

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>				
1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE		3. DATES COVERED (From - To)
		New Reprint		-
4. TITLE AND SUBTITLE			5a. CONTRACT NUMBER	
Bright two-photon emission and ultra-fast relaxation dynamics in a DNA-templated nanocluster investigated by ultra-fast spectroscopy			W911NF-09-1-0545	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
			611102	
6. AUTHORS			5d. PROJECT NUMBER	
Sung Hei Yau, Neranga Abeyasinghe, Meghan Orr, Leslie Upton, Oleg Varnavski, James H. Werner, Hsin-Chih Yeh, Jaswinder Sharma, Andrew P. Shreve, Jennifer S. Martinez, Theodore Goodson III				
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES			8. PERFORMING ORGANIZATION REPORT NUMBER	
University of Michigan - Ann Arbor Regents of the University of Michigan 3003 S. State St Ann Arbor, MI 48109 -1274				
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			ARO	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
			56696-MS.10	
12. DISTRIBUTION AVAILABILITY STATEMENT				
Approved for public release; distribution is unlimited.				
13. SUPPLEMENTARY NOTES				
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
14. ABSTRACT				
Metal nanoclusters have interesting steady state fluorescence emission, two-photon excited emission and ultrafast dynamics. A new subclass of fluorescent silver nanoclusters (Ag NCs) are NanoCluster Beacons. NanoCluster Beacons consist of a weakly emissive Ag NC templated on a single stranded DNA ("Ag NC on ssDNA") that becomes highly fluorescent when a DNA enhancer sequence is brought in proximity to the Ag NC by DNA base pairing ("Ag NC on dsDNA"). Steady state fluorescence was observed at 540 nm for both Ag NC on ssDNA and				
15. SUBJECT TERMS				
silver metal cluster NLO optical applications				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES
a. REPORT	b. ABSTRACT	c. THIS PAGE		
UU	UU	UU	UU	
				19a. NAME OF RESPONSIBLE PERSON
				Theodore Goodson III
				19b. TELEPHONE NUMBER
				734-647-0274

Report Title

Bright two-photon emission and ultra-fast relaxation dynamics in a DNA-templated nanocluster investigated by ultra-fast spectroscopy

ABSTRACT

Metal nanoclusters have interesting steady state fluorescence emission, two-photon excited emission and ultrafast dynamics. A new subclass of fluorescent silver nanoclusters (Ag NCs) are NanoCluster Beacons. NanoCluster Beacons consist of a weakly emissive Ag NC templated on a single stranded DNA ("Ag NC on ssDNA") that becomes highly fluorescent when a DNA enhancer sequence is brought in proximity to the Ag NC by DNA base pairing ("Ag NC on dsDNA"). Steady state fluorescence was observed at 540 nm for both Ag NC on ssDNA and dsDNA; emission at 650 nm is observed for Ag NC on dsDNA. The emission at 550 nm is eight times weaker than that at 650 nm. Fluorescence up-conversion was used to study the dynamics of the emission. Bi-exponential fluorescence decay was recorded at 550 nm with lifetimes of 1 ps and 17 ps. The emission at 650 nm was not observed at the time scale investigated but has been reported to have a lifetime of 3.48 ns. Two-photon excited fluorescence was detected for Ag NC on dsDNA at 630 nm when excited at 800 nm. The two-photon absorption cross-section was calculated to be similar to 3000 GM. Femtosecond transient absorption experiments were performed to investigate the excited state dynamics of DNA-Ag NC. An excited state unique to Ag NC on dsDNA was identified at similar to 580 nm as an excited state bleach that related directly to the emission at 650 nm based on the excitation spectrum. Based on the optical results, a simple four level system is used to describe the emission mechanism for Ag NC on dsDNA.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Continuation for Block 13

ARO Report Number 56696.10-MS
Bright two-photon emission and ultra-fast relaxa ...

Block 13: Supplementary Note

© 2012 . Published in Nanoscale, Vol. 4 (14) (2012), (14). DoD Components reserve a royalty-free, nonexclusive and irrevocable right to reproduce, publish, or otherwise use the work for Federal purposes, and to authroize others to do so (DODGARS §32.36). The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

Approved for public release; distribution is unlimited.

An Ultrafast Look at Au Nanoclusters

Sung Hei Yau^a, Oleg Varnavski^a, Theodore Goodson III^{*a}

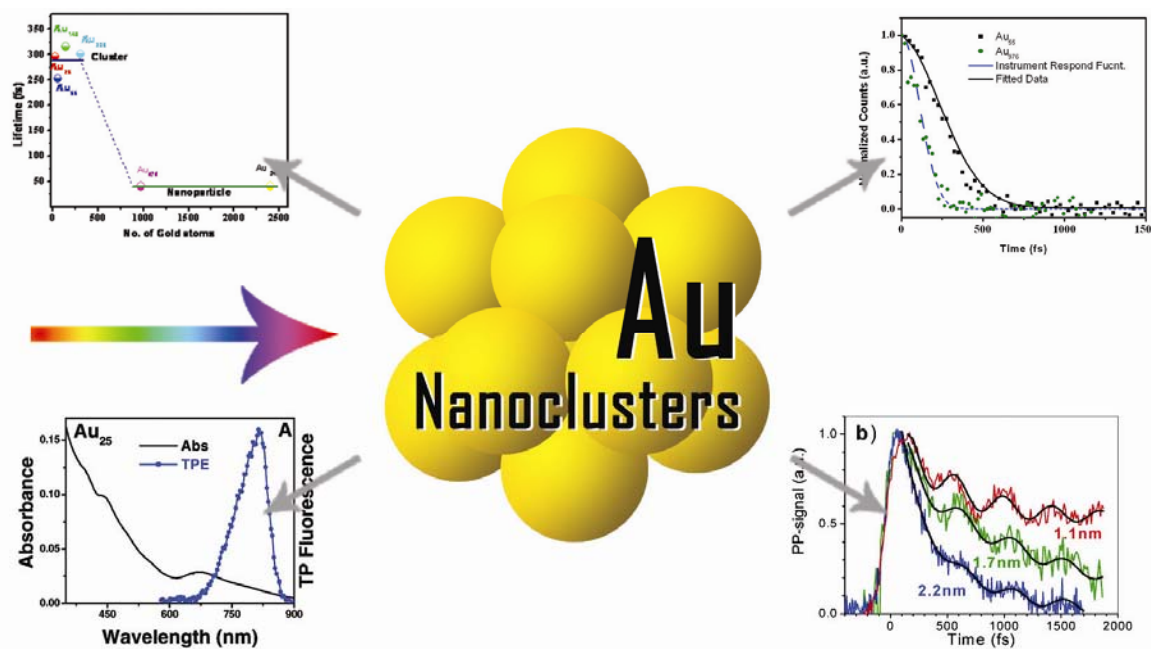
^a*Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109*

*tgoodson@umich.edu

Conspectus

The area of research involving nano-materials in the past 20 years is credited with the discovery of many new and interesting properties not found in bulk materials. Extensive research has focused on metal nanoparticles (> 3 nm) because of their useful applications. The discovery of metal nanoclusters (<3nm) has greatly expanded the horizon of nano-material research. These nanosystems exhibit molecular-like characteristics as their size approaches the Fermi-wavelength of an electron. The relationships between size and physical properties for nanomaterials are very interesting. Particularly, the changes in the optical properties have provided tremendous insight into the electronic structure of nanoclusters. The success of synthesizing monolayer protected clusters (MPCs) in the condensed phase has allowed scientists to probe the metal core directly. Au MPCs have become the “gold” standard in nanocluster science, thanks to the rigorous structural characterization already accomplished. The use of ultrafast laser spectroscopy on MPCs in solution provides the benefit of directly studying the chemical dynamics of metal nanoclusters (core), and their non-linear optical properties.

In this contribution, the optical properties of MPCs in the visible region are investigated using ultrafast spectroscopy. An emission mechanism for nanoclusters is proposed based on fluorescence up-conversion. Nanoclusters behave differently from nanoparticles in terms of emission life-times as well as two-photon cross-sections. Further investigation of the transient (excited state) absorption has revealed many unique phenomena of nanoclusters such as quantum confinement effects and vibrational breathing modes. In summary, based on the differences in the optical properties, the distinction between nanoclusters and nanoparticles appear at a size near ~2.2nm. This is consistent with simulations from a free-electron model proposed for MPCs. The use of ultrafast techniques on these nanoclusters can answer many of the fundamental questions about the nature of these exciting nano-materials and their applications.



I. Introduction

In the past 10 years, nanoscopic materials have elucidated new frontiers in science, medicine and engineering. The development of new types of nanomaterials has led to the discovery of metal nanoclusters which have gathered tremendous attention. Bulk metals are well-defined by classical dielectrics,^{1,2} and are very well-understood. Recent studies on metal nanomaterials focus on systems comprised of a small group of metal atoms in the nanometer scale. Metal nanosystems have interesting physical properties, such as quantum confinement,³⁻⁶ emission,^{7,8} two-photon absorption⁹ and other optical phenomena.^{10,11} Extensive research in the past decade^{6,12-14} initially focused on the synthesis of size-controlled metal systems; particularly those that approach the Fermi-wavelength of an electron. These metal nanosystems were classified as nanoparticles and nanoclusters.^{6,14-17} It is interesting to note that for metal nanosystems in this size regime, the electronic properties are dictated by their sizes and shapes. The tunable size of metal nanosystems offers the possibility of a wide range of applications, including molecular electronics,^{3-5,18,19} image markers^{8,20} and catalysts²¹.

Metal nanoparticles and nanoclusters are defined by their size. Nanoparticles have a metal core larger than about 3 nm, and nanoclusters smaller than about 3 nm.^{6,7}

However with the exact divide between nanoparticles and nanoclusters are not clear until recently. The division of nanoclusters and nanoparticles arises from their drastically different optical properties.^{7,9,16,17} Nanoparticles are already used in many fields, most notably in the field of imaging and extending the nano-tool box to an even smaller scale. Nanoclusters could provide an opportunity for an even wider array of potential applications. Metal topologies with a small number of atoms such as nanoparticles were first studied in the gas phase²². However, it was not until the condensed phase synthesis of metal nanomaterials that leads to tremendous interest experienced recently. The advancement of the synthesis processes also lead to an expansion of applications and, at the same time, the study of fundamental physics of these nanosystems.^{6,10,14,15,18,23–28} Of the many different synthetic routes developed, Brust's synthesis^{29,30} became a foundation for synthesis development, and is commonly used.^{6,18} In brief, the synthesis uses an organic shell (Glutathione) to stabilize and regulate cluster formation from metal salt, creating highly stable metal systems. These systems were later labeled as monolayered protected clusters (MPCs). Using a straightforward "single-pot" synthesis strategy³¹, Au(MPCs) can be synthesized with high stability^{6,15,18,29,32}, and receive much interest in the field. MPCs are considered to have two parts: a metal core and a single layer ligand shell.¹⁵ The simple outer shell allows direct investigation of the metal core in the condense phase and it can be functionalized and adjusted to both polar and non-polar solvents.^{13,33} The self-assembly nature of MPCs facilitates the synthesis of highly mono-dispersed products, and the metal core size can be adjusted by the reaction conditions.^{6,15,29,31} The high purity (mono-disperse) and yield of MPCs synthesis allows for the accelerated characterization efforts.^{7,18,34,35}

Detailed characterization work on Au nanoclusters leads to the identification of $\text{Au}_{25}(\text{SG})_{18}$ ^{6,18,36–38} and various other species. One of the most definitive characterizations of Au MPCs is the x-ray crystal structure of $\text{Au}_{102}(\text{SR})_{44}$ ³⁵ and $\text{Au}_{25}(\text{SR})_{18}$.^{6,10,38,39} The identification of $\text{Au}_{25}(\text{SG})_{18}$ also coincides with theoretical work done on Au_{25} ³⁹, giving further evidence to the structural details of the system. Theoretical works on Au_{25} gave insight into the bonding motif and the electronic structure of Au_{25} .^{10,15,27,28,39–42} This account focuses on various optical phenomena observed for Au MPCs. Utilizing different ultrafast spectroscopic techniques, we are able to study the chemical dynamics of these

systems in great detail. Our investigations target the emission properties and mechanisms, non-linear optical responses, as well as transient absorption properties. The goal is to understand the fundamental scientific questions behind nanoclusters, such as the effect of size on optical behavior and the investigation of new optical behavior to further the understanding of nanomaterials in general and to advance the development of these new materials.

A. Electronic Absorption and Structure of Gold Clusters

The structure of metal nanoparticles and their electronic and optical properties are directly related, so it is important to understand the structure of MPCs for our discussion. The characterization of various MPCs leads to the discovery of “magic numbers”:^{32,43} similar to metal nanoparticles in the gas phase,²² only metal core with certain sizes are found for MPCs. These magic number nanoclusters exhibit high stability and similar optical and physical properties, and can be modeled based on physical packing.²⁴ The stability of the larger nanoparticles can be well explained by the physical packing of the core. However, physical packing alone cannot account for the various sizes observed and leads to the development of the “super atom” theory.¹⁵ The super atom theory adopts ideas from semi-conductors and treats the metal core as a single atom within the system. The highly stable cluster numbers are the result of the systematic closing of outer electronic shells, similar to the Jellium and Kubo models.^{2,22} The simplest unit of Au MPCs was identified to be a 13 atom icosahedral core^{34,37,38} and some of the magic clusters are found to be based on the same motif (physical packing or electron shell closing). It should be noted that Au₁₀₂ does not follow the icosahedral packing, but it does follow the electronic shell closing regime.³⁵ Most of the MPCs share a fundamental unit (Au₁₃), and in theory, should exhibit very similar physical properties. The treatment of the metal core as a super atom also gives rise to the idea of discrete (molecular like) energy levels for metal nanoclusters. Beside the super atom theory, the free electron model⁶ can also be used to describe nanoclusters.

The direct effect of core size on the electronic structure for nanoclusters is known as the Quantum Size Effect. Our detailed investigations used various optical techniques to investigate the quantum size effect for Au MPCs and found that major optical difference can be observed between nanoparticles and nanoclusters at around 2.2-3 nm, in agreement with the free electron model. Moreover, nanoparticles were found to be similar to bulk metals and could be described by Mie theory.^{1,7,44} Mie Theory utilizes Maxwell's equation to describe light interaction with metal nanoparticles and accounts for the Surface Plasmon Resonance (SPR). SPR is the collective excitation mode of the conduction electrons in the metal core, and it has been shown that enhanced emission from metal nanoparticles is caused by the SPR.^{16,20,21} Control of the size and shape can directly affect the SPR, making nanoparticles a tunable image marker.²⁰ A comparison of the various steady state absorption spectra in figure 1 indicates the difference between nanoclusters and nanoparticles. The SPR is only observed for the nanoparticle, Au₂₄₀₆. Based on Mie theory,^{1,7,44} a simple model is used to simulate the absorption spectrum for a gold nanoparticle similar in size to Au₂₅. However, the calculation predicts the appearance of a surface plasmon band that can be observed at 520 nm, which is not observed in the experiments. This demonstrates that Mie theory (and its extensions),^{1,2,44-46} does not apply to nanoclusters.

It is reported that absorption peaks for Au₂₅ are correlated to the icosahedra structure of the core, and can be correlated to the transient absorption spectrum.^{15,25,27,34} In our transient absorption spectra, we observed an additional absorption feature that we proposed to be related to the ground state.⁷ The details will be discussed in the transient absorption section. In an attempt to resolve more details from the absorption spectrum, the Ramakrishna group¹¹ looked at the absorption spectra for Au₂₅ and Au₃₈ systems at low temperatures and observed a change in the absorption maximum, peak sharpening and an increase in the oscillator strength. Their model attributes the effect of the electron-phonon interaction with phonons in the metal-ligand interface.¹¹ Overall the absorption spectra of various Au nanoclusters and particles are clear evidence for quantum size effects.

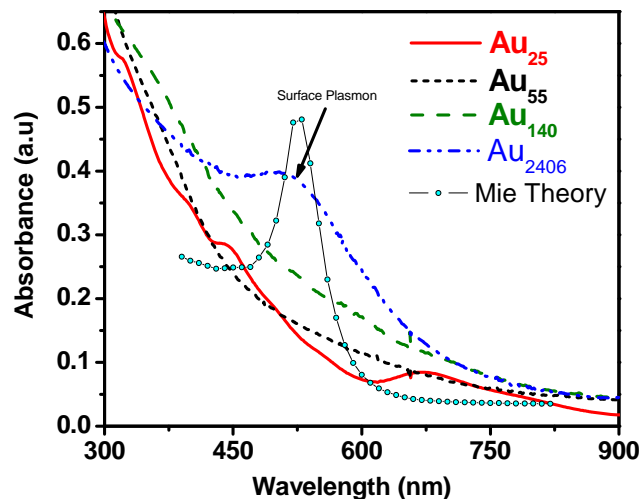


Figure 1: Steady state absorption for Au₂₅, Au₅₅, Au₁₄₀, Au₂₄₀₆ and Mie theory calculation using parameter similar to Au₂₅.⁷

B. Emission Mechanism of Gold Clusters

Quantum confinement effects clearly predict discrete energy levels within the nanoclusters systems, and it is theoretically possible to observe emission.^{2,7,15} Emission from MPCs was initially affronted with skepticism, due to the uncertainty in the purity of the materials and less-than-satisfactory characterization. Studies were carried out to look at the contribution from the ligand shell and the metal core separately, and it was found that neither component contributes to the emission.^{47,48} In our contribution, one-photon excitation was used to observe two different emission wavelengths in the steady state, confirmed by time-resolved kinetics.⁷ The emission is found to be in the visible and the near-infrared region.^{7,8,45,48} It is relatively strong in the near-infrared with quantum efficiency on the order of 10^{-4} . The visible emission is weaker in comparison, with an efficiency of 1.25×10^{-5} .⁷ Quantum efficiencies at both wavelengths are five orders of magnitude stronger than that of bulk gold (gold thin films).⁷

To understand the emission mechanism better, time-resolved fluorescence up-conversion is used to resolve the fluorescence life-time of various gold nanoparticles and nanoclusters (Figure 2,3).^{7,9} A femto-second Ti-sapphire laser system is used to achieve this goal with a time resolution of ~ 60 fs. The comparison of the fluorescence life-time of

nanoclusters and nanoparticles from 1.1 nm to 4 nm yields interesting results (Figure 2). There is a clear distinction between the emission life-times of nanoparticles and nanoclusters. In our previous investigation,¹⁶ emission from nanoparticles is associated with the recombination of the *d*-hole by an Auger type process, which has a short life-time of 50 fs (Figure 3). The emission life-time for nanoclusters, however, is much longer than that of nanoparticles and can be fitted with a single exponential, which is characteristic of molecular-like singlet decay relaxation process.⁷ (Figure 2, 3) The longer life-times are caused by the transition of discrete energy levels, similar to molecular emissions.

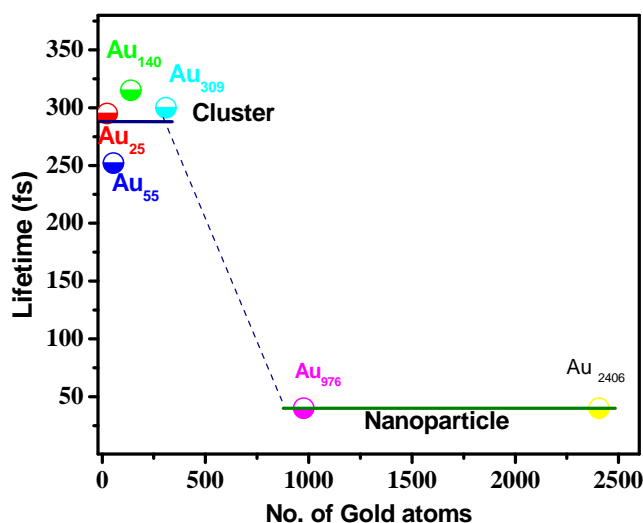


Figure 2: Fluorescence life time comparisons for MPCs of various sizes. The most notable difference is between the nanoparticle and nanoclusters.⁷

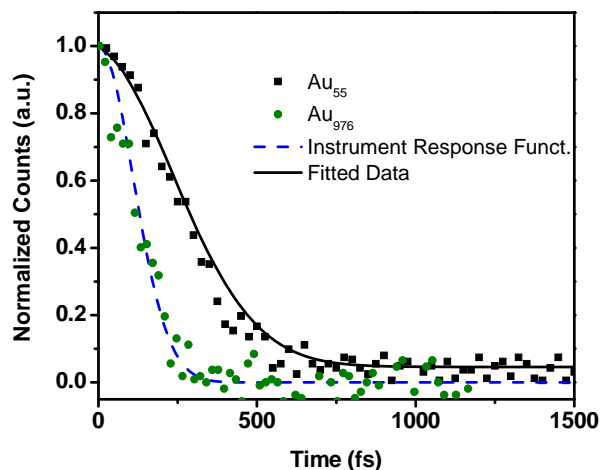


Figure 3: Time resolved visible emission for Au₅₅ and Au₉₇₆. The life time of Au₅₅ is about ~250fs. The emission from Au₉₇₆ is faster than the instrument response function (blue line).⁷

Based on our steady state and fluorescence life-time studies, we proposed an energy diagram for nanoclusters (Figure 4). The emission studies⁷ suggest that the dual-wavelength emission from Au MPCs follows two very different mechanisms. The emission in the visible region is fast and very short-lived (hundreds of fs), and it is most likely to be associated with the metal core (State B).^{7,17} The near-infrared emission is related to the surface states that arise from the interaction with the ligands.^{8,15,48} It has been reported that the polarity of the ligand has a direct effect on the emission efficiency.^{6,48} In MPCs, the metal core and the metal-ligands bonds do not contribute to the metal core, based on the super atom theory. When we treat the metal core as one “super atom”, the ligands can cause a change in the environment that affects the electronic states of the core as a whole.

The up-conversion studies suggest that the short-lived visible emission originates from the filling of the ground state hole by an electron from the excited state (Figure 4, B band).⁷ This mechanism, however, is very different from the Auger recombination process for nanoparticles with a much faster life-times.^{16,44} Compared to theoretical studies of Au₂₅ clusters, this transition is similar to the HOMO-LUMO+1 process.^{10,15} The small quantum efficiency forecasts the presence of non-radiative processes. These processes are represented by the transition from A band (LUMO) to the ground state (HOMO). The near-infrared emission is the result of the transition from the surface states, which originates from the A band, to the ground state. The absence of dynamic Stokes shift in our experimental results suggests that the energy is quickly transferred to the surface state, leading to the strong near infrared (NIR) emission.^{7,8,15,45,48}

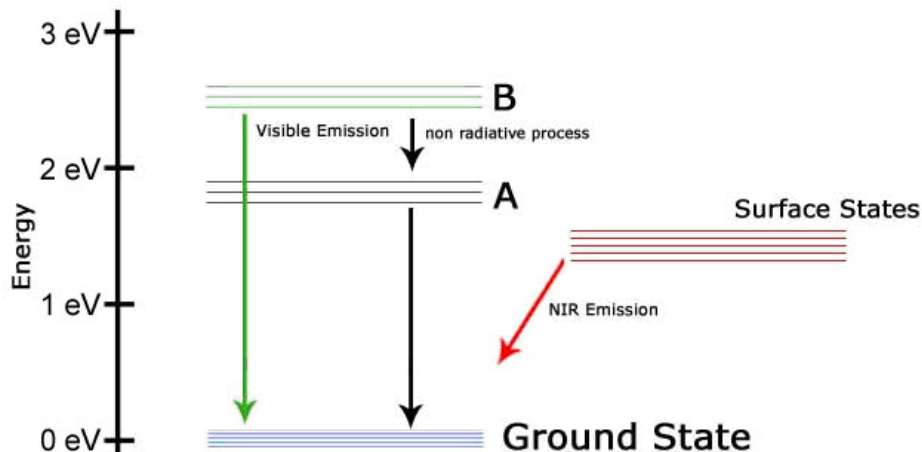


Figure 4: Transition energy diagram for the emissions for MPCs, using data from steady state emission, fluorescence up conversion and transient absorption.⁷

C. Two Photon Excited Emission in Gold Clusters

The relatively strong emission under single-photon excitation for Au MPCs leads to questions about the possibility of two-photon excited emission. Two-photon/multi photon excited emissions are beneficial for low power medical imaging. Au MPCs also have potential to be an optical limiting material with its large two-photon cross-section.⁹ We expected to observe a scaling law for the two-photon absorption (TPA) coefficient as a function of the core size.^{7,9} Two-photon excited emission was first with Au₂₅ under 1290 nm excitation, with an emission peak at 830 nm (Figure 5a). The quadratic intensity dependence of the fluorescence indicates that it is a two-photon excited emission (Figure 5b). The TPA cross-section was measured to be 2700 GM using H₂TPP (Tetraphenylporphyrin) in toluene as a standard, about 1-2 orders of magnitude higher than many organic chromophores.⁹

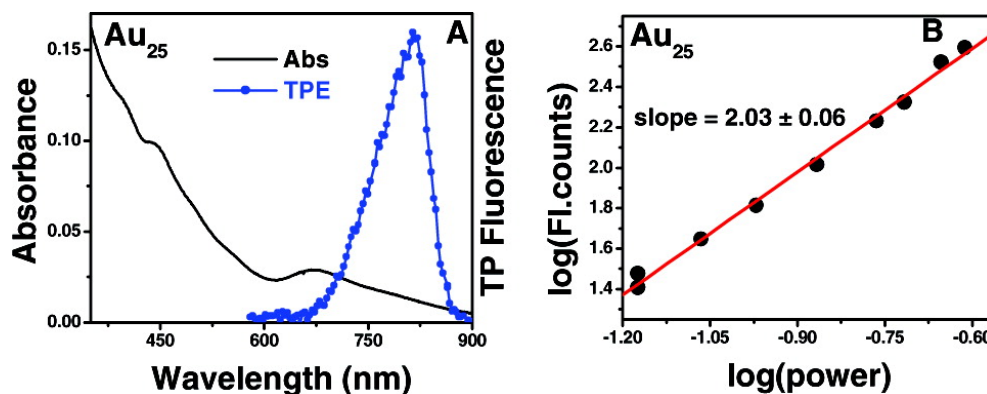


Figure 5. A) Two-photon excited fluorescence from Au₂₅. B) Pump power dependence for the two-photon excited emission.⁹

In addition to the two-photon emission in the near-infrared region, the emission in the visible region is also observed (Figure 6). Various sizes of Au MPCs are investigated, from gold nanoparticle (4 nm) down to Au₂₅ clusters (1.1 nm), under 800 nm excitation. The emission wavelength maxima are found to have dependence on size for both nanoparticles and nanoclusters. For nanoclusters, the emission is in the 500-535 nm range, while nanoparticles emit around 550 nm. The difference in the emission wavelengths for the nanoclusters and nanoparticles is the result of the different energy gaps between HOMO and LUMO affected by the variation in size.⁹ The fluorescence quantum yield under two-photon excitation is on the order of 10^{-7} to 10^{-8} . A clear illustration of the emission being a two-photon process is a quadratic power dependence of various clusters (Fig. 6b, d, f, h, j).⁹

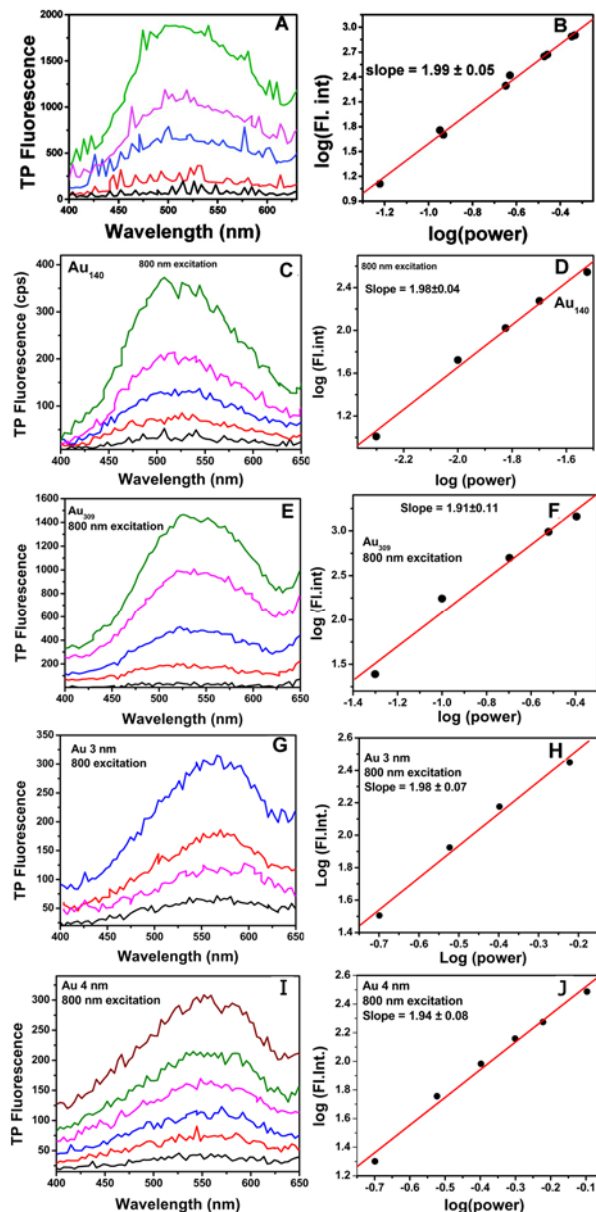


Figure 6. Two-photon excited emission and corresponding power dependence for MPCs of various sizes. A,C,E,G,I are the emission spectrum for Au₂₅, Au₁₄₀, Au₃₀₉, Au 3nm and Au 4nm respectively. B,D,F,H,J are corresponding power dependence.⁹

Due to the low quantum efficiency of these systems, measurement with a Spex-Fluorolog fluorimeter is difficult; two-photon excited femtosecond time-resolved fluorescence up-conversion⁹ is employed to ensure accurate measurement of the TPA cross-section. The fluorescence kinetic decay traces for all gold clusters are measured with both one- and two-photon excitation. Using the ratio of the relative counts per

second at 100 fs time delay, the TPA cross-sections for all the gold clusters are determined. Absolute TPA cross-sections observed for the gold clusters are much larger than any of the experimentally investigated organic macromolecules or semiconductor nanocrystals.⁹ The TPA cross-section for Au₂₅ is 427,000 GM and Au₃₀₉ 1,476,000 GM, much larger compared to a typical value of approximately 1000 GM at 800 nm for organic macromolecules. The large TPA cross-sections prophet the application of MPCs in optical power limiting, nanolithography, and multiphoton biological imaging. Comparisons of the two-photon cross sections of various MPCs also reveal scaling laws regarding core size and two-photon absorption cross-section (Figure 7a). There are two different trends, one for nanoclusters and the other nanoparticles. For nanoclusters, an increase in size is accompanied by an increase of the total two-photon cross-section. Nanoparticles Au₉₇₆ and Au₂₄₀₆ follow a separate but similar trend. Analysis of the cross-section per atom (Figure 7b) reveals that the cross-section decreases with increasing cluster size. However, the correlation of size vs. cross-section is much smaller for nanoparticles.

Results from our fluorescence life-time measurements and two-photon cross-sections clearly demonstrate that there are differences between nanoclusters and nanoparticles. The distinction occurs at 2.2 nm. Au nanoclusters are a promising imaging tool because of their large two-photon cross-section. In addition, the lifetime and cross-section trends demonstrate the difference between the two nanosystems with a clear divide at about 2.2 nm, supporting the quantum size effect. The very large cross section for Au nanoclusters in the infrared IR spectral regions hold tremendous potential as an imaging tool, due to the fact that two-photon excitation in the IR region would allow for much deeper penetration into tissues with lower overall energy,^{9,20} which is a very desirable trait for medical imaging.

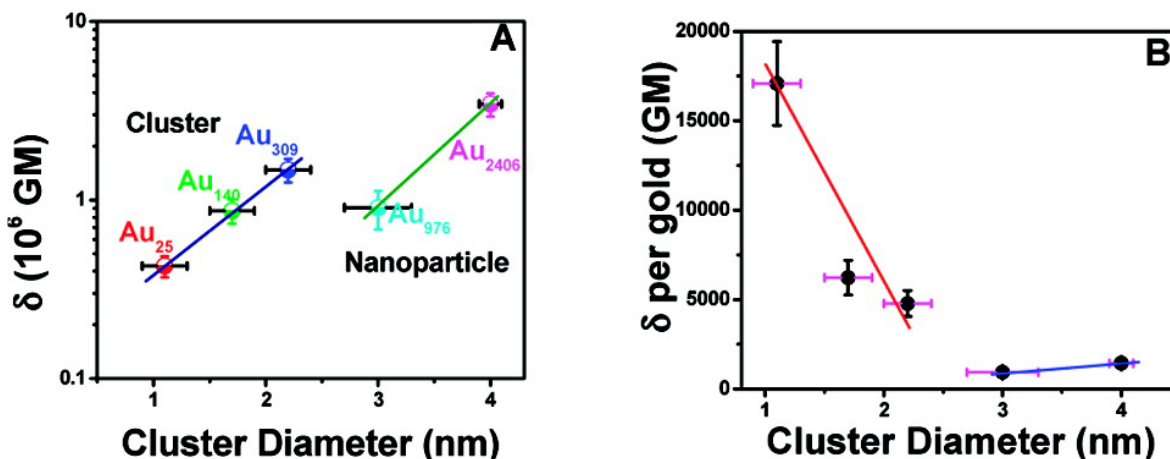


Figure 7. A) TPA cross sections for Au₂₅ to Au₂₄₀₆ using two-photon excited fluorescence up-conversion. B) The TPA cross section calculated per atom. Red is for nanoclusters and blue is for nanoparticles.⁹

D. Transient Electronic Effects in Gold Nanoclusters

Transient absorption spectroscopy in the femtosecond scale allows for the study of energy states. The system is first excited by a pump pulse and the excited state absorption is measured by the probe pulse and compared to the ground state absorption. The transient absorption of nanoparticles and nanoclusters has been studied previously.^{7,17,26,49,50} Our group focuses on the degenerate transient absorption (same wavelength pump and probe) as well as multi-color transient absorptions (450 nm – 750nm) of Au₂₅, Au₅₅ and Au₁₄₀.^{7,26} Transient absorption spectra of Au₂₅, Au₅₅ and Au₁₄₀ are compared at a time delay of 550 fs in figure 8.⁷ The characteristic SPR at 530 nm is not observed for the three nanoclusters. Excited state absorption (ESA) occurs at 500 nm and 675 nm. The analysis of transient dynamics of Au₂₅ nanoclusters with different charges (0,-1)⁴⁹ shows that the ESA signal near 670 nm can be bleached after 1 ns. This signal corresponds to the HOMO-LUMO transition in the Au core^{7,26,27}. Comparison of the various Au nanoclusters emphasizes a positive correlation between the absorption and the core size, which we believe to be related to the quantum size effect.⁷ The kinetic trace at 640 nm for Au₅₅ (Figure 9) exhibits a quick initial relaxation to the intermediate state and then a slow decay back to the ground state. This decay profile is analogous to molecular-like systems with single electron relaxation processes.^{7,16,50,16,55} Based on the work of Miller et al²⁶ and Qian et al⁴⁹, the observed dynamics of the nanoclusters suggest

a core-core HOMO-LUMO charge transfer (~ 1 ps) followed by a core-shell charge transfer (>1 ns).⁴⁹ However, the dynamics of the nanoparticles are very different from those associated with nanoclusters. Nanoparticles' transient signals follow Auger type kinetics, and the mechanism of relaxation is related to electron-phonon processes.^{7,16,44}

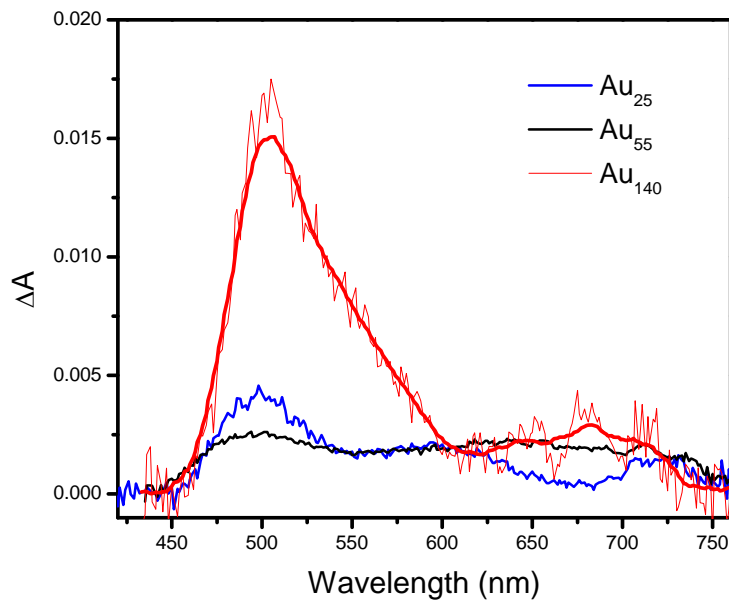


Figure 8: Transient absorption for Au₂₅, Au₅₅ and Au₁₄₀, at 550 fs.⁷

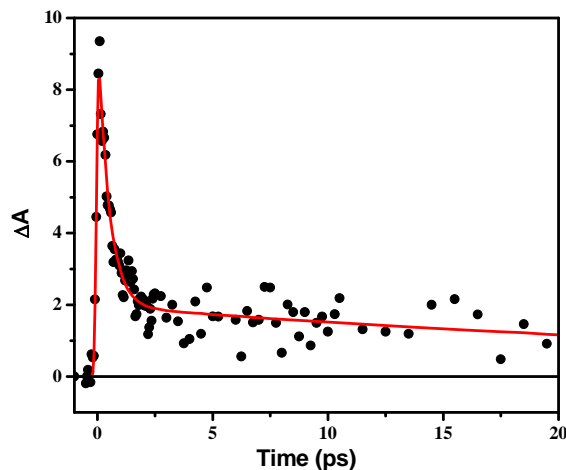


Figure 9: The kinetic trace from transient absorption for Au₅₅ at 640nm.⁷

Detailed analysis of the transient data also uncovers additional information about Au nanoclusters. The analysis of the transient absorption data in literature^{7,26} showed that the

bleaching observed at ~ 670 nm corresponds to a HOMO-LUMO absorption peak and can be assigned to the ground state bleach. In our experiments, we observed an additional bleach near 550 nm (Figure 11,12). This can be correlated to the weak shoulder observed in the steady state absorption spectrum (Figure 12).⁷ Using the same analysis, the bleach at 550 nm could be another ground state for the Au₂₅ system.⁷ In addition to the transient absorption comparison, the pump power dependence for Au₅₅ is also investigated to probe electron-electron and electron-phonon relaxation processes.⁷ Electron-electron scattering for the gold nanoparticles is attributed to the sharing of energy by excited electrons, followed by the thermal relaxation of the electronic gas^{16,44} and is weakly power dependent.⁷ Electron-phonon relaxation corresponds to the transfer of energy from electron system to the lattice.¹⁶ Larger nanoparticles exhibit electron-phonon relaxations which depend strongly on pump power.⁷ We do not observe these phenomena for nanoclusters because of their discrete energy levels (Figure 10).⁷

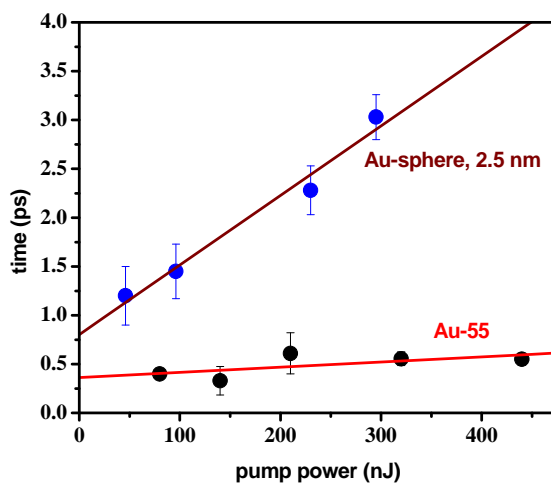


Figure 10: Pump power dependence against average life time for 2.5nm nanoparticle and Au₅₅ (1.4nm).⁷

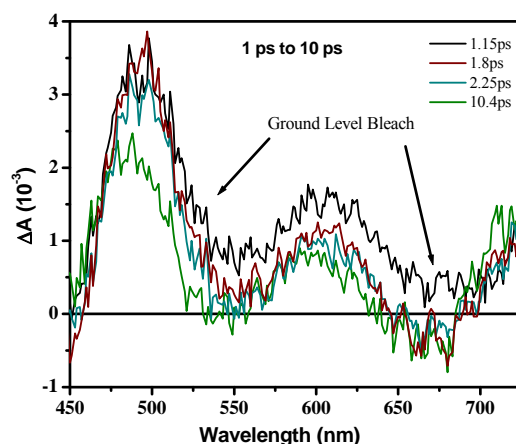


Figure 11: Transient absorption of Au₂₅ in hexane, probed from 450nm to 750nm. Ground level bleach can be observed at 550 nm and 675 nm.⁷

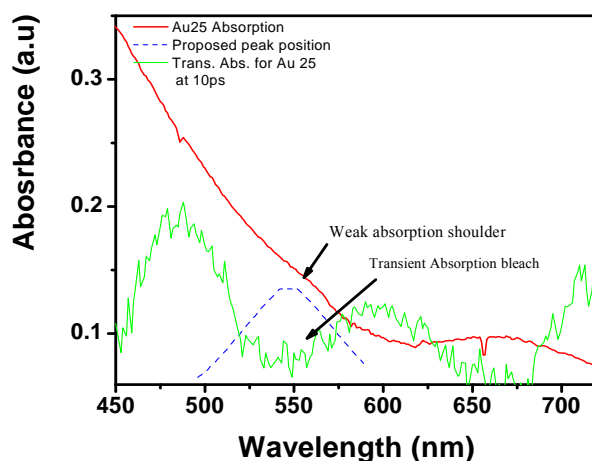


Figure 12: Steady state absorption compared to transient absorption for Au₂₅, with ground level bleach at 550 nm.⁷

Using degenerate pump-probe experiments, the excited state dynamics of the MPCs can be measured in a high time resolution.^{7,50} Acoustic modes and their excitation characteristics in nanomaterials contain important information about the structure, geometry, and their interactions with the environment. The structural assignment of both Au₇ and Au₂₀ in the gas phase is accomplished using vibrational spectroscopy, and it is also theoretically predicted that the nature of internal vibrational energy redistribution is a

key factor in promoting reactivity of small gold clusters.⁵¹ For gold nanoclusters with polypeptide chains, vibration transfer in the THz range has been predicted using molecular dynamics simulations.⁵² Coherently excited “breathing” vibrational modes for gold nanoparticles are proposed with a response time spanning from a few picoseconds to tens of picoseconds.^{53–56} The breathing mode frequency is also inversely proportional to the particle size. The mechanism for such breathing mode in nanoparticles can be explained by the impulsive heating of the particle lattice after short pulse laser excitation.^{53–55}

Our degenerate transient pump-probe^{44,57} detected oscillations with a period of ~ 450 fs (2.2 THz),⁵⁰ which compares well to a low-frequency vibrational density of states theoretically calculated for gold clusters.^{58,59} The fast oscillation period is similar to oscillatory features reported for Au₅ in femtosecond photoelectron spectroscopy experiment.⁵⁸ Based on the oscillatory period, the mechanism is different than nanoparticles and is more closely related to semiconductors and/or molecular systems.⁶⁰ Compare to the lack of oscillatory features for nanoparticles, the appearance of the oscillations for small MPCs can be correlated to the emergence of an optical energy gap near the Fermi level.⁵⁰ Au nanoclusters of various sizes were tested (Figure 13b) and showed frequency independent breathing mode. The lack of size correlation may be an indication that the oscillatory feature is a shared core phenomenon.

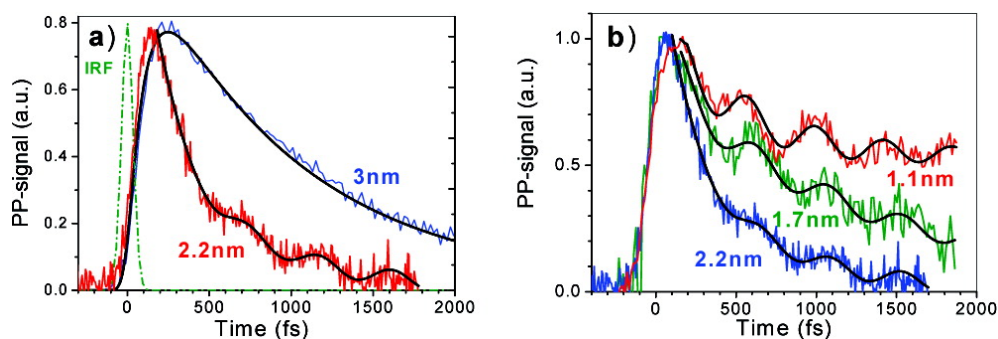


Figure 13: A) Degenerate pump-probe experiment on Au MPCs shows clear oscillatory features for nanoclusters. B) Comparison of oscillatory features of nanoclusters of various sizes.⁵⁰

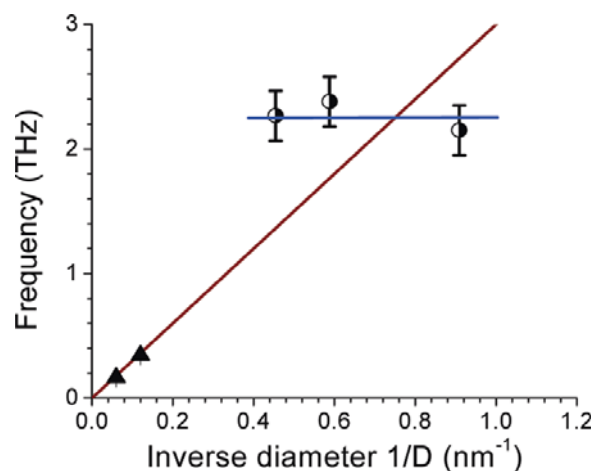


Figure 14: Acoustic vibration frequency size dependence. Solid triangles are frequencies of the “breathing” vibrational modes previously observed for larger gold particles. Solid brown line is the classical mechanical calculations for the elastic gold sphere. Horizontal blue solid line is a guide to the eye.⁵⁰

Summary

Monolayered protected clusters have unique physical and optical properties. The steady state absorption and emission illustrated the quantum size effect of MPCs. The dual emission nature for MPCs confirmed the super atom nature of these materials. Based on various ultrafast spectroscopy techniques, different mechanisms were proposed to explain the visible and infrared emissions of MPCs. Time resolved fluorescence spectroscopy serves as proof for the weak emission in the visible region for Au₅₅. The quantum yields in the visible region are five orders of magnitude larger than that of bulk gold; this emission enhancement is due to the discrete energy levels in the metal core, not the SPR. Very large two photon cross-sections were observed for Au MPCs, which suggests future applications of MPCs as an optical limiting material. Experimental evidence indicated that the size distinction between nanoparticles and nanoclusters is ~2.2 nm. Transient absorptions results identified an additional ground state absorption that has not been observed previously. The vibrational breathing mode found in degenerate transient absorption shows no size dependence on the mode frequencies and could be used in the characterization of nanoclusters. Overall, our optical studies yield many interesting results and also raised many more interesting questions. One of the biggest challenges ahead will be the refinement of unified laws (such as the super atom theory)

that govern all nanoclusters, and investigate in detail the relationship between the metal core and its environment. The field of MPCs is still at its infancy, with many application and fundamental science yet to be explored and we look forward to the new discoveries and opportunities ahead.

Acknowledgments

We would like to thank the Army Research Office (Materials program) and the National Science Foundation (Polymer program) for support of this work.

Reference

- (1) Mie, G. Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. *Annalen der Physik* **1908**, 330, 377–445.
- (2) Kubo, R.; Kawabata, A.; Kobayashi, S. Electronic properties of small particles. *Annual Review of Materials ...* **1984**, 49–66.
- (3) Chen, S. Gold Nanoelectrodes of Varied Size: Transition to Molecule-Like Charging. *Science* **1998**, 280, 2098–2101.
- (4) Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. 28 kDa Alkanethiolate-Protected Au Clusters Give Analogous Solution Electrochemistry and STM Coulomb Staircases. *Journal of the American Chemical Society* **1997**, 119, 9279–9280.
- (5) Schaaff, T. G.; Shafiqullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L.; Cullen, W. G.; First, P. N.; Gutiérrez-Wing, C.; Ascensio, J.; Jose-Yacamán, M. J. Isolation of Smaller Nanocrystal Au Molecules: Robust Quantum Effects in Optical Spectra. *The Journal of Physical Chemistry B* **1997**, 101, 7885–7891.
- (6) Jin, R. Quantum sized, thiolate-protected gold nanoclusters. *Nanoscale* **2010**, 2, 343–62.
- (7) Yau, S. H.; Varnavski, O.; Gilbertson, J. D.; Chandler, B.; Ramakrishna, G.; Goodson, T. Ultrafast Optical Study of Small Gold Monolayer Protected Clusters: A Closer Look at Emission †. *The Journal of Physical Chemistry C* **2010**, 114, 15979–15985.
- (8) Wang, G.; Huang, T.; Murray, R. W.; Menard, L.; Nuzzo, R. G. Near-IR luminescence of monolayer-protected metal clusters. *Journal of the American Chemical Society* **2005**, 127, 812–3.

- (9) Ramakrishna, G.; Varnavski, O.; Kim, J.; Lee, D.; Goodson, T. Quantum-sized gold clusters as efficient two-photon absorbers. *Journal of the American Chemical Society* **2008**, *130*, 5032–3.
- (10) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. Correlating the crystal structure of a thiol-protected Au₂₅ cluster and optical properties. *Journal of the American Chemical Society* **2008**, *130*, 5883–5.
- (11) Devadas, M. S.; Bairu, S.; Qian, H.; Sinn, E.; Jin, R.; Ramakrishna, G. Temperature-Dependent Optical Absorption Properties of Monolayer-Protected Au₂₅ and Au₃₈ Clusters. *The Journal of Physical Chemistry Letters* **2011**, *2*, 2752–2758.
- (12) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafiqullin, M.; Vezmar, I.; Whetten, R. L. Critical sizes in the growth of Au clusters. *Chemical Physics Letters* **1997**, *266*, 91–98.
- (13) Ackerson, C. J.; Jadzinsky, P. D.; Kornberg, R. D. Thiolate ligands for synthesis of water-soluble gold clusters. *Journal of the American Chemical Society* **2005**, *127*, 6550–1.
- (14) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. Monolayer-Protected Cluster Molecules. *Accounts of Chemical Research* **2000**, *33*, 27–36.
- (15) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. A unified view of ligand-protected gold clusters as superatom complexes. *Proceedings of the National Academy of Sciences of the United States of America* **2008**, *105*, 9157–62.
- (16) Varnavski, O.; Ispasoiu, R. G.; Balogh, L.; Tomalia, D.; Goodson, T. Ultrafast time-resolved photoluminescence from novel metal–dendrimer nanocomposites. *The Journal of Chemical Physics* **2001**, *114*, 1962.
- (17) Varnavski, O.; Ramakrishna, G.; Kim, J.; Lee, D.; Goodson, T. Critical size for the observation of quantum confinement in optically excited gold clusters. *Journal of the American Chemical Society* **2010**, *132*, 16–7.
- (18) Murray, R. W. Nanoelectrochemistry: metal nanoparticles, nanoelectrodes, and nanopores. *Chemical reviews* **2008**, *108*, 2688–720.
- (19) Hicks, J. F.; Miles, D. T.; Murray, R. W. Quantized Double-Layer Charging of Highly Monodisperse Metal Nanoparticles. *Journal of the American Chemical Society* **2002**, *124*, 13322–13328.
- (20) Rosi, N. L.; Mirkin, C. A. Nanostructures in biodiagnostics. *Chemical reviews* **2005**, *105*, 1547–62.

- (21) Daniel, M.-C.; Astruc, D. Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Reviews* **2004**, *104*, 293–346.
- (22) Knight, W.; Clemenger, K.; De Heer, W.; Saunders, W.; Chou, M.; Cohen, M. Electronic Shell Structure and Abundances of Sodium Clusters. *Physical Review Letters* **1984**, *52*, 2141–2143.
- (23) Gilbertson, J. D.; Vijayaraghavan, G.; Stevenson, K. J.; Chandler, B. D. Air and water free solid-phase synthesis of thiol stabilized au nanoparticles with anchored, recyclable dendrimer templates. *Langmuir*: the ACS journal of surfaces and colloids **2007**, *23*, 11239–45.
- (24) Schmid, G. The relevance of shape and size of Au₅₅ clusters. *Chemical Society reviews* **2008**, *37*, 1909–30.
- (25) Pyykkö, P. Theoretical chemistry of gold. III. *Chemical Society reviews* **2008**, *37*, 1967–97.
- (26) Miller, S. A.; Womick, J. M.; Parker, J. F.; Murray, R. W.; Moran, A. M. Femtosecond Relaxation Dynamics of Au₂₅L₁₈ – Monolayer-Protected Clusters. *The Journal of Physical Chemistry C* **2009**, *113*, 9440–9444.
- (27) Aikens, C. M. Origin of Discrete Optical Absorption Spectra of M₂₅(SH)₁₈ – Nanoparticles (M = Au, Ag). *The Journal of Physical Chemistry C* **2008**, *112*, 19797–19800.
- (28) Aikens, C. M. Effects of core distances, solvent, ligand, and level of theory on the TDDFT optical absorption spectrum of the thiolate-protected Au(25) nanoparticle. *The journal of physical chemistry. A* **2009**, *113*, 10811–7.
- (29) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. Synthesis and reactions of functionalised gold nanoparticles. *Journal of the Chemical Society, Chemical Communications* **1995**, 1655.
- (30) Brust, M.; Schiffrin, D. J.; Bethell, D.; Kiely, C. J. Novel gold-dithiol nano-networks with non-metallic electronic properties. *Advanced Materials* **1995**, *7*, 795–797.
- (31) Wu, Z.; Suhan, J.; Jin, R. One-pot synthesis of atomically monodisperse, thiol-functionalized Au₂₅ nanoclusters. *Journal of Materials Chemistry* **2009**, *19*, 622.
- (32) Negishi, Y.; Takasugi, Y.; Sato, S.; Yao, H.; Kimura, K.; Tsukuda, T. Magic-numbered Au(n) clusters protected by glutathione monolayers (n = 18, 21, 25, 28, 32, 39): isolation and spectroscopic characterization. *Journal of the American Chemical Society* **2004**, *126*, 6518–9.

- (33) Shibu, E. S.; Muhammed, M. A. H.; Tsukuda, T.; Pradeep, T. Ligand Exchange of Au₂₅SG₁₈ Leading to Functionalized Gold Clusters: Spectroscopy, Kinetics, and Luminescence. *Journal of Physical Chemistry C* **2008**, *112*, 12168–12176.
- (34) Briant, C. E.; Theobald, B. R. C.; White, J. W.; Bell, L. K.; Mingos, D. M. P.; Welch, A. J. Synthesis and X-ray structural characterization of the centred icosahedral gold cluster compound [Au₁₃(PMe₂Ph)₁₀Cl₂](PF₆)₃; the realization of a theoretical prediction. *Journal of the Chemical Society, Chemical Communications* **1981**, 201.
- (35) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution. *Science (New York, N.Y.)* **2007**, *318*, 430–3.
- (36) Negishi, Y.; Nobusada, K.; Tsukuda, T. Glutathione-protected gold clusters revisited: bridging the gap between gold(I)-thiolate complexes and thiolate-protected gold nanocrystals. *Journal of the American Chemical Society* **2005**, *127*, 5261–70.
- (37) Tracy, J. B.; Crowe, M. C.; Parker, J. F.; Hampe, O.; Fields-Zinna, C. A.; Dass, A.; Murray, R. W. Electrospray ionization mass spectrometry of uniform and mixed monolayer nanoparticles: Au₂₅[S(CH₂)₂Ph]₁₈ and Au₂₅[S(CH₂)₂Ph]_{18-x}(SR)_x. *Journal of the American Chemical Society* **2007**, *129*, 16209–15.
- (38) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. Crystal structure of the gold nanoparticle [N(C₈H₁₇)₄][Au₂₅(SCH₂CH₂Ph)₁₈]. *Journal of the American Chemical Society* **2008**, *130*, 3754–5.
- (39) Akola, J.; Walter, M.; Whetten, R. L.; Häkkinen, H.; Grönbeck, H. On the structure of thiolate-protected Au₂₅. *Journal of the American Chemical Society* **2008**, *130*, 3756–7.
- (40) Iwasa, T.; Nobusada, K. Theoretical Investigation of Optimized Structures of Thiolated Gold Cluster [Au₂₅(SCH₃)₁₈]⁺. *Journal of Physical Chemistry C* **2007**, *111*, 45–49.
- (41) Jiang, D.; Luo, W.; Tiago, M. L.; Dai, S. In Search of a Structural Model for a Thiolate-protected Au₃₈ Cluster. *Journal of Physical Chemistry C* **2008**, *112*, 13905–13910.
- (42) Lopez-Acevedo, O.; Tsunoyama, H.; Tsukuda, T.; Häkkinen, H.; Aikens, C. M. Chirality and electronic structure of the thiolate-protected Au₃₈ nanocluster. *Journal of the American Chemical Society* **2010**, *132*, 8210–8.

- (43) Negishi, Y.; Chaki, N. K.; Shichibu, Y.; Whetten, R. L.; Tsukuda, T. Origin of magic stability of thiolated gold clusters: a case study on Au₂₅(SC₆H₁₃)₁₈. *Journal of the American Chemical Society* **2007**, *129*, 11322–3.
- (44) Varnavski, O.; Goodson, T.; Mohamed, M.; El-Sayed, M. Femtosecond excitation dynamics in gold nanospheres and nanorods. *Physical Review B* **2005**, *72*, 235405–.
- (45) Lee, D.; Donkers, R. L.; Wang, G.; Harper, A. S.; Murray, R. W. Electrochemistry and optical absorbance and luminescence of molecule-like Au₃₈ nanoparticles. *Journal of the American Chemical Society* **2004**, *126*, 6193–9.
- (46) De Heer, W. The physics of simple metal clusters: experimental aspects and simple models. *Reviews of Modern Physics* **1993**, *65*, 611–676.
- (47) Parker, J. F.; Fields-Zinna, C. A.; Murray, R. W. The story of a monodisperse gold nanoparticle: Au₂₅L₁₈. *Accounts of chemical research* **2010**, *43*, 1289–96.
- (48) Wang, G.; Guo, R.; Kalyuzhny, G.; Choi, J.-P.; Murray, R. W. NIR luminescence intensities increase linearly with proportion of polar thiolate ligands in protecting monolayers of Au₃₈ and Au₁₄₀ quantum dots. *The journal of physical chemistry. B* **2006**, *110*, 20282–9.
- (49) Qian, H.; Y. Sfeir, M.; Jin, R. Ultrafast Relaxation Dynamics of [Au₂₅(SR)₁₈] q Nanoclusters: Effects of Charge State. *The Journal of Physical Chemistry C* **2010**, *114*, 19935–19940.
- (50) Varnavski, O.; Ramakrishna, G.; Kim, J.; Lee, D.; Goodson, T. Optically excited acoustic vibrations in quantum-sized monolayer-protected gold clusters. *ACS nano* **2010**, *4*, 3406–12.
- (51) Mitrić, R.; Bürgel, C.; Bonacić-Koutecký, V. Reactivity-promoting criterion based on internal vibrational energy redistribution. *Proceedings of the National Academy of Sciences of the United States of America* **2007**, *104*, 10314–7.
- (52) Miao, L.; Seminario, J. M. Molecular Dynamics Simulations of the Vibrational Signature Transfer from a Glycine Peptide Chain to Nanosized Gold Clusters. *Journal of Physical Chemistry C* **2007**, *111*, 8366–8371.
- (53) Hartland, G. V Coherent excitation of vibrational modes in metallic nanoparticles. *Annual review of physical chemistry* **2006**, *57*, 403–30.
- (54) Voisin, C.; Del Fatti, N.; Christofilos, D.; Vallée, F. Ultrafast Electron Dynamics and Optical Nonlinearities in Metal Nanoparticles. *The Journal of Physical Chemistry B* **2001**, *105*, 2264–2280.

- (55) Hodak, J. H.; Henglein, A.; Hartland, G. V. Size dependent properties of Au particles: Coherent excitation and dephasing of acoustic vibrational modes. *The Journal of Chemical Physics* **1999**, *111*, 8613.
- (56) Plech, A.; Cerna, R.; Kotaidis, V.; Hudert, F.; Bartels, A.; Dekorsy, T. A surface phase transition of supported gold nanoparticles. *Nano letters* **2007**, *7*, 1026–31.
- (57) Varnavski, O.; Goodson, T.; Sukhomlinova, L.; Twieg, R. Ultrafast Exciton Dynamics in a Branched Molecule Investigated by Time-Resolved Fluorescence, Transient Absorption, and Three-Pulse Photon Echo Peak Shift Measurements †. *The Journal of Physical Chemistry B* **2004**, *108*, 10484–10492.
- (58) Stanzel, J.; Burmeister, F.; Neeb, M.; Eberhardt, W.; Mitrić, R.; Bürgel, C.; Bonacić-Koutecký, V. Size-dependent dynamics in excited states of gold clusters: from oscillatory motion to photoinduced melting. *The Journal of chemical physics* **2007**, *127*, 164312.
- (59) Sun, D.; Gong, X.; Wang, X.-Q. Soft and hard shells in metallic nanocrystals. *Physical Review B* **2001**, *63*, 193412.
- (60) Zeiger, H.; Vidal, J.; Cheng, T.; Ippen, E.; Dresselhaus, G.; Dresselhaus, M. Theory for displacive excitation of coherent phonons. *Physical Review B* **1992**, *45*, 768–778.

Biographical information

Sung Hei Yau received his B.S in Chemistry from University of Michigan in 2003 and later returned to Michigan to pursue his Ph.D in Chemistry. Sung Hei met Professor Goodson during his undergraduate study and has been working closely with Professor Goodson ever since. Optical properties of nanoclusters have been a major focus of his work at Michigan using ultrafast systems. Sung Hei Yau received a Chemistry Research Excellence Awards fellowship from the Department of Chemistry, Best Paper Award at the 16th International Conference on Luminescence and a travel award at the Vaughan symposium.

Oleg Varnavski is a senior research associate at the Goodson Group. He received his Master of Science from the Moscow Institute of Physics and Technology in 1974 and his Ph.D. at the P.N. Lebedev Physics Institute of Russian Academy of Sciences. After receiving his PhD at Physics Institute he received the Alexander von Humboldt Fellowship (Germany) and worked at Stuttgart University. His research interests include excited state dynamics, relaxation processes, energy transfer processes in complex macromolecules (coherent and incoherent), multiphoton absorption, optical properties of metal nanocomposites and nanoclusters.

Theodore Goodson III is the Richard Bernstein Professor of Chemistry at the University of Michigan. He has received numerous awards including the Army Research Office Young Investigator Award, the National Science Foundation Career Award, Lloyd Ferguson Yong Scientist Award, the Percy Julian Award, The University Distinguished Faculty Achievement Award, and many others. After receiving his Ph.D. at the University of Nebraska, he went on to postdoctoral positions at the University of Chicago and University of Oxford. Using various spectroscopic techniques, the Goodson Group focuses on the investigation of optical properties and applications of novel organic macromolecular materials and metal nano-materials.