NANO LETTERS

2007
Vol. 7, No. 10
3227−3234

The Effect of Plasmon Field on the Coherent Lattice Phonon Oscillation in Electron-Beam Fabricated Gold Nanoparticle Pairs

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Received July 25, 2007

ABSTRACT

By using electron beam lithography, we fabricated pairs of gold nanoparticles with varying interparticle separation. Double-beam femtosecond transient absorption spectroscopy was used to determine the coherent lattice oscillation frequency as a function of the interparticle separation in the presence of the plasmon field excited by the monitoring probe light. We found that the fractional shift in the coherent lattice phonon oscillation frequency follows an exponential decay with respect to the interparticle gap scaled by the disc diameter with the same decay constant as that previously observed for the fractional shift in the surface plasmon electronic oscillation resonance frequency. This strongly suggests that it is the near-field coupling between the particles that shifts both the coherent electronic oscillation (plasmon) frequency and the coherent lattice oscillation (phonon) frequency. The similar trend in the effect of interparticle coupling on the plasmon frequency and the phonon frequency is essentially a reflection of the universal scaling behavior of the distance decay of the interparticle plasmonic near-field. It is shown that the observed decrease in the lattice oscillation frequency with decrease in the interparticle distance is the result of a reduction in the effective free electron density within each nanoparticle pair partner as a result of the polarizing perturbation of the plasmonic field of the other nanoparticle in the pair.

In recent years, great interest has been directed toward the effect of interparticle interactions on the surface plasmon resonance (SPR) in metal nanoparticle assemblies, including self-assembled two-dimensional superlattices,[1−3] solution-phase assemblies or aggregates,[4−7] electron beam lithography (EBL)-fabricated nanodisc or nanoprism structures,[2,8−13] as well as by electrodynamic simulations.[14−18] The observed shift in the surface plasmon resonance (SPR) with change in the interparticle separation between the metal nanoparticles has been utilized for optical biosensing[19] and also as a molecular ruler for dynamic distance measurement in biology.[20−22] Another interesting aspect of interacting noble metal nanoparticle chains is their ability to transfer and guide electromagnetic energy below the diffraction limit,[23] which can be attributed to the near-field coupling of the SPR modes of the adjacent nanoparticles in the chain. It has been found also that the plasmon coupling of particles results in the squeezing of the optical near-field to the junction between the neighboring nanoparticles.[8] The confinement of the optical near-field between the neighboring nanoparticles enhances the local electromagnetic field within the inter-nanoparticle gap, which has led to other applications, such as single-molecule traps,[24] single-molecule surface-enhanced Raman scattering (SERS),[25,26] and second-harmonic generation.[27]

Because of the above-listed interesting and useful attributes of SPR coupling, extensive studies have been performed on the near-field coupling between closely spaced plasmonic nanoparticles. The near-field interaction between sphere-, disk-, and prism-shaped nanoparticle pairs has been examined by several groups.[2,10−12,21,28,29] It has been found for nanosphere and nanodisc pairs that the surface plasmon resonance frequency of the particle pair decreases almost exponentially as the gap between the two nanoparticles is decreased.[2,12,21,29] When the fractional shift in the surface plasmon band is plotted against the interparticle gap in units of the particle diameter, the same near-exponential decay trend is observed for nanoparticles of different sizes.[2,12,29] This scaling law has been recently found to be valid for nanoparticle pairs of different size, shape, plasmonic material (gold and silver), and in different media.[29] To the best of our knowledge, all of these past studies have been focused on the effect of the interparticle interactions on the coherent electron oscillation (i.e., plasmon) observed by means of steady-state spectroscopy. Here, we study using ultrafast transient absorption spectroscopy the effect of interparticle coupling on the

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10.1021/nl071813p CCC: $37.00
Published on Web 08/31/2007

coherent phonon oscillation in lithographically fabricated gold particle pairs.

Ultrafast laser-induced coherent phonon vibrations have been optically detected in noble metal nanoparticles of different shapes and also in different environments.[30−35] However, the nanoparticles in all of these systems are randomly distributed in solution or in a matrix in which the interparticle interactions are negligible. We first studied the coherent phonon vibrations in a two-dimensional periodic array prepared using nanosphere lithography.[36] Recently, our group discovered the effect of interparticle coupling on the coherent phonon oscillation in monolayer periodic gold nanoparticle arrays.[37] The Pileni group has also reported the effect of interparticle coupling on the Raman-active lattice vibrations in self-assembled periodic face-centered cubic arrangement of silver nanocrystals coated with dodecanethiol chains.[38,39] However, the effect of the interparticle separation between the coupled nanoparticles on the lattice vibration has not been elucidated because limitations in the sample preparation methods employed in these previous studies did not allow the interparticle distance to be varied systematically. In the current study, we employed electron-beam lithography to fabricate gold nanoparticle pairs with varying interparticle separation and studied using an ultrafast pump−probe technique the changes in the coherent lattice oscillation frequency as a function of interparticle separation in the presence of the plasmonic field resulting from the surface plasmon resonance excitation of the nanoparticle pair. We observe that the fractional shift in the coherent lattice oscillation frequency decays as a function of the interparticle separation scaled by the nanoparticle size with the same near-exponential decay constant as that found previously for the surface plasmon oscillation.[29] This strongly suggests that the observed frequency shift of the coherent lattice oscillation is due to the near-field coupling between the nanoparticles resulting from the surface plasmon field induced by the monitoring light. Using a dipolar-coupling model, we show that the similarity in the trend and scaling of the interparticle gap dependence of the plasmon frequency and the phonon frequency is essentially a reflection of the distance decay of the interparticle plasmonic near-field. The polarizing effect of the plasmonic field of one nanoparticle on the effective electron density of the other pair partner gives rise to the decrease in the lattice oscillation frequency.

Nanodisc Pair Array Fabrication. The gold nanoparticle pairs were prepared on quartz slides by electron-beam lithography (EBL) using a JEOL JBX-9300FS 100 kV EBL system in the Microelectronics Research Center (MiRC) at Georgia Institute of Technology. Quartz slides (Technical Glass Products, Inc.) were cleaned in piranha solution (3:1 H_2SO_4/30% H_2O_2) at 80 °C for 1.5 h and dried in air. The cleaned quartz slide was spin-coated with 65 nm PMMA 950k electron-sensitive resist and cured at 180 °C for 3 min. The slide was mounted in a thermal evaporator and coated with 10 nm of gold to make the substrate conductive. After pattern writing, the gold film was etched in gold etchant GE-8148 (an aqueous solution of KI and I_2). The pattern was then developed in 1:3 MIBK/IPA (methyl isobutyl ketone: isopropyl alcohol) for 180 s, followed by washing in IPA for 30 s and drying in pure N_2. The substrate was mounted in an electron beam evaporator to deposit a thin Cr layer (∼0.4 nm), which increased the Au nanoparticle adhesion to the quartz substrate, followed by a deposition of 25 nm Au with a deposition rate of 0.5 Å/s. We performed the lift-off step in hot acetone (∼63 °C) to remove the resist and the metal film on top of it. Polarized microabsorption spectra were taken by a SEE 1100 microspectrometer in the transmission mode and the area examined with a 20× objective lens was $8 \times 8\ \mu m^2$.

Femtosecond Transient Absorption Spectroscopy.[36] To observe the effect of the surface plasmon near-field interaction on the coherent phonon oscillation frequency, a polarized 400 nm femtosecond laser pulse was used for the optical excitation of the lattice oscillation and a polarized white-light pulse was used to monitor the lattice oscillations while supplying a plasmonic field to the oscillating discs. The 400 nm pump laser pulses were generated by frequency-doubling the fundamental 800 nm wavelength pulse output from an amplified femtosecond Ti:sapphire laser system (Clark MXR CPA 1000) in a 1 mm BBO crystal. The white light continuum, ranging from 400 to 1100 nm, was generated by focusing a small portion of the fundamental pulse (∼40 μJ) onto a 1 mm sapphire plate. The detailed pump−probe experimental setup has been detailed previously.[37] In our experiment, the pump and probe beams, both with polarization parallel to the axis connecting the centers of the two nanodiscs in the pair, were focused and overlapped at the sample to a beam diameter of ∼250 μm. A spectrometer placed after the sample was used to select from the transmitted white light a specific wavelength overlapping with the surface plasmon absorption band of the nanodisc pair. The intensity of the transmitted white light at this wavelength was measured as a function of the delay time following the pump pulse. This intensity changed periodically with a period corresponding to the lattice oscillation period. This is due to the fact that as the lattice expands and contracts during the lattice oscillation, the surface plasmon absorption band shifts respectively to the red and to the blue.

It must be noted that we measure the oscillation amplitude of the lattice (from the intensity of the transmitted lights at the selected wavelength) at different delay times in the presence of the white light that excites the plasmon field. Thus, phenomenologically, one can think of the present experiment as the measurement of the lattice oscillation frequency while the plasmon field is turned "on".

SEM Images and Absorption Spectra of Nanodisc Pair Arrays. Parts a−f of Figure 1 show the representative SEM images of the lithographic nanodisc particle pair samples used in the experiments, with different interparticle gaps, i.e., 2, 7, 12, 17, 27, and 212 nm, respectively. The nanodisc diameter D is 88 nm and thickness of each nanodisc is 25 nm for all the samples. The size and the shape was almost the same for all nanodiscs, thus, the effects of sample heterogeneity could be excluded from the absorption and the coherent phonon oscillation measurements. Magnified images of the nanodisc pair are shown in Figure 1a−e insets, clearly

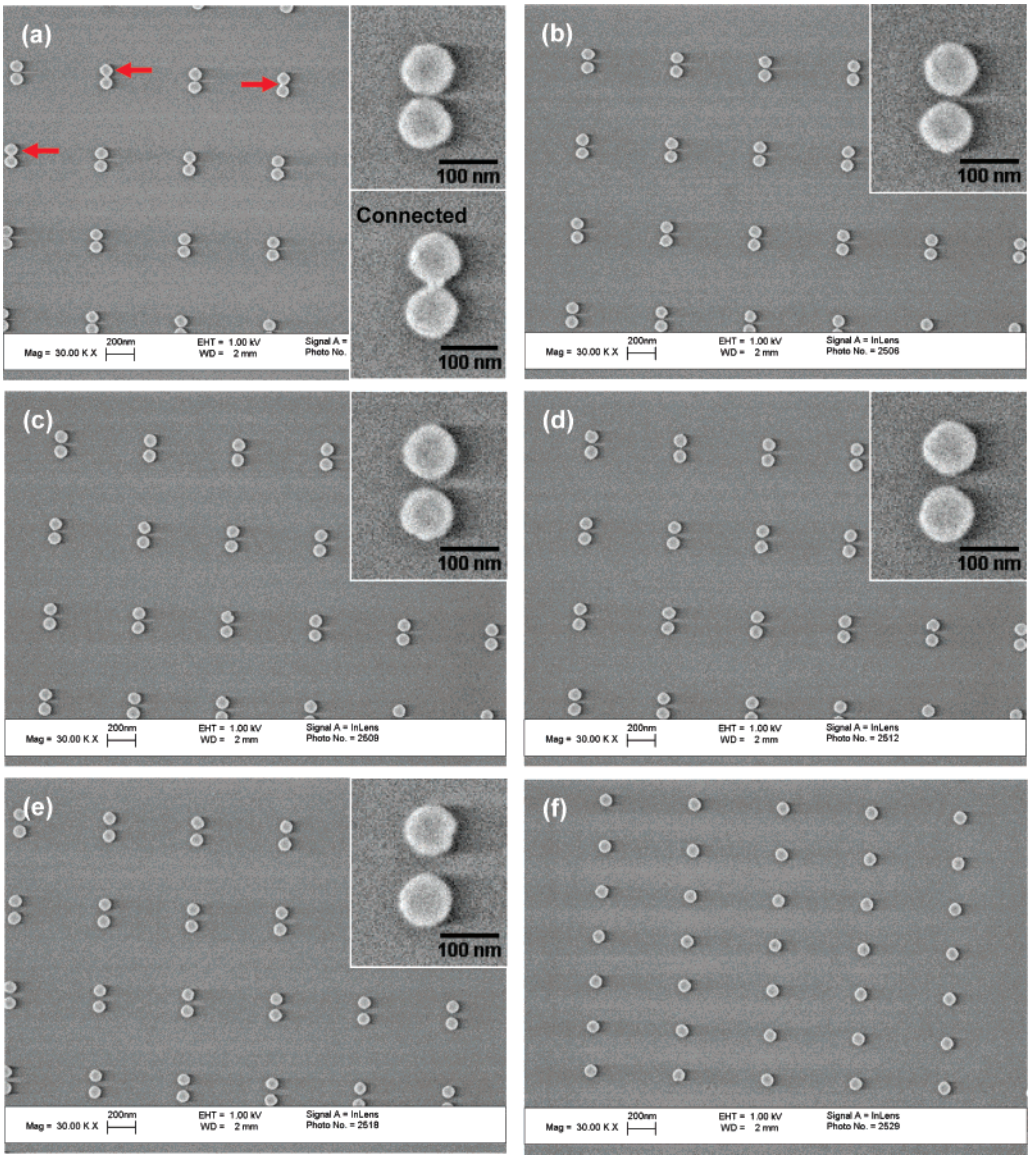

Figure 1. SEM images of the different nanodisc pairs used in the present study, having interparticle gaps of (a) 2 nm, (b) 7 nm, (c) 12 nm, (d) 17 nm, (e) 27, and (f) 212 nm. The insets in (a−e) are magnified images of a representative nanodisc pair clearly showing the controlled variation of the gap between the nanodisc pair partners. In (a), we show that, at 2 nm gap, some of the nanodisc pair partners are interconnected (as indicated by red arrows). The diameter of each nanodisc is 88 nm and the thickness of each nanodisc is 25 nm for all samples.

showing the controlled variation in the internanodisc gap. Extensive care was employed in the preparation of nanodiscs with sub-10 nm separation. While we attempted to go down to a gap as small as 2 nm, it is very difficult to control such a small gap, and as seen in Figure 1a, in some pairs, the nanodisc pair partners are interconnected (indicated by red arrows). Thus, the smallest interparticle gap without nanodisc partners touching each other is around 7 nm (Figure 1b).

Polarized microabsorption spectroscopy was used to characterize the optical properties of the nanodisc pairs for demonstrating the effect of interparticle coupling on the width and frequency of the surface plasmon resonance. The absorption was measured under two configurations: one in which the polarization of the incident light was parallel to the axis connecting the centers of the two nanodiscs in a pair (also called long-axis of the nanodisc pair) and another with a polarization perpendicular to this long axis. The parallel and perpendicular polarized microabsorption spectra are shown in parts a and b of Figure 2, respectively. The change in the surface plasmon resonance spectra with a change in the interdisc gap is in complete contrast for the two polarization configurations. For the incident light polarization parallel to the long axis of the nanodisc pair, the plasmon band red-shifts from 571 to 608 nm as the gap decreases from 27 to 7 nm (Figure 2a). We also notice that the plasmon band shifts only 4 nm as the gap is decreased from 27 to 17 nm, while a shift of 32 nm is observed when the gap is decreased from 17 to 7 nm. Thus, the magnitude of the shift of the plasmon band decreases dramatically with increasing interparticle gap, which suggests that the interaction strength between the nanodisc pair partners decays

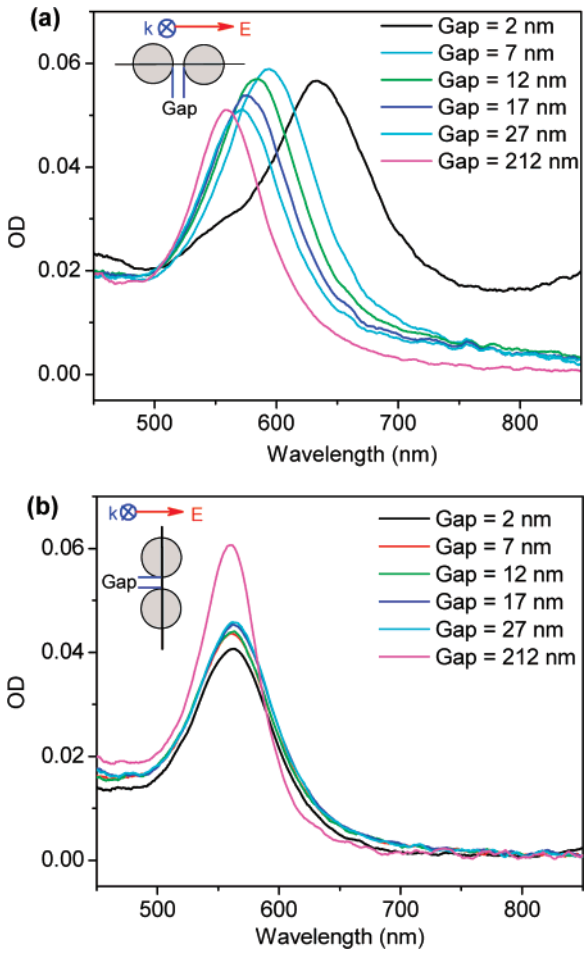

Figure 2. Absorption spectra of the nanodisc pairs as a function of decreasing interparticle separation with the incident light polarized (a) parallel and (b) perpendicular to the axis connecting the centers of the two nanodiscs in the pair. The plasmon band red-shifts with decreasing interparticle distance for the light polarized parallel to the interparticle axis but a slight blue-shift is observed when the polarization of the light is perpendicular to the connecting axis. This difference has been recently explained by the simple dipole or exciton picture.[4,9]

exponentially over the interparticle gap, consistent with earlier studies.[12,29]

For the incident light polarization perpendicular to the long axis of the nanodisc pair, the plasmon band maximum blue-shifts from 563 to 561 nm as the gap decreases from 27 to 7 nm. While in the parallel polarization case, the interparticle interaction is strongly attractive, resulting in the large plasmon red-shift; the small blue-shift in the perpendicular polarization case is due to a very weak repulsive interaction between the electronic dipoles of the particle pair partners in the side-by-side configuration.[4,9] We also observe in the perpendicular polarization case a slight decrease in the plasmon band intensity as the gap is decreased, whereas in the parallel polarization case, the plasmon band intensity increases, further supporting the dipolar-coupling picture. An interesting observation in the perpendicular polarization case is that, at the largest gap, i.e., 212 nm, the intensity of the plasmon absorption band is relatively higher. Besides, the band maximum for this gap is located at 560 nm, which is blue-shifted (~3 nm) with respect to the plasmon maximum

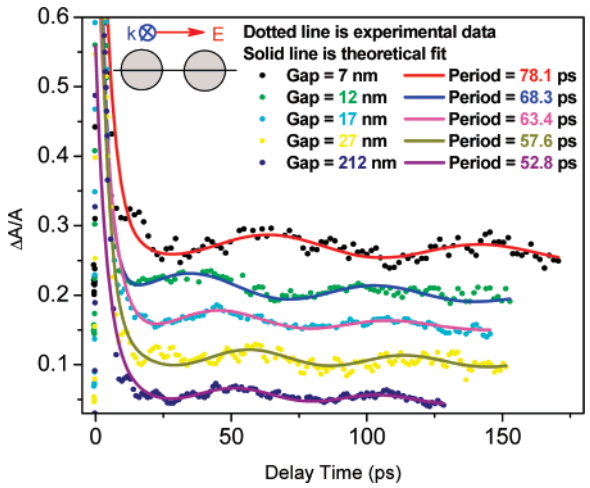

Figure 3. Optically detected coherent phonon oscillations in gold nanodisc pairs with different interparticle separations (gaps). The experimental traces (dotted lines) are fitted with two exponential decays plus a damped cosine function (solid line). The traces are normalized and vertically shifted for clear view. The exciting and monitoring light pulses are polarized parallel to the axis connecting the centers of the two nanodiscs in a pair. For the smallest gap (7 nm), the vibration period is 78.1 ps. As we increase the gap between the nanodiscs within the pair, we observe that the vibration period decreases. For the pairs with an interparticle separation of 212 nm, we observe a vibration period of 52.8 ps, which is very close to the theoretically calculated period ($2d/v_l = 53.7$ ps) for an isolated nanodisc (without coupling to its pair partner).

for the smaller 27 nm gap. The plasmon band for the 212 nm gap is also much sharper, with a full width at half-maximum = 1715 cm^{-1}, whereas the 7 nm gap has a bandwidth of 2005 cm^{-1}. This anomalous blue-shift and decrease in the bandwidth of the surface plasmon can be attributed to the diffractive coupling in arrays of cylindrical nanoparticles predicted and observed by the Schatz and Van Duyne groups.[15,16]

Coherent Phonon Oscillation in Nanodisc Pairs. To study the effect of interparticle coupling on the coherent phonon oscillation, we measured the coherent phonon oscillation frequency for nanodisc pairs with interparticle separation gap varying from 212 to 7 nm. We did not use the nanodisc pair with a 2 nm gap because, in this case, some of the pair partners are connected, leading to dramatic changes in the surface plasmon resonance. As shown in Figure 2a, the absorption spectrum of the nanodisc pair array with 2 nm gap shows three bands, a weak shoulder peak around 550 nm, a strong peak around 635 nm, and a peak beyond 850 nm. The 635 nm peak represents the nanodisc pair of 2 nm gap. The shoulder at 550 nm represents a higher order mode (quadrupole), and the peak in the infrared range is possibly the plasmon resonance of the connected nanodiscs.[12] Thus, for the 2 nm gap nanodisc pairs, the effect of interparticle coupling on the coherent phonon vibration cannot be identified clearly to be from the coupled nanodisc pairs or from the connected nanodisc pairs. Coherent phonon vibrations were excited in the nanodisc pair samples with different interparticle gaps by means of 400 nm femtosecond laser light (pump) polarized parallel to the long axis of the nanodisc pair (Figure 3). A femtosecond white-light con-

tinuum pulse polarized along the particle pair long axis was used to probe the lattice oscillation dynamics at various time delays following the pump excitation. It must be noted here that the white-light continuum probe pulse excites the surface plasmon resonance of the particle pair. Thus, phenomenologically, in this experiment, the lattice oscillation dynamics is being monitored in the constant presence of the resonant plasmon field of the nanoparticle pair. Figure 3 clearly shows that in the interacting particle pairs, the coherent lattice vibration period depends strongly on the interparticle gap. For gaps of 7, 12, 17, 27, and 212 nm, the corresponding vibration periods obtained from the transient absorption experiments are 78.1, 68.3, 63.4, 57.6, and 52.8 ps, respectively.

For the pair with the 212 nm gap, it is reasonable to suppose that there is negligible interparticle coupling, and the vibration period (52.8 ps) can be attributed to an isolated single nanodisc. The one-dimensional acoustic wave model[33] has been extensively used to precisely calculate the vibration period of isolated nonspherical metal nanoparticles, such as nanoprisms on the surface of quartz substrates[37] or in colloidal solution[40] and ellipsoid-shaped nanoparticles embedded in a glass matrix.[33] Unlike the coherent electronic vibration (plasmon) that is sensitive to the surrounding environment, the period (or frequency) of the coherent phonon vibration is independent of the dielectric constant of the medium. The insensitivity of the phonon vibration period is quite reasonable because the period is determined by the internal lattice interactions of the nanoparticle based on the elastic continuum model.[33,41−43] For Au nanodiscs with 88 nm diameter, the model gives a period of 53.7 ps ($T = 2d/v_l$, $v_l = 3240$ m/s for bulk gold), which is very close to the measured vibration period of 52.8 ps for the isolated nanodisc.[33]

We observe that with increasing interparticle gap, there is an exponential decrease in the vibration period, which is quite similar to the gap-dependence of the plasmon resonance wavelength maximum observed by steady-state absorption spectroscopy. This interesting similarity is carried even further. Figure 4 shows a comparison of the decay of the fractional shift of the coherent phonon oscillation frequency (Figure 4a) and that of the SPR frequency (Figure 4b) with the interparticle gap scaled by the nanodisc diameter. The decay constant (τ) for both the exponential dependencies are very close to one another ($\tau = 0.17$ for the phonon frequency f, and $\tau = 0.19$ for the plasmon frequency ω).

Recently, it has been shown that the fractional SPR shift decays near-exponentially with the interparticle gap over a distance that is roughly 0.2 times the particle size, independent of the nanoparticle size, shape, material, and the medium dielectric constant.[29] This universal scaling behavior of the plasmon resonance in nanoparticle pairs originates from the inherent distance decay of the interparticle near-field that couples the particles together.[29] From the result of Figure 4, it is obvious that the coupling affecting the phonon vibration frequency has the same distance dependence as that affecting the surface plasmon/electronic oscillation frequency. The similarity of the scaling behavior of the phonon oscillation

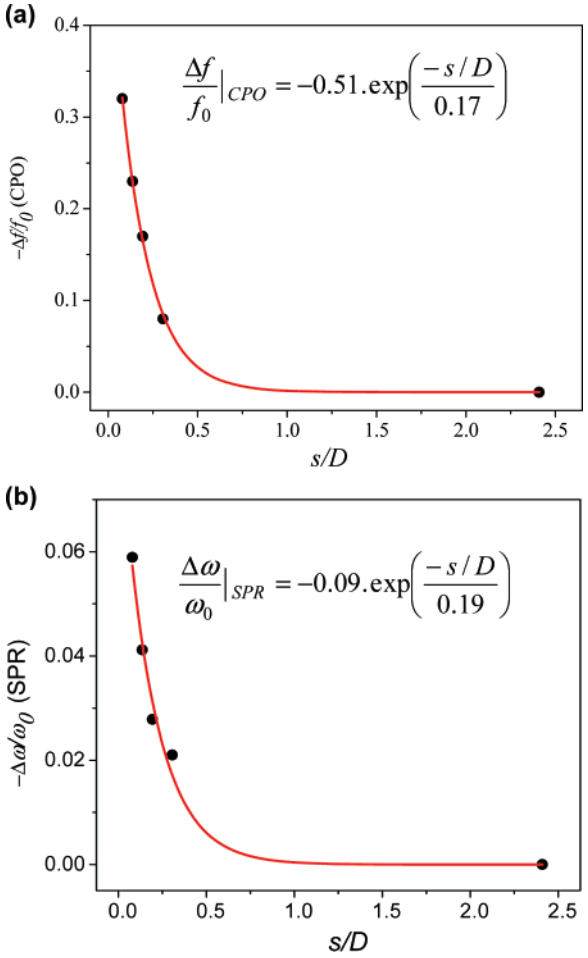

Figure 4. Exponential decay fits of the fractional shift of the frequency of (a) the coherent phonon oscillation (CPO) and (b) the surface plasmon resonance (SPR) with increasing interparticle separation s scaled by the particle diameter D. The fractional shift in both the CPO and SPR frequencies decreases exponentially with increasing s/D with similar exponential decay constant of ~0.20.

frequency to the surface plasmon resonance thus suggests that it is this same near-field coupling, which is responsible for the modulation of the phonon oscillation frequency with varying interparticle coupling distance. It must be noted here that, in our experiments, we probe the coherent phonon oscillation of the nanodisc pair using laser light (probe pulse), which is resonant with the plasmon absorption of the nanodisc pair. Thus, the coherent phonon oscillation is measured in the constant presence of the resonant plasmonic near-field of the particle pair excited by the monitoring probe light. Hence, it is reasonable to expect a perturbation of the coherent phonon oscillation due to the plasmonic near-field interaction between the two particles.

A simple dipolar-coupling model can help us elucidate this perturbation further. The dipolar polarizability α_0 of an isolated single metal nanoparticle is given by the Clausius−Mossotti relation[44] as:

$$\alpha_0 = \epsilon_0 V(1+\kappa)\frac{(\epsilon - \epsilon_m)}{(\epsilon + \kappa\epsilon_m)} \quad (1)$$

where ϵ_0 is the vacuum permittivity, $\epsilon(\omega) = \epsilon_r + i\epsilon_i$ is the

complex dielectric constant of the metal, which is a function of the light frequency ω, ϵ_m is the dielectric constant of the surrounding medium, V is the nanoparticle volume, and κ is a shape factor. At some frequency ω_0, where $\epsilon_r = -\kappa\epsilon_m$, the polarizability given by eq 1 shows a strong maximum, corresponding to the resonant interaction (absorption and scattering) of the incident light field with the nanoparticle, viz. the dipolar surface plasmon resonance. ω_0 thus corresponds to the dipolar surface plasmon resonance frequency of the nanoparticle. However, when the two nanoparticles are fairly close to each other, in addition to the incident light field, each particle feels an additional field due to the presence of the plasmon dipole on the neighboring particle, which results in a shift $\Delta\omega$ (which is $-ve$ for polarization parallel to the interparticle axis) in the position of the surface plasmon frequency.[29] We may alternatively represent the perturbative effect of this field induced by the neighboring plasmon dipole as a change in the effective electronic density of the single particle, which results in a shift of its surface plasmon resonance frequency. As per the Drude−Lorentz−Sommerfeld model,[44] which is a good representation of the free-electron behavior for gold in the visible region, the real part of the metal dielectric function is given as a function of frequency ω as:

$$\epsilon_r = \epsilon_\infty - \frac{{\omega_p}^2}{\omega^2 + \gamma^2} \tag{2}$$

where ϵ_∞ is the dielectric contribution due to the atomic core polarizability, γ is the electronic damping function, and ω_p is the bulk plasma frequency, which is given as:

$$\omega_p = \left(\frac{N_0 e^2}{\epsilon_0 m_e}\right)^{1/2} \tag{3}$$

where e is the electronic charge, m_e is the effective mass of the electron, and N_0 is the free electron density of the metal. Because $\gamma \ll \omega$ for gold in the visible region, combining eqs 2 and 3 and the resonance condition $\epsilon_r = -\kappa\epsilon_m$ gives a simple relationship between the electron density in the metal and the surface plasmon resonance frequency ω_0:

$$N_0 = {\omega_0}^2 \frac{\epsilon_0(\epsilon_\infty + \kappa\epsilon_m)m_e}{e^2} \tag{4}$$

Thus for small perturbations (due to the near-field interaction) from the surface plasmon resonance (SPR) of an isolated particle, the change in the "effective" electronic density with respect to the bulk electronic density N_0 can be given as:

$$d(\ln N) = 2 \cdot d(\ln \omega)|_{sp} \tag{5}$$

because other quantities in eq 4 are constant. Alternatively:

$$\frac{\Delta N}{N_0} = 2\left.\frac{\Delta\omega}{\omega_0}\right|_{sp} \tag{6}$$

With decreasing interparticle gap, the plasmon resonance of the two-particle system shifts to a lower frequency, which can be alternatively represented as a decrease in the "effective" electronic density within each particle. Thus, in the case of the nanoparticle pair, in the presence of a resonant plasmon field, the lattice oscillation of the individual nanodisc can be considered to be taking place in an electron gas with this effectively lowered or "softened" electronic density $N_0 - \Delta N$. Although the exact relationship between the phonon oscillation frequency and the metal free electron density would require a detailed treatment, it can be expected that the "bond force constant" and hence the frequency f of the coherent phonon oscillation (CPO) would have some direct functional dependence on the metal free electron density. It can thus be said for small perturbations that:

$$\left.\frac{\Delta f}{f_0}\right|_{CPO} \propto \frac{\Delta N}{N_0} \propto \left.\frac{\Delta\omega}{\omega_0}\right|_{SPR} \tag{7}$$

The fractional plasmon shift $\Delta\omega/\omega_0$ has already been shown to have a functional dependence on s/D determined by the inherent distance decay of the plasmonic near-field.[29] The simple relationship given by eq 7 elucidates that the fractional shift in the phonon oscillation frequency, if caused by the near-field coupling, would follow the same trend with distance as the fractional shift in the surface plasmon resonance, which is already known to be caused by the near-field interaction.[29] This model thus explains clearly the experimental observation of similar decay constants for the SPR and the CPO depicted in Figure 4. Our observations, therefore, show that the coherent phonon oscillation in the plasmonic nanoparticle pair system is strongly dependent on the near-field interaction between the particle pair partners.

This effect is qualitatively similar to the electronic softening of a semiconductor crystal lattice by optical excitation, which has been used to explain the decrease in the coherent phonon oscillation frequency with increasing photoexcited carrier density.[45,46] In our case, however, we propose that the reduction in the effective metal electronic density results in the softening of the metal interatomic potential (and hence the reduction of the coherent phonon oscillation frequency), as expected from the electron-sea theory of metallic bonding.[47] The effect of the near-field interaction has also been used by Pileni and co-workers to explain the shift in the Raman scattering band of silver nanocrystals self-organized in face centered cubic supracrystals.[38] In their Raman experiment, too, the phonon vibration takes place in the constant presence of the induced electric field due to the excited surface plasmon of the neighboring nanocrystal. Recently, Margueritat et al. have also reported the effect of surface plasmon coupling between silver nanocolumns, fabricated in an oriented assembly, on the Raman-active phonon vibrations of the nanostructure.[48]

While the plot of fractional frequency versus s/D shows the same exponential decay constant for the plasmon

oscillation and the phonon oscillation, the amplitude preceding the exponential fit function is almost five times larger for the phonon oscillation. This suggests that the magnitude of the fractional frequency shift is five times larger for the phonon oscillations. In fact, the particle pair with 7 nm separation does show a ratio of ~5 for the observed fractional shift in the phonon oscillation to that of the plasmon oscillation. While the shift in frequency is very small for the phonon oscillation compared to that for the electronic oscillation, the value of the lattice oscillation frequency is so much smaller (4 orders of magnitude) than that of the electronic oscillation frequency.[49]

Conclusion. We used electron beam lithography to fabricate pairs of nanodiscs each having diameter of 88 nm and thickness of 25 nm and interparticle separation that was systematically varied from 7 to 212 nm. We used femtosecond transient absorption spectroscopy method, in which the nanoparticle plasmon is constantly excited, to optically determine the phonon oscillation frequency as a function of the interparticle separation. It was found that the fractional shift in the oscillation frequency increases exponentially with decreasing ratio of the interparticle separation to the particle diameter. We found that the observed scaling behavior for the near-exponential decay of the coherent phonon vibration frequency with distance is the same as that observed for the surface plasmon electronic oscillation frequency. This strongly suggests that it is the near-field coupling between the particles that modulates both the coherent electronic oscillation (plasmon) frequency and the coherent lattice oscillation (phonon) frequency. Thus, it is the distance-decay of the plasmon near-field that is reflected in the similar interparticle gap-dependence of both these frequencies. The polarizing perturbation of the plasmonic field of one nanoparticle on the electron density of the other pair partner is proposed to be responsible for the observed decrease in its oscillation frequency.

Acknowledgment. This work is supported by the Division of Materials Research of the National Science Foundation (grant no. 0527297).

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(49) For the nanodisc pair of 7 nm gap (the situation with the strongest coupling), the magnitude of the frequency shift in the coherent phonon vibration with respect to the uncoupled situation (212 nm gap) is 6.14×10^9 Hz, which corresponds to an energy change of 2.54×10^{-5} eV. For the same nanodisc pair, the frequency change in the SPR (coherent electron oscillation) with respect to the uncoupled situation is 3.16×10^{13} Hz, which corresponds to an energy change of 1.31×10^{-1} eV. Therefore, the energy required to change the coherent vibration frequency of the phonon is four orders of magnitude smaller than that of the SPR.

NL071813P