultraviolet and visible absorbance may arise from transitions between molecular orbitals with either ligand contributions or metal character (LMCT and LMMCT), as well as from metal–metal electronic transitions. A rapid (<1 ps lifetime) decay pathway for clusters which have a core of metal atoms may lead to an emission in the visible range. A long-lived (>100 ns lifetime), charge transfer component is present for all clusters. NIR emission in the clusters is related to the surface states and originates from the charge transfer excited state.

References

1. Kreibig U, Vollmer M (1995) Optical properties of metal clusters. Springer, Berlin
2. Christensen NE (1972) The band structure of silver and optical interband transitions. *Phys Status Solidi (b)* 54:551
3. Christensen NE (1978) Spin-orbit projected d densities-of-states of Pd, Ag, Pt, and Au. *J Phys F: Met Phys* 8:L51
4. Jin R (2010) Quantum sized, thiolate-protected gold nanoclusters. *Nanoscale* 2:343
5. Ashcroft NW, Mermin N (1976) Solid state physics. Harcourt Inc., Orlando
6. Bonačić-Koutecký V, Veyret V, Mitrić R (2001) Ab initio study of the absorption spectra of Ag_n ($n = 5-8$) clusters. *J Chem Phys* 115:10450
7. Bonačić-Koutecký V, Mitrić R, Bürgel C, Noack H, Hartmann M, Pittner J (2005) Tailoring the chemical reactivity and optical properties of clusters by size, structures and lasers. *Eur Phys J D* 34:113

8. Bellina B, Compagnon I, Bertorelle F, Broyer M, Antoine R, Dugourd P, Gell L, Kulesza A, Mitrić R, Bonačić-Koutecký V (2011) Structural and optical properties of isolated noble metal-glutathione complexes. Insight into the chemistry of liganded nanoclusters. *J Phys Chem C* 115:24549
9. Markus R, Schwentner N (1987) Physics and chemistry of small clusters. Plenum, New York
10. Harbich W, Fedrigo S, Buttet J, Lindsay DM (1991) Optical spectroscopy on size selected gold clusters deposited in rare gas matrices. *Z Phys D At, Mol Clusters* 19:157
11. Harbich W, Fedrigo S, Buttet J, Lindsay DM (1992) Deposition of mass selected gold clusters in solid krypton. *J Chem Phys* 96:8104
12. Collings BA, Athanassenas K, Lacombe D, Rayner DM, Hackett PA (1994) Optical absorption spectra of Au₇, Au₉, Au₁₁, and Au₁₃, and their cations: gold clusters with 6, 7, 8, 9, 10, 11, 12, and 13s-electrons. *J Chem Phys* 101:3506
13. Kreibig U (1974) Electronic properties of small silver particles: the optical constants and their temperature dependence. *J Phys F: Met Phys* 4:999
14. Harbich W, Fedrigo S, Meyer F, Lindsay DM, Lignieres J, Rivoal JC, Kreisle D (1990) Deposition of mass selected silver clusters in rare gas matrices. *J Chem Phys* 93:8535
15. Sieber C, Buttet J, Harbich W, Félix C, Mitrić R, Bonačić-Koutecký V (2004) Isomer-specific spectroscopy of metal clusters trapped in a matrix: Ag₉. *Phys Rev A* 70:041201
16. Chen W, Wang Z, Lin Z, Lin L, Fang K, Xu Y, Su M, Lin J (1998) Photostimulated luminescence of AgI clusters in zeolite-Y. *J Appl Phys* 83:3811
17. Peyser LA, Vinson AE, Bartko AP, Dickson RM (2001) Photoactivated fluorescence from individual silver nanoclusters. *Science* 291:103
18. Hild U, Dietrich G, Krückeberg S, Lindinger M, Lützenkirchen K, Schweikhard L, Walther C, Ziegler J (1998) Time-resolved photofragmentation of stored silver clusters Ag_n⁺ (n = 8–21). *Phys Rev A: At Mol Opt Phys* 57:7
19. Zheng J, Dickson RM (2002) Individual water-soluble dendrimer-encapsulated silver nanodot fluorescence. *J Am Chem Soc* 124:13982
20. Richards CI, Choi S, Hsiang J-C, Antoku Y, Vosch T, Bongiorno A, Tzeng Y-L, Dickson RM (2008) Oligonucleotide-stabilized Ag nanocluster fluorophores. *J Am Chem Soc* 130:5038
21. Wu Z, Jin R (2010) On the ligand's role in the fluorescence of gold nanoclusters. *Nano Lett* 10:2568
22. Diez I, Ras RHA (1963) Fluorescent silver nanoclusters. *Nanoscale* 2011:3
23. Brust M, Walker M, Bethell D, Schiffrin DJ, Whyman R (1994) Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid-liquid system. *J Chem Soc, Chem Commun* 7:801
24. Negishi Y, Nobusada K, Tsukuda T (2005) Glutathione-protected gold clusters revisited: bridging the gap between gold(I)—thiolate complexes and thiolate-protected gold nanocrystals. *J Am Chem Soc* 127:5261
25. Negishi Y, Takasugi Y, Sato S, Yao H, Kimura K, Tsukuda T (2004) Magic-numbered Au_n clusters protected by glutathione monolayers (n = 18, 21, 25, 28, 32, 39): isolation and spectroscopic characterization. *J Am Chem Soc* 126:6518
26. Schaaff TG, Knight G, Shafigullin MN, Borkman RF, Whetten RL (1998) Isolation and selected properties of a 10.4 kDa gold: glutathione cluster compound. *J Phys Chem B* 102:10643
27. Zeng C, Chen Y, Das A, Jin R (2015) Transformation chemistry of gold nanoclusters: from one stable size to another. *J Phys Chem Lett* 6:2976
28. Jin R, Zeng C, Zhou M, Chen Y (2016) Atomically precise colloidal metal nanoclusters and nanoparticles: fundamentals and opportunities. *Chem Rev* 116:10346
29. Jin R (2015) Atomically precise metal nanoclusters: stable sizes and optical properties. *Nanoscale* 7:1549
30. Harkness KM, Cliffl DE, McLean JA (2010) Characterization of thiolate-protected gold nanoparticles by mass spectrometry. *Analyst* 135:868
31. Dass A, Stevenson A, Dubay GR, Tracy JB, Murray RW (2008) Nanoparticle MALDI-TOF mass spectrometry without fragmentation: Au₂₅(SCH₂CH₂Ph)₁₈ and mixed monolayer Au₂₅(SCH₂CH₂Ph)_{18-x}(L)_x. *J Am Chem Soc* 130:5940

32. Kumar S, Bolan MD, Bigioni TP (2010) Glutathione-stabilized magic-number silver cluster compounds. *J Am Chem Soc* 132:13141
33. Hamouda R, Bertorelle F, Rayane D, Antoine R, Broyer M, Dugourd P (2013) Glutathione capped gold $\text{Au}_N(\text{SG})_M$ clusters studied by isotope-resolved mass spectrometry. *Int J Mass Spectrom* 335:1
34. Jadzinsky PD, Calero G, Ackerson CJ, Bushnell DA, Kornberg RD (2007) Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution. *Science* 318:430
35. Wu Z, Gayathri C, Gil RR, Jin R (2009) Probing the structure and charge state of glutathione-capped $\text{Au}_{25}(\text{SG})_{18}$ clusters by NMR and mass spectrometry. *J Am Chem Soc* 131:6535

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