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## Nonlinear optical studies of single gold nanoparticles

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# Preface

This thesis reflects the results of four years of research in the MoNOS group at Leiden University on the development of new techniques for the detection of single gold nanoparticles, in particular by using a pulsed laser system to excite the particles. Gold nanoparticles are spherical clusters of gold atoms with diameters typically between 1 and 100 nm. Initially, our goal was to develop a method to detect the smallest possible particles, that could be used in biophysical experiments. Gold particles are useful labels for these experiments, since they do not suffer from photoblinking and photobleaching, as molecules and nanocrystals do. Therefore, unlimited observation times come within reach, which is of great importance for experiments in which the biological system is tracked for a long period. For a tracking experiment it is essential that the label has no influence on the mobility of the system to which it is attached. Therefore, for a method for detection of gold nanoparticles to be useful in biophysical applications, it has to enable detection of very small particles, preferably with diameters below 5 nm, with a high signal-to-noise ratio.

Pulsed lasers emit their light not continuously, but periodically in very short bursts. By concentrating the light in these short bursts, the peak powers become much higher. As an example, the laser system that I used emitted one pulse of 100 fs every 13 ns. In other words, all photons that would have been emitted in 13 ns are now emitted in 100 fs, which leads to an enhancement of the peak power by a factor of more than  $10^5$ . These high peak powers have opened windows towards new physical effects, such as frequency mixing. Two photons can form one new photon with a frequency that is the sum or the difference of the two old photons. A special case is second-harmonic generation (SHG), in which the two original photons have the same energy, as a result of which the frequency of the new photon is twice as high. These processes are of course not limited to two photons. One step beyond SHG is third-harmonic generation (THG), in which three photons form a new photon

of three times the frequency of the source.

Besides the benefit of high peak powers, pulsed lasers also allow for studying the time evolution of processes on extremely short time scales, in which the time resolution is limited only by the length of the pulse. The technique that is most common to study the dynamics of systems at this very short time scale is called pump-probe spectroscopy. In pump-probe spectroscopy, changes of a system can be measured on a time scale on the order of the pulse length. Two pulses, a pump pulse and a probe pulse, arrive at the sample with a tunable mutual delay that can be tuned simply by changing the optical path length of one of the beams, for example by translating a mirror. The pump pulse induces a perturbation of the system, and the probe measures the effect of this perturbation at variable time intervals, thereby mapping the complete time evolution of the induced perturbation. By modulating the intensity of the pump and demodulating the detected signal with a lock-in amplifier, only the difference in response between the perturbed and unperturbed state is measured, while much of the noise is subtracted away, which largely enhances the signal-to-noise ratio.

We have used both benefits of short pulses, the high peak powers and the high time resolution, to explore new methods for detection of single gold nanoparticles. The first method we have developed was the detection of third-harmonic generation of single gold nanoparticles. In this experiment, a gold particle was excited by an infra-red laser pulse. New frequencies were generated inside the particle, with values twice (second-harmonic generation) and three times (third-harmonic generation) the frequency of the source. For spherically symmetric particles, the second harmonic is forbidden, therefore we aimed to detect the third harmonic. The method worked and we have successfully detected single particles. Additionally, we have detected a size dependence that deviates from earlier assumptions. Nevertheless, the method was not sensitive enough to detect the really small particles that we were after, and we decided to try a different method. In chapter 2, the method and results of the THG experiment are presented in detail.

We proceeded with a new experiment, no longer dwelling on generation of new wavelengths in the particle, as in the THG experiment, but instead we tried to detect the absorption of light by a single particle. We have developed a common-path interferometer, in which the probe and reference waves are not separated in space, as for example in a Michelson interferometer, but in time. Splitting and recombination of probe and reference waves was done in a birefringent crystal in which the spatial overlap is guaranteed, which made alignment of the interferometer much easier. The interferometer was

combined with a pump-probe spectroscopy setup (described above). A full description and characterization of the pump-probe interferometer is given in chapter 3. The idea for this experiment was to detect the changes in absorption of a probe pulse in the first picosecond after excitation with a pump pulse. The very large and short-lived increase in electron temperature was expected to induce large changes in the absorption spectrum of the particle, and together with the size dependence of the absorption signal, which decreases much slower for small particles than more conventional methods as scattering, we hoped that this method would enable the detection of very small gold particles.

Unfortunately, most probably due to saturation of the absorption signal, it turned out that the method was limited to detection of particles larger than 10 nm. During the experiments, we observed a peculiar oscillation in our signals, which appeared to be acoustic vibrations of single gold nanoparticles, a periodic expansion of the lattice of the particle, caused by the sudden increase in electron and lattice temperature after excitation with a short pulse. These vibrations had been detected in large ensembles already, but never before on single particles. There appeared to be a lot of interesting physics in the acoustic oscillations, and eventually, these vibrations have filled a majority of the pages in this thesis. In chapter 4 and chapter 5, the results of the vibration experiments are described. In these chapters, I present a careful characterization of the signals that we have detected in the pump-probe experiments. Proof of detection of single particles is given, a probe-wavelength analysis is demonstrated and we have studied homogeneous damping times. An ensemble measurement of acoustic vibration detects the average vibration of many particles that all vibrate at a slightly different frequency, since their sizes differ (generally the size dispersion is in the order of 5%). This effect, which reduces the damping time of the ensemble vibration due to dephasing, is called inhomogeneous broadening and is obviously absent in single-particle measurements. Only by detecting single particles it is therefore possible to detect the homogeneous damping time of the particles.

Most of the vibrations we have detected were a plainly radial expansion and contraction of the particle, called the breathing mode. A fraction of the particles however, showed an additional vibration mode, associated with ellipsoidal deformation, which had so far never been detected in pump-probe experiments. For a long time, we were puzzled why only a small fraction of our particles showed a very strong sign of this mode. The very last experiments I did could shed light on the origin of this mode, and an explanation is given in chapter 5.

## *Preface*

The physics behind metal nanoparticles is addressed in chapter 1. Their optical and spectral properties, as well as the response of a metal nanoparticle to excitation with a short laser pulse are explained. Also, this chapter contains an overview of the field of single-particle detection (including experiments that *did* succeed in the detection of particles with a size useful for biologists).