Ultrafast Electron Dynamics in Thiolate-Protected

Plasmonic Gold Clusters

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KEYWORDS: Mie theory, transient absorption, ligand effect, quantum regime, electron-phonon coupling

ABSTRACT: The influence of passivating ligand on electron-phonon relaxation dynamics of smallest sized gold clusters was studied using ultrafast transient absorption spectroscopy and theoretical modeling. The electron dynamics in $\text{Au}_{279}$, $\text{Au}_{329}$, and $\text{Au}_{329}$ passivated with tertiary butyl benzene thiol (TBBT), Phenyl ethane thiol (SC$_2$Ph) and hexane thiol (SC$_6$), respectively, were investigated. These clusters were chosen as they were the smallest gold clusters (till date) that show plasmonic properties and the sizes are similar but with different passivating ligands. Ultrafast transient absorption measurements were also carried out on $\text{Au}_{1500}$ (SC$_6$) and $\text{Au}_{2500}$ (SC$_6$) to understand the influence of size on electron-phonon re-
laxation with the same passivating ligand. Furthermore, to compare the electron dynamics of ligand-free and ligand-conjugated samples, optical properties of citrate-stabilized Au NPs with a diameter of 13 nm was studied. The results show that all investigated clusters are plasmonic via power-dependent surface plasmon bleach recovery kinetics. However, relatively smaller power dependence was observed for Au$_{329}$ (SC$_2$Ph). The results also show that the ligands do influence the intrinsic electron-phonon coupling and electron-phonon coupling strength. To model the effect of ligands, free electron density reduction of all samples was determined using three-layered Mie theory, and the results show that hexane thiol interacts least with core-gold while TBBT and SC$_2$Ph have a greater effect on the surface electronic conductivity. In addition, our results show that with the same hexane thiolate ligand, the electron-phonon coupling has increased with an increase in the size of the cluster.

**Introduction**

Optical properties of noble metal nanoparticles have been the subject of widespread research interest for the past two decades.\textsuperscript{1–4} The coupling of the electromagnetic field to free electrons in metal nanoparticles create quasi-particles named surface plasmons and were the focus of research for both theoreticians and experimentalists alike.\textsuperscript{5} The surface plasmon resonance (SPR) of metal nanoparticles (NPs) strongly depends on the density of electrons, shape, type, size, the composition of the nanoparticles, the polarization direction of the incident light as well as the chemical environment that surrounds them.\textsuperscript{5–16} Among metallic nanoparticles, gold NPs have attracted significant interest owing to their high chemical and physical stability, biocompatibility, photo-stability and large optical cross sections.\textsuperscript{17–19} The SPR of gold NPs was applied in many areas\textsuperscript{20} such as optical sensing,\textsuperscript{21} biological imaging,\textsuperscript{22–24} plasmonic photo-thermal therapy,\textsuperscript{4} molecular diagnostics,\textsuperscript{2,23,25} surface-enhanced Raman spectroscopy,\textsuperscript{2} metal-enhanced luminescence and plasmonic rulers.\textsuperscript{3}

Enormous research has focused on the plasmonic properties of Au NPs and significant breakthroughs were made in the field.\textsuperscript{2,3,11,14,17,19,23–30} However, bulk of the surface plasmon research has fo-
cused on gold nanoparticles passivated with surfactants or gold nanomaterials in different matrices.\textsuperscript{26,31–37} The SPR properties seem to be influenced by the chemical environment around the NPs and can be greatly altered if the surface of the gold nanoparticles is chemically bound to ligands.\textsuperscript{26,31–34} The ligands that are chemically bound to Au NPs prevent coalescence of the NPs by counterbalancing the van der Waals attractive forces.\textsuperscript{38–40} Coupling NPs with chemical ligands can potentially reduce the electron density of the conduction electrons and thereby altering effective optical refractive index at the near field of the NPs.\textsuperscript{39–41} A remarkable work was carried out by Peng et. al\textsuperscript{40} on the plasmon absorption spectrum of spherical silver (Ag) NPs with diameters in the range of 2 to 20 nm. They observed an interesting trend where the absorption peak of the ligand-conjugated Ag NPs shifted to higher energies when size was decreased from 20 nm to 12 nm, while the absorption peak shifted to longer wavelengths with further reduction of the size. This unusual trend was assigned to the ligand effect on SPR absorption.

Although significant progress was made on gold nanoparticles of varying sizes and shapes, corresponding research on ligand-protected gold NPs such as thiolated gold nanoparticles was rather limited.\textsuperscript{2,4,10,14,15,19,23–25,42,43} In recent years, thiolate-protected gold clusters have received enormous research attention as the clusters with sizes less than 2 nm seem to show interesting quantum size behavior and excitonic properties.\textsuperscript{26,27,29,30,44–46} The advent of modern synthetic and characterization techniques have made the science of atomically protected gold clusters interesting for theoreticians and experimentalists. Even thiolate protected gold clusters show plasmonic properties and Au\textsubscript{329} protected with hexane thiol was found to be the smallest hexane thiolate protected gold nanoparticle. On the other hand, Au\textsubscript{333} was found to be the smallest gold cluster that has shown plasmonic properties that was protected with Phenyl ethane thiol.\textsuperscript{47}

One common way to study plasmons in metal nanoparticles is via the use of ultrafast transient spectroscopy and corresponding pump-power dependence that yields information of electron
Comprehensive understanding of the relaxation processes of metal nanoparticles yielded valuable information that were useful for applications like exciton-plasmon energy transfer and optical switching. Link and El-Sayed investigated pump-power, size and shape effects on electron-phonon (e-p) relaxation dynamics in gold and silver nanospheres and nanorods in size range from 10 to 100 nm. The studies demonstrated that e-p relaxation dynamics was independent of the size and shape of NPs. Similarly, Hodak and coworkers reported a size independent electron-phonon coupling in Au nanoparticles in the 2.5 to 8 nm range in aqueous solution. Link et al. embedded 14.5 nm and 12.1 nm Au NPs in MgSO₄ powder and solution to test the effect of surrounding medium on the relaxation time of plasmon bleach. They found that electron-phonon relaxation time of Au NPs in MgSO₄ powder is higher than in solution by a factor of 2 that was assigned to the effect of the medium. In a recent work, e-p dynamics of the different sized gold nanoparticles conjugated with the chemical-ligand has been studied. By mapping the bleach recovery dynamics of these nanoparticles, Zhou et al. demonstrated that Au NPs with diameter more than 2.3 nm show metallic behavior while NPs with diameter less than 1.7 nm display pure molecular behavior. In addition, it was shown that particles with 1.7 to 2.3 nm show both metallic and excitonic behavior. More recently, our group studied optical properties of Au₃₆ (SR)₂₄, Au₄₄ (SR)₂₈, Au₁₁₃ (SR)₅₂ and Au₂₇₉ (SR)₈₄ using steady-state and transient absorption, time dependent density function theory and density of state calculation. By observing power dependent bleach recovery kinetics in Au₂₇₉ (SR)₈₄, we reported that it is the smallest gold thiolate nanoparticle that has shown metallic behavior and support localized SPR.

However, the influence of ligands on e-p relaxation dynamics of the ultra-small nanoparticles has not been addressed. In addition, previous theoretical studies have neglected the chemical ligand effect on the conductivity of Au NPs and consequently on their e-p relaxation. In the present work, we studied the electron-phonon relaxation dynamics of smallest sized plasmonic gold clusters conjugated with different thiolate ligands using ultrafast pump-probe spectroscopy. To investigate the effect of aromatic
and aliphatic ligands on the electron dynamics, investigations were carried out on Au$_{279}$ (d ~ 2.1 nm) passivated with TBBT and Au$_{329}$ (d ~ 2.3 nm) passivated with phenyl ethane thiol (SC$_2$Ph), and hexane thiol (SC$_6$). To further study the ligand effects, the free electron density of these NPs was modeled using three-layered Mie theory$^{56,57}$, inspired by Peng et al.$^{40}$

**Results and Discussion**

**A. Ultrafast transient absorption measurements**

Optical absorption spectra of Au$_{279}$(TBBT), Au$_{329}$ (SC$_2$Ph) and Au$_{329}$ (SC$_6$) have shown absorption around 500 nm which is broad when compared to citrate stabilized gold nanoparticles (Figure S1). The electronic absorption spectrum of these ligand-protected gold clusters does not completely represent the SPR absorption as they are overlapped with interband transitions whose contribution increases monotonously with an increase in energy. Thus to understand the influence of ligand on SPR, transient absorption measurements were carried out after excitation at 370 nm. Pump-power dependent measurements were carried out to follow the electron dynamics. Parts A, B, C and D of Figure 1 show the ESA spectra at a pump energy of 120 nJ for Au$_{279}$ (TBBT), Au$_{329}$ (SC$_2$Ph), Au$_{329}$ (SC$_6$) and Au$_{13}$ nm (Citrate), respectively. Since the excitation energy is higher than the interband transition threshold (520 nm in gold NPs, corresponding 2.4 eV$^{58}$), the excitation increases the electronic temperature of the NPs, creating hot electrons.$^{48,52}$ As observed in Figure 1, a negative absorption centered around 545 nm with two positive wings are observed and are consistent with literature reports.

The negative bleach in the transient absorption spectrum of the metal NPs arise because of the rapid rise of the electronic heat capacity due to the sudden rise of electronic temperature.$^{52}$ Similar spectra features were also observed for Au$_{1500}$ (SC$_6$), Au$_{2500}$ (SC$_6$), and Au$_{13}$ nm (Citrate). The bleach maximum is attributed to SPR absorption of the clusters and the accurate maximum was determined by the fit of the bleach curve (see Figure S2).$^{43,47,52,55,59,60}$ The bleach maximum has shifted to higher energies for all samples with increase in time, except for Au$_{329}$ (SC$_2$Ph) that has shown two peaks (see Fig-
ure 1, Figure S2 and Figure S3). Presence of two peaks for Au\textsubscript{329} (SC\textsubscript{2}Ph) in bleach spectrum was also observed by Zhou and coworkers and is quite interesting to see why such behavior was observed for this cluster.\textsuperscript{47}

The shift of the bleach maximum to the higher energies can be explained by the fact that with increase in time delay, the electronic temperature of the illuminated NPs decreases because of heat transfer to phonon bath that leads to increased free electron density. Enhancing electron density increases the plasmon frequency and consequently shifts the bleach maximum to lower wavelengths. From Figure 1, it can be seen that the bleach maximum of the ligand-passivated NP is shifted to lower energies as well as broadened when compared to ligand-free gold nanoparticles.\textsuperscript{40} The FWHM of smaller Au clusters at t= 0.5 ps are ~ 91 nm, ~ 76 nm, ~ 74 nm for Au\textsubscript{279} (TBBT), Au\textsubscript{329} (SC\textsubscript{2}Ph)) and Au\textsubscript{329} (SC\textsubscript{6}), respectively, and is much bigger than ~ 42 nm that was observed for 13 nm- Au. This result clearly shows that chemically bound ligands do alter the SPR quality factor by altering the free electron density. This result can also be explained by the fact that ligands cause increased electron- surface scattering rate that dampens the plasmon band. Enhancing the electron-surface collision frequency adds extra potential to the electronic motion and discretize electronic levels in the NPs, leading to a reduced density of the electron and phonon states.\textsuperscript{63,64} However the bleach width of the samples with aromatic ligands (Au\textsubscript{279} (TBBT) and Au\textsubscript{329} (SC\textsubscript{2}Ph)) is wider than Au\textsubscript{329} (SC\textsubscript{6}), despite the similar size. This results can be explained by the fact that conjugating NPs with aromatic ligands will further reduce free electron density of the NPs resulting in further damping of SPR.
Figure 1. Transient absorption spectra at different time delays for (A) Au_{279} (TBBT), (B) Au_{329} (SC_{2}Ph) (C) Au_{329} (SC_{6}) and (D) Au_{13 nm} (citrate) after excitation at 370 nm laser.

As the central aim of the study is to understand the influence of passivating ligand on electron dynamics, transient bleach recovery dynamics was monitored as a function of pump power. Pump-power dependence of bleach recovery kinetics is a key feature for plasmonic nanoparticles as it alters the electronic temperature of the nanoparticle. Figure S3 A-F show the bleach recovery kinetic traces for the investigated clusters at different pump powers. As expected with an increase in pump-power, the bleach signal increases as the local temperature of cluster increases. Increasing pump energy will heat up more electrons and by deaccelerating e-p coupling leading to slowing down of electron relaxation. The pump-power dependence of bleach recovery can be modeled using a two-temperature model (TTM).
\[ C_e(T_e) \frac{\partial T_e}{\partial t} = -\gamma(T_e - T_l) + \alpha N \quad (1) \]

\[ C_l \frac{\partial T_l}{\partial t} = \gamma(T_e - T_l) + \beta N \quad (2) \]

where \( C_e, T_e \) and \( C_l, T_l \) are heat capacity and temperature of the electron gas and lattice, correspondingly. \( \alpha N \) describes the heating of the electron gas by the initial nonthermalized electrons, \( \beta N \) represents the direct coupling between the non-thermalized electrons and the lattice occurs during the electron gas thermalization process, \(^{69}\) and \( \gamma \) is electron-phonon coupling constant. \(^{49,70–72}\)
The electron heat capacity of the metals is proportional to the electron gas temperature. Increasing the temperature of electron gas reduces electron-phonon effective coupling rate \( \frac{\gamma}{C_e(T_e)} \) and deaccelerating electron-phonon coupling time. The normalized bleach recovery (-Norm. \( \Delta A \)) for the investigated clusters is shown in Figure 2 A-F. To extract electron-phonon relaxation for each cluster, the bleach recovery dynamics was fitted (see Figure 2) using:

\[
\Delta A(t) = \int_{-\infty}^{\infty} H(\tau) \left[ A(1 - e^{-\frac{\tau}{\tau_{ee}}}) e^{-\frac{\tau}{\tau_{ep}}} + B \left( 1 - e^{-\frac{\tau}{\tau_{ep}}} \right) \right] e^{-\left(\frac{\tau-t}{\tau_0}\right)^2/\tau_0^2} \, d\tau
\]  

where \( H(\tau) \) is Heaviside function, A and B are e-e and e-p scattering amplitudes, where \(|B| < |A|/10\). \( \tau_{ee} \) is e-e coupling time and is in order of few hundred femtoseconds, and \( \tau_{ep} \) is e-p coupling time and is in order of \( \sim 1 \) ps. \( \tau_0 \) is instrument response which is obtained by the cross correlation of the pump and probe beams. From the intercept and slope of the linear fit of e-p relaxation lifetime versus pump energy, intrinsic e-p coupling time and e-p coupling strength for all samples was determined and provided in Table 1.
Figure 3.A shows the plot of calculated $\tau_{e-p}$ at different pump energies for $\text{Au}_{279}$ (TBBT), $\text{Au}_{329}$ (SC$_2$Ph), $\text{Au}_{329}$ (SC$_6$) and $\text{Au}_{13 \text{ nm}}$ (Citrate) nanoparticles. As seen from the figure, the slopes and intercepts varied for different clusters. $\text{Au}_{279}$ (TBBT) and $\text{Au}_{329}$ (SC$_6$) has shown an intercept of close to 1 ps and 0.8 ps, respectively while $\text{Au}_{329}$ (SC$_2$Ph) t has shown an intercept of 1.44 ps. Similar higher intercept was also observed by Zhou et al. In addition, the slope that represents electron-phonon coupling strength is significantly smaller for $\text{Au}_{329}$ (SC$_2$Ph) when compared to $\text{Au}_{279}$ (TBBT) and $\text{Au}_{329}$ (SC$_6$). This unusual result can be ascribed to specific Au-π interaction in $\text{Au}_{329}$ (SC$_2$Ph) that significantly reduces electric conductivity of the surface layer of the cluster. One another interesting observation is the difference in slopes for $\text{Au}_{279}$ (TBBT), $\text{Au}_{329}$ (SC$_6$) and 13 nm Au cluster. The slope is smaller for $\text{Au}_{279}$ (TBBT) when compared to $\text{Au}_{329}$ (SC$_6$), which is much smaller than that of 13 nm Au cluster (See Table 1). This can again be ascribed to the difference in electric conductivity as it is influenced by the nature of passivated ligands. Aromatic passivating ligands seem to have smaller slopes and higher intercepts when compared to hexane thiol ligand. In addition, the plot of e-p relaxation as a function of pump power for different sized SC$_6$ protected gold cluster is shown in Figure 3B. It can be observed from the Figure 3B and Table 1 that with an increase in size, total electric conductivity increases slightly due to a decrease of the surface to volume ratio, and thereby increasing the intercept (intrinsic electron-phonon coupling time) and slope (electron-phonon coupling strength). However, the slope is definitely smaller when compared to Au 13 nm that was passivated with surfactant again signifying the importance of ligand.
Among all investigated clusters, unique behavior was observed for Au$_{329}$ (SC$_2$Ph). The transient bleach of Au$_{329}$ (SC$_2$Ph) has shown two negative bleach peaks around ~ 493 and 540 nm. A similar result was reported by Zhou and coworkers and assigned it to excitonic and plasmonic behavior of the cluster.\textsuperscript{33} Interestingly, a closer look to the ESA spectrum of the samples in Figure 1 reveals that transient bleach of the Au$_{329}$ (SC$_2$Ph) is higher and wider than Au$_{279}$ (TBBT) and Au$_{329}$ (SC$_6$), respectively.

### Figure 3.

Electron-phonon relaxation as a function of pump pulse energy for (A) Au$_{279}$ (TBBT), Au$_{329}$ (SC$_2$Ph), Au$_{329}$ (SC$_6$) and Au$_{13}$ nm (Citrate), (B) Au$_{329}$ (SC$_6$), Au$_{1500}$ (SC$_6$) and Au$_{2500}$ (SC$_6$).

### Table 1.

| Sample         | Au$_{279}$- TBBT   | Au$_{329}$-SC$_2$Ph | Au$_{329}$-SC$_6$ | Au$_{1500}$-SC$_6$ | Au$_{2500}$-SC$_6$ | Au$_{13}$ nm - Citrate |
|----------------|--------------------|---------------------|-------------------|--------------------|--------------------|------------------------|
| Slope          | (2.6 ± 0.11) x 10^{-3} | (1.2 ± 0.06) x 10^{-3} | (3.2 ± 0.19) x 10^{-3} | (3.7 ± 0.10) x 10^{-3} | (3.9 ± 0.18) x 10^{-3} | (6.0 ± 0.3) x 10^{-3}  |
| Intercept      | 0.99± 0.01         | 1.44 ± 0.01         | 0.81 ± 0.02       | 0.80± 0.01         | 0.95± 0.02         | 1.04 ± 0.03            |
These observations can again be ascribed to specific Au-\(\pi\) interaction\textsuperscript{74} between \(\text{Au}_{329}\) and \(\text{SC}_2\text{Ph}\) ligand (see Figure 4). This interaction is probably the reason for unusual transient absorption features observed for \(\text{Au}_{329}\) (\(\text{SC}_2\text{Ph}\)). This can potentially reduce the free electron density of \(\text{Au}_{329}\) significantly (refer to theoretical modeling (section 2.2.)) and thereby creating hybrid state\textsuperscript{47} (metallic- molecular) for it. Additional modeling is necessary to understand the influence of passivating ligands on electron density.

**Figure 4.** Cartoon diagram depicting the interaction of (A) \(\text{SC}_6\), (B) STBBT, and (C) \(\text{SC}_2\text{Ph}\), with the surface of gold atoms.

**B. Theoretical modeling**

From the transient absorption measurements, it was shown that ligand plays an important role in the bleach spectrum as well as electron-phonon relaxation time and coupling strength. To understand such behavior, the SPR bleach was modeled with three-layered Mie theory\textsuperscript{40,56,57} As illustrated in Figure 5, the three layers structure of gold clusters consists of a core region with a diameter of \(d_{\text{core}} = d_{\text{NPs}} - 2t\), skin layer with a thickness of \(t\) and chemical ligand with a width of \(l\). We fixed \(t\) to be roughly the thickness of an atomic Au layer (or Au-Au bonding length), \(t=0.28\) nm. In addition, in our
simulation, the diameter of NPs have been calculated using the relation of \( 0.578 \times (x - 1) \) where \( x \) representing number of layers and 0.578 is twice the Au-Au bond length. \(^{47}\) According to the aforementioned relation, the size of NPs are taken as: \( d_{279} = 2.1 \) nm, \( d_{329} = 2.3 \) nm, \( d_{1500} = 4.1 \) nm, \( d_{2500} = 4.9 \) nm. The thickness of chemical ligands have fixed to \( l = 0.8 \) nm. Finally, the refractive index was used as 1.492, 1.43, and 1.375 for the TBBT, SC\(_2\)Ph and SC\(_6\) ligands, respectively. Also, the refractive index of 1.394 for citrate and 1.497 for toluene were used. \(^{75}\)

By reducing the size of the NP (\( d < 40 \) nm), the mean free path of the conduction electrons will decrease leading to increased collision rate of the electrons with the surface of the NP as well as more damping of the plasmon band. To accurately simulate optical properties of these NPs, modification on damping constant of the bulk is necessary with shrinking dimension of the NPs. Existing classical models have described these changing by expressing size dependent damping factor as \(^{41,42,64,76}\)

\[
\Gamma(r) = \Gamma_0 + \frac{AV_F}{r} \quad (4)
\]

where \( \Gamma_0 \) represents the bulk damping constant, \( V_F = 1.39 \times 10^6 \) ms\(^{-1} \) is Fermi velocity, \( r \) is the effective radius of the NP and \( A \) is an empirical damping factor ranging from 0.1 to 2, depending on the experimental data and physical model.\(^{41,42,64,76}\)

The modified permittivity for the NPs with 10 nm < \( d < 40 \) nm can be expressed as \(^{41}\)

\[
\varepsilon_{np}(\omega, r) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + i\Gamma_0 \omega} - \frac{\omega_p^2}{\omega^2 + i\Gamma(r) \omega} \quad (5)
\]

where \( \varepsilon_{bulk} \) is permittivity of the bulk metal, \( \omega_p \) is plasma frequency \( (\omega_p = \sqrt{n e^2 / m \varepsilon_0}) \), and \( \omega \) is the angular frequency of the incident light.
When the size of NP is less than 10 nm, the quantum effect must be taken into account. For this small sized region, the energy levels of the conduction band are discretized, and only certain electronic or plasmonic transitions are allowed.\textsuperscript{64,77} By considering these quantum effects, the permittivity of the quantum-sized NP can be written as \textsuperscript{64,77}

\[
\varepsilon_{\text{QNP}}(\omega) = \varepsilon_{\text{IB}} + \omega^2 \sum_i \sum_f \frac{S_{if}}{(\omega_{if}^2 - \omega^2 - i\Gamma(\omega))} 
\]

where the sum is taken over all initial and final states. In Eq. 6, $\varepsilon_{\text{IB}}$ is the contribution of interband transitions that can be obtained elsewhere,\textsuperscript{78} and $\omega_{if}$ and $S_{if}$ represent transition frequency and oscillator strength between initial and final states of electrons, respectively.

![Figure 5](image)

**Figure 5.** Schematic illustration of three layers structure of spherical NPs consists of the core region of diameter $d_{\text{core}}$ and skin and surrounding chemical ligand with a thickness of $t$ and $l$, respectively.

As discussed above, conjugating the metallic NP with ligand reduces the density of the free electrons in the conduction band of the metal due to chemical bonding between the NPs and the ligand.\textsuperscript{40} These chemical interactions have the most effect on the outermost layer of the NPs by decreasing the number of free electrons. This caused a shift of bleach maximum to longer wavelength and dampened
the plasmon band.\textsuperscript{40} To consider the ligand effects on the permittivity of the NPs, it is necessary to model the electronic conductivity of the core and shell by a factor of $g_{\text{core}}$ and $g_{\text{skin}}$, respectively. By applying these modifications to the equations (5) and (6), the permittivity of NPs can be represented as below for classical sized NPs ($d \geq 10$ nm):

$$
\varepsilon_{\text{NP}}(\omega, r) = \varepsilon_{\text{bulk}}(\omega) + \frac{\omega_p^2}{\omega^2 + i\Gamma(\omega)} - \frac{g^2 \omega_p^2}{\omega^2 + i\Gamma(\omega)} 
$$

(7)

On the other hand, the modified electric permittivity for quantum sized NPs ($d \leq 10$ nm) can be expressed as:

$$
\varepsilon_{\text{QNP}}(\omega) = \varepsilon_{\text{IB}} + g^2 \omega_p^2 \sum_i \sum_f \frac{S_{if}}{(\omega_i^2 - \omega^2 - i\Gamma(\omega))} 
$$

(8)

As the transient bleach at initial times represents the SPR bleach, it was modeled to obtain the electronic conductivities and corresponding $g_{\text{core}}$ and $g_{\text{skin}}$.\textsuperscript{43,47,52,55,59,60} Obtained $g_{\text{core}}$ and $g_{\text{skin}}$ from the analysis for different samples are shown in Figure 6. A closer inspection of Figure 6 reveals interesting trends. Both $g_{\text{core}}$ and $g_{\text{skin}}$ values for aromatic passivating ligands are much smaller when compared to hexane thiol passivating ligand. Also, the $g_{\text{skin}}$ obtained for SC$_2$Ph is much smaller than TBBT, and the results are consistent with experimentally observed electron dynamics in these clusters. The modeling suggests that it is the electron density difference, which is crucial for electron dynamics in these clusters. Due to the direct interaction between the chemical ligand and surface layer, electron conductivity of the outermost layer of the metallic NPs is decreased more when compared to the core region. In agreement with our experimental results, aromatic ligands, especially SC$_2$Ph, lowered the conductivity of the NPs more when compare to hexane thiol. As mentioned above, owing to the specific $\pi$ interaction between the gold and SC$_2$Ph ligand, the free electron density of the skin and core regions of Au$_{329}$ are lowered by a factor of 0.64 and 0.9, respectively. This significant reduction of the electron conductivity,
especially for the outermost layer, is further justification of deaccelerated electron-phonon dynamics in 

**Au**\textsubscript{329} (SC\textsubscript{2}Ph).

For the clusters with the same SC\textsubscript{6} passivating ligand, the \(g_{\text{skin}}\) values have increased with an increase in cluster size while \(g_{\text{core}}\) values are same as that of 13 nm Au Np. This result is also consistent with what was observed from electron dynamics measurements. Present results show zero reduction on the number of free electrons in citrate capped 13 nm Au nanoparticles. The three-layered Mie theory results were able to accurately model the influence of ligand on electron density and their effect on plasmon quality factor. This ligand influence can have consequences for electric field enhancement offered by ligand-protected plasmonic clusters.

![Figure. 6.](image)

**Figure. 6.** Free electron density correction factor of the outermost layer \((g_{\text{skin}}^2)\) and core region \((g_{\text{core}}^2)\) of the investigated Au clusters.

**Conclusions**

The electron-phonon relaxation dynamics measurements carried out on smallest sized plasmonic gold clusters have shown interesting trends with regards to the effect of the ligand on the dynamics. The results showed that the gold clusters with aromatic passivating ligands (TBBT and SC\textsubscript{2}Ph) have broadened surface plasmon band width and smaller electron-phonon coupling strength when compared to the
gold cluster with hexane thiol passivating ligand. The electron dynamics of gold clusters with hexane thiol are in line with the results obtained for citrate stabilized gold clusters as well as larger gold cluster with the same passivating ligand. The different electron-dynamics observed for aromatic passivating ligands are ascribed to reduced electron conductivity. The electron conductivity was modeled with three-layered Mie theory and the results have shown that all ligand passivated gold clusters have smaller surface conductivity when compared to citrate stabilized gold nanoparticles. Within the ligand passivated clusters, TBBT, and SC$_2$Ph ligand passivated clusters have much smaller electron conductivity that can be attributed to the way the aromatic ligands interact with surface gold atoms. Especially, unique results were obtained for Au$_{329}$ (SC$_2$Ph) that has shown smaller surface electron conductivity as well as two bleach maxima in transient absorption spectra and can be attributed to specific $\pi$ interaction between the ligand and Au on the surface. In addition, it was found that the electron-phonon coupling of the samples conjugated with same chemical ligands (Au$_{329}$ (SC$_6$), Au$_{1500}$ (SC$_6$) and Au$_{2500}$ (SC$_6$)) depend on the size of the cluster where the electron conductivity increased with increase in the size of the cluster.

ASSOCIATED CONTENT

Supporting Information Available

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ACKNOWLEDGMENTS
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Figure S1. Transient absorption spectra of the (a) Au\(_{1500}\) (SC\(_6\)) and (b) Au\(_{2500}\) (SC\(_6\)) at pump-probe delay times of 0.1 ps, 0.5 ps, 1.5 ps, 5 ps and 8 ps, which are excited by 370 nm wavelength laser light at a pump energy of 120 nJ.
Figure S2. Temporal evolution of electron-phonon dynamics of (A) Au$_{279}$ (TBBT), (B) Au$_{329}$ (SC$_2$Ph), (C) Au$_{333}$ (SC$_6$), (D) Au$_{1500}$ (SC$_6$), (E) Au$_{2500}$ (SC$_6$), and (F) Au$_{13}$ nm (Citrate) for different pump pulse power at their corresponding LSPR wavelength.
Figure S3. Normalized temporal evaluation of the transient bleach of (A) Au_{1500} \text{(SC}_6\text{)} and (B) Au_{2500} \text{(SC}_6\text{)} for different pump beam power probed at their corresponding LSPR peak.