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Electron-phonon coupling dynamics in very small (between 2 and 8 nm diameter) Au nanoparticles

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Ultrafast laser experiments were used to study electron-phonon coupling in Au nanoparticles in the 2.5 to 8 nm size range in aqueous solution. The electron-phonon coupling constants for these samples were found to be independent of the particle size. This is attributed to a weak interaction between the electron gas and the surface phonon modes in Au. Calculations were performed which show that the coupling between the hot electrons and the surface accounts for less than 10% of the total electron energy losses for these particles. Thus, bulk electron-phonon coupling dominates the relaxation of excited electrons in Au particles, for particles as small as several hundred atoms. © *2000 American Institute of Physics.* [S0021-9606(00)70813-0]

I. INTRODUCTION

In recent years there has been considerable interest in investigating the dynamics of nanometer-sized metallic clusters.[1–9] It is important to obtain a comprehensive understanding of the relaxation processes in these systems because their fast optical response is potentially useful for applications such as optical switching.[10–17] Nanoparticles can in principle be used as building blocks for photonic or microelectronic devices that process high frequency signals. Ultrafast lasers are now capable of resolving the processes that occur following optical excitation of these materials. It is generally accepted that the excited electrons thermalize via electron–electron (e-e) scattering on a time scale of tens to a few hundreds of femtoseconds, generating a hot Fermi distribution that further relaxes through electron-phonon (e-ph) coupling.[1–9] A major focus of research in the past several years has been to determine how the time scales for e-e and e-ph coupling depend on the particle size. Steady-state absorption spectra show that the plasmon band broadens and dampens as the particle size decreases, due to a progressive reduction in the dephasing time from scattering of the electrons at the surface.[18,19] Whether the particle size has an effect on the e-ph interaction is a more difficult question.

Extensive work has been done on several different metal nanoparticle systems. Logunov and co-workers studied thiol modified Au particles with diameters of 1.9, 2.6 and 3.2 nm in toluene.[3] Link *et al.* obtained data for 9 and 50 nm diameter Au particles in aqueous solutions,[7] and Hodak *et al.* performed measurements on 10 and 50 nm Ag and 4.6 to 120 nm Au particles in aqueous solutions.[6,9] The relaxation time showed no effect due to the particle size in these systems. Furthermore, the electron-phonon coupling constant was found to be similar to the corresponding bulk value.

On the other hand, Del Fatti *et al.* observed a decrease in the relaxation time for Ag when the particle diameter was decreased from 30 to 4 nm.[8] Similarly, Nisoli and co-workers reported a decrease in the relaxation time with decreasing the size for 12 to 4 nm diameter Sn particles,[4] and for 18 to 10 nm diameter Ga particles (in both the solid and liquid phases).[5] Zhang and co-workers studied 3 and 35 nm Pt particles, and 15 nm Au particles and the Au_{13} and Au_{55} clusters.[2] Interestingly, they observed a decrease in the relaxation time when the particle size decreased, but the relaxation time was found to be very long for the molecular like Au_{13} clusters. These results, in particular those of Del Fatti *et al.*[8] show that changes in the e-ph coupling time should only be expected for particles smaller than ca. 5 nm diameter.

One of the difficulties in these experiments is the preparation of monodisperse samples of different sizes, while keeping the same environment, i.e., eliminating any possible contribution from changes in the surface. This is especially a problem for very small particles stabilized by strongly adsorbed ligands. In the experiments of Nisoli and co-workers[4,5] and Del Fatti et al.[8] the particles were prepared on (or in) a solid support and, thus, the surrounding medium was similar for the different sizes. On the other hand, the studies with Au particles have been performed in a wide range of environments.

It has recently become possible to use radiolytic techniques to synthesize Au particles in aqueous solution with sizes anywhere between 2 and 120 nm.[20,21] The aim of this paper is to examine the e-ph coupling for very small Au particles in aqueous solution. In a previous report we gave preliminary values of g (the electron-phonon coupling con-

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stant) for particles down to 4.6 nm diameter. In the present paper we give a full description of these experiments and present results for very small (2.5 nm) diameter Au particles. The samples were prepared radiolytically and are stabilized by weakly adsorbed Cl^- ions and nonadsorbed PVA. We consider the Cl^- ions to be only weakly adsorbed because they do not distort the absorption spectrum of the particles, unlike species such as alkyl thiols.[22] Because there are no strongly adsorbed molecules that can perturb the electronic structure of the metal core, these systems provide a unique opportunity to examine how the properties of metal particles depend on their size.

II. EXPERIMENT

The ultrafast pump–probe experiments were performed with a laser system that has been described elsewhere.[6] The pump laser pulses were centered at 390 nm, and a white light continuum provided the probe laser pulses. An overall time resolution of 150–200 fs (full-width-half-maximum, sech^2 deconvolution) was determined by optical parametric amplification of the probe. The pump laser intensity was varied by a $\lambda/2$-waveplate/polarizer combination, and the intensity was monitored with a photodiode operating in the linear range.

The 2.5 nm gold particles were prepared by radiolytic reduction of $AuCl_4^-$, and the larger particles by enlarging the 2.5 nm seeds. As the procedures have already been reported,[20,21] a brief description should suffice here: A deareated aqueous 4×10^{-4} M $NaAuCl_4$ solution, which also contained 0.5 M methanol and 10^{-2} M polyvinyl alcohol, was γ-irradiated for 6 min at a dose rate of 1.5×10^6 rad/h. All the trivalent gold in $AuCl_4^-$ was reduced and the solution had a weak red color. Electron microscopy revealed that 2.5 nm gold particles were formed with a rather wide size distribution. This solution was directly used in the laser excitation experiments. To enlarge the particles up to 4 nm the solution was diluted by a factor of 2, and then one volume of the diluted solution was mixed with 3 volumes of a solution containing 2.0×10^{-4} M $KAu(CN)_2$, and the mixture was then irradiated at 8.5×10^4 rad/h until all the gold was reduced. A final enlargement to obtain 8 nm Au particles was then made using the 4 nm Au particles as seeds by irradiating a mixture of 1 volume of solution with 7 volumes of 2.0×10^{-4} M $KAu(CN)_2$. With increasing enlargement, the size distribution of the particles became narrower, as previously reported.[21]

III. RESULTS AND DISCUSSION

The absorption spectra of the samples used in this work are presented in Fig. 1. A blue shift and broadening of the plasmon band with decreasing size are clearly noticeable. The maximum of the plasmon band occurs at 522 nm for the 8.3 nm diameter particles, 517 nm for the 4.6 nm particles, and 502 nm for the 2.5 nm particles. Note that due to the damping of the plasmon band, the interband transitions dominate the absorption spectrum for the 2.5 nm Au particles.

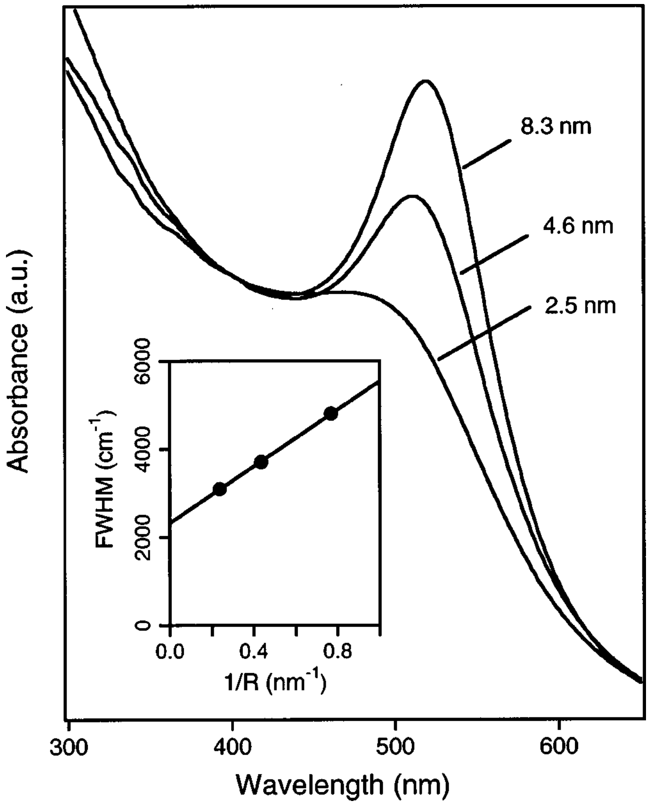

FIG. 1. Absorption spectra of Au particles in aqueous solution. The concentration of Au is $\sim2\times10^{-4}$ M for each sample. The insert shows the full-width-at-half-maximum of the plasmon band (in cm^{-1}) plotted against the inverse of the particle radius (in nm^{-1}).

The increased broadening of the plasmon band for small particles is usually attributed to electron-surface scattering.[18,19] Kreibig and co-workers have shown that the damping constant γ for the plasmon band can be described by the equation

$$\gamma=\gamma_0+\frac{Av_F}{R}, \tag{1}$$

where γ_0 is the bulk damping constant, v_F is the Fermi velocity, R is the particle radius and A is a constant that is near unity.[18,19] Calculations of the value of A depend on how the electron-surface interaction is modeled, and whether the electrons are treated quantum mechanically.[18,19] The insert in Fig. 1 shows a plot of the full-width-at-half-maximum (in cm^{-1}) of the plasmon band versus $1/R$ for our samples. A straight line fit to the data yields values for the slope and intercept of $A=0.43$ and $\gamma_0=4.4\times10^{14}$ Hz, which in turn yields an intrinsic dephasing time of $\tau_0=1/\gamma_0=2.3$ fs. These values are in good agreement with previous studies of the plasmon bandwidth in Au.[18,19] Note that because the position of the plasmon band is only weakly dependent on the particle size, the polydispersity in the samples does not significantly affect the bandwidth measurements.[23] Indeed, near-field scanning optical microscopy studies of Au particles have shown that the width of the plasmon band in the ensemble averaged spectrum is within a factor of 2 of that for single particles.[24] In comparison, luminescence spectra from single CdSe quantum dots are ca. 50 times narrower than the ensemble averaged spectrum.[25]

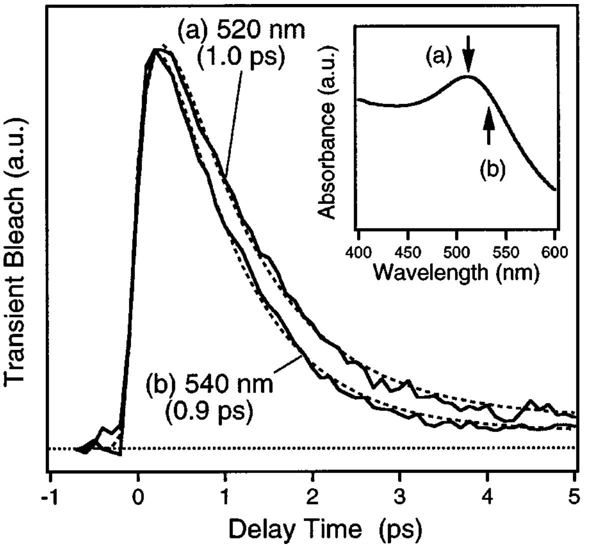

FIG. 2. Wavelength dependence of the relaxation dynamics for 4.6 nm diameter Au particles. The dashed lines are exponential fits to the data. The relaxation times obtained from fitting the data are indicated in parenthesis. These experiments were performed with the same pump laser power and, therefore, the same initial electronic temperature.

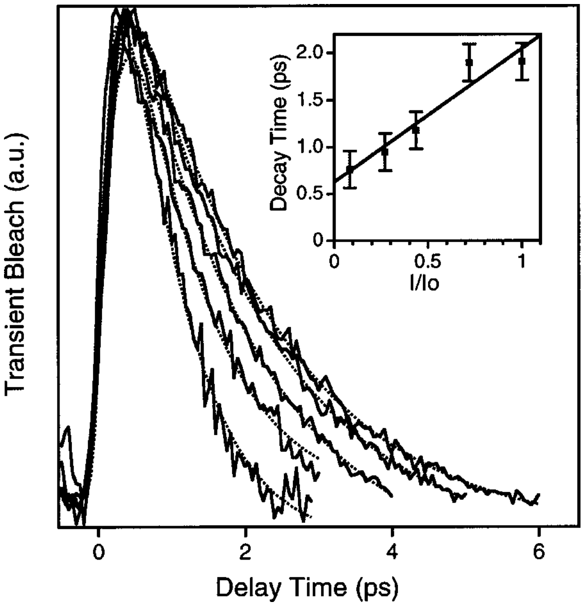

FIG. 3. Bleach recovery data for 2.5 nm diameter Au particles obtained with 390 nm pump and 500 nm probe laser pulses (solid lines). The pump laser power was varied from 0.03 to 0.3 μJ per pulse for these experiments. The dotted lines are exponential fits to the data. The insert shows a plot of the relaxation time (τ) versus the relative pump laser power (I/I_0). A straight line fit to this data is also shown.

Laser excitation of the particles increases their electronic temperature, which broadens the plasmon band. This creates a strong transient bleach signal for probe laser wavelengths near the plasmon band maximum.[3,6,7] The recovery of the bleach maps out the cooling of the electron gas due to coupling between the electrons and the lattice.[3,6,7] Note that the samples shown in Fig. 1 have approximately the same concentration of Au. Thus, the absorbance per Au atom in the 370 to 430 nm region is similar for the different sized particles. This means that experiments performed with 390 nm pump pulses that have the same power will produce the same temperature rise in the particles. It is also important to note that the relaxation time depends to some extent on the probe laser wavelength. This can be seen in Fig. 2 for the 4.6 nm diameter Au particle sample. This effect has also been observed for Cu particles by Bigot *et al.*[1] Qualitatively, the reason for this is that both the magnitude and the width of the plasmon bleach decrease as the electrons equilibrate with the lattice. Thus, experiments performed at different wavelengths can give different results. Because of this we have chosen to perform our experiments with the probe laser tuned to the peak of the plasmon band for the different particles. Specifically, for the data presented and discussed below the probe wavelengths used were 520 nm for the 4.6 and 8.3 nm Au particles, and 500 nm for the 2.5 nm Au particles (note that our probe laser has a bandwidth of ca. 10 nm).

Bleach recovery data for the 2.5 nm Au particles are presented in Fig. 3. Logunov *et al.* observed an absorption signal in the 500 nm region, not a bleach, for very small 1.9 nm diameter thiol capped Au particles.[3] This shows that thiol capping can significantly affect the electronic properties, and the transient response, of very small particles.[22,23] The set of scans shown in Fig. 3 correspond to pump laser intensities ranging from approximately 0.03 to 0.3 μJ per pulse, with the higher pump powers giving longer decays. This power dependence of the decay time has been previously studied, and is usually interpreted in terms of the two-temperature-model.[1,3,6,7,23,26] In this frame the free-electron gas and the lattice compose two sub-systems of the metal, each characterized by a different heat capacity and temperature. Energy can flow from one sub-system to the other through electron-phonon coupling. This is described by the following pair of differential equations:

$$\begin{aligned} C_e(T_e)\frac{\partial T_e}{\partial t} &= -g(T_e - T_l), \\ C_l\frac{\partial T_l}{\partial t} &= g(T_e - T_l), \end{aligned} \tag{2}$$

where $C_e = \gamma T_e$ is the temperature dependent electronic heat capacity, $\gamma = 66\ \mathrm{Jm^{-3}\,K^{-2}}$ for Au,[27] C_l is the lattice heat capacity, T_e and T_l are the electronic and lattice temperatures, and g is the *e-ph* coupling constant. It is the temperature dependence of the electronic heat capacity that causes the intensity dependence in the relaxation time.

The primary aim of this paper is to understand how the *e-ph* coupling constant, g, depends on size for very small Au particles. A reliable value of g can be obtained by extrapolating the lifetime measured at different pump intensities to zero pump power.[6,7,23] An example of this extrapolation is shown in the insert in Fig. 3. In the low power regime the relaxation time is given by $\gamma(T_0 + \Delta T)/g$, where T_0 is the ambient temperature and ΔT is the electronic temperature increase induced by the pump laser pulse.[6] Thus, extrapolation to zero pump power yields the value of $\gamma T_0/g$. Table I summarizes the values of g obtained for the samples studied in this work. The key result from these experiments is that the *e-ph* coupling constant *does not vary with size* for

TABLE I. Relaxation time (zero power limit) and electron-phonon coupling constants obtained for the different sized Au particles. The probe wavelength used in each case is also included.

Mean radius (nm)	Wavelength (nm)	Intercept (ps)	g ($\mathrm{W\,m^{-3}\,K^{-1}}$)
1.3 ± 0.3	500	0.63 ± 0.1	$(3.1\pm0.5)\times10^{16}$
2.3 ± 0.3	520	0.63 ± 0.1	$(3.1\pm0.5)\times10^{16}$
4.2 ± 0.5	520	0.57 ± 0.1	$(3.5\pm0.5)\times10^{16}$

TABLE II. Electron-surface and effective electron-phonon coupling constants ($\mathrm{W\,m^{-3}K^{-1}}$) calculated with the model of Belotskii and Tomchuk (Refs. 33,34).

Particle radius (nm)	g_C	g_A	g_{eff}
1.3	1.75×10^{15}	5.57×10^{14}	3.18×10^{16}
2.3	9.97×10^{14}	1.64×10^{13}	3.05×10^{16}
4.2	1.58×10^{14}	5.05×10^{12}	2.97×10^{16}
Bulk			2.95×10^{16}

our samples. Furthermore, the value of g obtained is similar to the values for larger (>10 nm diameter) Au particles,[6,7] and for bulk Au.[28]

Note that an alternative way to compare *e-ph* coupling for different sized metal particles is to perform measurements at a single pump power, and ensure that the same initial electronic temperature is obtained for each sample. In this case the decay times give an indication of the relative magnitudes of the *e-ph* coupling constants. However, to do this the same number of excited electrons per Au atom must be produced in each experiment, which requires the product of the laser power density and the absorbance per Au atom to be the same for each sample. This is rather difficult to achieve for a series of different sized samples. An advantage of the extrapolation technique detailed above is that it eliminates the pump laser intensity dependence in the dynamics and, therefore, the requirement to exactly reproduce the experimental conditions (laser intensity, spot size, etc.) from day to day.

However, there are several difficulties that are associated with these experiments. First, at low pump laser power the rise and decay times are comparable. The signal-to-noise also becomes worse, which makes it difficult to extract accurate decay times (the rise and decay times become strongly correlated in the fitting routine). The rise times in these experiments are on the order of 200 fs. The noninstantaneous rise in the bleach signal is due to electron–electron scattering processes that equilibrate the absorbed energy over the entire electron distribution.[7,23] However, transient absorption experiments are not particularly well suited for studies of *e-e* scattering. Much more detailed information can be obtained from time-resolved two-photon photoemission spectroscopy.[29–32]

A second disadvantage of the extrapolation method is that the values of g obtained from the intercept are noisy (typically 20% error) and, thus, it is difficult to detect small effects. However, the previous studies performed by Nisoli and co-workers[4,5] and Del Fatti *et al.*[7] show that changes in the relaxation times on the order of 20% to 50% are expected, which should be detectable in spite of the rather low sensitivity of this method.

The relaxation of the hot electron gas can be assumed to occur through two different channels: bulk electron-phonon interactions, and electron-surface interactions. The last process occurs by coupling between the electrons and two kinds of surface modes, namely, acoustic and capillary surface modes.[33] The acoustic surface modes change the volume of the particle, while the capillary surface modes deviate the shape of the particles without changing their volume. Since these mechanisms occur in parallel, the effective electron-phonon coupling constant is determined by summing the different contributions:

$$g_{\mathrm{eff}}=g_{\mathrm{Bulk}}+g_A+g_C\,, \tag{3}$$

where the last two terms stand for the acoustic and capillary surface mode coupling terms, respectively. These terms account for all the size dependence. In the following calculations we will assume that the bulk contribution is equal to 2.95×10^{16} $\mathrm{Wm^{-3}\,K^{-1}}$, which is the value measured by Groenveld *et al.* for Au.[28]

The contribution of the surface modes to the electronic relaxation is calculated using the theory developed by Belotskii *et al.*,[33,34] where the electron gas is assumed to be in a spherical potential well with the dimensions of the particle and with a depth V_0, which is equal to the Fermi energy. The coupling constant between the electrons and the capillary modes is given by:[34]

$$g_C=\frac{3}{16\pi}k_B\frac{v_F}{R}n\,\frac{m_e\omega_l^2}{\sigma}\left(\frac{V_0}{\varphi_0}\right)^2, \tag{4}$$

where k_B is Boltzmann's constant, n is the free electron density, m_e is the electron mass, σ is the surface tension, φ_0 is the work function of the metal, and ω_l is the maximum frequency of the capillary modes. This assignment of the parameters in Eq. (4) follows that given in Ref. 5. The limiting frequency ω_l is approximately given by:[35]

$$\omega_l=\sqrt{\frac{\sigma}{\rho R^3}l(l-1)(l+2)}, \tag{5}$$

where ρ is the density of the metal, and l is the angular momentum number corresponding to the shortest possible surface wave, which is given by the integer part of $\pi R/d$ where d is the lattice parameter. Note, that the surface tension cancels when ω_l from Eq. (5) is substituted into Eq. (4). In turn, the energy loss associated with excitation of the acoustic surface modes is given by:[34]

$$g_A=\frac{1}{16\pi}k_B\frac{v_F}{R^2}n\,\frac{m_e}{\rho}\left(\frac{\omega_D}{c_l}\right)^2\left(\frac{V_0}{\varphi_0}\right)^2, \tag{6}$$

where c_l is the longitudinal speed of sound in the material, ω_D is the Debye frequency, and all the remaining symbols have been defined above.

The results of calculations for the different sized Au particles used in our experiments are shown in the Table II. Because both g_A and g_C have an inverse dependence on radius, the time scale for electron-phonon coupling decreases with decreasing size according to this model.[2,4,5] Also, the contribution of the capillary modes to the relaxation is much larger than that for the acoustic modes. As can be seen from Table II, for Au the contribution of the surface modes is less than 10% of the total *e*-*ph* coupling constant, which is on the order of the error in our measurements of the *e*-*ph* coupling constant. Thus, these calculations show that the energy loss to the surface modes does not significantly affect the effective electron-phonon coupling constant g_{eff} for Au particles >2 nm diameter, which is consistent with our experimental data.

This model has been applied to gallium nanoparticles with diameters between 10 and 18 nm, where it was shown that it almost exactly accounts for the variation in the relaxation times with the particle size.[5] The same model applied to silver nanoparticles with diameters between 4 and 30 nm accounts for ca. 50% of the variation in the relaxation time with the particle radius.[8] Thus, the results of the calculations performed using this theory are in good agreement with the available experimental data for Ga, Ag and Au nanoparticles. In all cases the surface coupling is dominated by g_C.

What appears to determine the magnitude of g_C for the different metals is the ratio of the electron density to the metal density (n/ρ), which is proportional to the valence of the metal divided by its atomic mass. Thus, Au $(n/\rho=3.1\times10^{21}\ \mathrm{g}^{-1})$ which has high atomic mass, has a smaller electron surface coupling than Ga $(n/\rho=2.6\times10^{22}\ \mathrm{g}^{-1})$ or Ag $(n/\rho=5.6\times10^{21}\ \mathrm{g}^{-1})$. The physical picture that emerges is that collisions of the electrons with the surface will not significantly displace the surface atoms from their equilibrium position for heavy elements, such as Au. This means that the surface phonon modes will not be efficiently excited, and there will be little energy transfer to these modes. For metals with a large free electron density, such as Ga, the number of electron-surface collisions is larger, which increases the probability of energy transfer from the electrons to the surface atoms. Likewise, metals with lighter nuclei will have larger *e*-*ph* coupling constants. It should also be noted that the ratio V_0/φ_0 is larger for Ga than for Au, but this factor does not cause a big difference in the values of the *e*-*ph* coupling constant for these two metals.

Thus, we expect the electron-phonon relaxation time to be strongly size dependent for metals with low atomic mass, and for those that have more than one valence electron. For example, nanoparticles of Al or Cr should show size dependent *g* values. Of course, whether a size dependent electron-phonon coupling constant can be observed also depends on the magnitude of the intrinsic (bulk) electron-phonon interaction. Thus, size dependent electronic relaxation may not be observable for Al, because it has a high bulk electron-phonon coupling constant.[36]

IV. CONCLUSIONS

The coupling between the electrons and phonons in Au has been examined for nanoparticles with diameters between 2.5 and 8.3 nm. The results show that—to within our signal-to-noise—the characteristic time-scale for electron-phonon coupling does not change with the particle size *for Au*. This rather surprising result suggests that there is no effect from surface scattering on the electronic relaxation: phonon emission ''inside'' the particle dominates the dynamics. Calculation of the coupling of the excited free electron gas to the capillary and acoustic surface phonon modes shows that this coupling is at least one order of magnitude smaller than the bulk electron-phonon coupling for our particles. On the other hand, the excitation of the capillary modes will contribute to the relaxation of the hot electron gas in the case of metals with a larger number of valence electrons and/or low atomic mass. For metals with massive atoms the surface acts as a rigid wall from which the electrons scatter elastically. These considerations are important for designing devices with fast time responses that are tunable through changing the size or composition of the nanoparticles.[10–17]

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