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Time-Resolved Investigation of the Acoustic Vibration of a Single Gold Nanoprism Pair

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The acoustic vibration of single gold nanoprism pairs on a glass substrate has been investigated in the time-domain combining a spatial modulation spectroscopy microscope with a high-sensitivity femtosecond pump–probe setup. Three modes were observed and ascribed to two in-plane and one out-of-plane vibration of the nanoprisms forming the pair, in agreement with a theoretical analysis. The periods of the two former modes with similar nature show weak (about 10%) and well correlated pair to pair fluctuations that can be unambiguously ascribed to variation of the prism geometry. In contrast, strong fluctuations, by almost a factor of 6, of the mode damping are evidenced with no correlation with their period. This indicates large variations of the prism-substrate coupling, providing a unique way for its local investigation.

The acoustic response of nanometric size materials has attracted a large interest during the past decade. It is motivated by fundamental aspects, i.e., acoustic properties at the nanoscale, but also by its large potential for application and nanomaterial characterization. In particular, the properties of the acoustic modes of a nanoobject contain information on its geometry1–13 and structure14–16 through its period, and its interaction with its environment through its damping.2,18–20 Since the first time-domain investigations of the acoustic vibration of semiconductor quantum dots,21,22 and metal nanoparticles,2,3 time-resolved optical spectroscopy has emerged as a powerful tool for the investigation of the low-frequency acoustic modes of nanoobjects.23 It very complementary to spontaneous Raman spectroscopy,11 different modes dominating the spectral- and time-domain responses,25 and has also the important advantage of yielding information on both the mode period and damping.

In time-resolved studies, the vibrational modes of metal nanoparticles are impulsively excited by a femtosecond pump pulse.2,3,23,26 In this process, the energy injected by the pump pulse in the conduction electrons is quickly damped to the lattice by electron–phonon coupling. This lead to a fast heating of the lattice, on a picosecond time-scale in noble metals.24 This fast lattice heating triggers dilation of each particle with an imposed phase, launching the acoustic modes associated to a volume change. The lowest frequency modes, with no or a minimum number of displacement nodes, are preferentially launched as their displacement better matches particle dilation.5 For each excited mode, the periodic change of the nanoparticle volume translates into a time-modulation of its optical response that can be detected by a time-delayed probe pulse.2

Up to now most investigations were performed on large ensembles of nanoparticles. Correlation of the vibrational properties with the particle geometry and environment coupling is then frequently hampered by their particle to particle fluctuations. Actually, environment has a limited influence on the measured vibrational mode period.27 Its mean value can be precisely compared to theoretical models provided the nanoparticle geometry (size, shape) and structure are well controlled.5,7,14,18 In contrast, the observed decay of the time-domain oscillations strongly depends on the dispersion of the particle characteristics.2,3 As each nanoparticle oscillates with its own period imposed by these characteristics, their initially in-phase contribution drifts out of phase with time and destructively interferes. This inhomogeneous contribution adds-up to the intrinsic one due to acoustic energy transfer from the nanoparticles to their environment. The latter is only observable for a strong enough coupling as for glass embedded particles.2,20,27 Its investigation in different environment conditions thus requires addressing a small number or a single nanoparticle. With the development of far-field time-resolved absorption or scattering spectroscopy techniques, time-resolved experiments can now be performed on a single nanoparticle.28–31 In particular, the vibrational response of a single nanosphere has been recently addressed using time-resolved interferometry, the results confirming the central role of inhomogeneous damping in ensemble measurements.31

Combining the spatial modulation spectroscopy technique32,33 with a high-sensitivity femtosecond pump–probe setup we have investigated the acoustic response of single nanoprism-pairs in a 2D organized prism monolayer fabricated by nanosphere lithography.9,34 The good size and shape dispersion control of the nanoprisms and their direct growing on the substrate make this system a prototype nanostructure for investigating the impact of nanoobject geometry and substrate interaction on their vibrational properties. Observation of different modes permits separation of the role of these two parameters and to ascribe the correlated pair to pair fluctuation of the mode periods to variation of the nanoprism geometry. Strong fluctuations of the mode damping are demonstrated and associated to large local variation of nanoprism-substrate energy exchanges.

The nanoprism array was prepared using a classical nanosphere lithography technique.35 Briefly, a mask is first fabricated by self-organization of monodisperse polystyrene spheres on a
As discussed earlier, the optical spectrum of these systems is characterized by a large surface plasmon resonance around 800 nm and an absorption rise below 500 nm due to interband absorption. In order to in situ localize the nanoparticles, optical images of the sample were realized using the recently developed spatial modulation spectroscopy (SMS) technique.32,33 It is based on modulating at the frequency $f$ the position of isolated nanoparticles in the focal spot of a tightly focused laser beam. When a nanoparticle is under the spot, the transmitted power is modulated by an amount proportional to its extinction cross section. This is detected at $f$ or $2f$ frequency by a lock-in amplifier. An image of the sample is then obtained by scanning its position in the focal plane ($XY$).32,33 This technique developed for nanoobjects much smaller than the beam spot size and with a low surface density, has been extended here to the high density and large size nanoparticles fabricated by nanosphere lithography.

To optimize spatial resolution, optical mapping was performed at 410 nm in the interband absorption region of gold. The blue beam was created by frequency doubling in a BBO crystal part of the 100 fs pulse train delivered by a Ti-sapphire oscillator operating at 820 nm with a repetition rate of 76 MHz. It was focused by a 100× microscope objective onto the sample surface. The intensity profile at the focal spot exhibits a Gaussian shape with a full width at half-maximum $d \approx 0.3$ µm (shaded area in Figure 1). Though a single nanoparticle cannot be observed with the present spatial resolution, $d$ being twice the bisection of a prism, the optical image shows well defined extinction maxima (the modulation amplitude of the sample position is $\delta_Y \approx 0.2d$). Correlation with the SEM image shows that each maximum corresponds to a single nanoprism pair with its axis along $X$, i.e., perpendicular to the modulation direction $Y$ (Figure 1). This directional selection can be understood using a shadowing argument: for a focal spot centered on a $X$ axis prism pair, modulation leads to a larger reduction of the illuminated prism surface than for pairs along other directions. When imaging the sample, a maximum transmission modulation at $2f$ is then expected at the position of these pairs.

After their optical localization, individual nanoprism pairs were investigated using a high-sensitivity femtosecond pump–probe setup. Measurements were performed with the same femtosecond Ti-sapphire oscillator as used for optically mapping the sample. Both the femtosecond frequency doubled and fundamental beams were then sent into the spatial modulation microscope.28 The former is used as the pump beam to excite the electrons by interband absorption. The latter, at 820 nm, monitors the induced optical transmission change of the nanoprin pair around their surface plasmon resonance. The induced probe transmission change $\Delta T/T$ was then monitored as a function of the pump–probe delay using a classical pump–probe setup. It uses mechanical chopping of the pump beam at 2 kHz and lock-in detection of the transmitted probe beam energy after its spectral selection with color filters.

The time-dependent transmission change measured in a single nanoprin pair is shown in Figure 2 for two different pairs. It exhibits a short time scale transient reflecting fast heating-up of the electrons by the pump pulse and their subsequent cooling via electron–lattice energy transfer. The observed kinetics is consistent with that previously reported for ensemble measurement in large gold nanospheres.24 It will thus not be further discussed here and we will focus on the long delay signal. This shows pronounced oscillations with a few tens of picosecond period, overlapped with short period ripples for delays smaller than about 40 ps (Figure 2). As in ensemble measurements, we ascribed these oscillations to modulation of the optical transmission by impulsively excited acoustic vibration modes of the nanoobjects.2,3,6,9

To extract the characteristics of the different modes contributing to the oscillating part of $\Delta T/T$ we have reproduced it by a sum of cosine functions with period $T_i$ and damping time $\tau_i$:
The short delay ripples correspond to a period of about \( T_0 = 14 \) ps. They are ascribed to thickness mode oscillation of the nanoprism forming the pair, i.e., a contraction–dilation movement in the \( Z \) direction perpendicular to the sample surface. This out-of-plane mode is similar to the thickness mode observed in thin metal films whose period \( T_{th} \) is given by:

\[
T_{th} = 2e/c_L
\]

where \( c_L \) is the longitudinal sound velocity in the metal. For a film thickness \( e = 30 \) nm, one obtains \( T_{th} \approx 18 \) ps consistent with the period \( T_0 \). This comparison is justified by the large aspect ratio, \( a/e \approx 4 \), of the prisms, leading to a large decoupling of the out- and in-plane vibrations. The discrepancy between \( T_0 \) and \( T_{th} \) is ascribed to modification of the mode period due to the truncated pyramid shape of the nanostructures. This assignment is corroborated by recent time-resolved experiments performed using high-speed asynchronous optical sampling in ensemble of nanoprism fabricated by the same technique. In these measurements, for similar size prisms, the thickness mode dominates the measured response and no long period oscillations were observed, in contrast to our results.

Long period nanoprism oscillations were previously observed in ensemble measurement of similar arrays and ascribed to a single in-plane vibration mode. Detailed time- and frequency-domain analysis of the oscillating signal show that it is dominated by the same mode with period \( T_1 \), but also contains a weaker contribution from a mode of smaller period \( T_2 \), not observed before (Figure 2). Actually, this additional mode is similar to that detected in ensemble measurements in colloidal solutions of silver nanoprism. \(^9,34\) It has to be noted that a small deviation between the obtained fit and the measured data is observed for some nanoprism pairs but not for all. This is partly due to the fact that the signal background exhibits a long delay rise for some pairs (for instance, for pair 1 but not for pair 2 in Figure 2) that is not included in the fitting procedure. As in colloidal solutions, \(^{35}\) this effect is ascribed to modification of the nanoparticle environment, i.e., substrate heating here, that translates into a shift of the surface plasmon resonance of the prisms.

Measurements performed in different nanoprism pairs show similar results. No modification of the signal temporal shape was observed over the accessible probe wavelength range (from 790 to 850 nm). The main mode periods \( T_1 \) and \( T_2 \) are comparable but exhibit significant pair to pair fluctuations, with a maximum amplitude of about \( \pm 10\% \) of their mean value \( \langle T_1 \rangle = 68 \) ps and \( \langle T_2 \rangle = 50 \) ps for the eight investigated prism pairs (Figure 3a). The \( T_1 \) and \( T_2 \) variations are very well correlated indicating that they have the same origin. The mean periods are consistent with those measured in ensemble studies, \( T_1^{ens} = 68 \) ps and \( T_2^{ens} = 41 \) ps, performed on the same sample over about 5000 nanoprism (i.e., using 30 \( \mu \)m diameter spot size for the pump and probe beams). Though the mean \( T_1 \) value is in excellent agreement with \( T_1^{ens} \), a deviation of about 20\% is observed for the \( T_2 \) mode (Table 1). This discrepancy is ascribed to the lower precision in determining \( T_2 \) due to the small contribution of this mode to the measured signal (Figure 2).

To identify the involved modes, we have computed the vibrational eigenmodes of a nanoprism in the usual model of a homogeneous isotropic elastic object. \(^{36}\) They are solution of the Navier–Stokes equation with the proper boundary conditions for displacement and stress.\(^{2,4,26,36}\) We first considered a perfect free prism of 120 nm side and 30 nm thickness, i.e., neglecting shape deviation as well as prism–substrate and prism–prism interactions. The corresponding equations were solved using a finite element method using the bulk gold elastic constants. The

\[
R(t) = \sum_{i} A_i \exp(-t/\tau_i) \cos[2\pi t/T_i - \phi_i]
\]

\( T_{th} \) is the time delay between the excitation and the signal, \( c_L \) is the longitudinal sound velocity in the metal, and \( e \) is the film thickness. The main mode periods are consistent with those measured in ensemble studies, \( \langle T_1 \rangle = 68 \) ps and \( \langle T_2 \rangle = 50 \) ps for the eight investigated prism pairs (Figure 3a). The \( T_1 \) and \( T_2 \) variations are very well correlated indicating that they have the same origin. The mean periods are consistent with those measured in ensemble studies, \( T_1^{ens} = 68 \) ps and \( T_2^{ens} = 41 \) ps, performed on the same sample over about 5000 nanoprism (i.e., using 30 \( \mu \)m diameter spot size for the pump and probe beams). Though the mean \( T_1 \) value is in excellent agreement with \( T_1^{ens} \), a deviation of about 20\% is observed for the \( T_2 \) mode (Table 1). This discrepancy is ascribed to the lower precision in determining \( T_2 \) due to the small contribution of this mode to the measured signal (Figure 2).

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two lower frequency eigenmodes associated with a volume change are identical to those modeled by Bonacina et al. They correspond almost entirely to movement in the prism plane (Figure 4). The fundamental (lowest frequency) mode is associated to contraction and dilation of the prism tips along their bisector, with a much weaker displacement of the prism edge centers (Figure 4a,c). In contrast the second mode corresponds to large in and out displacement of the prism edge centers with almost unmoving tip (Figure 4b,d). The computed mode periods are consistent with but significantly larger than the measured ones, especially for $T_1$ (Table 1).

To analyze the role of the prismatic shape assumption in this discrepancy, we have performed the same modeling for a more realistic truncated pyramid. A regular tetrahedron of edge length 120 nm, truncated in the Z direction to 30 nm thickness is assumed. The two lowest frequency modes are similar to the prism ones (Figure 5), but exhibits significantly reduced periods in better agreement with the experimental data (Table 1). This agreement is further confirmed by comparing the computed and experimental prism size dependencies (Figure 5). As only the average prism size is known, single nanoprisms pair measurements were not repeated and comparison has been been performed with available ensemble measurement data on the $a$ dependence of $T_1$. In both gold and silver, excellent agreement is obtained for the truncated pyramid shape, while a significant deviation is observed for a prism shape (Figure 5). Note that, in agreement with experimental data, the larger thickness (50 nm instead of 30 nm) of the two largest size gold prisms has little influence on the computed $T_1$ (it increases by less than 3% and 1.5% with increasing $e$ from 30 to 50 nm for $a = 160$ and 190 nm, respectively). Actually, for large aspect ratio prisms the in- and out-of-plane movements are largely decoupled and $T_1$ (and $T_2$) is almost proportional to $a$ (Figure 5, with a displacement given in Figure 4a,c). For smaller $a/e$, the movements couple and $T_1$ become $e$ dependent, the fundamental mode eventually switching to an extensional movement along $Z$ for very small $a/e$. A crude estimation of $T_1$ can also be obtained using a simple dimensional analysis. For a large $a/e$ ratio prism this translates into the condition: $T_1 = \sqrt{3a/e} L$.

which yields a $T_1$ value consistent but significantly different from the computed and experimental ones, especially for gold (Figure 5a).

Agreement between the mode periods computed assuming free isolated nanoobjects and the experimental data suggests a weak influence of the substrate and thus a large acoustic decoupling. The periods then almost entirely reflects the nanoparticle geometry and their fluctuations are ascribed to changes of the lateral size ($a$) and shape of the nanoprisms forming the pairs. Correlation between the $T_1$ and $T_2$ variations measured in different pairs confirms this analysis. The role of $a$ variation is further confirmed by the amplitude of the period fluctuations, about 10% of the mean period, comparable with the individual nanoprisms size dispersion (about 8%). The measured $T_1$ and $T_2$ correlation ($T_2 = 0.76T_1$, (Figure 3)) is, however, slightly different from the computed one for a truncated regular tetrahedron with varying $a$ ($T_2 \approx 0.62T_1$ for large $a/e$) suggesting that local variation of the nanoobject shape also plays a role.

In contrast to their period, the acoustic mode damping time strongly depends on the coupling between the two media. In the case of the investigated pair of prisms, it directly translates in the measured oscillation damping, permitting to analyze prism-substrate energy transfer. The damping time $\tau_1$ of the $T_1$ mode measured in different nanoprisms pairs is shown in Figure 3-b. Because of the weak contribution of the $T_2$ mode, its damping time, in the 50 ps range, cannot be extracted with a sufficient precision to analyze its fluctuations. $\tau_1$ exhibits very large pair to pair variations as illustrated by the very different oscillation damping observed for the two pairs of Figure 2. For the eight investigated prisms, it has been found to vary from 110 to 600 ps with a mean value $\langle \tau_1 \rangle = 260$ ps. This indicates very large local variations of the prism-substrate coupling (i.e., of the surface contact of the prism with the substrate), probably associated to the fabrication technique by metal evaporation. These fluctuations are not correlated with those of the $T_1$ period (Figure 3b), indicating that geometry fluctuation does not influence $\tau_1$. This also confirms the minor influence of the substrate on the mode periods.

Finally, we emphasize that the decay time deduced from ensemble measurement, $\tau_1^{1/e} \approx 70$ ps, is always smaller than the $\tau_1$ values measured in the different prism pairs (Figure 3b), and
considerably smaller than their mean value (Table 1). This indicates that, as expected in ensemble studies, the homogeneous contribution largely dominates the observed damping times. This large contribution is making $\tau_{\text{ens}}^{\text{nu}}$ smaller than the decay time measured for pairs, even for those most efficiently coupled to the substrate. As a rough approximation, assuming that $T_1$ follows a Lorentzian distribution with a full width at half-maximum of 10% of $\langle T_1 \rangle$, an inhomogeneous decay time $\tau_{\text{ens}}^{\text{nu}} \approx 110$ ps is estimated. Taking into account the homogeneous contribution, a total decay time of about 80 fps is roughly estimated in ensemble measurement. This is consistent with the experimental value, $\tau_{\text{ens}}^{\text{nu}}$, further confirming the above analysis.

In conclusion, combining a spatial modulation apparatus with a time-resolved pump–probe technique, we have investigated the acoustic vibration of single pairs of gold nanoprism on a glass substrate. Three modes were observed and associated to two in-plane and one out-of-plane vibrations of the individual prisms forming the pair. As the in-plane modes dominate the response and are simultaneously investigated on the same single nanoobject, their periods can be compared. Correlated pair to pair fluctuations were demonstrated and associated to change in the prism geometry. Comparing the measured and the computed periods, quantitative agreement is obtained when assuming a realistic truncated pyramid shape rather than a prismatic one, stressing the strong shape sensitivity of the nanoparticle mode period. Relaxation of the acoustic vibration of the individual prism pairs has been found to be strongly pair dependent and uncorrelated to the mode period variation, i.e., details of their geometry. This relaxation has been ascribed to their coupling with the substrate, indicating a strong local variation of the latter. These results demonstrate the potential of time-resolved studies of acoustic vibrational modes as new and powerful tool for local analysis of individual nanoobjects.

Using their acoustic signature, i.e., mode period and intrinsic damping, information can be independently obtained on their shape and coupling with their environment, respectively. In particular, they constitute a quasi unique tool for investigating the latter and its fluctuations at a local nanoscale level, an important parameter for many applications.

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References and Notes