

Coherent Acoustic Vibration of Metal Nanoshells

C. Guillon,[†] P. Langot,[†] N. Del Fatti,^{†,‡} and F. Vallée^{*,†,‡}

*Centre de Physique Moléculaire Optique et Hertzienne CNRS and
Université Bordeaux I, 351 cours de la Libération, 33405 Talence, France, and
Laboratoire de Spectrométrie Ionique et Moléculaire CNRS and Université Lyon I,
43 Bd. du 11 Novembre 1918, 69622 Villeurbanne, France*

A. S. Kirakosyan and T. V. Shahbazyan

*Department of Physics and Computational Center for Molecular Structure and
Interactions, Jackson State University, P.O. Box 17660, Jackson, Mississippi 39217*

T. Cardinal and M. Treguer

*Institut de Chimie de la Matière Condensée de Bordeaux CNRS and Université
Bordeaux I, 87 Av. du Dr. Albert Schweitzer, 33608 Pessac, France*

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ABSTRACT

Using time-resolved pump–probe spectroscopy, we have performed the first investigation of the vibrational modes of gold nanoshells. The fundamental isotropic mode launched by a femtosecond pump pulse manifests itself in a pronounced time-domain modulation of the differential transmission probed at the frequency of nanoshell surface plasmon resonance. The modulation amplitude is significantly stronger, and the period is longer than that in a gold nanoparticle of the same overall size, in agreement with theoretical calculations. This distinct acoustical signature of nanoshells provides a new and efficient method for identifying these versatile nanostructures and for studying their mechanical and structural properties.

Metal nanoshells—metal shells grown on dielectric spheres—are among the highlights of nanostructures with versatile optical and mechanical properties.¹ As for fully metallic nanoparticles, absorption and scattering of light by nanoshells are dominated by the surface plasmon resonance (SPR).² However, they offer wide new possibilities of controlling the SPR characteristics, such as its frequency position, by varying, for instance, the shell thickness vs overall size, or the constituent materials.^{3,4} Furthermore, recent measurements of scattering spectra of single nanoshells^{5,6} indicated enhanced sensitivity to their environment and narrowing of their resonance line shape as compared to solid gold particles.⁷ The unique tunability and characteristics of nanoshell optical properties spurred a number of proposals for their applications including optomechanics,⁸ sensing,^{9,10} and drug delivery.^{11,12}

While the optical response of nanoshells has been extensively studied, much less is known about their acoustical

properties. In fact, the low-frequency vibrational modes of nanostructures bear a unique signature of their structural and mechanical properties directly reflecting the impact of confinement on the ionic movement. This is in contrast to the optical frequency domain whose features are determined by the electronic response. The vibrational modes thus constitute an additional source of information that could be particularly important in the case of complex systems. This is especially the case for hybrid or layered systems with structurally distinct constituents, such as nanoshells.^{13,14} Due to their structural sensitivity, vibrational modes are also expected to constitute acoustic signatures permitting further nanoshell identification, complementary to the optical one.

Time-resolved optical techniques are powerful tools for investigating the low-frequency vibrational modes of nanostructures. They have been applied to the study of the acoustic properties of semiconductor and metal nanoparticles^{15–18} and have recently been extended to bimetallic particles.^{19,20} In these experiments, vibrational modes are impulsively excited as a result of rapid expansion of metal particles induced by absorption of a femtosecond pump pulse.^{15,21} In this process, the energy initially injected into the electron

[†] Centre de Physique Moléculaire Optique et Hertzienne CNRS and Université Bordeaux I.

[‡] Laboratoire de Spectrométrie Ionique et Moléculaire CNRS and Université Lyon I.

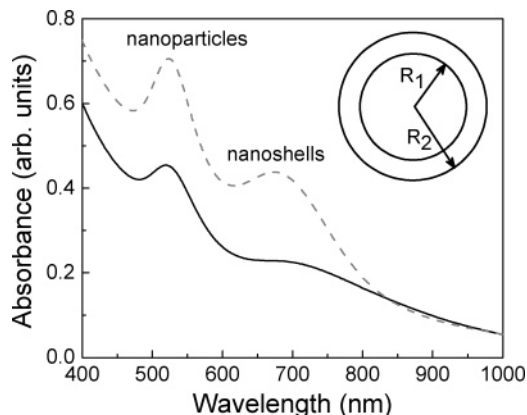


Figure 1. Measured linear absorption spectrum of Au₂S/Au core/shell particles in water for two different sizes, with $R_1 = 9.0$ nm inner radius and $R_2 = 11.5$ nm outer radius (solid line) and for $R_1 = 10.3$ nm and $R_2 = 13.5$ nm (dashed line). Inset: schematic geometry of a nanoshell.

gas is quickly damped to the lattice on the time scale of the electron–phonon energy transfer, about 1–2 ps in noble metals. Due to lattice anharmonicity, this lattice heating leads to an isotropic force on ions triggering in-phase dilation of each particle that subsequently undergoes radial contractions and expansions around its new equilibrium size. The periodic change in nanoparticle volume translates into a modulation in time of the electronic properties. This can be detected by a time-delayed probe pulse monitoring the concomitant modulation of the wavelength of the SPR.¹⁵ The triggered initial expansion being homogeneous, the modulation is dominated by the fundamental breathing mode that closely corresponds to particle expansion as a whole.

Using time-domain spectroscopy, we have performed the first investigation of acoustic vibrational modes in metal nanoshells. As in fully metallic particles, we observed in nanoshells a pronounced time modulation of the measured probe differential transmission indicating coherent excitation of the fundamental breathing mode. The modulation amplitude is significantly stronger and its period is considerably longer than those in pure gold nanoparticles of the same size. At the same time, the damping time of the oscillations is much shorter than that for gold particles suggesting a faster energy transfer from nanoshells to the surrounding medium. Such distinct signatures allow unambiguous identification of nanoshell acoustic vibration and separation of their contribution from that of other entities possibly present in a colloidal solution. These results are consistent with theoretical analysis of vibrational modes in nanoshells.

Experiments were performed in colloidal solution of Au₂S-core/Au-shell nanoshells prepared using the method described in ref 1. Both nanoshells and gold nanoparticles are simultaneously synthesized, as shown by the linear absorption spectra of the colloidal solution (Figure 1). It exhibits two characteristic bands centered around 700 and 530 nm that have been associated to SPR in core–shell nanoparticles and gold nanospheres, respectively.^{1,22} This assignment is confirmed by the spectral displacement of the former band during nanoshell growth, while, in contrast, the spectral position of the latter remains almost unchanged as expected

for small nanospheres.¹ This is further corroborated by transmission electron microscopy (TEM) measurements showing the presence of large nanoparticles (mean radius R_2 in the 14 nm range) that have been identified as nanoshells and of smaller ones (mean size of about 4 nm) identified as pure gold.^{1,14} The nanoshell SPR energy is determined by the ratio of the inner to outer radius R_1/R_2 ; the latter was thus estimated by fitting the experimental spectrum with $A(\omega) = P_p A_p(\omega) + P_s A_s(\omega)$, where P_p and P_s are the volume fractions of nanoparticles and nanoshells, respectively, and $A_{p,s}(\omega)$ are the corresponding absorbances.¹ For the investigated nanoshells, R_1 ranges from 9 to 10.3 nm with a shell thickness $d = R_2 - R_1$ of 2.5–3.7 nm; i.e., R_1/R_2 ranges from 0.78 to 0.73 nm.

Time-resolved measurements were performed using a femtosecond Ti:sapphire oscillator delivering 20 fs pulses at 860 nm with a 80 MHz repetition rate. Part of the pulse train is selected to create the pump pulses. Absorption in this spectral range being dominated by the broad SPR of the nanoshells, they are predominantly excited. The pump-induced transient change of the sample transmission ΔT is detected at the same wavelength around the nanoshell SPR using the remaining part of the beam. This probe wavelength permits further selection of the nanoshells that thus dominate the detected $\Delta T/T$ signal. This has been confirmed by the fact that pure gold nanoparticle colloidal solutions yield an undetectable signal in this pump–probe configuration. The two beams were focused on a 30 μ m diameter focal spot, and the pump beam average power was about 100 mW. Measurements were performed with a standard pump–probe setup with mechanical chopping of the pump-beam and lock-in detection of ΔT .

The measured time-dependent transmission change shows a fast transient, ascribed to photoexcitation of nonequilibrium electrons and their cooling via electron–lattice energy transfer (Figure 2). The observed kinetics is consistent with that previously reported in gold nanoparticles and films for similar excitation conditions.²³ This signal is followed by pronounced oscillations that can be reproduced by a phenomenological response function

$$R(t) = A \exp(-t/\tau) \cos[2\pi t/T_{\text{osc}} - \varphi] \quad (1)$$

using a period $T_{\text{osc}} \approx 38$ ps and a decay time $\tau \approx 60$ ps for the nanoshells of Figure 2a. Such long probe-delay response is similar to that reported in fully metallic nanoparticles,^{15,18} but the measured period of the oscillations is by far too long to ascribe them to the residual fully metallic small nanoparticles. We thus ascribed them to the acoustic vibration of the nanoshells. Furthermore, their amplitude relative to that of the short time delay electronic signal is much larger than that in metal nanospheres (about 75% as compared to 10%¹⁵). The measured period is also much longer (about four times) than that predicted for solid Au nanospheres of the same overall size, about 9 ps for $R_2 = 13.5$ nm. Furthermore, the phase of the oscillation $\varphi \approx 1.1$ is significantly larger than that predicted for a purely displacive type of excitation in a harmonic oscillator model (about 0.2). As this phase is a

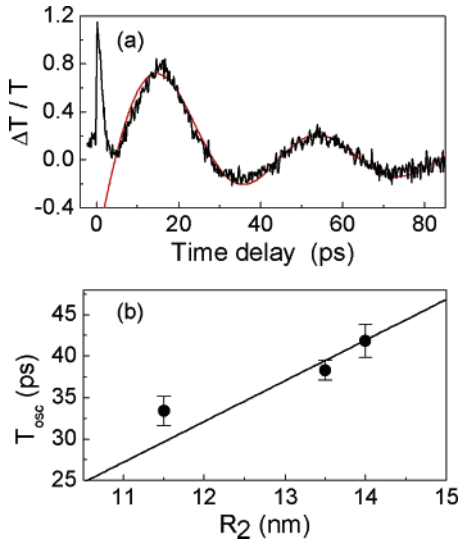


Figure 2. (a). Time-dependent differential transmission $\Delta T/T$ measured in Au₂S/Au nanoshells in water with near-infrared pump and probe pulses is shown together with a fit using eq 1. The inner and outer radii are $R_1 = 10.3$ and $R_2 = 13.5$ nm, respectively. (b) Oscillation period T_{osc} measured in different Au₂S/Au nanoshells as a function of their outer radius R_2 . The aspect ratios for R_1/R_2 are 0.78, 0.76, and 0.74, in increasing R_2 order. The line is a fit assuming that T_{osc} is proportional to R_2 .

signature of the excitation mechanism, this suggests a modified launching process as compared to the breathing mode of nanospheres.²¹

Measurements performed in different nanoshells show similar behaviors with an almost linear increase of the oscillation period with the outer nanoshell size R_2 (Figure 2b). The effective decay time τ of the oscillations can also be extracted from the time-domain data. It varies from 30 to 60 ps for the three investigated samples (30, 60, and 42 ps in increasing order of R_2), but conversely to the period, no systematic variation with the nanoshell size is experimentally found. This suggests that, as for nanosphere colloidal solutions, inhomogeneous relaxation due to the particle size and structure fluctuations dominates over the homogeneous one due to matrix–water coupling.^{16,24}

To further correlate the observed oscillation mode with the nanoparticle structure, we have theoretically analyzed the radial vibrational modes of a spherical nanoshell in a dielectric medium. The motion of nanoshell boundaries is determined by the radial displacement $u(r)$ that satisfies the Helmholtz equation (at zero angular momentum)

$$u'' + \frac{2u'}{r} + k^2 u = 0 \quad (2)$$

where $k = \omega/c_L$ is the wave vector. In the presence of core and outer dielectric medium, the boundary conditions impose that both the displacement $u(r)$ and the radial diagonal component of the stress tensor

$$\sigma_{rr} = \rho \left[c_L^2 u' + (c_L^2 - 2c_T^2) \frac{2u}{r} \right] \quad (3)$$

are continuous at the core/shell and shell/medium interfaces (ρ and $c_{L,T}$ are density and longitudinal/transverse sound velocities, respectively). In the core, shell, and medium regions, solutions are of the form $u \sim [\sin(kr)/r]'$, $u \sim [\sin(kr + \phi)/r]'$, and $u \sim [e^{ikr}/r]'$, respectively, where ϕ is the phase mismatch and prime stands for derivative over r . Matching u and σ_{rr} at $r = R_1, R_2$ yields the equations for the eigenvalues

$$\begin{aligned} \frac{\xi^2 \kappa^2}{\xi \kappa \cot(\xi \kappa + \phi) - 1} - \frac{\eta_c \xi^2 \kappa^2}{(\xi \kappa / \alpha_c) \cot(\xi \kappa / \alpha_c) - 1} + \chi_c &= 0 \\ \frac{\xi^2}{\xi \cot(\xi + \phi) - 1} + \frac{\eta_m \xi^2}{1 + i\xi / \alpha_m} + \chi_m &= 0 \end{aligned} \quad (4)$$

where $\xi = kR_2 = \omega R_2 / c_L$ and $\kappa = R_1 / R_2$ are shorthand notations for the normalized eigenenergies and aspect ratio, respectively. The parameters

$$\begin{aligned} \alpha_i &= c_L^{(i)} / c_L^{(s)} \quad \eta_i = \rho^{(i)} / \rho^{(s)} \quad \chi_i = 4(\beta_s^2 - \eta_i \delta_i^2) \\ \beta_i &= c_T^{(i)} / c_L^{(i)} \quad \delta_i = c_T^{(i)} / c_L^{(s)} \end{aligned} \quad (5)$$

characterize the metal/dielectric interfaces ($i = c, s, m$ stand for core, shell, and outer medium). From eq 4, the ideal case of a nanoshell in vacuum is obtained by setting $\alpha_c = \alpha_m = \eta_m = \eta_c = 0$ and $\chi_c = \chi_m = 4\beta_s^2$; in the thin shell limit, $1 - \kappa = d/R_2 \ll 1$, we then recover the well-known result $\xi_0 = 2\beta_s(3 - 4\beta_s^2)^{1/2}$.²⁶ For a nanoshell in a dielectric medium, the eigenvalues are complex reflecting energy exchanges with the environment, $\xi = \omega R_2 / c_L + i\gamma R_2 / c_L$, where $\omega = 1/T_{\text{osc}}$ and $\gamma = 1/\tau$ are the mode frequency and damping rate, respectively.

This general model provides an equilibrium description of the nanoshell acoustic response. However, under ultrafast excitation, the role of the dielectric core is expected to diminish. Indeed, the dielectric core is not directly affected by the pump pulse but experiences thermal expansion as a result of heat transfer from the metal shell. At the same time, this expansion is much weaker than that of the metal, so that when new equilibrium size is established, the core is almost fully disengaged from the shell. This should be contrasted to bimetallic particles where the core remains engaged after the expansion and thus contributes to the acoustical vibration spectrum.^{19,20}

To take into account this effect, calculations were performed for gold nanoshells with disengaged core ($\eta_c = 0$ in eq 4). The calculated frequency, ω , and damping rate, $\gamma = 1/\tau$, are plotted in Figure 3 versus the aspect ratio R_1/R_2 , for the fundamental breathing mode of gold nanoshells immersed in water. The data are normalized in units of c_L/R_2 so that the corresponding curves for solid nanoparticles are horizontal lines starting at $R_1/R_2 = 0$. The sound velocities and the density were taken as $c_L^{(s)} = 3240$ m/s, $c_T^{(s)} = 1200$ m/s, $\rho^{(s)} = 19700$ kg/m³ for Au, and $c_L^{(m)} = 1490$ m/s, $c_T^{(m)} = 0$, and $\rho^{(m)} = 1000$ kg/m³ for water.

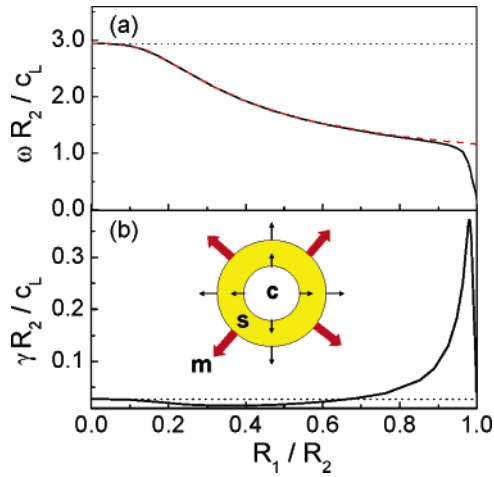


Figure 3. Calculated frequency (a) and damping rate (b) of the fundamental breathing mode of a gold nanoshell with disengaged core in water versus its aspect ratio R_1/R_2 . The dashed line in (a) is for a gold nanoshell in vacuum. The horizontal dotted lines show the normalized frequency and damping for a gold nanosphere of the same overall size (radius R_2). The inset indicates mechanical movement associated to the fundamental mode (thin arrows) and the energy damping mechanism to the environment (thick arrows).

The computed frequency of the fundamental mode is significantly smaller for nanoshells as compared to gold particles of the same overall size (Figure 3). It is about two times smaller for $R_1/R_2 = 0.5$ and further decreases to about a factor of 3 for thin nanoshells. In contrast, the aspect ratio dependence of the computed damping rate is non-monotonic. A minimum is reached at $R_1/R_2 = 0.4$, followed by a large increase for thin shells that can be understood on the basis of energy consideration: the deposited energy is proportional to the nanoshell volume, V , while the efficiency of energy exchange is determined by the surface area, A . Then, the characteristic time of energy transfer from the shell to the outer medium is $\tau \sim V/Ac_L^{(m)} \propto d/c_L^{(m)}$, as opposed to the $R/c_L^{(m)}$ dependence for solid particles.²⁵ With further decrease of the nanoshell thickness, a sharp change in behavior is seen for both ω and γ , indicating a crossover to an overdamped regime (Figure 3). In this thin shell limit, the spectrum of vibrational modes is mostly determined by the energy exchange with environment, as shown by the large deviation of the computed frequency for a water or vacuum environment for $R_1/R_2 \geq 0.9$ (Figure 3).

The behavior for the thin shell regime can be better analyzed using approximated analytical solutions for the vibrations frequency and damping. For $1 - \kappa = d/R_2 \ll 1$, eq 4 (with $\eta_c = 0$) reduces to

$$\frac{\chi_c}{1 - \kappa} \left(\chi_m - \chi_c + \frac{\alpha_m \eta_m \xi^2}{\alpha_m - i\xi} \right) = \left(\chi_m + \frac{\alpha_m \eta_m \xi^2}{\alpha_m - i\xi} \right) \xi_0^2 - \chi_c \xi^2 \quad (6)$$

In the typical case when the metal shell density is much higher than that of the surrounding medium, i.e., $\eta_m = \rho^{(m)}/\rho^{(s)} \ll 1$, eq 6 further simplifies to

$$x^2 - 1 = \frac{\alpha_m \eta_m}{\xi_0(1 - \kappa)} \left[\frac{4\alpha_m \beta_m^2}{\xi_0} - \frac{x^2}{\alpha_m/\xi_0 - ix} \right] \quad (7)$$

where $x = \xi/\xi_0$ and we used $\chi_m - \chi_c = -4\eta_m \alpha_m^2 \beta_m^2$ and $\chi_m/\chi_c = 1 - \eta_m \beta_m^2$. Two regimes can now be clearly identified, governed by the ratio $\eta_m/(1 - \kappa) = R_2 \rho^{(m)}/d \rho^{(s)} \approx M_m/M_s$, where M_s is the metal shell mass, and M_m is the mass of outer medium displaced by the core-shell particle. Explicit expressions can be obtained for the cases of “heavy” and “light” shells. For a “heavy shell”, $M_s \gg M_m$, the complex eigenvalue is given by

$$\xi \approx \xi_0 - \frac{\lambda}{2} \left[\frac{\alpha_m + i\xi_0}{(\alpha_m/\xi_0)^2 + 1} - 4\alpha_m \beta_m^2 \right] \quad (8)$$

where ξ_0 is the eigenvalue for a nanoshell in vacuum and $\lambda = \alpha_m \eta_m / \xi_0(1 - \kappa)$. In a good approximation, the real part is simply $\xi' \sim \xi_0$ and is thus independent of the medium or aspect ratio, in agreement with the full calculation for $R_1/R_2 \leq 0.9$ (Figure 3). In contrast the imaginary part, although small ($\xi'' \ll \xi'$), is only nonzero in the presence of a matrix and thus depends on both. Putting this all together, we obtain in the “heavy shell” regime

$$\omega \approx \frac{2c_L^{(s)}\beta_s}{R_2} (3 - 4\beta_s^2)^{1/2}$$

$$\gamma \approx \frac{c_L^{(m)}}{d} \frac{2\eta_m \beta_s^2 (3 - 4\beta_s^2)}{\alpha_m^2 + 4\beta_s^2 (3 - 4\beta_s^2)} \quad (9)$$

As discussed above, here the damping rate is determined by the shell thickness rather than by the overall size. In the opposite case of a “light shell”, $M_s \ll M_m$, the eigenvalue is given by $\xi \approx 2\alpha_m \beta_m ((1 - \beta_m^2)^{1/2} - i\beta_m)$, yielding

$$\omega \approx 2c_T^{(m)}/R_2, \quad \gamma \approx \omega c_T^{(m)}/c_L^{(m)} \quad (10)$$

Note that for a light nanoshell in water ($c_T^{(m)} = 0$) the limiting frequency vanishes. In the crossover region, the nanoshell frequency is significantly lower than that in vacuum (Figure 3).

The above theoretical analysis of the nanoshell vibrational modes is consistent with experimental data. In the aspect ratio of interest, $R_1/R_2 \approx 0.75$, the fundamental mode period is considerably longer than that for a pure metal particle of the same overall size. For the investigated particles, the aspect ratio R_1/R_2 lies in the range where the normalized frequency $\omega R_2/c_L$ varies weakly so the period is almost proportional to R_2 , in agreement with the experimental data (Figure 2b). A deviation from a simple R_2 dependence toward longer T_{osc} is apparent for the nanoshell with largest aspect ratio (smallest R_2), in agreement with the calculated vibrational modes spectra. However, the measured period for a nanoshell in Figure 2a, $T_{osc} \approx 38$ ps is larger by about a factor of 2 than that calculated for the *ideal* nanoshell. This discrepancy

could be attributed to structural inhomogeneity of the metal shell. Its porous (“bumpy”) structure with interstices increases the surface to volume ratio and, thus, moves the vibrational modes toward those of effectively *thinner* nanoshells. Importantly, such structural defects drive nanoshell acoustical response *away* from solid nanoparticle, as long as the shell is continuous. Note that clusterization or aggregation processes that effectively break the shell geometry will result in an increase, as compared to ideal shell, of the vibration frequency contrary to the experimentally observed reduction. This specific acoustic response can thus be used to unambiguously distinguish different nanoobjects produced during nanoparticle synthesis, such as nanoparticle clusters and nanoshells.

The computed damping rate τ is smaller than the experimental one by almost a factor of 1.5. A similar discrepancy has been reported for nanosphere colloidal solutions.¹⁵ In theoretical models, computation is made for one nanoparticle with a given mean geometry. Damping is then associated to energy transfer to the surrounding medium and is thus weak in the case of a water matrix. As a large number of nanoparticles are simultaneously investigated, inhomogeneous damping due to dephasing of the coherently excited acoustic oscillations of the nanoparticles is thus expected to play a dominant role.^{16,24} This statistical effect that reflects the particle size, shape, and structure distribution is also probably at the origin of the sample to sample fluctuations of the measured damping rate.

In summary, using a time-resolved pump–probe technique, we have investigated the acoustic vibration of gold nanoshells in colloidal solution. The results clearly show oscillations with a period in the 40 ps range, much longer than the oscillations expected for pure gold nanospheres. In agreement with our theoretical model, they have been ascribed to fundamental breathing vibration of the gold nanoshells, whose acoustic signature is thus observed here for the first time. Note that such low-frequency vibrational modes (in the 1 cm^{−1} range) are extremely difficult to observe using spontaneous Raman spectroscopy. These results stress the importance of time-resolved studies of acoustic vibrational modes as a new and powerful tool for unambiguous determination of the structure of synthesized nanoobjects via their specific acoustic properties.

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