ULTRAFAST SPECTROSCOPIC STUDIES
OF METAL NANOPARTICLES

A Dissertation

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An important aim of nanoparticle research is to understand how the properties of materials depend on their size and shape. In this thesis, time-resolved spectroscopy has been used to measure the physical properties of nanometer sized objects, such as the characteristic time scale for heat dissipation and their elastic moduli. In our experiments, metal nanoparticles are excited with a sub-picosecond laser pulse, which causes a rapid increase in the lattice temperature. In the first project, the rate of heat dissipation from Au nanoparticles to their surroundings was examined for different size gold nanospheres in aqueous solution. Laser induced lattice heating can also impulsively excite the phonon modes of the particle that correlate with the expansion co-ordinates. For spherical Au particles the symmetric breathing mode is excited. Experimental results for ~50 nm diameter Au particles were compared to a model calculation where the expansion coordinate is treated as a damped harmonic oscillator. This gives information about the excitation mechanism. In the second project, the extensional and breathing modes of cylindrical gold nanorods were studied by
time-resolved spectroscopy. These experiments yield values for the elastic constants for the rods. Both the extensional mode and the breathing mode results show that gold nanorods produced by wet chemical techniques have a smaller elastic moduli than bulk gold. HR-TEM and SAED studies show that the rods have a 5-fold twinned structure with growth along the [110] crystal direction. However, neither the growth direction nor the twinning provide a simple explanation for the reduced elastic moduli measured in the experiments. In a final project, polydisperse silver nanoparticle samples were investigated. A signal due to coherently excited vibrational motion was observed. The analysis shows that the observed signal arises from the triangular-shaped particles, rather than the rods or spheres that are present in the sample. The triangles dominate the response because they have a much narrower size distribution than the rods.
CONTENTS

FIGURES ................................................................................................................................iv

ACKNOWLEDGMENTS ..............................................................................................................x

CHAPTER 1: INTRODUCTION .......................................................................................... 1
  1.1 Metal Nanoparticles ................................................................................................. 2
      1.1.1 Spherical Nanoparticles .............................................................................. 2
      1.1.2 Mie Theory .................................................................................................. 3
      1.1.3 Elongated Nanorods-Gans Model ............................................................... 5
  1.2 Time-resolved Spectroscopy ................................................................................... 7
  1.3 References ............................................................................................................... 12

CHAPTER 2: EXPERIMENTAL ...................................................................................... 17
  2.1 Ultrafast Laser System ........................................................................................... 17
      2.1.1 Ultrafast Pulse Generation ........................................................................ 17
      2.1.2 Transient Absorption Experiments ............................................................. 20
      2.1.3 Detection Electronics ................................................................................ 22
  2.2 Synthesis of Nanoparticles .................................................................................... 23
      2.2.1 Radiation Method and Spheres .................................................................. 23
      2.2.2 One-dimensional Structures ...................................................................... 26
          2.2.2.1 Electrochemical Method ................................................................... 26
      2.2.2.2 Seed Mediated Method ........................................................................ 28
      2.2.3 Other Shape Controlled Synthesis ............................................................. 30
  2.3 References ............................................................................................................... 33

CHAPTER 3: SPHERICAL METAL NANOPARTICLES ............................................ 35
  3.1 Introduction .............................................................................................................. 35
  3.2 Experimental .......................................................................................................... 37
  3.3 Coherent Vibrational Motion in Nanospheres ....................................................... 40
  3.4 Heat Dissipation from a Sphere ............................................................................ 48
      3.4.1 Theory ......................................................................................................... 48
      3.4.2 Transient Experiment Results .................................................................... 51
  3.5 Summary and Conclusions .................................................................................... 61
  3.6 References .............................................................................................................. 62
FIGURES

1.1 Calculated absorption spectra for a Au nanorod using Gan’s model ........7

1.2 Calculated absorption spectra of gold particles (top) and nanorods (bottom: aspect ratio = 3) in water at room temperature (solid line) and for an increase in electronic temperature of 1000°C (dashed line). The insert shows the difference spectra, which displays a strong bleach signal at the plasmon resonance .................................................................10

1.3 Top: transient absorption data for ~ 40 nm diameter gold particles in aqueous solution with time and wavelength resolution. The bottom two panels show transient absorption spectra recorded at different times (left), and traces of the signal versus time at two wavelengths (right) .................................11

2.1 Diagram of the regeneratively amplified laser system. BS: Beam Splitter .................................................................18

2.2 Chirped Pulse Amplification procedure. See text for details ............19

2.3 Transient absorption experiment set-up for most of the experiments performed in this work. The dashed line panel shows the signal detection system. BS = Beam splitter, WP = Wave plate, POL = Polarizer, L = Lens, SHG = Second harmonic generation, WLG = White light generation, PD = Photodiode .................................................................21

2.4 Upper panel: the extinction spectra of the gold spheres with different diameters produced by radiation method. Lower panel: TEM images of 20 nm diameter Au nanoparticles prepared using the Turkevich method (lower left), and after coating with Ag (lower right). The molar ratios are Au:Ag = 1:1..........................25

2.5 TEM images of gold nanorods with an aspect ratio of 18 prepared by seed-mediated growth method from Murphy group [24] .........................29
2.6 A proposed growth mechanism model for the seed mediated method by Murphy and co-workers [27]. The bilayer structure formed by C₁₆TAB, which absorbed on specific crystallographic faces of the Au nanorods, may facilitate the growth of rods along a specific direction while more gold ions are introduced .........................................................29

2.7 The TEM images of Ag nanospheres before irradiation with fluorescent light (A) and Ag nanoprisms (B) produced after 70 hours irradiation from Mirkin group. (C) and (D) show the SEM images of Ag nanocubes and Ag-Au nanoboxes produced by Xia and coworkers, the insets at upper right-hand corners of panel (C) and (D) are the electron diffraction patterns taken from individual Ag nanocubes and Ag-Au nanoboxes, respectively ...............32

3.1 Transient absorption data for ca. 50 nm diameter Au particles in aqueous solution, recorded with different probe laser wavelengths. Note that the strong bleach signal in the 520 nm to 560 nm region has been cut-off to better illustrate the modulated portion of the data ..............................................41

3.2 Change in radius versus time for the Au particles in Figure 3.1. (●) Experimental data; (—) calculated using Equations 3.4−3.6; (---) calculations that ignore hot-electron pressure effects in the coefficient for thermal expansion .................................................................44

3.3 Calculated temperature versus time profiles using Equation 3.9. From top to bottom, the different traces correspond to particles with diameters of 50, 40, 26, and 15 nm. The insert shows the characteristic time constant for energy dissipation (τ) obtained from fitting the temperature profiles to Equation 3.10, plotted against the square of the radius (in nm²) .......................50

3.4 Transient bleach data for 15 nm diameter Au particles recorded with 530 nm probe pulses and a pump laser power of 0.4 µJ/pulse. The different regions of the decay (coupling between the electrons and phonons within the particles and coupling between the particles and their environment) are labeled in the figure ..............................................................52

3.5 Transient bleach data for different sized Au particles recorded with pump laser powers of (a) 0.2 or (b) 0.4 µJ/pulses. The different traces correspond, from top to bottom, to particles with diameters of 50, 40, 26, or 15 nm. The initial temperature rise induced by the pump laser is included in the figure. The dashed lines show fits to the data using Equation 3.10 ..................54

3.6 Transient bleach data for 15 nm diameter Au particles recorded with pump powers of 0.2, 0.4, 0.6, and 0.8 µJ/pulses. The temperature rise in the particle created by the pump laser is given in the figure. The dashed lines show fits to
the data using Equation 3.10 with the values of $\tau$ and $\beta$ constrained to $\tau = 40$ ps and $\beta = 0.5$ (i.e., only the amplitude was allowed to vary). These results show that the form of the decay does not depend on the initial temperature

3.7 Characteristic time constant for energy dissipation determined using Equation 3.10 versus diameter: (○) experimental data; (—) calculated temperature versus time profiles. The dashed line shows a fit to the data assuming a parabolic dependence of $\tau$ on diameter (i.e., $\tau \propto R^3$) …………..57

3.8 Transient bleach data for the 4 nm diameter particles recorded with 0.4 $\mu$J pump laser pulses. The dashed line shows a fit to the data using Equation 3.10. The characteristic time scale for energy relaxation obtained from this fit is $\tau = 10 \pm 5$ ps …………………………………………………………..60

4.1 Diagram Showing the Fundamental Extensional and Breathing Modes of a Cylindrical Rod. Calculations performed under the assumption that the length greatly exceeds the width. In the breathing mode, a pure radial expansion and contraction is observed; there is no change in length. In the extensional mode, an increase in length is accompanied by a contraction in radius ……………………………………………………………………….69

4.2 Representative TEM images of the gold nanorods used in our experiments. The images correspond (from top left) to the samples with average lengths of: (a) $L = 108 \pm 7$, (b) $L = 89 \pm 7$ nm, (c) $L = 75 \pm 6$ nm, (d) $L = 73 \pm 4$ nm, (e) $L = 61 \pm 5$ nm, and (f) $L = 46 \pm 6$ nm ………………………………………75

4.3 UV-visible absorption spectra of the “high quality” gold nanorod samples. The average lengths for the different spectra are as follows: (a) $\bar{L} = 108 \pm 7$, (b) $\bar{L} = 89 \pm 7$ nm, (c) $\bar{L} = 75 \pm 6$ nm, (d) $\bar{L} = 73 \pm 4$ nm, (e) $\bar{L} = 61 \pm 5$ nm, and (f) $\bar{L} = 46 \pm 6$ nm ………………………………………………...76

4.4 Transient absorption traces for Au nanorods with average lengths of (a) $\bar{L} = 46 \pm 6$ nm, (b) $\bar{L} = 61 \pm 5$ nm, (c) $\bar{L} = 75 \pm 6$ nm and (d) $\bar{L} = 89 \pm 7$ nm, for two different probe laser wavelengths. In all cases, the probe wavelengths presented lie on opposite sides of the longitudinal plasmon band of the sample. Note the different scale for the time axes in panel (d) …………….79

4.5 Period versus probe laser wavelength for all the different samples listed in Table 4.1. The different symbols indicate average lengths of $\bar{L} = 46 \pm 6$ nm (▲), $\bar{L} = 61 \pm 5$ nm (○),$\bar{L} = 73 \pm 4$ (●),$\bar{L} = 75 \pm 6$ (○),$\bar{L} = 89 \pm 7$ nm (●)and $\bar{L} = 108 \pm 7$ (□). The error bars are contained within the symbol ……………………………………………………………………………………………81
4.6 Transient absorption data for a gold nanorod sample with an average length of $61 \pm 5$ nm and an average width of $21.5 \pm 1.9$ nm. (a) The pump laser wavelength was 795 nm and the probe laser ($\lambda = 540$ nm) was tuned to the transverse plasmon band of the sample. For comparison, transient absorption data for the extensional mode (pump laser wavelength 400 nm, probe wavelength 700 nm) for the same rod sample is shown in (b). Note the different scale for the time axes .....

4.7 Vibrational period for the extensional mode versus average length for the gold nanorods samples used in the transient absorption experiments. The solid line is a fit to the data using Equation 4.4 and allowing $E$ to vary. The dashed lines show calculations for different crystal directions, see text for details ...

4.8 Temperature dependence of Young’s modulus for bulk gold .......

4.9 (Top) HRTEM image of a gold nanorod produced by seed-mediated growth. The image on the right shows an expanded view of the outlined rectangle on the left. {111} lattice fringes characteristic of imaging the $<110>$ and $<111>$ crystallographic zones can be clearly seen on the lower half of the rod. (Bottom Left) Corresponding diffraction pattern from the rod. The outlined hexagon of $\{220\}$ spots arises from diffraction from the $<111>$ zone, and the smaller reciprocal lattice inside this arises from the $<110>$ zone. The drawing at the bottom right shows the structure of the rods ...

5.1 SEM images of (a) elongated Ag nanorods or nanowires with a high concentration and (b) multi-twinned structure of the Ag nanorods. The inset shows the EDX data from a nanorod [2] ...

5.2 Representative TEM images of samples A – D. The average dimensions of the rods, triangular-shaped particles and spherical particles are summarized in Table 5.1 ...

5.3 The UV-Vis absorption spectra for samples A – D used in our transient absorption experiment ...

5.4 (a) The percentage of spheres, rods and triangular-shaped particles in the samples A – D. Over 1000 particles were counted for each sample. (b) Dimensions of the spheres (diameter), rods (length and width) and triangular-shaped particles (bisector) for the different samples ...

5.5 Transient absorption traces for samples A – D. All experiments were performed with the probe tuned to the red side of the long wavelength
plasmon band. The probe wavelengths used were 520 nm, 540 nm, 600 nm and 710 nm, respectively, for samples A – D. Dashed lines are fits to the data using a damped cosine function ………………………………………..112

5.6 Representative transient absorption traces for sample C. The wavelengths range from the red side to the blue side of the plasmon band. The phase of the modulations changes by 60° as the probe laser is tuned from the red to the blue ……………………………………………………………..114

5.7 (a) Observed vibrational periods and (b) phases of the modulations versus probe wavelength for the different samples used in experiments. The different symbols correspond to sample A (△), B (▲), C ( ) and D (O) ………………………………………………………………………………..115

5.8 Calculated absorption spectra of silver nanorods with different aspect ratios using the Gans model, see Ref. [15] for details. The dielectric constant of the medium is fixed to be 2.5 and the dielectric constant of silver was taken from Ref. [16] ………………………………………………………………………………..117

5.9 Average vibrational period versus dimension for the different samples, in (A) the x-axis is the length of the rods and in (B) the x-axis is the bisector of the triangles. Solid lines in both figures are the calculated period, see text for details, and dashed lines are fits to the experimental data assuming a linear relationship between period and dimension. The open symbol in (B) represents the triangles synthesized using the procedure in ref [4] ………………………………………………………………………………..120

A.1 TEM image which shows how we define the dimensions measured for the rods and triangular-shaped particles …………………………………….127

A.2 (a-d): Histograms and normal distribution fits for samples A-D, respectively. The width of the rods and the bisector of the triangular-shaped particles have a narrower size distribution than the length of rods. The dimensions of the spheres, the rods and the triangular shaped particles are reported in Table 5.1 in main text ………………………………………………………………………………..128

A.3 (a): Transient absorption data for a sample of triangular shaped particles produced using the recipe in Ref. [1]. The probe wavelengths used were 600 nm and 640 nm. The measured periods are 33.0 ps for 600 nm and 31.0 ps for 640 nm, and the change in phase between the two traces is 120°; (b): UV-Vis absorption spectra for the sample in Figure A.3(a) …………………..132

A.4 Representative TEM image for the above sample ……………………..134
A.5  Size histogram and normal distribution fit for the sample in Figure A.4. Over 100 particles were counted and the average size was 61 nm, with a standard deviation of 23 nm
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CHAPTER 1

INTRODUCTION

During the last two decades, the synthesis and characterization of inorganic nanocrystals have drawn a lot of attention in the scientific and industrial fields [1-7]. These materials have very unique physical and chemical properties compared to the bulk materials due to their small size (within the nanometer range). They have found useful applications in variety of industrial applications, including nanoelectronics [8-14], chemical catalysis [15-21], biomolecule detection [22-28] and optical data storage devices [29]. These tiny materials may lead to a new era of science and technology which may benefit the whole of human society, like what semiconductors did fifty years ago. This is termed “Nanoscience and Nanotechnology”. Different types of nanomaterials have been investigated to date from nanoparticles [30-32], nanotubes [33, 34] to complicated nanodevices [14, 35, 36] and nanocomposites [37-39]. With the development of microscopy techniques such as TEM, SEM and STM, scientists can begin to manipulate single atoms or nanoparticles [40-43] to make targeted structures by physical methods. For example, nanocircuits can be constructed by assembly of semiconductor nanounits [35, 36].
Since nanoparticles are the basic construction block for complicated nanostructures, the research on different nanoparticles is very intense in recent years. Both metal and semiconductor particles have been studied. Nanoparticles can be also modified to achieve desirable features, for example core-shell nanoparticles can be created to make high-efficiency catalysts [44-46]. The shape of the nanoparticles can also be controlled [5, 32]. Metal nanorods and nanoshells have found unique application in cancer treatment [47, 48]. This is called nanoengineering. The major focus of this thesis is metal nanoparticles, specifically, how their properties depend on size and shape.

1.1 Metal nanoparticles

1.1.1 Spherical nanoparticles

Metal nanoparticles have been a topic of interest for thousands of years. For example, gold nanoparticles have been used to make colorful glasses for over one hundred years. This is probably the first practical application of nanoparticles, although clearly the people who made the glasses did not know the principle behind the fascinating colors. One of the most famous examples is the Lycurgus cup (Roman 400 A.D.) [49] which reflects green light and transmits ruby red light. This is because of the unique optical absorption and scattering properties of nanoparticles contained in the glass. The first proper scientific research on metal nanoparticles was carried out by Michael Faraday [50]. This initiated the interest
of many scientists and this interest continues to today. For spherical gold nanoparticles, there is a strong absorption band in the visible region near 520 nm, which is not observed in small nanoparticles and bulk gold. This absorption is called the Surface Plasmon Resonance (SPR), and is due to the oscillation of the free electrons in the conduction band of the nanoparticles. In 1908, Mie developed a theoretical explanation for the color of metal nanoparticles by solving Maxwell’s equation for the absorption and scattering of electromagnetic radiation [51].

Light scattering theory falls into two categories. One is the theory of Rayleigh scattering that is applicable to small, dielectric (non-absorbing) and spherical particles. The second is the theory of Mie scattering. Compared to Rayleigh scattering theory, the latter can be applied to the general scattering solution (absorbing or non-absorbing) without a size limit on the particles. Thus, Mie theory is very useful for describing the optical properties of spherical particle, and includes within it Rayleigh scattering [52-54].

1.1.2 Mie theory

Mie theory is an exact solution of Maxwell’s electromagnetic field equations for a plane light wave interacting with a homogenous sphere of a radius $R$ with a fixed relative index of refraction $n$, which is defined as the ratio between the refractive index of the sphere ($n_s$) to the refractive index of the surrounding medium ($n_m$) [53, 54]. The scattering and extinction efficiency factors ($Q$) using
full Mie theory expression can be obtained by solving the Maxwell’s equations under specific boundary condition. The scattering (or extinction) efficiency factor \( Q_{\text{sca}} \) (or \( Q_{\text{ext}} \)) is defined as the ratio of the scattering (extinction) cross-sectional area, \( C_{\text{sca}} \) (or \( C_{\text{ext}} \)), divided by the physical cross-sectional area \( \pi R^2 \). \( Q_{\text{sca}} \) and \( Q_{\text{ext}} \) can be expressed as:

\[
Q_{\text{sca}} = \frac{C_{\text{sca}}}{\pi R^2} = \frac{2}{x^2} \sum_{l=1}^{\infty} (2l + 1) \left[ |a_l|^2 + |b_l|^2 \right]
\]

\[
Q_{\text{ext}} = \frac{C_{\text{ext}}}{\pi R^2} = \frac{2}{x^2} \sum_{l=1}^{\infty} (2l + 1) \Re(a_l + b_l)
\]

(1.1)

where \( Q_{\text{ex}} = Q_{\text{sca}} + Q_{\text{abs}} \), and the coefficients \( a_l \) and \( b_l \) are given as:

\[
a_l = \frac{m \psi_j(nx)\psi'_j(x) - \psi'_j(nx)\psi_j(x)}{m \psi_j(nx)\zeta'_j(x) - \psi'_j(nx)\zeta_j(x)},
\]

\[
b_l = \frac{\psi_j(nx)\psi'_j(x) - m \psi'_j(nx)\psi_j(x)}{\psi'_j(nx)\zeta_j(x) - m \psi_j(nx)\zeta'_j(x)},
\]

(1.2)

where \( x = 2\pi n_s R / \lambda = kR \), \( n = n_s / n_m \), \( \psi_j(z) \) and \( \zeta_j(z) \) are Riccati-Bessel function defined as:

\[
\psi_j(z) = \sqrt{\pi z/2} \times J_{l+1/2}(z),
\]

\[
\zeta_j(z) = \sqrt{\pi z/2} \times \left[ J_{l+1/2}(z) - i Y_{l+1/2}(z) \right]
\]

(1.3)

When the size of particle is much smaller than the wavelength of the radiation, the above expression can be simplified by ignoring higher order terms. This gives the more popular form of Mie Theory for spherical particles:
In this equation, $\varepsilon_m$ is the dielectric constant of the surrounding medium, $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is the complex dielectric constant of the particles. From Equation 1.4, an absorption peak is expected to show up when the condition of $\varepsilon_1 = -2\varepsilon_m$ is satisfied [52]. This is the surface plasmon band which accounts for the brilliant color of metal nanoparticles.

1.1.3 Elongated nanorods-Gans model

The shape of the particle plays an important role on the surface plasmon absorption. Mie theory has to be modified to describe such a system. However, it may be impossible to obtain a direct solution for some shapes. Gans predicted in 1912 that for rod shaped particles the surface plasmon band would split into two different modes due to the orientation of the rod with respect to the electric-magnetic wave [55]. According to Gans, the extinction coefficient can be expressed as [56]:

$$C_{\text{ext}} = \frac{2\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2}{\left(\varepsilon_1 + 2\varepsilon_m\right)^2 + \varepsilon_2^2}$$

(1.4)

$$C_{\text{ext}} = \frac{2\pi V}{3\lambda} \varepsilon_m^{3/2} \sum_j \frac{(1/P_j^2)\varepsilon_2}{\left(\varepsilon_1 + \frac{1 - P_j}{P_j^2}\varepsilon_m\right)^2 + \varepsilon_2^2}$$

(1.5)
where $V$ is the volume of the rod, $P_j$ ($j = A, B, C$; $A > B = C$, $A =$ length, $B = C =$ width) are the depolarization factors for the elongated particles (nanorod), which are given by:

$$P_A = \frac{1 - e^2}{e^2} \left[ \frac{1}{2e} \ln \left( \frac{1 + e}{1 - e} \right) - 1 \right]$$ (1.6a)

$$P_B = P_C = \frac{1 - P_A}{2}$$ (1.6b)

$$e = \sqrt{1 - \left( \frac{B}{A} \right)^2} = \sqrt{1 - \left( \frac{1}{\xi} \right)^2}$$ (1.6c)

where $\xi = A/B$ is the aspect ratio of the rod. Figure 1.1 shows a calculated spectrum using the Gans model above for a Au nanorod with an aspect ratio of $\xi = 3.5$ embedded in a solution with $\varepsilon_m = 2.5$. The intense peak at $\sim 850$ nm is termed the longitudinal plasmon resonance, and the weaker peak at $\sim 520$ nm is the transverse plasmon resonance. The longitudinal resonance corresponds to electron oscillation along the axis of the rod, and the transverse resonance is oscillation across the rod.
1.2 Time-resolved Spectroscopy

The study of the interaction between the metal nanoparticles and intense sub-picosecond light pulses has become a topic of much interest recently [57-65]. For gold particles visible radiation excites the inter-band transition of the $d$-band electrons to the $sp$ conduction band [66]. This causes the temperature of the electrons to increase very rapidly [67]. The Drude model is also not a complete description of the system and an additional inter-band contribution must be included. To do this, the complex dielectric function for the metal is split into two terms [68, 69]:

Figure 1.1 Calculated absorption spectra for a Au nanorod using Gan’s model.
\[ \epsilon_1 = \epsilon_1^{\text{Drude}} + \epsilon_1^{\text{Interband}} \quad \text{and} \quad \epsilon_2 = \epsilon_2^{\text{Drude}} + \epsilon_2^{\text{Interband}} \] (1.7)

The Drude model or free electron model is given by the following expression [68-70]:

\[ \epsilon^{\text{Drude}} = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma \omega} \] (1.8)

where \( \omega_p = \sqrt{Ne^2/(\epsilon_0 m_e)} \) is the plasma frequency determined by the free electron density \( N \), the electron charge \( e \), the permittivity in vacuum \( \epsilon_0 \) and the electron effective mass \( m_e \). \( \Gamma \) is damping factor which has a form of \( \Gamma = \Gamma_0 + Av_F/R \).

Here \( \Gamma_0 \) is the bulk damping constant, \( v_F \) is the Fermi velocity, and \( R \) is the radius, \( A \) is a parameter depending on the electron scattering process [52]. The temperature dependence of inter-band dielectric constants can be obtained from the Rosei model and the Kramer-Kronig relation as [68, 70-73]:

\[ \epsilon_2^{\text{Interband}}(T) = \frac{f}{\pi} \int_0^{\nu_d(\omega - \omega_{\text{Interband}})} \frac{1 - g(E, T)}{\sqrt{\nu_d^2 h(\omega - \omega_{\text{Interband}}) - E}} dE \] (1.9a)

\[ \epsilon_1^{\text{Interband}}(T) = \frac{2}{\pi} P \int_0^{\infty} \frac{\nu_{\text{Interband}}^2}{(w^2 - \omega^2)} dw \] (1.9b)

where \( g(E, T) \) is the Fermi distribution, \( \omega_{\text{Interband}} \) is the frequency of the inter-band transition, \( \nu_d \) is related to the relative dispersion of the conduction and valence bands, \( f \) is related to the transition matrix elements, and \( P \) represents the principle value for the integral [73].

From above formulas, the change in the dielectric constant of the metals with temperature can be calculated, and thus the extinction spectra can be
determined by using numerical methods. The main result from the interaction with a short laser pulse is a broadening of the plasmon band [74-80]. This causes a strong bleach signal at the plasmon band maximum and creates two absorption shoulders in the transient difference spectra [74, 77, 80]. Figure 1.2 shows calculated transient spectra for gold particles and gold nanorods for an increase in electronic temperature of 1000 °C.

Figure 1.3 shows a typical transient absorption spectra taken by the Hartland group for 40 nm diameter Au nanospheres in solution [80]. This shows bleach signal at the plasmon maximum and the absorption features in the wings of the band can be clearly seen. In lower right panel of Figure 1.3, the coherent vibrational mode due to the laser-induced lattice heating can be observed, this will be discussed in following chapters. The general features of the calculated and experimental spectra are in good agreement.
Figure 1.2 Calculated absorption spectra of gold particles (top) and nanorods (bottom: aspect ratio = 3) in water at room temperature (solid line) and for an increase in electronic temperature of 1000°C (dashed line). The insert shows the difference spectra, which displays a strong bleach signal at the plasmon resonance.
Figure 1.3  Top: transient absorption data for ~40 nm diameter gold particles in aqueous solution with time and wavelength resolution. The bottom two panels show transient absorption spectra recorded at different times (left), and traces of the signal versus time at two wavelengths (right).
1.3 References


CHAPTER 2

EXPERIMENTAL

2.1 Ultrafast Laser System

2.1.1 Ultrashort pulse generation

All the experiments in the following chapters were performed with a commercial ultrafast laser system (Clark-MXR, CPA-1000). The system layout is shown in Figure 2.1. Briefly, a Spectra Physics Millenia Vs diode pumped Nd:YAG laser was used to pump a mode-locked Ti:Sapphire oscillator (Clark-MXR, NJA-4). A pulse-train at a 100 MHz repetition rate and energy of 4 nJ/pulse was delivered from the oscillator. The average power is roughly 400 mW and the FWHM is approximately 40-60 femtoseconds. The central wavelength can be tuned within 760-840 nm. In all the transient experiments performed in this work, a tunable probe laser pulse is needed. This can be obtained from a white light continuum, but white light generation requires a relatively high peak powers. This is achieved by the chirped pulse amplification technique illustrated in Figure 2.2. The pulses are expanded first in time (over 200 ps FWHM) by a grating-telescope combination in the “stretcher”, then the seed laser beam is directed into
Figure 2.1  Diagram of the regeneratively amplified laser system. BS: Beam Splitter.
the regenerative amplifier. The amplifier is a second Ti:Sapphire crystal pumped with 532 nm radiation from a Q-switched Nd-YAG laser operating at 1 kHz repetition rate. The amplified pulses are finally re-compressed to obtain very short and high power pulses (0.5 mJ/pulse) by a grating “compressor”. The output from the “compressor” now can be used to perform the transient experiments. During the experiment, it is necessary to measure the width of the pulse to obtain an optimal output. In all the following chapters, the FWHM of the pulse is usually compressed to below 150 fs, which is measured by an autocorrelator. In this measurement, a 50:50 beam splitter is used to create two identical intensity pulses.

Figure 2.2  Chirped Pulse Amplification procedure. See text for details.
These two pulses are directed into a nonlinear crystal leading to a Second
Harmonic Generation (SHG) signal. The timing between the two pulses is
controlled by a motor-driven translation stage. When the pulses overlap in time,
the intensity of the SHG signal reaches a maximum. A LabVIEW program on a
computer records the intensity versus the delay time, and fits this to a $\text{sech}^2$
function to determine the pulse-width.

2.1.2 Transient Absorption Experiments

A “pump” and a “probe” beam are used in all the transient absorption
experiments. Figure 2.3 shows the optical set-up for most of the experiments in
the following chapters. The output of the regenerative amplifier (780-800 nm; 0.5
mJ/pulse; 120-150 fs fwhm sech$^2$ deconvolution; 1 kHz repetition rate) is split by a
90:10 beamsplitter. The 90% portion of the pulse train supplies the pump laser
pulses. The intensity of these pulses is controlled with a $\lambda/2$-waveplate/polarizer
combination. For most of the transient experiments, the pump pulses are frequency
doubled in a BBO doubling crystal to create a 400 nm pump beam. For some
experiments, the fundamental wavelength (800 nm) is used as the pump beam. The
10% portion of the pulses is directed to a 3 mm sapphire window to generate a
white light continuum for the probe light and then steered towards the sample. The
pump and probe are cross-overlapped at the sample, usually by focusing with a 10
cm lens. The white light continuum ensures a wide selection range for the probe
light in different transient experiments. A monochromator (Jobin-Yvon Spex H-10)
Figure 2.3 Transient absorption experiment set-up for most of the experiments performed in this work. The dashed line panel shows the signal detection system. BS = Beam splitter, WP = Wave plate, POL = Polarizer, L = Lens, SHG = Second harmonic generation, WLG = White light generation, PD = Photodiode.
is placed after the sample to detect specific wavelengths. Signal normalization is achieved by splitting off a small portion of the probe beam before the sample. The reference is monitored by another monochromator (Jobin-Yvon Spex H-10). Both the signal and reference are detected by Thorlabs photodiodes (PDA55, 13 mm²). The large area of the detectors helps to minimize thermal lensing signals. The timing between the pump and probe pulses is controlled by a stepper motor driven translation stage (Newport UTM150PP.1) controlled by the same computer used for the autocorrelation. To acquire the transient data, a pre-scan is performed to define the zero time in the transient signal. Then the translation stage is scanned back and forth in steps while a lock-in amplifier averages the signal during the scan.

### 2.1.3 Detection Electronics

The signal detection and processing set-up is highlighted in Figure 2.3. Both the “signal” and “reference” from the photo-diodes are gated by boxcar integrators (Stanford Research Systems, Model SR250) triggered at the laser frequency. The boxcars produce quasi-dc voltages with an amplitude that is proportional to the probe laser intensity. The outputs from the signal and reference channels of the boxcar are divided with an IC divider (Burr&Brown, DIV 100) and then fed into a lock-in amplifier (Stanford Research Systems, Model SR830) which is referenced to a synchronous optical chopper (New Focus 3501) that modulates the pump laser pulses. The voltage detected by the lock-in amplifier is proportional to the change in absorbance of the sample induced by the
pump laser beam. Thus, it allows us to perform time-resolved spectroscopy on the sample through running the LabVIEW data acquisition program from the computer.

2.2 Synthesis of nanoparticles

The nanoparticles used in the transient experiments were synthesized via different techniques. Both the size and shape of the nanoparticles can be controlled. In the following sections, a variety of synthesis methods will be discussed.

2.2.1 Radiation method and spheres

γ-radiation has been widely used in the preparation of metal nanoparticle colloids, and has proved to be a very successful method to grow larger metal nanoparticles [1-7], and core-shell type bimetallic particles [8-12]. Compared to conventional chemical methods, radiation chemistry has several advantages. It produces monodisperse nanoparticles, and the reduction of metal ions can be very well controlled without adding excess reducing agents. For example, to grow Au particles, a solution of seed particles is first synthesized via the well-known “Turkevich method” [13]. In this method, citrate is used as reducing agent and
yields roughly 15 nm Au nanoparticles with a fairly narrow size distribution. This is accomplished via the following reaction:

\[
6\text{AuCl}_4^- + \text{C}_6\text{H}_5\text{O}_8 + 5\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 24\text{Cl}^- + 6\text{Au}^0 + 18\text{H}^+ \quad (2.1)
\]

Then a solution containing the Au seed particles, \(\text{Au(CN)}_2^-\) and methanol (\(\text{CH}_3\text{OH}\)) and nitrous oxide is \(\gamma\)-irradiated with a \(\text{Co}^{60}\) source, this produces 1-hydroxymethyl radicals (\(\cdot\text{CH}_2\text{OH}\)). These radicals can react with the colloid particles by transferring electrons, thus a large number of electrons can be stored at the seed particles. These electrons assist the reduction of \(\text{Au(CN)}_2^-\) directly onto the surface of the seed particles. The reactions occurring in the irradiation process are proposed as \([7]\):

\[
x \cdot\text{CH}_2\text{OH} + \text{Au}_n \rightarrow x \cdot\text{CH}_2\text{O} + x\text{H}^+ + \text{Au}_n^{x-}
\]

\[
x \cdot\text{Au(CN)}_2^- + \text{Au}_n^{x-} \rightarrow \text{Au}_{(n+x)} + 2x \cdot\text{CN}^- \quad (2.2)
\]

The \(\text{CN}^-\) ions can be removed from the reaction system by ion-exchange resin.

Figure 2.4 shows the UV-Vis spectra of different sized Au nanoparticles used in our experiments. The radiation method can also be applied to synthesize core-shell bimetallic particles. In this case the seed particles are different from the metal complex ions to be deposited on the surface of the seeds. The TEM micrographs of both the “Turkevich sample” and Au-Ag core-shell particles are shown in lower panel of Figure 2.4.
Figure 2.4 Upper panel: the extinction spectra of the gold spheres with different diameters produced by radiation method. Lower panel: TEM images of 20 nm diameter Au nanoparticles prepared using the Turkevich method (lower left), and after coating with Ag (lower right). The molar ratios are Au:Ag = 1:1.
2.2.2 One dimensional structures

There are several different synthesis methods for preparation of metal nanorods. For example, the template method introduced by Martin and co-workers [14-16], the electrochemical synthesis demonstrated by Wang et.al. [17, 18], the seed mediated growth method in solution reported by Natan and Murphy [19-27], and recently Yang and co-workers prepared gold nanorods via a photochemical method [28]. The emphasis in this chapter is the electrochemical method and seed mediated growth route, as these were the techniques used to produce the particles in our experiments.

2.2.2.1 Electrochemical method

This synthesis is conducted within a simple two-electrode-type electrochemical cell. A gold metal plate is used as the anode and the cathode is a platinum plate. Both electrodes are immersed in an electrolytic solution which contains a cationic surfactant, hexadecyltrimethylammonium bromide (C\textsubscript{16}TAB) and a much more hydrophobic cationic cosurfactant, tetradecylammonium bromide (TC\textsubscript{12}AB). The C\textsubscript{16}TAB serves not only as the supporting electrolyte but also as the stabilizer for nanoparticles, to prevent their further growth while the TC\textsubscript{12}AB acts as a rod-inducing regent. The electrolytic cell containing the mixed solution is then placed into an ultrasonic bath. A small amount of acetone and cyclohexane are added into the electrolytic solution before the electrolysis.
Acetone is used for loosening the micellar framework, and cyclohexane is necessary for enhancing the formation of the elongated rodlike $C_{16}$TAB micelles [29]. Electrolysis is carried out under constant current mode for a typical electrolysis time of 30 min. During the synthesis, the bulk gold metal is converted from the anode to form gold complex ions $AuBr_4^-$, and these ions are driven by the current to the cathode. The reduction reaction takes place at the interfacial region of the cathodic surface and within the electrolytic solution. At the same time, the gold ions form a complex with the cationic surfactants, and this facilitates the formation of rod-like particles.

To better control the aspect ratio of the gold nanorods, an additional Ag plate is immersed into the electrolytic solution. The $AuBr_4^-$ produced from the anode oxidizes the silver metal to ions (in the form of AgBr), and it is found that the concentration of silver ions and their release rate affects the length of the nanorods [18]. However, the complete mechanism is still not very clear so far. Yang et. al. proposed a mechanism for the role of the Ag ions in the synthesis of Au nanorods from their photochemical method. Briefly, silver exists in either AgBr or neutral cluster form because of the competition between the photoreduction and chemical reactions with $AuCl_4^-$ . This redox dynamics modulates the nascent surfaces of Au nanocrystals (produced by UV reduction), and subsequently the growth rate along a particular direction is enhanced. Yang et. al. believe that this mechanism is shared with the electrochemical method here [28].
2.2.2.2 Seed mediated method

A variety of groups reported the use of seeds to facilitate the formation of monodisperse metal nanorods. Different reducing regents were employed, such as hydroxylamine, sodium citrate and ascorbic acid. A systematic study has been reported recently by Murphy and co-workers [24, 25]. In a typical synthesis, a 3.5 nm gold seed particles solution is first prepared by sodium borohydride (NaBH₄) reduction in the presence of citrate, which serves only as the capping agent since it cannot reduce gold salt at room temperature. A growth solution containing gold salt (HAuCl₄) and cetyltrimethylammonium bromide (C₁₆TAB) is mixed with freshly prepared ascorbic acid solution (a mild reductant). Then a two or three-step seeding process is used for the nanorod synthesis. This synthesis also produces spheres. The excess surfactant is removed by performing centrifugation. Figure 2.5 shows a representative TEM image of long Au nanorods from the Murphy group [24].

The mechanism of formation of rod-like nanoparticles in aqueous surfactant medium has been investigated by both the Murphy and El-Sayed groups [27, 30]. Murphy proposed that the trimethylammonium headgroup of the C₁₆TAB selectively binds on specific crystallographic faces of the seeds or rods, while the tails of the C₁₆TAB molecules form a bilayer structure with each other through van der Waals interactions. Figure 2.6 presents such a scheme from
Figure 2.5  TEM images of gold nanorods with an aspect ratio of 18 prepared by seed-mediated growth method from Murphy group [24].

Figure 2.6  A proposed growth mechanism model for the seed mediated method by Murphy and co-workers [27]. The bilayer structure formed by C\textsubscript{16}TAB, which absorbed on specific crystallographic faces of the Au nanorods, may facilitate the growth of rods along a specific direction while more gold ions are introduced.
Murphy’s research work [27]. These bilayers play an important role for promoting the formation of rods. Experimental studies found that surfactants with longer chain lengths lead to longer rods, and higher yield compared to shorter ones. The seed mediated method can also be applied to the synthesis of other noble metal nanorods, for example silver. The final shapes generated from the seed mediated growth method depend on which crystallographic surface of the seed the surfactant molecules select to bind. Different binding area and different seed crystal will assist different growth directions and yield different shapes. Thus, in a seed mediated synthesis, a variety of shapes may be produced. For gold, the majority of shapes are rods and spheres, while silver can yield other shapes, such as triangles as well as spheres and rods.

2.2.3 Other shape controlled synthesis

Two and three dimensional structures have been synthesized via variety of techniques such as wet chemistry and lithography. Jin and Mirkin demonstrated a pioneering work in the controlled synthesis and optical characterization of metal nanotriangles [31]. They converted Ag nanospheres into (truncated) triangular shaped particles by irradiation with a fluorescent lamp. In a typical experiment, a Ag nanosphere colloid solution was first prepared by reduction of AgNO$_3$ with sodium borohydride (NaBH$_4$) in the presence of citrate. A small amount of Bis($\rho$-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt solution (BSPP) was subsequently added to the solution as a particle stabilizing agent. The system
was then irradiated with a conventional fluorescent light. The surface plasmon band of the Ag particles was monitored by UV-Vis spectroscopy. The color changes of the solution from yellow to green and blue after adequate irradiation indicates the transformation of nanospheres to nanotriangles. The optical spectra of the nanotriangles display a strong in-plane dipole resonance in the visible to near-IR range. Discrete dipole approximation (DDA) calculation shows that this resonance is very sensitive to the sharpness of the tips on the triangles [31, 32]. Other bands observed include in-plane and out-of-plane quadrupole resonances in the visible and UV regions. The out-of-plane dipole band is very weak and broad, and only reflected as a small shoulder. Other shapes like Ag nanocubes and nanoboxes have been synthesized by Xia and coworkers [33, 34]. They demonstrated that the polyol method can be applied to the large-scale production of Ag nanowires by reducing AgNO$_3$ with ethylene glycol in the presence of PVP, and they then developed this method to generate uniform Ag nanocubes by simply controlling the concentration of AgNO$_3$ and the molar ratio between PVP and AgNO$_3$. These nanocubes were used to make several other structures, like hollow Au nanoboxes, through a galvanic replacement reaction between the silver nanostructures and HAuCl$_4$ in aqueous medium. This makes the surface plasmon resonance tunable from UV across to the near-IR range. These materials are expected to find useful applications in photothermal cancer therapy and photothermally triggered drug release. Representative TEM images of these particles are shown in Figure 2.7.
Figure 2.7  The TEM images of Ag nanospheres before irradiation with fluorescent light (A) and Ag nanoprisms (B) produced after 70 hours irradiation from Mirkin group [31]. (C) and (D) show the SEM images of Ag nanocubes and Ag-Au nanoboxes produced by Xia and coworkers [33], the insets at upper right-hand corners of panel (C) and (D) are the electron diffraction patterns taken from individual Ag nanocubes and Ag-Au nanoboxes, respectively.
2.3 References


[34] Sun, Y. G.; Xia, Y. N. *Science* 2002, 298, 2176.
CHAPTER 3

SPHERICAL METAL NANOPARTICLES

3.1 Introduction

The research on nanoparticles has become very intense during the last several years. Due to the interdisciplinary nature of nanotechnology, it draws a lot of attention not only in the chemistry community, but also in other science and engineering fields. Recently, the interaction of intense ultrafast light pulses with nanoparticles received a lot of attention from physical chemistry research [1-5]. The basic procedure in this interaction is that the ultrafast laser pulse excites the conduction band electrons of the nanoparticles, which subsequently relax by electron-electron (e-e) scattering to give a hot electron distribution. The temperature of the electrons can increase by up to thousands of Kelvin. The hot electrons then equilibrate with the lattice by electron-phonon (e-ph) coupling. This sequence of events is identical to what happens in bulk metals [6, 7]. In bulk metals, the energy deposited by the laser diffuses away from the excitation region in a way that depends on the thermal conductivity of the metal. In contrast, for particles, the final step in the relaxation process is transfer of energy from the hot electron/phonon system to the environment [1, 2]. Another interesting topic is the
lattice expansion. As we will show in this chapter, the time scale for heating is faster than the period of the phonon mode that correlates with the expansion coordinate – the symmetric breathing mode for spherical particles. This means that this mode can be coherently excited. The mechanism for coherent excitation will be discussed in detail.

Most of the recent experimental work in this area has focused on the relatively fast e-e and e-ph relaxation processes. However, the particle-to-surroundings energy transfer process is also important and is not very well understood. This is an important topic for applications. For example, heat dissipation from bio-functionalized Au nanoparticles has been used to selectively kill cells and study denaturation of proteins [8]. This process is the rate determining step for energy dissipation; that is, it controls how long the particles remain hot after laser excitation. Our interest in energy transfer from the particles to their environment stems from studying laser-induced alloying in core-shell bimetallic particles [9]. To calculate an effective interdiffusion time for these systems we needed to know how long the particles remain hot after excitation, which means we needed to know the time scale for energy transfer to the environment.

The particles usually take up to several hundred picoseconds to dissipate the energy to the environment [1, 2, 10, 11]. Nanoparticles with different sizes and shapes, or surface properties, may have different heat dissipation time scales and mechanisms. El-Sayed and coworkers investigated the heat dissipation for 15
nm gold nanoparticles in different environments [12, 13]. Their studies showed that the relaxation depends on the surroundings, specifically, liquids with higher thermal conductivities give faster relaxation times [12]. Another set of experiments on gold nanoparticles in MgSO₄ powder were also performed, and in this case they concluded that the relaxation time scale again depends on the surroundings [13].

3.2 Experimental

The experiments described in this chapter were performed with a regeneratively amplified Ti:sapphire laser. Briefly, the output of the laser (λ = 780 nm; 0.5 mJ/pulse; 120 fs fwhm sech² deconvolution; 1 kHz repetition rate) was split by a 90:10 beam splitter. The 90% portion was frequency doubled in a 1 mm BBO crystal to generate 390 nm pump pulses. The intensity of these pulses was controlled with a λ/2-waveplate/polarizer combination. The 10% portion was used to generate a white light continuum in a 3 mm sapphire window, which was used as the probe. The pump and probe were crossoverlapped at the sample by focusing with a 10 cm lens, and the polarizations were set to parallel for all of the experiments described below. Specific probe wavelengths were selected using a Jobin-Yvon Spex H-10 monochromator (10 nm spectral resolution) placed after the sample. Fluctuations in the probe laser intensity were normalized by splitting-off and monitoring a small portion of the probe beam before the sample. The
timing between the pump and probe pulses was controlled by a stepper motor driven translation stage (Newport UTM150PP.1).

The pump laser intensity at the sample was measured by a Molectron J3-02 Energy Detector, and the pump laser spot size was $(6 \pm 1) \times 10^{-4} \text{ cm}^2$ for these experiments. The spot size was measured using both standard laser burn paper and by observing the laser-induced color change in a thin film of Au particles deposited on a glass slide. These measurements gave equivalent results, but the images of the beam are much clearer from the thin Au particle films.

Au particles with a 15 nm diameter were prepared using the standard citrate reduction recipe [14]. Smaller 4 nm diameter Au particles were made using NaBH$_4$ as the reductant rather than citrate. Particles with 26, 40, and 50 nm diameters were made by depositing Au onto the surface of the 15 nm particles using radiation chemistry [15, 16]. In this technique, the excess citrate is removed by ion exchange with Cl$^-$, and $\gamma$ irradiation is carried out under an atmosphere of nitrous oxide with ~0.3 M methanol added to the solution. Thus, the 15 nm particles are stabilized by adsorbed citrate ions, the 4 nm particles are (probably) stabilized by BO$_2^-$ (the oxidized form of BH$_4^-$), and the larger particles prepared by radiation chemistry are stabilized by Cl$^-$. These different anions are not expected to significantly change the energy relaxation dynamics. The particle sizes were measured either by TEM or by observed quantum beats due to the symmetric breathing mode of the particles in transient absorption experiments [17, 18]. The samples were held in 2 mm cuvettes, and the experiments were
performed without flowing. However, the relatively low pump laser powers and repetition rates used in these experiments mean that thermal effects, which arise from heat accumulation in the solvent, are not a problem. The concentration of Au was adjusted to \(1.2 \times 10^{-4}\) M for all of the experiments presented below.

The probe laser wavelength used was \(\lambda = 530\) nm, i.e., at the maximum of the Au plasmon band. This wavelength was chosen for several reasons. First, tuning the probe to the maximum of the plasmon band maximizes the signal intensity, which allows us to perform experiments at low excitation levels. Second, the contribution from the beat signal mentioned above is minimized at this wavelength [19]. Third, the signal in this spectral region is dominated by the broadening of the plasmon band induced by the increase in the electronic temperature [20-22]. This creates a transient bleach at the plasmon band maximum, the magnitude of which tracks the electronic temperature [20, 21]. The transient absorption signals at wavelengths significantly displaced from the plasmon band maximum have a more complicated temperature dependence [21].

Careful measurement of the power absorbed by the sample shows that the pump laser absorption follows Beer's law under the experimental conditions. In this case, the temperature rise in the particles can be simply calculated from the pump laser intensity \((I_0)\), the spot size \((\sigma)\), the sample absorbance \((A)\), and the concentration and heat capacity \((C_p)\) of Au:

\[
\Delta T = \frac{I_0(1-\theta)^2(1-10^{-4})}{C_p[Au]\sigma l} \tag{3.1}
\]
In this equation, the \((1 - \theta)^2\) factor accounts for scattering of the pump laser at the front and back surfaces of the input window of the sample cell \((\theta \approx 0.04)\) and \(l\) is the length of the cell. Equation 3.1 assumes that no energy is lost to the environment during the e-ph coupling process. It will be shown below that this is a reasonable assumption for ultrafast experiments with particles larger than ca. 10 nm diameter. Note that the temperature increase in the particles primarily depends on the heat capacity of Au, the absorption coefficient of the particles at the pump laser wavelength, and the pump laser flux \((I_0/\sigma)\) at the sample. In addition, for 390 nm pump pulses, the absorption coefficient is \(\varepsilon \approx 2000 \text{ M}^{-1} \text{ cm}^{-1}\) for all of the samples examined, i.e., \(\varepsilon\) does not strongly depend on size at this wavelength [15, 16]. Also note that under the conditions of the experiments (<\(\mu\)J pulse energies) the temperature increases created by the pump laser are <200 °C. The error in the calculated temperatures from Equation 3.1 is ±15% and is almost completely due to the uncertainty in the laser spot size.

### 3.3 Coherent Vibrational Motion in Nanospheres

The heat deposited into the lattice causes the particles to expand. For Au nanoparticles larger than ca. 6 nm, the time scale for heating is faster than the period of the phonon mode that corresponds to the expansion co-ordinate (the symmetric breathing mode) [17, 18, 23-25]. This means that this mode can be impulsively excited. Figure 3.1 shows results from transient absorption
Figure 3.1  Transient absorption data for ca. 50 nm diameter Au particles in aqueous solution, recorded with different probe laser wavelengths. Note that the strong bleach signal in the 520 nm to 560 nm region has been cut-off to better illustrate the modulated portion of the data.
experiments with ca. 50 nm diameter Au particles performed with a series of
probe wavelengths. Modulations due to the symmetric breathing mode can be
clearly seen in the data. The maximum in the modulations occurs at ca. 550 nm,
which is 25 nm red-shifted from the maximum of the plasmon band for these
samples. Careful inspection of the transient absorption data shows that the
modulations for probe wavelengths on the red and blue sides of the plasmon band
are 180° out-of-phase. This implies that this signal arises from a periodic change
in the position of the plasmon band [18, 26]. The coherently excited vibrational
motion shows up as a modulation in the transient absorption traces because it
changes the electron density of the particles and, therefore, the position of the
plasmon resonance. The observed period depends on the size and shape of the
particles, and their elastic properties. For spherical particles the period of the
symmetric breathing mode is given by [27-29]

\[
T_{br} = \frac{2\pi R}{\eta c_l}
\]

(3.2)

where \( R \) is the particle radius, \( c_l \) is the longitudinal speed of sound, and \( \eta \) is an
eigenvalue that depends on the transverse and longitudinal speeds of sound. The
value of \( \eta \) can be obtained by solving the boundary condition equation:

\[
\eta \cot \eta = 1 - \eta^2 / 4 \delta^2
\]

where \( \delta = c_c / c_l \) and \( c_c \) is the transverse speed of sound [27-29]. This result assumes that the particles are isotropic, i.e., polycrystalline.
Calculations using Equation 3.2, and values of \( c_c \) and \( c_l \) for bulk gold, are in
excellent agreement with the experimental data for Au particles with diameters
between 8 nm and 120 nm [18]. This means that the elastic property of 8 nm diameter particles are the same as those for bulk gold.

The transient absorption data in Figure 3.1 can be used to determine how the position of the plasmon resonance (\(\omega_{\text{max}}\)) changes with time. The peak position versus time data, in turn, allows us to estimate how the size of the particles changes with time [19]. Assuming that the dielectric function of the metal is dominated by free electron contributions [30], it can be shown that the maximum of the plasmon band occurs at [31]:

\[
\omega_{\text{max}} = \frac{\omega_p}{\sqrt{1 + 2\epsilon_m}}
\]

(3.3)

where \(\epsilon_m\) is the dielectric constant of the medium and \(\omega_p\) is the plasma frequency. The plasma frequency is given by \(\omega_p = \sqrt{Ne^2/\epsilon_0 m_e}\) where \(N\) is the electron density, \(m_e\) is the effective mass of the electrons, and \(\epsilon_0\) and \(e\) have their usual meanings [30]. Thus, changes in the size of the particles affect \(N\) and, therefore, the position of the plasmon resonance. Calculations using Equation 3.3 to convert the \(\omega_{\text{max}}\) data to radius versus time are shown in Figure 3.2 [19]. The important points to note are that: (i) in these experiments laser excitation produces an overall increase in the radius of the particles of \(~0.4\%\), just after the electrons and phonons have reached equilibrium. (ii) The oscillations in the radius are \(~50\%\) of the overall increase in size.

A simple way to understand how this beat signal is generated is as follows. The pump laser deposits energy in the electronic degrees of freedom, which
Figure 3.2 Change in radius versus time for the Au particles in Figure 3.1. (●) Experimental data; (—) calculated using Equations 3.4–3.6; (---) calculations that ignore hot-electron pressure effects in the coefficient for thermal expansion.
subsequently flows into the phonon modes on a picosecond time scale. This increases the lattice temperature, and causes the particles to expand. Because lattice heating is faster than the phonon mode that correlates with the expansion coordinate, the nuclei cannot respond instantaneously. Thus, following excitation the nuclei start to move along the expansion coordinate (the symmetric breathing mode) and pick-up momentum. When they reach the equilibrium radius of the hot particles their inertia will cause them to overshoot. The elastic properties of the particle then provide a restoring force that makes the nuclei stop, and reverse their motions. The competition between the impulsive kick from the rapid laser induced heating, and the restoring force from the elastic response of the particles, cause the nuclei to “ring” around the equilibrium radius of the hot particles.

The response of the nuclei to the rapid laser induced heating can be modeled by treating the symmetric breathing mode as a harmonic oscillator [17-19, 25]:

\[
\frac{d^2R}{dt^2} + 2\Gamma \frac{dR}{dt} + \left(\frac{2\pi}{\tau}\right)^2 \{R - [R_0 + \Delta R_0(T)]\} = 0
\] (3.4)

In this equation \(\tau\) is the period of the vibrational motion, \(\Delta R_0(T)\) is the increase in the radius of the particles due to heating, and \(\Gamma\) is a phenomenological damping constant. \(\Delta R_0\) can be simply calculated from the coefficient for thermal expansion (\(\kappa\)) by \(\Delta R_0/R_0 = (\kappa/3)\Delta T\), where \(\Delta T\) is the temperature increase [18, 19]. The change in the lattice and electronic temperature after ultrafast laser excitation can be calculated using the Two-Temperature Model [7, 32-34]. In this model the electron
and phonon sub-systems are characterized by two separate temperatures, $T_E$ and $T_L$, and they exchange energy in a way that depends on the temperature difference. Specifically,

$$C_E \frac{dT_E}{dt} = -g(T_E - T_L)$$

(3.5a)

$$C_L \frac{dT_L}{dt} = g(T_E - T_L)$$

(3.5b)

where $C_E$ and $C_L$ are the electronic and lattice heat capacities, and $g$ is the electron-phonon (e-ph) coupling constant [7, 32-34]. The electronic and lattice heat capacities play off each other in an interesting way. The lattice heat capacity is over two orders of magnitude larger than the electronic heat capacity [30], which means that the overall change in the temperature (once the electrons and phonons have reached equilibrium) is determined by $C_L$, and is much less than the initial electronic temperature. However, inspection of Equation 3.5a shows that the time scale for coupling between the electrons and phonons is controlled by $C_E / g$ [26]. Because $C_e = \gamma T_e$ is temperature dependent, this time scale depends on the initial electronic temperature.

It is important to note that the coefficient for thermal expansion contains contributions from the lattice and the electronic degrees of freedom. This can be seen by writing $\kappa$ in terms of the heat capacities [30]:

$$\kappa = \frac{1}{B} (\gamma_L C_L + \frac{2}{3} C_E(T_E))$$

(3.6)
where $B$ is the bulk modulus, $\gamma_L$ is the Grüneisen parameter for the lattice [30], and the temperature dependence of $C_E$ has been explicitly noted. For metals $C_E \ll C_L$ when the electrons and lattice are in thermal equilibrium, which means that the anharmonicity in the potential energy surface for the ions dominates expansion. However, in ultrafast experiments $T_E \gg T_L$ at early times, which makes the electronic and lattice contributions to expansion approximately equal. The effect of the electronic degrees of freedom on $\kappa$ is known as hot-electron pressure [6, 35]. The force due to the hot electrons decays rapidly as the electrons equilibrate with the phonons. On the other hand, the contribution to expansion from the nuclei reaches a maximum when the electrons and phonons reach thermal equilibrium, and decays slowly as energy is transferred from the particle to the environment. Thus, the nuclear heating contribution to expansion is a step function like perturbation, whereas, the electronic contribution is a delta-function like perturbation. In the harmonic oscillator model these two driving forces produce modulations that have a different phase [19, 25, 36].

Calculations using the harmonic oscillator model with Equation 3.6 for $\kappa$ are included in Figure 3.2 as the solid line. The time dependent temperatures for the electrons and the lattice were calculated using Equations 3.5a and 3.5b, and the initial temperature rise was determined from the pump laser intensity and spot size, and the absorbance of the sample at 400 nm [19]. The harmonic oscillator model does a good job of reproducing the magnitude and the phase of the oscillations. Importantly, calculations that do not include the contribution from
hot-electron pressure (shown as the dashed line in Figure 3.2) do not correctly reproduce the phase of the modulations. The difference in phase between the two calculations is $\sim 45^\circ$. This analysis provides strong evidence for the existence of hot electron pressure effects in ultrafast experiments with metal nanoparticles. Our conclusions are in excellent agreement with recent work on spherical and ellipsoidal Ag particles in a glass matrix [25, 36]. It is important to note that the instantaneous force due to hot electron pressure may make it possible to coherently excite vibrational motion in very small metal particles, where the period of the symmetric breathing mode is comparable to or faster than the time-scale for lattice heating.

3.4 Heat Dissipation from a Sphere

3.4.1 Theory

Heat transfer or conduction is a classic problem [37]. Here, it is a specific situation, i.e., heat transfer from a solid sphere to an infinite medium. Cooper reported the heat fluxes and temperature profiles for the conduction heat-transfer problem of having a sphere initially at temperature $T_{1i}$ inside a medium initially at temperature $T_{2i}$ [38]. The differential equations that describe this heat transfer process are [37, 38]:

$$\frac{\partial T_p}{\partial t} = \alpha_p \frac{1}{r} \frac{\partial^2}{\partial r^2}[r T_p(r, t)]$$  \hspace{1cm} (3.7a)
Here the subscript “p” and “m” refer to the particle and medium respectively, and \( \alpha \) is the thermal diffusivity of the particle or the medium. \( \alpha \) is related to the thermal conductivity \( k \) by \( \alpha = k/\rho C_p \), where \( \rho \) is the fluid density and \( C_p \) is the heat capacity. At the interface \( R \) (\( R \) is the radius of the particle), the boundary condition is that the temperature and the heat flux are the same for the particle and the medium, that is,

\[
T_p[R,t] = T_m[R,t], \quad k_p \left( \frac{\partial T_p}{\partial r} \right)_{r=R} = k_m \left( \frac{\partial T_m}{\partial r} \right)_{r=R} \tag{3.8}
\]

where \( k_i \) is the thermal conductivity of the particle or the medium. The initial state of the system is that at \( t = 0 \), \( T_p = T_{pi} \), \( T_m = T_{mi} \). By using Laplace transform methods, the temperature profiles were obtained as:

\[
T_p = T_{mi} + \frac{2}{\pi} k_p k_m (T_{mi} - T_{pi}) \sqrt{\frac{\alpha_p \alpha_m}{r}} \times 
\int_0^\infty \frac{e^{(-u^2 R^2/\delta_p)} (u \cos u - \sin u) \sin \left( \frac{uR}{R} \right)}{\alpha_p k_p u^2 \sin^2 u + \alpha_m [k_p (u \cos u - \sin u) + k_m \sin u]^{2}} du \tag{3.9}
\]

Here \( \delta_p \) is the relaxation time of particle and \( \delta_p = R^2/\alpha_p \). By using the numerical solution command in Mathematica\textsuperscript{\textregistered}, the temperature profile of the spherical particles with different diameter can be plotted. The results are shown in Figure 3.3. The initial temperature rise in the particles can be calculated from Equation 3.1 as 80 Kelvin. The values of the parameters used are \( k_p = 317 \text{ W m}^{-1} \text{ K}^{-1} \), \( k_m = 0.611 \text{ W m}^{-1} \text{ K}^{-1} \), \( C_p(\text{Au}) = 0.129 \text{ J g}^{-1} \text{ K}^{-1} \), \( C_p(\text{H}_2\text{O}) = 4.18 \text{ J g}^{-1} \text{ K}^{-1} \), \( \rho(\text{Au}) = 19.3 \text{ g cm}^{-3} \).
Figure 3.3 Calculated temperature versus time profiles using Equation 3.9. From top to bottom, the different traces correspond to particles with diameters of 50, 40, 26, and 15 nm. The insert shows the characteristic time constant for energy dissipation ($\tau$) obtained from fitting the temperature profiles to Equation 3.10, plotted against the square of the radius (in nm$^2$).
g cm\(^{-3}\), and \(\rho(\text{H}_2\text{O}) = 1.0 \text{ g cm}^{-3} \) [39, 40]. The precise value of the particle temperature depends on the chosen value of the radius. In this calculation, \(r = 2R/3\) was chosen. The exact value of \(r\) is not critical (as long as it is not \(r = 0\) or \(R\)). The calculations show that heat dissipation from the particles does not follow a single (or even double) exponential decay. The temperature versus time profiles can be conveniently fitted using a stretched exponential function:

\[
F(t) = A \times \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right]
\]  \hspace{1cm} (3.10)

Compared to a double exponential function, stretched exponential function makes it more convenient to define a characteristic time scale for heat dissipation. The decay time is plotted versus the square of the radius of the particles as the insert of Figure 3.3. This clearly indicates that the heat dissipation process is closely related to the surface area of the particles, i.e., the decay time scales \(\tau \propto R^2\). For different particles, the stretching parameter \(\beta\) obtained from the fit changes from 0.35 for the 15 nm diameter particles to 0.44 for the 50 nm diameter particles. Another interesting feature is that for a given particle, the decay time \(\tau\) and the stretching parameter \(\beta\) do not change with the initial temperature of the particle.

### 3.4.2 Transient Experiment Results

Typical transient bleach data obtained from 15 nm diameter gold nanoparticles is shown in Figure 3.4. The pump laser power was set at 0.2 \(\mu\)J and the probe light was tuned to the plasmon band maximum, i.e., 530 nm. At this
Figure 3.4 Transient bleach data for 15 nm diameter Au particles recorded with 530 nm probe pulses and a pump laser power of 0.4 μJ/pulse. The different regions of the decay (coupling between the electrons and phonons within the particles and coupling between the particles and their environment) are labeled in the figure.
specific wavelength the temperature of the electron distribution is proportional to the bleach signal [20, 21], thus, the temperature changes in the particles can be easily tracked from the transient data. It is very clear that two separate processes occur after the ultrafast laser excitation in Figure 3.4. The initial fast decay corresponds to the electron-phonon (e-ph) coupling process, which results in energy flow from the excited electron distribution into the phonon modes. The subsequent slow decay is the heat transfer process from the particles to the medium, after the electrons and lattice have reached equilibrium. The “break point” represents the point where the electrons and lattice are in equilibrium.

To compare with the theoretical results, transient experiments for different sized gold nanoparticles (4, 15, 26, 40 and 50 nm in diameter) have been conducted. Figure 3.5 shows two sets of the transient bleach data obtained at different pump laser intensity, which result in temperature rises in the particles of 40 K for 0.2 μJ/pulses (Figure 3.5a), and 80 K for 0.4 μJ/pulses (Figure 3.5b). Note that the data have been normalized at the break point where the electrons and the lattice reach equilibrium. The 4 nm particles will be shown separately later. Also shown in Figure 3.5 are fits to the transient bleach data using Equation 3.10. In Figure 3.5, the amplitude of the bleach signal at the break point for each sample is linearly proportional to pump laser power. Equation 3.1 also shows that the temperature increase in the lattice is proportional to the pump laser power. This indicates that the temperature of the lattice can be conveniently tracked from the signal in these experiments. The results in Figure 3.5 show that, similar to the
Figure 3.5 Transient bleach data for different sized Au particles recorded with pump laser powers of (a) 0.2 or (b) 0.4 \( \mu \)J/pulses. The different traces correspond, from top to bottom, to particles with diameters of 50, 40, 26, or 15 nm. The initial temperature rise induced by the pump laser is included in the figure. The dashed lines show fits to the data using Equation 3.10.
calculations, the characteristic time scale for energy dissipation increases as the particle size increases. In addition, for particles of the same size, the form of the bleach recovery is very similar for experiments performed at different laser powers (i.e., Figure 3.5 part (a) compared to part (b)). This is shown in Figure 3.6, where data for the 15 nm diameter particles is plotted for different pump laser powers. Fits to the data using Equation 3.10 are also presented. The values of the time constant and stretching parameter used in these fits are identical for the four traces ($\tau = 40$ ps and $\beta = 0.5$), and only the amplitude was varied. Clearly, each trace can be well fitted using the same $\tau$ and $\beta$ values; that is, the characteristic time scale for energy dissipation is the same for each laser power. Again, this result is consistent with the calculations using the general formula presented in ref [38]. The amplitude extracted from the data is proportional to the laser power (which determines the initial temperature of the particles). This result is consistent with our assumption that the bleach signal is proportional to the temperature of the particles. The values of the time constant $\tau$ obtained from fitting the experimental results in Figure 3.5 are plotted in Figure 3.7, along with the results from the calculations described above. The values of $\tau$ and $\beta$ obtained from this analysis are also collected in Table 3.1. The dashed line in Figure 3.7 is a fit to the experimental time constants assuming that $\tau = \gamma R^2$. Specifically, we find that $\gamma = 0.64 \pm 0.01$ ps/nm$^2$, which means that the temperature in the particles at time $t$ can be estimated by:
Figure 3.6 Transient bleach data for 15 nm diameter Au particles recorded with pump powers of 0.2, 0.4, 0.6, and 0.8 μJ/pulses. The temperature rise in the particle created by the pump laser is given in the figure. The dashed lines show fits to the data using Equation 3.10 with the values of $\tau$ and $\beta$ constrained to $\tau = 40$ ps and $\beta = 0.5$ (i.e., only the amplitude was allowed to vary). These results show that the form of the decay does not depend on the initial temperature.
Figure 3.7 Characteristic time constant for energy dissipation determined using Equation 3.10 versus diameter: (○) experimental data; (—) calculated temperature versus time profiles. The dashed line shows a fit to the data assuming a parabolic dependence of $\tau$ on diameter (i.e., $\tau \propto R^2$).
TABLE 3.1

TIME CONSTANTS (τ) AND STRETCHING PARAMETERS (β) OBTAINED FROM ANALYSIS OF EXPERIMENTAL TRANSIENT ABSORPTION DATA AND CALCULATED TEMPERATURE VERSUS TIME PROFILES

<table>
<thead>
<tr>
<th>diameter (nm)</th>
<th>experiment$^a$</th>
<th>Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ (ps)</td>
<td>β</td>
</tr>
<tr>
<td>5</td>
<td>10 ± 5</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>15</td>
<td>50 ± 10</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>26</td>
<td>130 ± 20</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>40</td>
<td>270 ± 30</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>50</td>
<td>380 ± 40</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>

$^a$ Note that the values of τ and β from the experimental data are correlated. This correlation is reflected in the reported errors.

\[ \frac{T(t) - T_0}{T(i) - T_0} = \exp \left[ -\left( \frac{t}{0.64 \times R^2} \right)^{0.7} \right] \]  \hspace{1cm} (3.11)

where \( T_i \) is the initial temperature, \( T_0 \) is the temperature of the surroundings, and \( t \) and \( R \) are expressed in ps and nm, respectively. It is important to remember that Equation 3.11 is purely phenomenological, there is no fundamental reason heat dissipation should follow a stretched exponential function.

Both the experiments and calculations show that the characteristic time scale for heat dissipation is proportional to the surface area of the nanoparticles, and that the time scale does not depend on the initial temperature of the system. For the calculations, the time constants are uniformly faster than those obtained from the transient experiments. This difference was attributed to the boundary
conditions used in the calculations. Specifically, to obtain a solution to the heat transfer equations for the particle/solvent system, the particle surface was assumed to have the same temperature as the contacting solvent, and that the solvent properties at the particle surface are the same as bulk solvent. However, in the real particle/solvent system, there will be an intermediate region between the particles and the solvent due to the nanoparticle synthesis procedure. In the calculation used in this chapter, the energy transfer between the gold atoms in the particle and the molecular layer was ignored. For small particles, this feature will become important. Therefore, the calculations effectively yield an upper bound for the rate of energy dissipation. To obtain a more accurate estimation of the heat transfer procedure requires a molecular description of the interaction between gold and the solvent [41].

Figure 3.8 presents experimental data for the small (4 nm diameter) Au nanoparticles recorded with 0.4 $\mu$J energy pump laser pulses. The temperature increase for the lattice was estimated to be 80 K. In this case, the signal is almost completely dominated by the e-ph relaxation. A fit to the data yields an estimate of the characteristic time scale for ph-ph coupling of 10 ps. This time constant is comparable to that for the e-ph coupling process (several picoseconds for this experiment). Thus, these results show that significant energy dissipation can occur before the electrons and phonons have reached equilibrium. In other words, for very small particles, the solvent molecules may interact with nonthermal electrons.
Figure 3.8 Transient bleach data for the 4 nm diameter particles recorded with 0.4 \( \mu l \) pump laser pulses. The dashed line shows a fit to the data using Equation 3.10. The characteristic time scale for energy relaxation obtained from this fit is \( \tau = 10 \pm 5 \text{ ps} \).
3.5 Summary and Conclusions

Excitation of metal nanoparticles with an ultrafast laser pulse causes a rapid increase in the electronic temperature. The hot-electrons subsequently equilibrate with the phonon modes on a several picosecond time scale. These rapid heating processes can impulsively excite the phonon mode that correlates with the expansion co-ordinate. For spherical particles the symmetric breathing mode is excited. For particles with diameters between 8 nm and 120 nm the frequency of this mode can be exactly calculated using continuum mechanics [17, 18].

By performing wavelength dependent transient absorption measurements for a ca. 50 nm diameter Au particle sample we have been able to calculate how the radius changes with time. These results can be directly compared to model calculations where the expansion co-ordinate (the symmetric breathing mode) is treated as a harmonic oscillator. A careful analysis of the phase of the modulations shows that both hot-electron pressure and lattice heating contribute to the impulsive excitation process [19]. The force due to the hot electrons is only significant at early times, when the electronic temperature is much greater than the lattice temperature. The overall expansion of the particles, and the magnitude of the oscillations in the particle radius, are controlled by the lattice heating contribution.

The rate of energy dissipation from Au nanoparticles to their surroundings was also examined by time-resolved spectroscopy. It shows that the rate of energy dissipation for Au nanoparticles in aqueous solution depends on size: small particles have faster relaxation times because of their larger surface-to-volume
ratios. The relaxation times do not depend on the initial temperature of the system, a surprising result that is consistent with calculations of the expected cooling times for Au particles in water. The calculated time scales are consistently faster than the experimental results. This is attributed to the assumptions used in the calculations. Specifically, that the temperatures of the gold and the solvent are equal at the interface, which implies that energy exchange at the interface is instantaneous. For very small particles (~4 nm diameter), the time scale for energy dissipation (~10 ps) is comparable to the time scale for e-ph coupling (several ps). This implies that significant energy transfer to the environment can occur before the electrons and phonons have reached equilibrium [42]. These results form an important step in our efforts to understand laser induced heating effects in metal nanoparticles.

3.6 References


CHAPTER 4

GOLD NANORODS

4.1 Introduction

Recent research shows that low-frequency vibrational modes of metal nanoparticles can be excited by ultrafast laser pulses [1-9]. The excitation mechanism has been discussed in the previous chapter. Different types of nanoparticles and different shapes of particles have been investigated, such as metallic [2, 4, 5, 7, 8] and semiconductor nanoparticles [1, 3, 6], spherical nanoparticles [4, 5, 8] and ellipsoidal shaped particles [7], as well as aggregates of metal particles [9]. The excitation mechanism is slightly different for metallic versus semiconducting materials. For semiconductors, the vibrational modes are excited by a displacive mechanism: band-gap excitation changes the dimensions of the unit cell, which can impulsively excite totally symmetric phonon modes [10]. In contrast, for metal particles excitation occurs via the lattice expansion that follows rapid laser-induced heating [11, 12]. In both cases, the phonon modes observed are those that correlate with the expansion coordinate of the particle, which for spherical particles is the symmetric breathing mode [11, 12]. For spherical particles the measured vibrational frequencies are in excellent
agreement with calculations based on continuum elastic theory, for both homogeneous particles [13, 14] and heterogeneous core-shell particles [15]. In terms of practical applications, these measurements provide a way of determining the material properties of nanometer sized objects if the dimensions are accurately known, or the dimensions of the objects if the material properties are known.

Since synthetic chemists have invented various methods to synthesize different shaped nanoparticles [16-27], it is very important and worthwhile to make some progress in theoretical and experimental studies of vibrational modes for these non-spherical particles. It is well known that non-spherical particles will behave very differently to spherical particles in physical properties. In this chapter, one dimensional nanorods will be discussed.

Perner et al. observed modulations due to coherently excited vibrational modes in silver ellipses [7], which were produced by deforming spherical particles embedded in a glass [28]. Experiments were performed with the probe laser resonant to either the longitudinal or the transverse plasmon bands, which correspond to electron oscillation along the major or minor axes of the ellipse, respectively [29, 30]. Experiments that probed the longitudinal plasmon band showed a modulation with a period that matches $2L/c_1$, where $c_1$ is the longitudinal speed of sound and $L$ is the length. On the other hand, experiments that probed the transverse plasmon band gave $2w/c_1$, where $w$ is the width of the particle [7]. These are the results expected for an expansion/compression wave generated by ultrafast heating. In this chapter, both a theoretical treatment of the response of a
cylindrical rod to ultrafast heating and the experimental investigation of the gold nanorods with different aspect ratio will be addressed.

4.2 Theory

In this section, the temporal response of a cylindrical rod following excitation by a thermal pulse is calculated. Because in practice the length $L$ of the rod greatly exceeds its radius $a$, only the limiting case of $L/a \gg 1$ is addressed here. In practice, the rod is excited by a thermal pulse whose duration is much smaller than the characteristic time scale of rod vibration [11, 12], i.e., the inverse of its fundamental resonance frequency. As such, this thermal pulse can be considered to be of infinitesimal duration. In addition, the rod is assumed to remain at constant temperature following excitation, because the time scale for heat diffusion from the rod to its surroundings is also typically much longer than the vibrational period [31-33]. Under these assumptions, two classes of modes are excited: the extensional mode and the breathing mode of the rod. See Figure 4.1. The details of the theoretical analysis have been presented elsewhere [34]. The extensional modes are well studied [35], and exhibit an axial expansion combined with a radial contraction. As such, these modes probe the Young’s modulus of the material. In contrast, the breathing modes exhibit a pure radial expansion and, consequently, probe the bulk modulus of the material.
Figure 4.1  Diagram Showing the Fundamental Extensional and Breathing Modes of a Cylindrical Rod. Calculations performed under the assumption that the length greatly exceeds the width. In the breathing mode, a pure radial expansion and contraction is observed; there is no change in length. In the extensional mode, an increase in length is accompanied by a contraction in radius.
The natural resonant frequencies of the extensional and breathing modes are given by the following respective formulas

\[
\omega^{(n)}_{\text{ex}} = \frac{2n + 1}{L} \pi \sqrt{\frac{E}{\rho}}, \quad (4.1a)
\]

\[
\omega^{(n)}_{\text{br}} = \frac{\tau_n \sqrt{\frac{E(1-\nu)}{\rho (1+\nu)(1-2\nu)}}}{a} \quad (4.1b)
\]

where \( \tau_n \) is the \( n \)-th root of the following equation

\[
\tau_n J_0(\tau_n) = \frac{1-2\nu}{1-\nu} J_1(\tau_n) \quad (4.2)
\]

In these equations, \( \nu \) is Poisson’s ratio of the rod, \( E \) is Young's modulus, and \( \rho \) is the density of the rod. Comparison to rigorous finite element (FE) analysis [36] of elastic rods subjected to an instantaneous heating pulse shows that Equations 4.1a and 4.1b give an accurate expression of the vibrational frequencies of the rod, especially for cases where \( L/a \gg 1 \) (this is the regime where the above analytical formulas are derived and corresponds to the case encountered in practice). The finite element analysis also shows that other modes can be excited besides the extensional and breathing modes, but their contributions are insignificant in comparison to these dominant modes. Experimentally, the change in absorption spectrum of the rods is monitored. Variation in the absorption spectrum is expected to have contributions from both the rod deformation (change in aspect
ratio) and the change in its volume. Therefore, both the extensional and breathing
modes should be detected in the transient absorption experiment. The theoretical
analysis above can be used to determine which mode is excited by the ultrafast
laser pulse in the transient absorption experiments.

Interestingly, the above calculations show that the ratio of the resonant
frequencies \( \omega \) (or the vibrational periods \( T \)) for the fundamental breathing and
extensional modes is directly connected to the aspect ratio of the rod. From
Equations 4.1a and 4.1b we obtain

\[
\frac{\omega_{br}^{(0)}}{\omega_{ext}^{(0)}} = \frac{T_{ext}^{(0)}}{T_{br}^{(0)}} = \tau_0 \left( \frac{L}{a} \right) \sqrt{\frac{1 - \nu}{(1 + \nu)(1 - 2\nu)}}
\] (4.3a)

which for gold (Poisson’s ratio \( \nu = 0.42 \)) becomes

\[
\frac{\omega_{br}^{(0)}}{\omega_{ext}^{(0)}} = \frac{T_{ext}^{(0)}}{T_{br}^{(0)}} = 2.32 \times \zeta
\] (4.3b)

where \( \zeta \) is the aspect ratio \((L/d)\) of the rod. This finding should enable the aspect
ratio of the rod to be determined from a single measurement of its temporal
response following thermal excitation. This predicted behavior will be examined
in the following sections.

Note that in practice the heating pulse is not quite instantaneous, and the
amplitudes of the excited modes depend on their period compared to the duration
of the heating process [11, 12]. Although the calculations (both analytical and
exact finite element) predict that the amplitude of the extensional mode is much less than that of the breathing mode, the extensional mode may dominate the dynamics in a real experiment because of its much lower frequency. In addition, because the period of the breathing mode is proportional to the width of the rod, this mode will be more prominent for samples of “fat” rods with larger widths.

4.3 Experimental Apparatus and Techniques

4.3.1 Synthesis of Au Nanorods

The gold nanorods discussed in this chapter were prepared using a modified version of the solution phase synthesis developed by Jana and Murphy [23]. Compared to the electrochemical method developed by Wang et al. [17], the seeded growth method in solution led to much narrower size distributions and allowed much more control over the aspect ratio of the gold particles. The original protocol from Jana and Murphy [23] was modified to minimize the creation of spheres [37]. The UV-vis absorption spectra were recorded on a Cary 5 UV-vis-NIR spectrophotometer. The mean size and dispersity of the gold rods were determined using a Philips CM-10 electron microscope at 100kV. In these measurements, a 10-μL volume of colloidal solution was pipetted onto carbon-coated copper grids. Spheres were not included in any histograms.
4.3.2 Transient Absorption Apparatus

The transient absorption experiments were conducted with a regeneratively amplified Ti:Sapphire laser system that has been described in detail in Chapter 2. For the experiments described below, pump laser pulses at 400 nm with energies of approximately 0.1 μJ/pulse were used, and probe pulses in the visible to near-IR were obtained from a white-light continuum. The samples were contained in a 2 mm cuvette and the experiments were performed without flowing. The concentration of the sample was adjusted to give an absorbance at the pump laser wavelength of ~1. Care was taken to keep the pump laser power below the damage threshold for the sample—laser induced damage is easy to observe as it produces a dramatic color change in the sample [38]. It is estimated that these experimental conditions produce temperature increases in the gold lattice on the order of 20-40 °C, after the electrons and phonons have reached equilibrium [39]. Fits to the modulated portion of the data, using a damped cosine function with a decaying offset, were performed using the "Solver" routine in Microsoft Excel X for Mac.
4.4 Experimental Results

4.4.1 Characterization of Au nanorods

Representative TEM images of the gold nanorods used in our experiments are presented in Figure 4.2. The average length ($L$) and width ($w$) for the different samples were (from the top): (a) $L = 108 \pm 7$ nm, $w = 22.8 \pm 1.6$ nm; (b) $L = 89 \pm 7$ nm, $w = 22.2 \pm 2.0$ nm; (c) $L = 75 \pm 6$ nm, $w = 22.4 \pm 1.7$ nm; (d) $L = 73 \pm 4$ nm, $w = 22.1 \pm 1.5$ nm; (e) $L = 61 \pm 5$ nm, $w = 21.5 \pm 1.9$ nm; and (f) $L = 46 \pm 6$ nm, $w = 20.7 \pm 2.3$ nm. The errors represent the standard deviation (500-1000 particles counted for each measurement). The average values and standard deviations were obtained by fitting histograms of the length or width to Gaussian functions. Detailed high resolution TEM analysis has shown that the rods produced by this technique are 5-fold twinned crystals, that grow along a specific direction [40, 41]. This can be seen in the low resolution TEM images in Figure 4.2: the rods typically appear as all light or all dark depending on the orientation of the lattice with respect to the electron beam [42].

UV-Vis-NIR absorption spectra of the samples used in the transient absorption experiments are shown in Figure 4.3. Compared to Au nanospheres, the plasmon resonance for gold nanorods splits into two modes: the transverse mode which corresponds to electron oscillation along the short axis of the rod, and the longitudinal mode which corresponding to oscillation of the conduction
Figure 4.2 Representative TEM images of the gold nanorods used in our experiments. The images correspond (from top left) to the samples with average lengths of: (a) $L = 108 \pm 7$ nm, (b) $L = 89 \pm 7$ nm, (c) $L = 75 \pm 6$ nm, (d) $L = 73 \pm 4$ nm, (e) $L = 61 \pm 5$ nm, and (f) $L = 46 \pm 6$ nm.
Figure 4.3  UV-visible absorption spectra of the “high quality” gold nanorod samples. The average lengths for the different spectra are as follows: (a) $\bar{L} = 108 \pm 7$ nm, (b) $\bar{L} = 89 \pm 7$ nm, (c) $\bar{L} = 75 \pm 6$ nm, (d) $\bar{L} = 73 \pm 4$ nm, (e) $\bar{L} = 61 \pm 5$ nm, and (f) $\bar{L} = 46 \pm 6$ nm.
electrons along the length of the rod [30]. The transverse plasmon band appears at ca. 520 nm for all the samples, which is similar to the position of the plasmon resonance for spherical particle. In contrast, the longitudinal resonance appears between 600 nm and 1100 nm, depending on the aspect ratio. All the data are summarized in Table 4.1. Note that the different rod samples produced by the seed mediated growth technique have very similar widths (see Table 4.1), thus, the aspect ratio is mainly determined by the length of the rod.

### TABLE 4.1

<table>
<thead>
<tr>
<th>sample</th>
<th>$\bar{\zeta}$</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\bar{L}$ (nm)</th>
<th>$\bar{w}$ (nm)</th>
<th>$\bar{T}$ (ps)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>2.23 ± 0.55</td>
<td>699</td>
<td>46 ± 6</td>
<td>20.7 ± 2.3</td>
<td>54.6 ± 1</td>
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<tr>
<td>2</td>
<td>2.81 ± 0.42</td>
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<td>21.5 ± 1.9</td>
<td>65.4 ± 1</td>
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<tr>
<td>3</td>
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<td>786</td>
<td>73 ± 4</td>
<td>22.1 ± 1.5</td>
<td>77.4 ± 1</td>
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<tr>
<td>4</td>
<td>3.34 ± 0.45</td>
<td>822</td>
<td>75 ± 6</td>
<td>22.4 ± 1.7</td>
<td>80.0 ± 1</td>
</tr>
<tr>
<td>5</td>
<td>4.05 ±0.52</td>
<td>902</td>
<td>89 ± 7</td>
<td>22.2 ± 2.0</td>
<td>101.0 ± 1</td>
</tr>
<tr>
<td>6</td>
<td>4.75 ±0.49</td>
<td>976</td>
<td>108 ± 7</td>
<td>22.8 ± 1.6</td>
<td>119.9 ± 1</td>
</tr>
</tbody>
</table>

*The errors for $\bar{\zeta}$, $\bar{L}$ and $\bar{w}$ represent the standard deviations obtained by fitting histograms of the parameter to a normal distribution.*
4.4.2 Transient Absorption Experiment

4.4.2.1 Extensional Mode

Note that the near-UV absorbance for the spectra in Figure 4.3 does not strongly depend on aspect ratio, which means that all the particles in the sample (rods and spheres) are equally excited by the 400 nm pump laser pulses. However, only the rods that have their longitudinal plasmon bands resonant to the probe laser contribute to the signal [43]. In addition, the spheres do not significantly contribute to the transient absorption signal at the wavelengths used in these experiments [39]. Thus, even though ~50% of the particles in the sample are spheres, only the rods were monitored in the transient absorption measurements presented below.

Representative transient absorption traces for different rod samples are presented in Figures 4.4. Figure 4.4 shows data from the Au nanorods samples with average lengths of (a) $L = 89 \pm 7$ nm, (b) $L = 75 \pm 6$ nm, (c) $L = 61 \pm 5$ nm and (d) $L = 46 \pm 6$ nm, for two different probe laser wavelengths. The traces presented correspond to experiments performed on opposite sides of the longitudinal plasmon band (i.e., red of the maximum versus blue of the maximum). In each case the signal shows a fast component, which is attributed to energy transfer from the initially excited electron distribution into the phonon modes, electron-phonon ($e$-$ph$) coupling [11, 12], and a modulation due to the coherently excited vibrational modes. Note that in several cases the signal from
Figure 4.4  Transient absorption traces for Au nanorods with average lengths of (a) \( \bar{L} = 46 \pm 6 \) nm, (b) \( \bar{L} = 61 \pm 5 \) nm, (c) \( \bar{L} = 75 \pm 6 \) nm and (d) \( \bar{L} = 89 \pm 7 \) nm, for two different probe laser wavelengths. In all cases, the probe wavelengths presented lie on opposite sides of the longitudinal plasmon band of the sample. Note the different scale for the time axes in panel (d).
the hot electron distribution has been truncated to highlight the modulated portion of the data. The modulation is superimposed on a slowly varying background, which corresponds to heat dissipation to the environment [31-33, 44, 45]. Also shown in the figures are fits to the experimental data using a damped cosine function. It is very obvious that the modulations are \( \sim 180^\circ \) out-of-phase for probe wavelengths on opposite sides of the longitudinal plasmon band for all the samples. This implies that the signal arises from a periodic shift in the position of the longitudinal plasmon band - similar to what occurs for spherical particles [39].

In Figure 4.5 the period versus probe wavelength results for the modulations are presented for all the Au nanorods samples. For a given sample, the period of vibration increases very slightly when the probe wavelength is tuned from blue to red. This arises because longer probe wavelengths interrogate longer rods in the samples. From the probe wavelength dependent period relationship, it is clear that the nanorods used in the experiments have a relatively narrow size distribution. In contrast, in polydispersed nanorods samples, an almost linear relationship between the period and the probe wavelength is observed [34, 43]. Thus, the way the period changes with wavelength is a clear indicator of the quality of the samples.
Figure 4.5  Period versus probe laser wavelength for all the different samples listed in Table 4.1. The different symbols indicate average lengths of $\bar{L} = 46 \pm 6$ nm (▲), $\bar{L} = 61 \pm 5$ nm (○), $\bar{L} = 73 \pm 4$ (●), $\bar{L} = 75 \pm 6$ (○), $\bar{L} = 89 \pm 7$ nm (●) and $\bar{L} = 108 \pm 7$ (□). The error bars are contained within the symbol.


4.4.2.2 Breathing Mode

Transient absorption data for the breathing mode of a nanorod sample with an average length of $61 \pm 5$ nm and an average width of $21.5 \pm 1.9$ nm (Sample 2 in Table 4.1) is presented in Figure 4.6(a). For comparison, the extensional mode for the same rod sample is shown in Figure 4.6(b). The breathing mode is much harder to observe than the extensional mode. Since we excited the sample at near-IR region (resonant to the longitudinal plasmon band of the rods) and probed the transverse plasmon band, it is safe to say that there is no contribution from the spheres in this case because only the rods are excited. The experimental trace in Figure 4.6(a) was also fitted by a damped cosine function and the fit yields the vibration period of $11.4 \pm 0.5$ ps, which is very close to the value expected for the breathing mode of the rods [34]. This vibrational signal is extremely weak in the experiment, and it is very difficult to observe the breathing mode for other samples. Extensive averaging of scans was needed to obtain the data shown in Figure 4.6(a).

The slower modulation in Figure 4.6(b) has a period of $65.4 \pm 1$ ps for $\lambda = 700$ nm. From the theoretical analysis presented in this chapter, it is expected that for gold (Poisson’s ratio $\nu = 0.42$) the ratio of frequencies for the fundamental breathing and extensional modes should be proportional to the aspect ratio of the rod $\zeta$ (See Equation 4.3b). In the transient absorption experiments, the probe laser interrogates rods according to their aspect ratio, however, for a specific probe
Figure 4.6 Transient absorption data for a gold nanorod sample with an average length of 61 ± 5 nm and an average width of 21.5 ± 1.9 nm. (a) The pump laser wavelength was 795 nm and the probe laser (\( \lambda = 540 \text{ nm} \)) was tuned to the transverse plasmon band of the sample. For comparison, transient absorption data for the extensional mode (pump laser wavelength 400 nm, probe wavelength 700 nm) for the same rod sample is shown in (b). Note the different scale for the time axes.
wavelength, the aspect ratio is not necessarily the same as the average aspect ratio \( \bar{\zeta} \) of the sample. For the nanorods used in our experiments, the wavelength of the longitudinal plasmon resonance is related to the aspect ratio by \( \lambda_{\text{max}} = 114 \times \zeta + 434 \). Note this relation is derived from the experimental absorption spectra and the TEM analysis, see Table 4.1. It is not a general relationship between the longitudinal plasmon resonance and aspect ratio for nanorods. The rod synthesized by other methods may have different relationships because of different surfactant coatings.

For Figure 4.6(b), using the above relationship, the 700 nm probe pulses should interrogate rods with an aspect ratio of \( \zeta \approx 2.33 \). Thus, Equation 4.3b predicts that the ratio of frequencies should be \( \omega_{\text{br}}^{(0)} / \omega_{\text{ext}}^{(0)} = T_{\text{ext}}^{(0)} / T_{\text{br}}^{(0)} \approx 5.4 \) for a probe wavelength of 700 nm. In comparison, analysis of the transient absorption data for the fast and slow modulations gives a ratio of 5.7. The reasonable agreement between the calculated and experimental ratios of the fundamental frequencies supports the conclusions that the fast modulation is the breathing mode and the slow modulation is the extensional mode of the rod.
4.4.3 Elastic Properties of Gold Nanorods

4.4.3.1 Young’s Modulus

Since the extensional mode is related to the Young’s modulus of material, the elastic property of the nanorod can be determined. It is very difficult to measure the elastic constant of nanometer sized objects by conventional methods, thus, time-resolved spectroscopy provides a way to make such a measurement possible. Other ways of measuring Young’s modulus are to examine thermal vibrations by TEM [46, 47], to measure force versus distance curves by AFM [48], or by nanoindentation [49, 50]. All these experiments examine single objects and, therefore, are statistically less accurate than our experiments.

The measured vibrational period (extensional mode) versus the length of the rods (determined by TEM) is presented in Figure 4.7. The period of the fundamental extensional mode is given by

\[ T_{\text{ext}}^{(0)} = \frac{2L}{\sqrt{E/\rho}} \]  

(4.4)

where \( L \) is the length of the rod, \( E \) and \( \rho \) are the Young’s modulus and density respectively. Fitting the experimental data to a linear relationship (solid line in Figure 4.7) yields a value of Young’s modulus of \( E = 0.64 \pm 0.08 \) MB for \( \rho = 19.3 \) g/cm\(^3\). The density of the rod was assumed to have the same value as bulk gold in the calculation. The value of \( E \) obtained from the fit is significantly lower (~19%) than the room-temperature value for bulk gold of \( E = 0.78 \) MB.
Figure 4.7  Vibrational period for the extensional mode versus average length for the gold nanorods samples used in the transient absorption experiments. The solid line is a fit to the data using Equation 4.4 and allowing $E$ to vary. The dashed lines show calculations for different crystal directions, see text for details.
4.4.3.2 Bulk and Shear Modulus

Continuum mechanics calculations for a cylindrical rod give the period of the breathing mode of the rods as Equation 4.1b, this can be rewritten as the following formula:

\[
T^{(n)}_{br} = \frac{2\pi R}{\tau_n c_l}
\]  

(4.5)

where \( R \) is the radius of the rod, \( c_l \) is the longitudinal speed of sound, and \( \tau_n \) is an eigenvalue which is obtained from Equation 4.2, i.e.,

\[
\tau_n J_0(\tau_n) = (1-2\nu)J_1(\tau_n)/(1-\nu),
\]

where \( \nu \) is again Poisson’s ratio. For bulk gold \( \nu = 0.42 \), which yields \( \tau_0 = 2.281 \).

Since the longitudinal speed of sound \( c_l \) is related to the bulk \( (K) \) and shear \( (\mu) \) moduli by \( c_l = \sqrt{(K + 4/3\mu)/\rho} \) [51], it is possible for us to probe the value of the bulk plus shear modulus for nanorods. Using formula 4.5 and the measured period from Figure 4.6(a), the value of the longitudinal speed of sound in the rods is determined to be \( c_l = 2600 \pm 300 \text{ ms}^{-1} \). This is significantly lower than the value in bulk gold \( (3300 \text{ ms}^{-1}) \). Assuming that the density of the nanorods is the same as that for bulk gold, the above data can be used to calculate a value for \( K + 4/3\mu = 130 \pm 30 \text{ GPa} \). For bulk gold \( K + 4/3\mu = 210 \pm 2 \text{ GPa} \) [52], which means that this sum of the bulk and shear moduli is almost 40% smaller for the nanorods.
compared to bulk gold. We have chosen to use the breathing mode data to generate information about $K$ and $\mu$ because these are the natural elastic moduli to describe expansion. These results show that the gold nanorods produced by seed-mediated growth have much smaller elastic moduli (i.e., they are less stiff) than bulk gold.

4.4.4. Discussion of the Elastic moduli of Metal Nanorods

Usually nanomaterials such as nanowires and nanotubes have larger Young’s modulus compared to their bulk counterparts [46-48]. This has been attributed to the fact that when nanotubes or nanowires grow, they eliminate defects in their structure, which yields a stronger material [48]. Therefore, the results of a lower value of Young’s modulus in our experiments for metal nanorods is quite surprising. We don’t think that this results from either the contribution from the surface energy to the overall cohesive energy of the rods, or quantum confinement effects in the electronic states of the material. This is because at room temperature, both the surface energy and quantum confinement effects are only important for particles with dimensions on the order of a few nanometers [53, 54]. Thus, these effects are unlikely to play a role for our particles, which have dimensions over 20 nm. In the following, we will discuss several possibilities for the observed decrease in the elastic moduli ($E$, $K$ and $\mu$) of the nanorods.
4.4.4.1 Crystal growth direction

The first possibility considered is the crystal growth direction. The nanorods used in the transient absorption experiments have a specific structure and are not elastically isotropic. Our experiments on the extensional mode probe Young’s modulus along the axial direction of the rod. Because the rods grow along a specific crystal direction \([40, 41]\), the value of Young’s modulus measured will be different to the value for bulk, polycrystalline gold \([51, 52]\). For a cubic crystal, Young’s modulus depends on the crystal direction in the following way \([51]\):

\[
E = \left( \frac{c_{11} + c_{12}}{(c_{11} + 2c_{12})(c_{11} - c_{12})} + \frac{1}{c_{44}} - \frac{2}{c_{11} - c_{12}} \right) \times \left[ n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2 \right]^{-1}
\]  

(4.6)

where \(n_i\) are the components of the unit vector that give the crystal direction, and \(c_{ij}\) are the single-crystal elastic stiffnesses \([55]\). Calculations of the period versus length for different crystal directions \(<100>, <110>\) and \(<111>\) (for example) are included in Figure 4.7 as the dashed lines. There are several important things to note. First, the value of \(E\) calculated using Equation 4.6 is different for different crystal directions: \(E(<100>)>E(<110>)>E(<111>)\). Second, the value of \(E\) for the \(<110>\) direction, which is the growth direction determined by Murphy and coworkers, and confirmed in our HR-TEM studies (see below), is the same as the bulk value. Third, none of the calculated values of Young’s modulus in Figure 4.7
can reproduce the experimental results. Therefore, the crystal growth direction alone can not provide a satisfying explanation for the decrease in Young’s modulus in the nanorods.

4.4.4.2 Temperature dependent Young’s modulus

The second possibility is that the increase in the temperature of the rods during the laser heating process results in a reduced Young’s modulus. The value of Young’s modulus for gold is plotted versus temperature in Figure 4.8. The data are taken from ref. [52]. We estimated the temperature increase should be less than 100 °C in our experiments, based on our previous studies of laser induced heating in spherical Au nanoparticles [56, 57]. It is very important to note that temperature increases greater than 200 °C would cause a thermal-reshaping effect for the rod [58], which is not observed in our experiments. Thus, the laser induced heating in our experiments can not be greater than 200 °C. For bulk gold a temperature rise of 100 °C would produce a decrease of approximately 4% in Young’s modulus. This is much smaller than the experimentally observed change in $E$. Therefore, laser induced heating is not the cause of the reduced value of $E$ for the nanorods.
4.4.4.3 Structure of the rods

The structures of metal nanorods have been studied in the past several years by high resolution TEM and selected area electron diffraction. Research on gold [40], silver [59-62], and copper [63, 64] reveals that the nanorods synthesized via seed mediated growth method have 5-fold twinned structures with \{100\} facets on the sides, and \{111\} facets at the ends. The growth direction is [110] [40, 59-63]. However, different synthesis methods yield different
structures, and even the same solution methods may lead to different structures. For example, the gold nanorods produced from the electrochemical technique are single crystals and grow along the [001] direction [65], while Gai gives the structure of the rods as 5-fold twinned but with \{110\} sides, \{111\} ends, and growth along the [100] direction — even though these rods were produced by the seed mediated growth technique [66]. Therefore, it is necessary for us to perform structural studies for the gold nanorods used in our transient absorption experiments.

Figure 4.9 shows HRTEM image and an electron diffraction pattern of a gold nanorod from the samples used in the transient absorption experiments. The HRTEM image shows \{111\} fringes on one side of the rod, at an angle of approximately 55° to the rod axis. The diffraction pattern is a superposition of the \textbf{<110>} and \textbf{<111>} crystallographic zones. Specifically, the large hexagon outlined in the figure shows the \{220\} reciprocal lattice expected for diffraction from the \textbf{<111>} zone, and the smaller hexagon inside this can be assigned to diffraction from the \textbf{<110>} zone. The line that runs down the center of the rod arises from the twin boundaries [61]. Both the HRTEM image and the diffraction pattern are consistent with a 5-fold twinned structure, with elongation along the [110] axis [40, 59-63]. A diagram of this structure is also shown in Figure 4.9. This model for the nanorods is adapted from a model developed for decahedral particles of fcc metals [63]. The decahedral particles are constructed from 5
Figure 4.9 (Top) HRTEM image of a gold nanorod produced by seed-mediated growth. The image on the right shows an expanded view of the outlined rectangle on the left. \{111\} lattice fringes characteristic of imaging the \(<110>\) and \(<111>\) crystallographic zones can be clearly seen on the lower half of the rod. (Bottom Left) Corresponding diffraction pattern from the rod. The outlined hexagon of \{220\} spots arises from diffraction from the \(<111>\) zone, and the smaller reciprocal lattice inside this arises from the \(<110>\) zone. The drawing at the bottom right shows the structure of the rods.

distorted tetrahedral subunits that each contain four \{111\} faces. The tetrahedra share \{111\} faces along a common \([110]\) axis. Nanorods are generated by elongation along this axis, that is, by adding \(110\) planes in the center of the particle (this is clearly not how they really grow in solution) \[63\]. Depending on the orientation of the rod with respect to the electron beam, this structure can give diffraction from the \(<110>\) and \(<111>\) crystallographic zones, or the \(<100>\) and \(<112>\) zones \[40, 59-63\].
Both HRTEM and selected area electron diffraction studies confirm that the gold nanorods used in our experiments have the same structure as that given in ref [40]. The 5-fold twinned (decahedral) structure is a common feature for small particles of fcc metals, particularly silver and gold [67]. This structural model (see Figure 4.9) requires that each twin has an apex angle of 72° at the nanorod axis. However, the actual angle between {111} planes is 70.53°. An extra 1.47° means that each twin plane is actually a low-angle tilt boundary consisting of edge dislocations that run parallel to the nanorod axis, i.e., along the [110] direction. It is well known that dislocations have a significant effect on the mechanical properties of solids, for example, motion of edge dislocations through the crystal is the basis for plastic deformation of metals [68, 69]. However, the relevant motion in this case is perpendicular to the direction of the edge dislocation. Therefore, the presence of edge dislocations parallel to the axis of the rod does not explain the reduced value of Young’s modulus for extension and contraction along this axis (i.e., motion parallel to the direction of the dislocation). Likewise, these edge dislocations should not affect radial expansion and compression and, therefore, cannot rationalize the smaller value of $K + 4/3\mu$ determined from the breathing mode experiments. Thus, the reduced values for the elastic moduli of gold nanorods cannot be simply explained from the orientation of the dislocations that arise from their 5-fold twinned structure.

Although we can not find an appropriate explanation for our results at this stage, it is important to note that our experimental results of reduced elastic
properties \((E \text{ and } K + 4/3\mu)\) are consistent with the reduced thermal stability of the nanorods. Recent temperature-dependent TEM experiments reveal that the nanorods melt at a temperature \((\sim 550 \text{ K})\) much lower than the bulk melting point [55, 70]. The melting point of a material is proportional to the cohesive energy \(U\) [55, 71]. On the other hand, the bulk modulus depends on the second derivative of this energy with respect to volume \((\partial^2 U / \partial V^2)\) [51, 55]. Therefore, reduced elastic moduli of the nanorods should be accompanied by reduced melting point and visa-versa [69].

4.5 Summary and Conclusion

In this chapter, we showed that the rapid heating from the ultrafast pump laser coherently excites the phonon modes that correspond to the expansion coordinates of the particles. The period of the excited vibrational motion is closely related to the mechanical properties of nanoparticles. The exact relationship between the modulation period and the mechanical properties is established through continuum mechanics. For example, for cylindrical nanorods the period of the extensional mode is related to Young’s modulus and the length of the rod. On the other hand, the period of the breathing mode is determined by the longitudinal speed of sound and the radius of the rod. Thus, the elastic properties of nano-sized materials can be determined from time-resolved spectroscopy.
To validate the theory, time-resolved experiments were performed for gold nanorods in solution synthesized via a seed mediated growth method. From the extensional mode, we found that Young’s modulus is 19% lower than the corresponding bulk value. We further investigated the breathing mode of the nanorods and found a similar 21% lower value for the longitudinal speed of sound. The longitudinal speed of sound is related to the bulk \( (K) \) and shear \( (\mu) \) moduli by \( c_l = \sqrt{\frac{K + 4/3\mu}{\rho}} \), which means the sum of the bulk and shear moduli for the nanorods is nearly 40% lower than the value for bulk gold. Usually, nano-sized materials are mechanically stiffer than the corresponding bulk materials, for example, see Refs [46-48]. Thus, our results are unusual in this field. High resolution TEM and SAED studies show that nanorods and nanowires produced by seed mediated growth have a five fold twinned structure. However, it is not clear how this leads to the reduced elastic moduli for the nanorods.

### 4.6 References


[36] LUSAS is a trademark of, and is available from, FEA Ltd., Forge House, 66 High Street, Kingston Upon Thames, Surrey, KT1 1HN, U.K.


5.1 Introduction

In order to understand how structure and shape affect the mechanical properties of nanoparticles, we decided to investigate Ag. Silver nanorods have similar structural motifs as gold, for example, they also form a 5-fold twinned structure when grown from solution [1, 2]. Figure 5.1 shows SEM images of Ag nanowires recently obtained by Chen and coworkers [2]. It is clear that the Ag wires have pentagonal ends, which is consistent with the 5-fold twinned structure.

Solution phase recipes for producing Ag rods [3], triangles [4], cubes [5, 6] and tetrahedrons [7] have been reported. In this chapter, time-resolved experiments were performed on silver nanoparticle samples synthesized via seed mediated growth. These samples are extremely polydisperse in shape. A vibrational beat signal was observed, and analysis of the data shows that the signal arises from the triangular shaped particles. The period is given by $2h/c_l$, where $h$ is the bisector of the triangle and $c_l$ is the longitudinal speed of sound in silver. This phenomenological relationship is similar to that used to explain the vibrational beat signal observed for Au nanoprisms by the El-Sayed group [8].
Figure 5.1  SEM images of (a) elongated Ag nanorods or nanowires with a high concentration and (b) multi-twinned structure of the Ag nanorods. The inset shows the EDX data from a nanorod [2].
5.2 Experimental Section

5.2.1 Preparation of Metal Colloid Solution

Silver nanoparticles were synthesized via the seed mediated growth method described by Murphy et al [3]. All the glassware was cleaned before synthesis by aqua regia solution and all the chemical solutions were freshly prepared without aging. The 4 nm Ag seeds were first prepared by injecting 0.6 ml of 10 mM NaBH$_4$ solution into a vigorously stirring 20 ml solution that contains a final concentration of 0.25 mM AgNO$_3$ and 0.25 mM trisodium citrate in water. A light yellow color appeared upon adding NaBH$_4$. Stirring was stopped after 30 seconds and the color became a darker yellow. The seeds were stored without avoiding light, and used within 2 h of preparation. Different amounts of seed solution (1 ml = A, 0.5 ml = B, 0.25 ml = C and 0.125 ml = D) were added to four sets of 10 ml CTAB (80 mM) solutions. To avoid crystallization of CTAB from solution, the temperature was kept at 35° C during the preparation. The following solutions were then added in sequence: 0.25 ml AgNO$_3$ (10 mM), 0.50 ml ascorbic acid (100 mM) and 0.10 ml NaOH (1M). Right after adding the NaOH, the solutions were gently shaken to ensure they were homogeneously mixed. The solutions changed color from red to grey, brown and green depending on the amount of seed present. Centrifugation was performed at room temperature. For the samples which contain 0.25 ml of seeds or more (i.e., samples A-C), 10 ml aliquots were centrifuged at 6000 rpm for 30
min. For sample D, 10 ml of solution was centrifuged at 2000 rpm for 6 min. The supernatant (which contained most of the surfactant) was carefully removed, and the remaining solid was redispersed in DI water for characterization.

The UV-vis absorption spectra were recorded by a Cary 50 Bio-spectrophotometer. The shape and size distributions were measured from TEM images, recorded on a HITACHI H-600 TEM operating at 75 kV, by using Adobe Photoshop CS software. Histogram graphs and normal distribution curves for the samples used in our experiments are presented in Appendix A, and were obtained by using SPSS 12.0 for Windows. Carbon-coated copper grids (Carbon Type-A, 300 Mesh) from Ted Pella were used in the TEM measurements. To prepare the grids, samples were diluted and dropped on the darker side of grids (the carbon film side). The grids and a beaker full of water were then placed close together and covered with another beaker. The saturated water vapor environment ensures that the samples dry very slowly (1-2 hours).

5.2.2 Transient Absorption Apparatus

The transient absorption experimental set-up was described in detail above. The probe wavelengths used were resonant to the long wavelength band observed in the UV-vis absorption spectra. The pump laser intensity was kept below the damage threshold of the samples to avoid thermal reshaping. No degradation of the signal (either magnitude or form) was observed during the course of the experiments. This implies that the samples are stable under our
conditions. The temperature rise in the silver lattice was estimated to be 20 - 40°C for the laser powers used in these experiments [9]. Fits to the transient absorption data were performed using the “solver” function in Microsoft Excel for Windows.

5.3 Results and Discussion

5.3.1 Characterization of the polydisperse Ag sample

Although centrifugation was carefully undertaken to purify the silver nanoparticles, the samples still contained different shapes, including spherical particles, cylindrical rods and triangular-shaped particles. These are the majority shapes found in all samples. In addition, there are a few other odd-shaped particles, such as dimers or trimers of triangles, and cubes. However, the relatively low proportion of these particles implies that they do not significantly contribute to the UV-vis spectra or the transient absorption experiments. Figure 5.2 shows typical TEM images of the four samples: A, B, C and D. The particle dimensions increase in that order. The corresponding UV-Vis absorption spectrum are presented in Figure 5.3. The spectra show a resonance near 400 nm, which is mostly due to the spherical particles and the transverse plasmon band of the rods. The second red-shifted peak corresponds to the longitudinal plasmon band of the rods, and the plasmon resonance of the triangular-shaped particles [4, 10]. Note that, first, the distribution of shapes in our samples is very different to
Figure 5.2: Representative TEM images of samples A – D. The average dimensions of the rods, triangular-shaped particles and spherical particles are summarized in Table 5.1.
Figure 5.3: The UV-Vis absorption spectra for samples A – D used in our transient absorption experiment.
that reported by Murphy et al [3]. Second, the dimensions of all the particles (rods, spheres and triangles) increase as the concentration of seeds decreases. This causes the red shift in the long wavelength plasmon band as we go from sample A to D [10]. The dimensions of the samples were characterized by the diameter of the spheres, the length and width of the rods, and the bisector of the triangular shaped particles. Over 1000 particles were counted from several TEM images for each sample, and the averaged dimensions are summarized in Table 5.1. The average dimensions and standard deviation were obtained from Gaussian fits to the size histograms, see Appendix A for details. It is important to note that the triangular shaped particles are not perfect, they are “snipped” at the ends. Snipping leads to a blue shift of the plasmon resonance compared to perfect triangles [4, 10].

The relative amounts of spheres, rods and triangles, and their dimensions are shown in Figs. 5.4 (a) and (b), respectively. Figure 5.4 (b) clearly shows that the dimensions of all the particles increase with decreasing amount of seed particles. In addition, the length of rods is very polydisperse, while the size distributions for the bisector of the triangular-shaped particles are relatively narrow. The polydispersity is defined as $\Delta = \sigma_x / \bar{x}$, where $\sigma_x$ is the standard deviation and $\bar{x}$ is the average dimension of the particles. For the rods $\Delta$ is in the range of 20-60% for the length, while for the triangles $\Delta$ is 10-15% for the bisector. This polydispersity produces the broad absorption spectra in Figure 5.3.
TABLE 5.1

AVERAGE DIMENSIONS FOR THE BISECTOR OF TRIANGULAR-SHAPED PARTICLES ($\bar{h}$); LENGTH ($\bar{L}$), WIDTH ($\bar{w}$) AND ASPECT RATIO ($\bar{\xi} = \langle L/w \rangle$) OF THE NANORODS; AND DIAMETER OF THE SPHERICAL PARTICLES ($\bar{d}$) MEASURED FROM TEM IMAGES$^a$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Triangles</th>
<th>Nanorods</th>
<th>Spheres</th>
<th>$T_{exp}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{h}$</td>
<td>$\bar{L}$</td>
<td>$\bar{w}$</td>
<td>$\bar{\xi} = \langle L/w \rangle$</td>
</tr>
<tr>
<td>A</td>
<td>43 ± 5</td>
<td>48 ± 11</td>
<td>31 ± 6</td>
<td>1.6 ± 0.5</td>
</tr>
<tr>
<td>B</td>
<td>60 ± 7</td>
<td>73 ± 28</td>
<td>36 ± 9</td>
<td>2.2 ± 1.4</td>
</tr>
<tr>
<td>C</td>
<td>83 ± 12</td>
<td>151 ± 97</td>
<td>39 ± 10</td>
<td>4.5 ± 3.9</td>
</tr>
<tr>
<td>D</td>
<td>106 ± 16</td>
<td>172 ± 100</td>
<td>48 ± 16</td>
<td>4.1 ± 3.0</td>
</tr>
</tbody>
</table>

$^a$ All dimensions are in nm. $T_{exp}$ is the average vibrational period (in ps) measured in the transient absorption experiments. The errors reported are the standard deviations, which for the particle dimensions were obtained from fitting gaussian distributions to the size histograms.
Figure 5.4: (a) The percentage of spheres, rods and triangular-shaped particles in the samples A – D. Over 1000 particles were counted for each sample. (b) Dimensions of the spheres (diameter), rods (length and width) and triangular-shaped particles (bisector) for the different samples.
5.3.2 Transient experiment data

For the transient absorption experiments, the near-UV pump pulses excite all the nanoparticles (including the spheres) in the solution. However, the probe wavelengths used in this study were resonant to the long wavelength band, so the transient signals mainly have contributions from the rods and triangular-shaped particles. In the present study we did not tune the probe laser to the 400-500 nm region where the spherical particles are expected to absorb. Spherical particles of silver and gold have been extensively studied and their vibrational response is well understood [11-13]. Figure 5.5 shows representative transient absorption data recorded with probe wavelengths on the red side of the long wavelength absorption band for each sample. All the traces have been normalized by the maximum bleach signal at zero delay time. A general feature of these data is the fast initial decay, which corresponds to the electron-phonon coupling process, and results in energy flow from the excited electron distribution into the phonon modes [11-13]. This signal is followed by a modulation which corresponds to the coherently excited vibrational modes. The dashed lines in Figure 5.5 are fits to the data using a damped cosine function, $S(t) = A_0 \cos\left(\frac{2\pi t}{T_{\text{exp}}} + \phi\right) e^{-t/\tau}$ where $T_{\text{exp}}$ is the period of vibration, $\phi$ is the phase and $\tau$ is the damping constant of the modulation. This function fits the data very well. The measured periods increase from samples A to D, i.e., with increasing dimensions of the particles. We have previously shown that for polydisperse systems the damping should go as
Figure 5.5: Transient absorption traces for samples A – D. All experiments were performed with the probe tuned to the red side of the long wavelength plasmon band. The probe wavelengths used were 520 nm, 540 nm, 600 nm and 710 nm, respectively, for samples A – D. Dashed lines are fits to the data using a damped cosine function.
\[ \exp[-(t/\tau)^2] \] [9]. However, using this damping term gave a significantly worse fit to the data, presumably because this expression is only correct when all the particles in the sample contribute equally to the transient absorption signal [9, 13]. For non-spherical particles the absorption spectrum depends on the dimensions, and the damping due to polydispersity is very complex.

Figure 5.6 shows representative transient absorption traces for sample C probed at different wavelengths, which range from the blue side of the long wavelength absorption band to the red side. The measured vibrational periods and the phase of the modulations are plotted versus probe wavelength in Figure 5.7 for all the samples. The vibrational period is fairly insensitive to the probe wavelength -- it increases slightly with probe wavelength -- which indicates that the detected particles have a relatively uniform size distribution [14]. The phase of the modulation changes by approximately 60° with probe wavelength, which is much less than the expected 180° phase change [13]. The average vibrational period for each sample is included in Table 5.1.
Figure 5.6: Representative transient absorption traces for sample C. The wavelengths range from the red side to the blue side of the plasmon band. The phase of the modulations changes by 60° as the probe laser is tuned from the red to the blue.
Figure 5.7: (a) Observed vibrational periods and (b) phases of the modulations versus probe wavelength for the different samples used in experiments. The different symbols correspond to sample A (△), B (▲), C (▼) and D (●).
5.3.3 Calculation of nanorod spectra

The main issue to resolve from these experiments is whether we are detecting the nanorods or the triangles. Figure 5.8 shows spectra for Ag nanorods with different aspect ratios calculated using the Gans model [15] (see Chapter 1, Equations 1.5-1.6). The dielectric constant of the medium was fixed to 2.5, and the dielectric constant of silver was taken from Ref. [16]. The value of $\varepsilon_m = 2.5$ was determined from analysis of our previous gold nanorod data [14], since both the Au and Ag nanorods were synthesized under a similar chemical environment. Using the aspect ratios listed in Table 5.1, we calculate the positions of the corresponding absorption maxima for samples A-D to be 473 nm, 565 nm, 895 nm and 834 nm, respectively. In contrast, the experimentally measured absorption maxima are at 500 nm, 528 nm, 591 nm and 709 nm. The difference between the calculated and observed absorption maxima for samples A and B could be due, in part, to the choice of $\varepsilon_m$. However, for samples C and D the experimental absorption maxima are not in the order expected from the aspect ratios of the rods. This indicates that for samples C and D the absorption spectra have a significant contribution from the triangular shaped particles. This is consistent with the TEM results, which show a larger fraction of triangles for these samples. Note that the wavelength ranges where the vibrational beat signals were observed were 480-580 nm for samples A and B, 550-640 nm for sample C,
Figure 5.8: Calculated absorption spectra of silver nanorods with different aspect ratios using the Gans model, see Ref. [15] for details. The dielectric constant of the medium is fixed to be 2.5 and the dielectric constant of silver was taken from Ref. [16].
and 640-740 nm for sample D, see Figure 5.7. For samples C and D these wavelengths are blue-shifted from where we expect the nanorods to absorb. This implies that the modulations do not arise from the rods.

### 5.3.4 Assignment for vibrational signal

More concrete information about the identity of the particles being probed in our experiments comes from the period of the observed vibrational modes. In the following we present an analysis of the expected periods for vibrational modes of rods, spheres and triangles. For nanorods two types of modes can be excited, the breathing mode and the extensional mode. From continuum mechanics, the period of the breathing mode is given by [14]:

$$T_{br}^{(n)} = \frac{\pi w}{\varphi_n c_l}$$  \hspace{1cm} (5.1)

In this equation $w$ is the width of rods, $c_l$ is the longitudinal speed of sound in silver (3650 ms$^{-1}$ at room temperature), and $\varphi_n$ is an eigenvalue which satisfies

$$\varphi_n J_0(\varphi_n) = (1 - 2 \nu) J_1(\varphi_n)/(1 - \nu),$$

where $\nu$ is Poisson’s ratio. For silver, $\nu = 0.372$ at room temperature [17], which yields $\varphi_0 = 2.22$. Using Equation 5.1, the calculated period for the fundamental breathing mode of the silver nanorods in sample C (for example) is 15.2 ps, whereas, the observed period is 48 ± 2 ps. The large difference between the calculated and the experimental period shows that the modulations are not due to the breathing mode of the rods.
The period for the extensional mode of the nanorods can be calculated from the formula [14, 18]:

\[ T^{(n)}_{\text{ext}} = \frac{2L}{(2n+1)\sqrt{E/\rho}} \]  

where \( L \) is the length of rods, and \( E \) and \( \rho \) are Young’s modulus and the density, respectively. For bulk silver, \( E = 0.78 \text{ Mb} \) and \( \rho = 10.5 \text{ g/cm}^3 \). Figure 5.9 (A) shows a plot of the average vibrational period from the transient absorption measurements and the values calculated for the fundamental extensional mode, versus the length of the rods determined by TEM. The measured periods are much faster than the calculated values, which shows that the modulations are not due to the extensional mode of the rods. In addition, according to the TEM analysis, the rods also have relatively broad length distributions. Our previous experiments with gold nanorods shows that polydisperse samples have a strong damping and a wavelength dependent period [14, 19], which is not consistent with the data in Figs. 5.5 – 5.7.

We also consider the possibility that we are detecting the breathing mode of the spheres, even though the probe wavelengths used are well beyond where we expect the signal for spheres. The period of the symmetric breathing mode for spherical particles is given by [20]:

\[ T^{(n)}_{\text{br,sp}} = \frac{\pi d}{\xi_n c_l} \]  

where \( d \) is the diameter of the sphere, and \( \xi_n \) is an eigenvalue obtained from the
Figure 5.9: Average vibrational period versus dimension for the different samples, in (A) the x-axis is the length of the rods and in (B) the x-axis is the bisector of the triangles. Solid lines in both figures are the calculated period, see text for details, and dashed lines are fits to the experimental data assuming a linear relationship between period and dimension. The open symbol in (B) represents the triangles synthesized using the procedure in ref [4].
equation $\xi_n \cot \xi_n = 1 - \xi_n^2 / 4\delta^2$, where $\delta = c_t/c_l$ is the ratio of the transverse and longitudinal speeds of sound. For silver, these values are 1610 ms$^{-1}$ and 3650 ms$^{-1}$, respectively, which yields $\xi_0 = 2.85$. The sizes of the spheres in our samples are given in Table 5.1. Again, using sample C as an example, the calculated period for the fundamental breathing mode is 26.0 ps, which is much faster than the observed period of 48 ± 2 ps. Thus, we conclude that the modulations detected do not arise from the rods or spheres, even though these shapes represent the majority of the particles in the samples.

The measured vibrational periods are plotted against the dimensions of the triangular-shaped particles in Figure 5.9 (B). The solid line shows the period calculated by:

$$T_{tri} = \frac{2h}{c_l}$$

(5.4)

where $h$ is the bisector of the triangles. Equation 5.4 is a phenomenological expression for the vibrational period, which is expected from dimensional analysis [8, 21, 22]. The agreement between the calculated and experimental periods is very good. The dashed line in Figure 5.9 (B) shows a fit to the data. The fit yields a value for longitudinal sound speed of 3400 ± 200 ms$^{-1}$, which is slightly lower (7 %) than the bulk value of 3650 ms$^{-1}$. However, this slight deviation is clearly within the experimental errors.

The above analysis shows that the triangular shape particles dominate the vibrational response of the samples, even though the majority of the non-spherical
particles are rods. We believe that this is because of differences in the polydispersity of the rods and triangles. Specifically, the relative polydispersity in the length of the rods ($\sigma_L/L$) ranges from 20-60% for the different samples, see Table 5.1. In comparison the relative polydispersity for the triangles ($\sigma_h/h$) is only 10-15%. A large polydispersity will produce a rapid decay in the modulations. Thus, even though we may coherently excite the extensional vibrational mode of the rods, this motion will not produce modulations in our transient absorption experiments because of the strong damping. Note that the signals at early times are not well fitted in our analysis for any of the samples. This may be due to the strongly damped contribution from the nanorods.

5.3.5 “Mirkin” Triangles

To test the conclusion that the signal in these experiments arises from triangles, we also performed experiments on triangular shaped particles synthesized using the “Mirkin recipe” [4]. These samples had a bisector of 61 nm and gave a period of 32 ps, consistent with the data in Figure 5.9 (B). The experimental results are presented in Appendix A. The average period for the "Mirkin recipe" sample is also include in Figure 5.9 (B) as the open symbol.
5.3.6 Comparison to Other Data

Our results can be compared to the recent experiments by El-Sayed and co-workers on prismatic nanoparticle arrays produced by nanosphere lithography [8]. In this work the authors observed a period that varied between 70 ps and 110 ps, depending on the size of the prisms. The measured periods were consistently ~15% higher than the expected period of $2h/c_l$ where $h$ is now the bisector for the prism, whereas, our results show an almost perfect match with Equation 5.4. A possible reason for the deviation for the prisms is that, in this case, the bisector is not the appropriate dimension for the vibrational modes. The measured periods for the nanoprisms do not depend on probe wavelength (similar to our results), and show a phase change of 180° as the probe is tuned from the red side to the blue side of the plasmon band.

5.3.7 Excitation mechanism

The last point considered here is how the excited vibrational modes cause a signal in the transient absorption experiments. In general, for metal nanoparticles, the coherently excited vibrational modes will appear in transient absorption traces if they modulate a parameter that affects the position of the plasmon resonance. For example, for spheres the plasmon resonance depends on the electron density [23], thus, the breathing mode can be detected in transient absorption experiments [11, 12]. Likewise, for rods the longitudinal plasmon
band depends on the aspect ratio [15], which allows the extensional mode to be detected [14]. Because the pump laser induced heating causes expansion, the coherently excited vibrational motion red-shifts the plasmon resonance [9]. For the triangles the wavelength of the plasmon resonance is proportional to the edge length or, equivalently, the bisector of the triangle [24]. Ultrafast laser-induced heating generates a periodic increase in this dimension, which produces the modulations in the transient absorption traces. In monodisperse samples, this would produce a phase change of 180° for experiments performed on the red side of the plasmon band compared to the blue side, with no change in the measured period [8, 11-14]. Our samples show a slight increase in the period with wavelength and a 60° phase change. The increase in period is easy to understand – larger particles have longer vibrational periods and red-shifted spectra [24]. However, we do not have a satisfactory explanation for the <180° phase change at this time.

5.4 Summary and Conclusion

Time-resolved experiments have been performed on polydisperse silver colloid samples. The synthesis used in these experiments generated multi-shaped nanoparticles, with nanorods, triangles and spheres all present. Transient absorption experiments were performed by tuning the probe laser to the long wavelength absorption band of the samples, which arises from the non-spherical particles. Despite the polydispersity in shape, we still observed pronounced
vibrational modulations in our experiments. The modulations are due to the triangular shaped particles. The vibrational period is given by \(2h/c_l\), where \(h\) is the bisector of the triangle and \(c_l\) is the longitudinal speed of sound in silver. The triangles dominate the response in the transient absorption experiments, even though they are outnumber by the rods for all the samples studied. This is because the rods are much more polydisperse in their length, which strongly damps the coherent vibrational response from the rods.

5.5 References


A.1 Particle Analysis

The Ag nanoparticles used in our time-resolved experiments contain different shapes. To characterize these shapes, we measured the diameter of the spheres, the length and the width of the rods, and the bisector of the triangular shaped particles. Note that the triangular shaped particles are “snipped” triangles rather than perfect ones.

Figure A.1 TEM image which shows how we define the dimensions measured for the rods and triangular-shaped particles.
Figure A.2(a)
Figure A.2(b)
Figure A.2(c)
Figures A.2(a-d): Histograms and normal distribution fits for samples A-D, respectively. The width of the rods and the bisector of the triangular-shaped particles have a narrower size distribution than the length of rods. The dimensions of the spheres, the rods and the triangular shaped particles are reported in Table 5.1 in the main text.
A.2 Experimental Results for “Mirkin” Samples

Figure A.3(a): Transient absorption data for a sample of triangular shaped particles produced using the recipe in Ref. [1]. The probe wavelengths used were 600 nm and 640 nm. The measured periods are 33.0 ps for 600 nm and 31.0 ps for 640 nm, and the change in phase between the two traces is 120°.
Figure A.3(b): UV-Vis absorption spectra for the sample in Figure A.3(a).
Figure A.4: Representative TEM image for the above sample.
Figure A.5: Size histogram and normal distribution fit for the sample in Figure A.4. Over 100 particles were counted and the average size was 61 nm, with a standard deviation of 23 nm.

A.3 Reference

REFERENCES


http://www.thebritishmuseum.ac.uk/science/text/lycurgus/sr-lycurgus-p1-t.html


Li, X.; Gao, H.; Murphy, C. J.; Caswell, K. K. *Nano Lett.* **2003**, *3*, 1495.


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Mirkin, C. A. Small, 2005, 1, 14.


Mulvaney, P.; Perez-Juste, J., unpublished results.


Shephard, D. S.; Maschmeyer, T.; Sankar, G.; Thomas, J. M.; Ozkaya, D.;
1214.


Simmons, G.; Wang, H. Single-Crystal Elastic Constants and Calculated

Son, S. U.; Jang, Y.; Park, J.; Na, H. B.; Park, H. M.; Yun, H. J.; Lee, J.; Hyeon,

1994, 50, 15337.


Sun, Y. G.; Xia, Y. N. Science 2002, 298, 2176.


Thoen, E. R.; Steinmeyer, G.; Langlois, P.; Ippen, E. P.; Tudury, G. E.; Cruz, C.


