

Ultrafast study of electronic relaxation dynamics in Au₁₁ nanoclusters

Christian D. Grant^a, Adam M. Schwartzberg^a, Yiyun Yang^b,
Shaowei Chen^b, Jin Z. Zhang^{a,*}

^a Department of Chemistry, University of California at Santa Cruz, 1156, High Street, Santa Cruz, CA 95064, USA

^b Department of Chemistry, Southern Illinois University, Carbondale, IL 62901 USA

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Abstract

Ultrafast electronic relaxation measurements in thiol-capped Au₁₁ reveal an excited state lifetime of >500 ps, similar to Au₁₃ and Au₂₈. Upon extended exposure to laser light, a small amplitude, fast relaxation component was observed and attributed to formation of larger particles or aggregates. The long lifetime, combined with a lack of excitation intensity dependence, indicates that Au₁₁ behaves more molecule-like rather than a typical, bulk-like gold metal nanoparticle. The main relaxation pathway is proposed to be non-radiative mediated by a large number of surface trap states.

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1. Introduction

Electronic relaxation dynamics in metal nanoparticles occur on the ultrafast time scales and have been studied using femtosecond laser spectroscopy. Initial studies were first conducted on gold [1], silver [2] and copper [3] nanoparticles. Subsequent investigations have been performed on a number of metal nanoparticle systems, including Au [4–10], Ag [10–12], Sn [13], Pt [5,14], Cu [15,16], and Ga [17]. The relaxation time in most of these metal nanoparticles has been found to be on the order of a few ps, which was not significantly different from that in bulk metal. The relaxation is dominated by electron–phonon interaction. Most of these studies are done on nanoparticles that contain at least several hundred to several thousand atoms per particle with excitation near the surface plasmon absorption band. The similar relaxation times between these relatively large nanoparticles and bulk metal indicate that these nanoparticles have bulk-like metal properties.

One fundamental issue of interest is the possible size dependence of electronic relaxation, especially when the size is very small, e.g. with a few or few tens of atoms per

particle or cluster. It is expected that when the size is small enough a metal to non-metal (molecule) transition should occur. There is some evidence that this transition happens for Au clusters of less than 55 atoms [18]. There is also evidence of a metal to molecule transition between 55 to 13 atoms for Au in the study of the relaxation times [5]. The relaxation time was much longer in Au₁₃ than in Au₅₅, which is taken as evidence that Au₁₃ is molecule-like while Au₅₅ is still more like bulk Au metal. A more recent study of Au₂₈ clusters capped with glutathione molecules has found a double exponential relaxation with a subpicosecond component and a longer ns component [19]. The fast component was assigned to relaxation from a higher lying excited state populated by the 400 nm excitation to a lower electronic state. The longer nanosecond component was attributed to the radiative lifetime of the first excited state of the Au₂₈ clusters [20].

In this Letter, we report the first measurement of electronic relaxation dynamics in possibly the smallest stable Au cluster, Au₁₁ (~0.8 nm diameter), capped with different thiol agents. The data reveal a lifetime that is similar to that previously observed for Au₁₃ and Au₂₈ clusters. This further supports the conjecture that very small metal clusters are molecule-like and their excited electronic state lifetime is relatively long (>500 ps).

* Corresponding author. Fax: +831-459-2935.

E-mail address: zhang@chemistry.ucsc.edu (J.Z. Zhang).

2. Experimental

Au₁₁ thiol clusters were synthesized by a procedure already published [21]. Thiol capping agents used are as follows: 4-nitrothiol phenol (NTP), 4-hydroxythiol phenol (HTP), *n*-dodecanethiol (SC₁₂), and SC₂H₄Ph (ETP). The thiol capped gold clusters have a core diameter of 0.8 nm as determined from TEM and UV–Vis spectroscopy [21,22]. Particle composition was also performed via elemental analysis which verified stoichiometry as that of Au₁₁ [21].

Transient absorption measurements were performed using a regeneratively amplified, mode locked femtosecond Ti-Sapphire laser [23]. Pulses of approximately 50 fs duration and 4 nJ/pulse energy at a repetition rate of 100 MHz were generated and amplified in a Ti-sapphire regenerative amplifier using chirped-pulse amplification. The final output pulses were typically 150 fs with a pulse energy of 250 μJ, centered at 780 nm at 1 kHz. The amplified output was doubled in a 1 mm BBO crystal to generate 30 μJ/pulse of 390 nm light, which was used as a pump source to excite the sample contained in a quartz cell. The remaining fundamental was focused onto quartz to generate a white light continuum and the desired probe wavelength was selected using an interference band-pass filter. The probe beam was split into a signal and reference, which were detected by two photodiodes. Pulse to pulse fluctuation was eliminated by dividing the signal by reference for each laser shot. The time delay between pump and probe was controlled by a translation stage. The pump and probe beams were focused with a 10 cm focal length lens and cross overlapped over a spot size of 1mm² in the sample before the focal point. The pump power was attenuated such that there was no signal observed from the pure solvent due to multiphoton ionization.

3. Results and discussion

Fig. 1 shows representative ground state electronic absorption spectra of Au₁₁ nanoclusters with different capping agents. What is immediately apparent is the lack of the surface plasmon resonance near 520 nm typical of larger gold nanoparticles [24]. As the metal particle size decreases and approaches the mean free path of the electrons in bulk gold, more scattering between electrons and the surface takes place. This damps the coherent motion of the electrons and affects the dielectric constant of the metal, and results in broadening and blue shifting the plasmon [24]. In addition to the lack of a surface plasmon, there is significant structure to the UV–Visible spectra that is indicative of molecule-like features of the clusters [18]. Three main features are of interest for the Au₁₁ clusters capped with NTP and SC₁₂. First, there is a strong absorption at approxi-

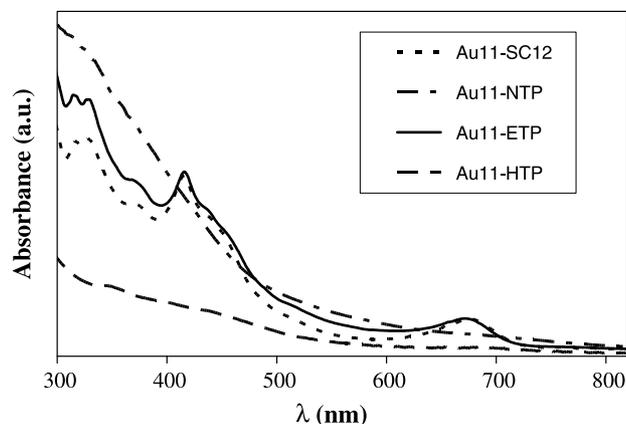


Fig. 1. Static ground state electronic absorption spectra of Au₁₁ clusters capped with different thiol capping agents.

mately 676 nm, which has been attributed to an excitonic transition similar to semiconductor quantum dots and reflects the band gap of the particle. The band gap of the undecagold (SC₁₂) was found to be ~1.8 eV by electrochemical and spectroscopic measurements [21]. Secondly, there are two higher energy transitions at 370 and 416 nm. These absorption bands were attributed to interband electronic transitions [21]. The structures in the absorption spectra are dependent on the capping agents of the Au₁₁ clusters. This could possibly be due to the change in the lattice as well as electronic structures of the clusters induced by the capping agents. Further studies are needed to better understand the origin of this dependence.

Fig. 2 shows representative short (top) and long (bottom) time scale transient absorption profiles of the excited state relaxation dynamics of Au₁₁ capped with *n*-dodecanethiol probed at 790 nm following excitation at 390 nm with excitation power of ~6 μJ/pulse. The decay can be fit to a single exponential with a lifetime of 526 ps. However, the experimental window was only 660 ps we cannot claim that the lifetime is not actually longer than what the fit to the data yielded. Most interesting is that there is no fast component (few ps) to the overall decay in contrast to Au₁₃ and Au₂₈ nanoclusters [5,19] as well as to larger gold nanoparticles [25]. In the Au₁₃ study, the small initial fast component (~1 ps) was attributed to aggregates of Au₁₃ clusters, while the fast (~750 fs) component in the Au₂₈ clusters was attributed the initial relaxation from a higher lying excited state populated by 400 nm excitation to a lower lying electronic state. The single component long lifetime observed here for Au₁₁ is tentatively assigned to the lifetime of the excited electronic state reached by the 390 nm excitation. Similar excited state lifetimes (~500 ps) have been found for Au₁₁ clusters with the other capping agents. The experiments were repeated for different fresh samples and the results are reproducible.

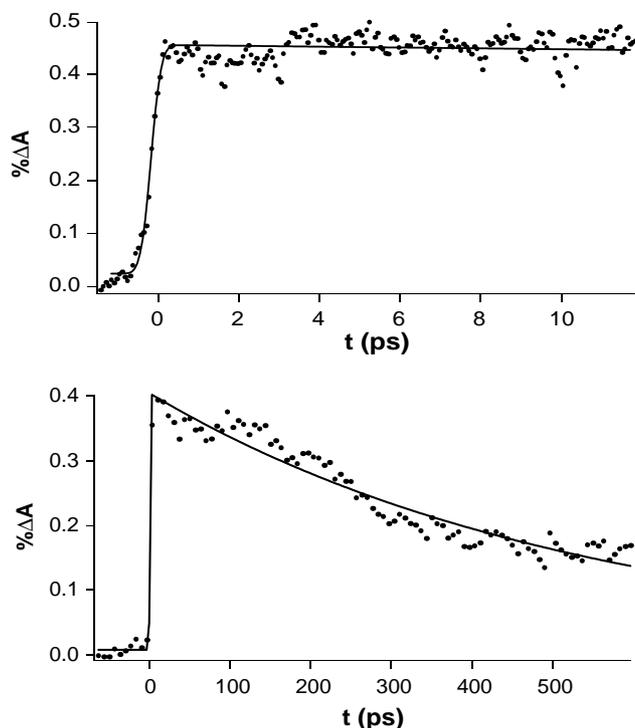


Fig. 2. Representative transient absorption profiles (dotted lines) of excited state decay of Au_{11} clusters capped with *n*-dodecanethiol on the short (top) and long (bottom) time scales. Single exponential fits are shown in solid lines. The nanoclusters were excited at 390 nm and probed at 790 nm with excitation intensity 2.5 $\mu\text{J}/\text{pulse}$.

It was noted that upon exposure to laser light at 390 nm for a period of hours, a small amplitude, fast decay component (~ 1 ps) appeared in the transient absorption data (not shown). This is possibly due to formation of aggregates or larger particles as a result of photoexcitation of the Au_{11} clusters, e.g. photodetachment of the protecting ligand. Only 3–5 Au_{11} clusters would need to aggregate in order to start to show the 1 ps fast component present in larger Au nanoparticles since the metal to non-metal transition appears to occur in the 28–55 gold atom range [5,19]. However, since there were no major changes in the ground state electronic absorption spectrum after laser irradiation, the number of larger particles or aggregates formed must be relatively small compared to the number of Au_{11} clusters. To obtain results as those shown in Fig. 2, the data were collected from fresh samples and before the fast component started to appear.

In larger gold nanoparticles (diameter > 2 nm) with excitation of interband transitions, a continuum of states are excited and undergo rapid (< 150 fs [2]) equilibration with other excited states via electron–electron scattering, the subsequent fast ~ 1 ps decay is primarily due to electron–phonon interaction. This decay is also strongly excitation intensity dependent, slower at higher excitation intensities, due to the tem-

perature dependant electronic heat capacity [25]. For all Au_{11} clusters studied here, 390 nm excitation probably involves a transition to an individual electronic state due to the discretization of electronic states in small clusters (separation of the metal conduction band into a semiconductor type valence and conduction band in the solid state band picture) and the relaxation time measured by the probe pulse is therefore the lifetime of the excited state and not cooling of hot electrons. This lifetime was found to be independent of the excitation intensity (shown in Fig. 3) in the range studied (2.5–6 $\mu\text{J}/\text{pulse}$), which is similar to Au_{13} and Au_{28} but in contrast to larger Au nanoparticles. The Au_{11} clusters have also been shown to fluoresce [21], which is consistent with the observed relatively long lifetime of the excited electronic state (526 ps as a lower limit). However, the fluorescence quantum yield was estimated to be $\sim 10^{-8}$ which is 5 orders of magnitude smaller than clusters of 28 gold atoms capped with glutathione. It has been suggested that these Au_{11} clusters behave much like indirect bandgap semiconductors with a significant amount of surface trap states [21]. In this case, the primary relaxation pathway in Au_{11} is proposed to be non-radiative mediated through a large amount of surface trap states. The relative long lifetime and lack of power dependence strongly suggest that Au_{11} is primarily molecular in character, instead of bulk metal like.

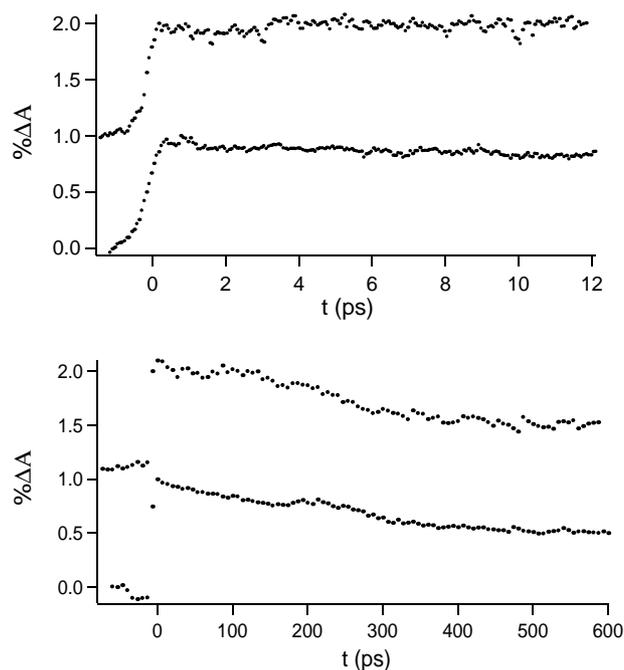


Fig. 3. Representative transient absorption profiles at two different excitation intensities (top trace: 2.5 $\mu\text{J}/\text{pulse}$ and bottom trace: 6.0 $\mu\text{J}/\text{pulse}$) normalized and offset for clarity. The amplitude of the signal scales linearly with increasing laser excitation intensity while the decays are essentially the same, indicating a single photon excitation process. Excitation wavelength is at 390 nm with probe wavelength at 790 nm.

4. Summary

In summary, we have directly measured the excited electronic state lifetime of Au₁₁ clusters capped with *n*-dodecanethiol and other capping agents using femto-second transient absorption spectroscopy. The long lifetime (>500 ps) observed was tentatively assigned as the lifetime of the excited electronic state reached by 390 nm excitation, not cooling of hot electrons as in larger Au nanoparticles with excitation of the interband transitions. The main relaxation pathway is proposed to be non-radiative mediated by a significant number of surface trap states. The lack of power dependence, in conjunction with a long lifetime, is taken as evidence that Au₁₁ behaves more like a molecule rather than a bulk-like, large gold metal nanoparticle.

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