

## Ultrafast Electronic Relaxation and Coherent Vibrational Oscillation of Strongly Coupled Gold Nanoparticle Aggregates

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**Abstract:** We report the first direct observation of the ultrafast electronic relaxation and coherent vibrational oscillation of strongly interacting gold nanoparticle aggregates measured by femtosecond laser spectroscopy. The electronic relaxation, reflected as a fast decay component with a time constant of 1.5–2.5 ps, becomes faster with decreasing pump power, similar to earlier observations of isolated gold nanoparticles. Surprisingly, periodic oscillations have been observed in the transient absorption/bleach signal and have been attributed to the coherent vibrational excitation of the gold nanoparticle aggregates. The oscillation period has been found to depend on the probe wavelength. As the probe wavelength is varied from 720 to 850 nm, the period changes from 37 to 55 ps. This suggests that the broad extended plasmon band (EPB) contains contributions from gold nanoparticle aggregates with different sizes and/or different fractal structures. Each of the different probe wavelengths therefore interrogates one subset of the aggregates with similar size or structure. Interestingly, the observed oscillation period for a given aggregate size determined by dynamic light scattering is longer than that predicted based on a elastic sphere model. One possible explanation is that the actual size of the aggregates is larger than what was observed from dynamic light scattering. An alternative, perhaps more likely, explanation is that the vibration of the aggregates is “softer” than that of hard spherical gold nanoparticles possibly because the longitudinal speed of sound is lower in the aggregates than in bulk gold. Persistent spectral hole burning was performed and yielded a hole in the nanoparticle aggregate’s extended plasmon band, further supporting that the near-IR band is composed of absorption subbands from differently sized/structured aggregates.

### Introduction

Metal nanoparticles have attracted considerable attention recently because of their many interesting properties and potential technological applications.<sup>1–10</sup> One classic metal nanoparticle system is gold. The optical properties of isolated gold nanoparticles have been extensively studied.<sup>11–13</sup> The main optical signature of these nanoparticles is the transverse plasmon band (TPB), which arises from the collective oscillations of the

conduction band electrons. The absorbance of the TPB is usually centered around ~520–540 nm, but small deviations are known to occur because of surface adsorbates, variation in particle size, or changes in the dielectric constant of the embedding solvent or matrix.

Interaction between metal nanoparticles is a fundamentally intriguing issue. It is critical to understanding the mechanism of self-assembly and formation of superlattices. The interaction can be roughly divided into the weakly and strongly interacting regimes. In the weakly interacting regime, the TPB shifts to the red because of interparticle interaction. For example, in weakly coupled systems of gold nanoparticles linked with DNA oligomers,<sup>14–16</sup> the TPB shifts to redder wavelengths. The DNA linkages induce aggregation, which shifts the TPB because of coupling between nanoparticles and changes in aggregate size. Similarly, a red shift of the TPB has been observed in Au nanoparticle superlattice structures, which indicates weak to moderately strong interparticle interaction.<sup>17</sup> The degree of interparticle separation controls the coupling between the

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particles; particles with a smaller separation show a larger shift because of stronger interaction.

In the strongly interacting regime, for example, aggregates with very short interparticle separation, a whole new absorption band in the 700–950 nm region appears because of strong interparticle interaction.<sup>18–23</sup> This type of band has been observed in other systems that deviate from spherical geometry, for example, gold nanorods<sup>13,24–29</sup> and gold nanoshells.<sup>30,31</sup> In these cases, the transverse and longitudinal polarizabilities are no longer equivalent. The extended plasmon band (EPB) gives rise to this new absorption in the near-IR in addition to the TPB at 520–540 nm.

The electronic relaxation of isolated colloidal gold nanoparticles has been extensively studied and found to be on the time scale of 1–2 ps, similar to that of bulk gold.<sup>32–34</sup> An interesting oscillatory behavior has been observed by both Hartland et al. and Vallee et al. in monitoring the electronic relaxation on longer time scales. These oscillations have been attributed to the excitation of the breathing vibrational modes of the nanoparticles because of energy transfer from the hot electrons into the lattice via electron–phonon coupling.<sup>35–38</sup> The vibrational frequency has been found to be inversely proportional to the radius of the nanoparticles, and the frequency can be calculated quite accurately on the basis of classical mechanics.<sup>39</sup> Similar observations have been recently made on gold nanorods and silver ellipsoids.<sup>40,41</sup> To our best knowledge, such observations have only been made on isolated particles or nanorods to date.

The ultrafast electronic relaxation and coherent vibrations of gold nanoparticles with strong interaction, for example, aggregates, have not been studied. While we expect to observe similar electronic (electron–phonon coupling) relaxation times in aggregates as that in isolated nanoparticles, coherent vibrational oscillations are not, at first thought, expected. If it is assumed that the aggregates have a broad distribution of sizes and structures that all contribute toward the EPB with similar absorption bandwidth, then no oscillations should be observed, since the differently sized and/or structured aggregates have different oscillation periods and any oscillations would be averaged out.

Contrary to expectation, we have observed directly, for the first time, coherent vibrational oscillations in the transient absorption/bleach measurement of strongly interacting gold nanoparticle aggregates. The oscillation period has been found to be longer at the redder probe wavelengths (55 ps at 850 nm) than at bluer probe wavelengths (37 ps at 720 nm). This suggests that the steady-state electronic absorption of the broad EPB contains contributions from aggregates of different sizes and/or fractal structures. Previous experimental and theoretical studies on small gold aggregates are consistent with this conclusion.<sup>42–44</sup> It has been further observed that, for a given aggregate size determined by dynamic light scattering, the oscillation period is longer than that predicted on the basis of an elastic sphere model. This possibly indicates that the vibration of the aggregates is “softer” than that of hard spherical gold nanoparticles. The electronic relaxation (1.5 ps) due to electron–phonon coupling is similar to that of isolated, strongly coupled Au nanoparticles<sup>45</sup> as well as bulk gold, as expected.

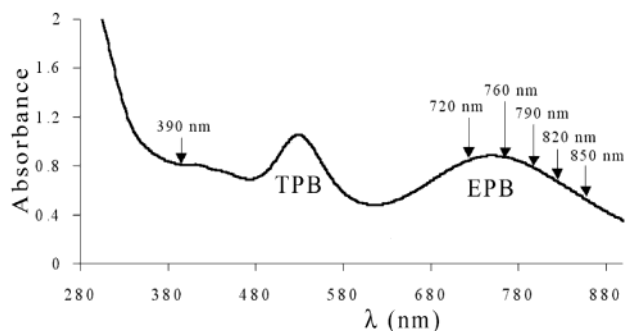
## Experimental Section

Gold nanoparticle aggregates were synthesized using a previously reported technique.<sup>18</sup> Briefly, 100  $\mu$ L of an aged 0.1 M Na<sub>2</sub>S solution were added to 40 mL of a  $5 \times 10^{-4}$  M chloroauric acid solution at room temperature. Upon addition of the Na<sub>2</sub>S, the solution turned from a straw yellow color to red/purple. Aggregation took approximately 40 min to complete and was monitored using a Perkin-Elmer Lambda 40 UV–visible spectrometer. Upon appropriate aggregation, enough polyvinylpyrrolidone was added to make a 3 wt % solution to halt the reaction. Aggregate size was determined via dynamic light scattering (DLS) experiments, on a DynaPro DLS instrument from Protein Solutions.

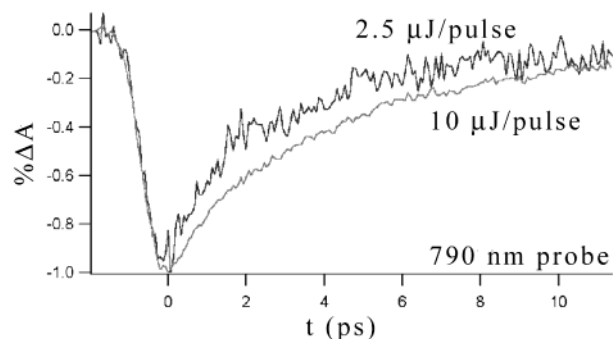
The transient bleach/absorption measurements were performed using a regeneratively amplified, mode locked femtosecond titanium–sapphire laser, which has been described previously.<sup>46</sup> Briefly, pulses of 50 fs duration with 4 nJ/pulse energy at a repetition rate of 100 MHz were generated and amplified in a titanium–sapphire regenerative amplifier using chirped-pulse amplification. The final output pulses were typically 150 fs with a pulse energy of 250  $\mu$ J, centered at 780 nm at 1 kHz. The amplified output was doubled in a 1 mm BBO crystal to generate 30  $\mu$ J/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

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**Figure 1.** UV-visible absorption spectrum of strongly interacting gold nanoparticle aggregates. The excitation (390 nm) and probe wavelengths used in the dynamics studies are indicated by arrows.



**Figure 2.** Ultrafast electronic relaxation dynamics of gold nanoparticle aggregates at two very different excitation intensities to illustrate the power dependence of the fast component of the decay.

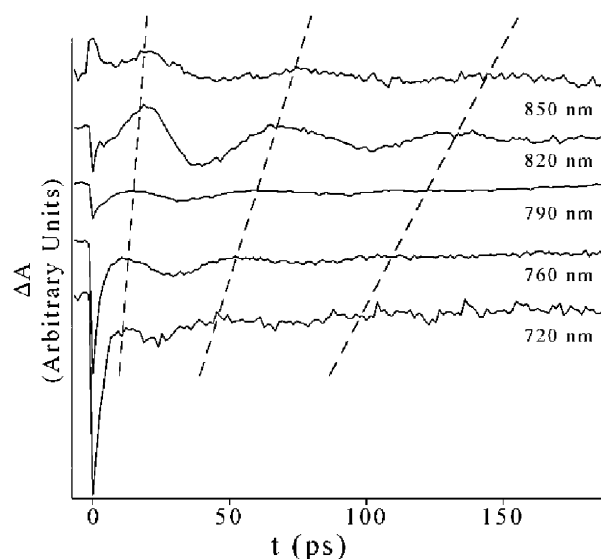
by dividing the signal by the reference for each laser shot. The time delay between pump and probe was controlled by a translation stage. The pump and probe beams were focused with a 10 cm focal length lens and cross overlapped over a spot size of 1 mm<sup>2</sup> in the sample before the focal point. The pump power was attenuated such that there was no signal observed from the pure solvent because of multiphoton ionization.

Persistent spectral hole burning experiments were conducted by using the output from the titanium-sapphire regenerative amplifier at a power of  $\sim 200 \mu\text{J/pulse}$  near 800 nm. Samples were irradiated for up to 2.5 h in a 1 cm quartz cuvette, and the hole burning process was monitored using UV-vis spectroscopy.

## Results and Discussion

Figure 1 shows the electronic absorption spectrum of one representative aggregate sample. The peak at  $\sim 540$  nm corresponds to the TPB from individual gold nanoparticles, while the broad near-IR absorption band is assigned as the EPB due solely to nanoparticle aggregates.<sup>18</sup> The EPB arises from strong particle-particle interaction. The aggregates in Figure 1 have an average radius ( $R_{\text{DLS}}$ ) of 40 nm with a polydispersity of 44% based on DLS measurement.

Figure 2 shows the electronic relaxation (transient bleach) of the aggregates probed at 790 nm following excitation at 390 nm for two different excitation intensities (10 and 2.5  $\mu\text{J/pulse}$ ). At high power, the fast component of the relaxation is slower than that at lower power, with time constants of  $\sim 2.5$  and  $\sim 1.5$  ps for high and low power, respectively. On the short time scale (a few ps), the relaxation is dominated by electron-phonon coupling. Energy transfer from the hot electrons to the lattice is dependent upon excitation intensity. This can be accounted for by the two temperature model.<sup>36,47,48</sup> Higher pump powers produce higher electronic temperatures which yield longer



**Figure 3.** Ultrafast electronic relaxation dynamics of gold nanoparticle aggregates at varying probe wavelengths (shown at right) with excitation at 390 nm at 8  $\mu\text{J/pulse}$ . Trend lines (dashed) demonstrate an increase in oscillation period and shift of the first peak toward a longer time as probe wavelength is shifted to redder wavelengths.

relaxation times because of the temperature dependence of the electronic heat capacity. Faster relaxation at lower power is consistent with previous observations in isolated gold nanoparticles.<sup>13,34</sup> The relaxation is also similar to strongly coupled gold nanoparticle films<sup>45</sup>

Figure 3 shows probe wavelength dependent transient absorption/bleach profiles of gold nanoparticle aggregates. The most striking feature is the periodic oscillations. Since the EPB is due solely to strongly coupled gold nanoparticle aggregates, the oscillations observed must be due to the aggregates, not isolated nanoparticles. Similar measurements on isolated gold particles alone in the same probe wavelength region show no oscillations. The oscillations are attributed to coherent vibrations of the aggregates that are excited following the initial hot electron relaxation. The observation of such periodic oscillations in these nanoparticle aggregates is somewhat surprising. If all of the differently sized and/or fractally structured aggregates contribute to the EPB with the same absorption bandwidth, then each aggregate will vibrate with its own frequency upon excitation. The observed signal would be a sum of all the oscillations with different frequencies or periods that would “wash out” any overall observable oscillation. This is apparently not the case.

The oscillations observed suggest that the broad EPB is composed of absorption sub-bands from gold nanoparticle aggregates with different sizes and/or different fractal structures. In other words, the EPB is inhomogeneously broadened by the different aggregate sizes and/or structures. For a given probe wavelength, only a subset of the aggregates with similar size or structure are probed. To use the size analogy, smaller aggregates will likely have an absorption in the bluer part of the EPB, while the larger aggregates will absorb in the redder part of the EPB. This conjecture is strongly supported by the

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probe wavelength dependence of the oscillation period, as discussed next.

A closer examination of the data reveals that the first peak of the oscillation appears later in time, as the probe wavelength is shifted more to the red. This can be explained by proposing that the redder probe wavelengths probe aggregates with a larger size, which takes a longer time to start vibrating following hot electron relaxation.

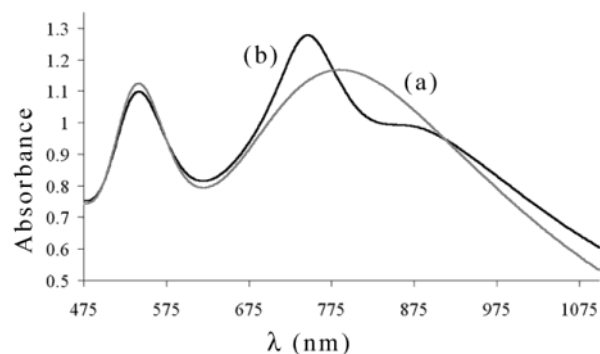
Another important feature of the oscillations is the change in period as a function of probe wavelength. As the probe wavelength is varied from 720 to 850 nm, the period changes from 37 to 55 ps. The likely explanation is that smaller aggregates with an absorption in the bluer part of the EPB have a shorter oscillation period because of smaller mass. Larger aggregates with an absorption in the red part of the EPB have a longer oscillation period because of heavier mass. The change in oscillation period could also be due to differences in the fractal structure of the aggregates, not necessarily just size.<sup>42–44,49</sup>

To gain some further insight into the oscillations, we use the elastic sphere model of Hartland et al.<sup>36</sup> as a starting point to calculate the particle size from the observed oscillation periods, since currently there is no theoretical model to describe the oscillations of gold nanoparticle aggregates. Using the oscillation period of  $\tau = 42$  ps observed at 760 nm, which is close to the peak (750 nm) of the EPB, the radius of the aggregates would be predicted to be  $R = 64$  nm if the elastic sphere model is assumed to apply. The radius is calculated from

$$R = \frac{\eta\tau}{2\pi} c_1 \quad (1)$$

where  $\eta$  is the vibrational eigenvalue, which is 2.95 from experiment or 2.93 from theory for gold particles,  $\tau$  is the observed oscillation period, and  $c_1$  is the longitudinal speed of sound in gold, 3240 ms<sup>-1</sup>.<sup>36</sup> However, the DLS measurement yielded an average radius of  $\sim 40$  nm for the aggregates. It is assumed that this average size of the aggregate corresponds to the peak of the EPB. Therefore, the size of the aggregates calculated on the basis of the oscillation period is much larger than the size measured from DLS. There are two possible explanations for this discrepancy. First, the aggregates are actually larger than what was measured by DLS; that is, DLS does not provide a good measure of the real aggregate size. Second, the elastic sphere model does not apply for aggregates; the calculated size is thus incorrect. Since the observed oscillation period is longer than what would be predicted using the size from DLS and the elastic sphere model, the results imply that the actual vibration of the aggregates is “softer” (longer period or lower frequency) than that of the hard gold spheres. This seems plausible, since the aggregates are not solid structures such as elastic spheres. However, the discrepancy in the calculation of the size of the aggregates from the period measurements might be accounted for by a change in the longitudinal speed of sound in the aggregates. An estimate of  $c_1$ , from eq 1, in the aggregates is approximately  $2/3$  that of bulk gold. This reduced  $c_1$  value may be the underlying reason for the “softness” of the aggregate vibrations.

It should be pointed out that the vibrational frequencies corresponding to the oscillations observed are on the order of



**Figure 4.** Persistent spectral hole burning experiment using  $\sim 800$  nm laser light at 200  $\mu\text{J}/\text{pulse}$ . Trace (a) is prior to laser irradiation. Trace (b) is after 2.5 h of hole burning. A hole is clearly seen in trace (b) as well as a growth and shift of the maximum absorbance to bluer wavelengths.

less than 1 cm<sup>-1</sup> (e.g., 0.8 cm<sup>-1</sup> for 42 ps). Such low frequencies are generally very difficult to measure for condensed phase systems such as solids, liquids, or aggregates because of significant inhomogeneous spectral broadening. If the above explanation is correct, the transient absorption/bleach technique provides a unique method for probing the low-frequency vibrational modes of systems such as nanoparticle aggregates.

The oscillations as well as the probe wavelength dependence of the period discussed previously imply that the EPB is composed of many absorption subbands from differently sized and/or structured aggregates. To further test this model, we have performed preliminary persistent hole burning experiments, for which the data are shown in Figure 4. The hole burning technique has been successfully used to measure homogeneous line widths of surface plasmon resonances in metal nanoparticles<sup>50,51</sup> but not in aggregates. If the EPB is composed of many absorption subbands, then certain sized or structured aggregates can be selectively excited and their structure or size altered. It is clearly evident that a hole is burned into an EPB part of the spectrum after laser irradiation around 800 nm. Also evident is a growth and shift to bluer wavelengths of the absorption maximum. This can tentatively be explained by the alteration or destruction of those particular aggregates of a certain size or structure that absorb the incident radiation to create aggregates with a smaller size or different fractal structure that absorb more in the blue region. These results are also consistent with earlier experimental and theoretical studies on small gold aggregates.<sup>42–44</sup>

## Conclusion

In summary, ultrafast electronic relaxation and coherent vibrational oscillations of strongly interacting gold nanoparticle aggregates have been studied using femtosecond laser spectroscopy. The electronic relaxation, reflected as a fast decay component with a time constant of 1.5–2.5 ps, becomes faster with decreasing pump power, which is similar to earlier observations of isolated gold nanoparticles. Interestingly, periodic oscillations have been observed in the transient absorption/bleach signal, and they have been attributed to the coherent vibrational excitation of the nanoparticle aggregates. The oscillation period has been found to depend on the probe wavelength. This indicates that the broad EPB band in the

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steady-state electronic absorption spectrum contains subbands that are contributed from aggregates of different sizes and/or fractal structures. Each of the different probe wavelengths interrogates one subset of the aggregates with similar size or structure. Aggregates that absorb in the redder part of the EPB have a longer oscillation period, which is likely associated with either a larger aggregate size or a particular fractal structure. Conversely, aggregates that absorb in the bluer part of the EPB have shorter oscillation periods. The observed oscillation period for a given aggregate size determined by dynamic light scattering is longer than that predicted on the basis of an elastic sphere model. One possible explanation is that the vibration of the aggregates is "softer" than that of spherical gold nanoparticles because of a lower longitudinal speed of sound in the aggregates

than in bulk gold. Spectral hole burning experiments performed showed a hole burned into the nanoparticle aggregate EPB, further supporting that this near-IR absorption is composed of subbands from differently sized and/or structured aggregates. This transient absorption technique provides a useful tool for probing the low-frequency vibrational modes of metal nanoparticle aggregates.

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