Ultrasonics xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Ultrasonics

journal homepage: www.elsevier.com/locate/ultras

Time-domain investigation of the acoustic vibrations of metal nanoparticles: Size and encapsulation effects ☆

Aurélien Crut *, Paolo Maioli, Natalia Del Fatti, Fabrice Vallée

FemtoNanoOptics Group, Institut Lumière Matière UMR5306, Université Lyon 1-CNRS, 69622 Villeurbanne, France

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Ultrafast spectroscopy
Metal nanoparticles
Acoustic vibrations
Pump–probe
THz domain

ABSTRACT

The acoustic vibrations of single-metal and multi-material nanoparticles are studied by ultrafast pump–probe optical spectroscopy and described in the context of the continuous elastic model. The applicability of this model to the small size range, down to one nanometer, is discussed in the light of recent experimental data and *ab initio* calculations. Investigations of multi-material nano-objects stress the impact of the intra-particle interface on the characteristics of their vibrational modes, also yielding information on the composition and spatial distribution of the constituting materials.

1. Introduction

Nano-objects exhibit discrete vibrational modes, whose spectral characteristics are imposed by the size, morphology and composition of the objects (macroscopic-like description), or equivalently by the number, nature and spatial organization of the atoms they are formed of (molecular-like image). The connection of these two descriptions has raised fundamental questions about the applicability limit of the continuous models and elasticity laws when reducing the size of an object down to the nanoscale range [1–5]. Size reduction also translates in increase of the vibrational mode frequencies, offering the possibility to create high-frequency nanoresonators operating in the THz domain, with potential applications such as high-precision nanobalances [6,7]. Moreover, acoustic vibrations of nano-objects can be exploited for their nanocharacterization, as measurement of the mode characteristics (frequency and damping) provides information on parameters such as their morphology, i.e., size [5,8–12], shape [13–17], crystalline structure [2,13,16,18], and their mechanical contact with the surrounding material [19,20] or (for multicomponent objects, such as core–shell ones) between different constituting materials [21–27].

Optical methods are powerful tools to study the vibrational response of nano-objects in optically transparent media. They offer the key advantage of being noncontact, in contrast with nanomanipulation methods whose analysis requires to take into account interactions between the nano-object and the local probe [28–30], and permit the addressing of embedded nano-objects. In this context, spectrally and temporally resolved optical techniques are complementary, as they usually lead to dominant responses from different vibrational modes [16,26,31,32], and are best adapted to different size regimes [33]. Spectrally resolved methods are most frequently based on inelastic scattering (i.e., Raman [8,34–36] and Brillouin [37,38] spectroscopies) or, as recently demonstrated, far-infrared absorption (i.e., THz spectroscopy [33,39]) by the object vibrational modes. Time-resolved methods use impulsive excitation and time-domain detection of the acoustic vibration in a pump–probe scheme. This approach, first developed in Maris's group to study acoustic wave propagation in thin films [40,41], was further extended to investigate acoustic vibrations of ensembles of nano-objects, i.e. semiconductor and metal nanoparticles [9–11,42]. This method has been extensively used to investigate the size and shape dependencies of the frequency of the acoustic vibrations of nanoparticles [11,13,43,44], as well as their environment-dependent damping in samples with small dispersions in size and shape [11,17,20]. Their high sensitivity has been exploited to extend them to single-particle studies, yielding information on the vibrational damping processes of deposited [4,45–49], optically trapped [50] or suspended [51] metal nanoparticles, free from spurious inhomogeneous effects which affect ensemble experiments [11].

In this paper, we describe time-resolved investigations of the vibrational modes of single-material or multi-material nanoparticles with spherical or elongated geometries. Modeling of their characteristics (frequency, damping rate and excitation amplitude)

☆ Paper for the special issue "Ultrafast acoustics: probing matter down to nanometers scale and up to terahertz frequencies".

* Corresponding author. Tel.: +33 472448182.
E-mail address: aurelien.crut@univ-lyon1.fr (A. Crut).

http://dx.doi.org/10.1016/j.ultras.2014.02.013
0041-624X/

is discussed, and compared to experimental results, focusing on the effect of size on the measured breathing mode frequencies. Extension to the vibrations of bimetallic and metal-dielectric core–shell nano-objects shows the impact of the mechanical contact at the core–shell interface and of the material spatial distribution within one particle on the observed vibrational modes of bicomponent nano-objects.

2. Time-resolved pump–probe experiments

In optical time-resolved pump–probe experiments, energy is deposited into nanoparticles by a "pump" light pulse and their ultrafast response is monitored by measuring the pump-induced reflection or transmission changes of a time-delayed "probe" pulse. The 2-color pump–probe setup used in our experiments is sketched in Fig. 1. It is based on a Ti-sapphire laser source, either a home-made oscillator delivering 20 fs near-infrared pulses at a repetition rate of 76 MHz, or an amplified system producing 150 fs pulses at 250 kHz. The output pulse train is split into two parts, one being frequency converted, either by frequency-doubling in a BBO crystal (as illustrated in Fig. 1) or by generation of a white light quasi-continuum and optical parametric amplification of part of it. The two beams are independently focused on the sample using two different lenses and used as the pump and probe pulse trains. The time delay between the pump and probe pulses is varied using a mechanical delay stage (or, alternatively, by asynchronous optical sampling (ASOPS) [52,53]). High sensitivity detection of the time-dependent relative change $\Delta T/T$ of the sample probe-beam transmission is achieved using a temporal modulation approach, involving mechanical chopping of the pump beam at ≈60 kHz and lock-in detection of the induced probe beam transmission change. A similar scheme is used for studying the ultrafast response of a single metal nano-object [54–56], after its initial detection using spatial modulation spectroscopy technique [57–60].

Pump absorption by metal nanoparticles initially generates non-thermal electronic distributions [12]. Internal nanoparticle thermalization occurs by electron–electron (on a few hundred fs timescale for noble metals [12,61]) and electron–phonon (on a typically one ps timescale [4,62]) scattering processes. Both electron and ionic lattice heating launch acoustic vibration of the excited nanoparticles *via* the two mechanisms responsible for lattice dilation upon heating, i.e., hot electron pressure and lattice anharmonicity, respectively [11,19,63]. Acoustic modes whose associated displacement most closely matches particle dilation are thus excited (see below). They are subsequently damped by mechanical energy dissipation in the particle environment [11,20,64], with possible contribution from internal or defect-related mechanisms [17,50,51]. The final temporal step in relaxation of an excited nanoparticle is its global cooling, i.e., release of its excess heat energy to its environment [26,65,66]. Both vibrational damping and cooling kinetics are connected to particle-environment energy transfers, and thus strongly depend on nano-object size and environment, with for instance typical timescales of 10 and 100 ps, respectively, for 20 nm diameter glass-embedded silver nanospheres [3,11].

All the processes mentioned above affect the material optical response, and thus the observed probe transmission (Fig. 2). In the case of metal nanoparticles, measurements are usually performed using a probe wavelength close to the particle surface plasmon resonance to enhance the signal sensitivity [11,67]. The acoustic vibrations of a nano-object (inducing shape and/or volume changes) modify the interatomic distances, and consequently its dielectric function, reflecting into oscillations in time-resolved signals. Their period directly reflects that of the dominantly excited and detected modes, while their damping contains information on the mode damping rates [11]. This is illustrated in Fig. 2a showing the time-dependent transmission change $\Delta T/T$ measured in an ensemble of 26 nm diameter glass-embedded silver nanospheres. The signal is accurately reproduced by the sum of two decaying exponentials and two damped sinusoidal functions. The two first contributions describe fast electron cooling dynamics after excitation by the pump pulse, due to energy transfer to the lattice (with a 850 fs characteristic time) [4,12,62], and slow nanoparticle heat transfer to the embedding glass matrix (with a characteristic time of about 150 ps), respectively. At intermediate timescales (<30 ps), the signal presents marked oscillations, which result from the coherent vibrations of nanoparticles. The oscillating part of the signal (deduced from the bare one by subtraction of the exponential contributions due to electron-lattice and nanoparticle-environment energy transfer) is dominated by a damped oscillation with 8 ps period, and a smaller second oscillation mode with approximately half period, which are reproduced by two damped sinusoi-

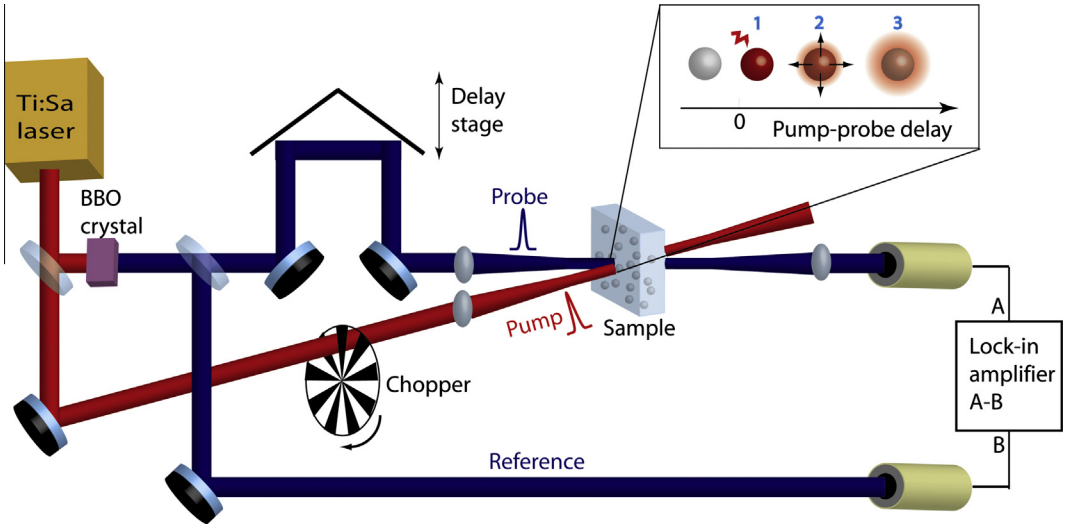

Fig. 1. Schematic view of a high-sensitivity optical pump–probe setup. Metal nanoparticles are excited by a femtosecond pump pulse. The different steps of their ultrafast response (internal thermalization (1), acoustic vibrations (2) and cooling (3)) are monitored through the measurement of probe pulse transmission changes, $\Delta T/T$, as a function of pump–probe delay (mechanical delay stage). High sensitivity, $(\Delta T/T)_{min} \sim 10^{-6}$, is achieved by mechanical modulation (chopper) and differential synchronous detection (lock-in).

Please cite this article in press as: A. Crut et al., Time-domain investigation of the acoustic vibrations of metal nanoparticles: Size and encapsulation effects, Ultrasonics (2014), http://dx.doi.org/10.1016/j.ultras.2014.02.013