

Invited paper

Time-resolved 2-photon photoionization on metallic nanoparticles

 M. Fierz¹, K. Siegmann¹, M. Scharfe², M. Aeschlimann²
¹Laboratory for Combustion Aerosols and Suspended Particles, ETH Zürich, Switzerland
 (Fax: +41-01/633-1080, E-mail: fierz@solid.phys.ethz.ch)

²Institute for Laser and Plasma Physics, University of Essen, Germany
 (Fax: +49-202/183-2120, E-mail: ma@ILP.Physik.Uni-Essen.DE)

Received: 16 October 1998/Revised version: 11 December 1998

Abstract. A new method for investigating the electron dynamics of free metallic nanoparticles suspended in a carrier gas is described. Monodisperse nanoparticles in the size range from 10 to 80 nm pass through a photoionization tube, where they are irradiated by a pump and a probe fs laser pulse. The nonlinear effect caused by the two photon photoionization process allows to study the inelastic lifetime of optically excited electrons in the intermediate state in the time domain by means of a crosscorrelation experiment.

PACS: 78.47.+p; 71.24.+q; 72.15.Lh

Excitation and relaxation of electrons in solids play a key role in a number of important physical phenomena including the interaction of molecules with surfaces. Relaxation of optically excited electrons in solids is caused by different mechanisms, such as electron–plasmon, electron–electron and electron–phonon scattering. In the case of metals without the unoccupied orbitals being restricted by a band gap, the hot electrons relax directly to a thermal equilibrium with the whole electron gas. Therefore, the lifetime of single excited electronic states is always short, typically of the order of only a few femtoseconds. Detailed studies of relaxation phenomena in the time domain began just half a decade ago [1, 2]. For optically excited electrons with excitation energies $\gg kT$ and at low carrier densities, the dominant relaxation process is inelastic scattering of the excited electrons with electrons at and just below the Fermi level, leaving both electrons in previously unoccupied states above the Fermi level. The standard theory of $e-e$ scattering is based on Landau's theory of Fermi liquids [3]. In the free electron approximation the probability of $e-e$ scattering depends on the available phase space (i.e. on the density of states (DOS) around E_F) and the interaction between the electrons, which can be described by a screened Coulomb potential [4].

When the dimensionality of the metallic system is reduced, both parameters, the DOS around E_F and the screening length, will change considerably, resulting in a different energy dependence of the scattering rate. Therefore, the dynamics of hot electrons in metallic particles is assumed to strongly depend on particle size and shape [5]; for instance, an increased lifetime is expected compared to the metallic bulk value, which is caused by the reduced phase space for

electron–electron scattering [6, 7]. This could be one of the reasons for the observed huge yield enhancement in photoemission in metallic nanoparticles [8] and their high catalytic activity. To our knowledge, unfortunately, no theoretical calculation has yet been published dealing with the scattering rate of optically excited electrons in nanoparticles, where the electronic system is confined in all three dimensions.

Nearly all experimental studies on optically excited metallic nanoparticles carried out so far have been concentrated on the investigation of the surface plasmon (SP) resonance, which is a collective electron–plasma oscillation [9, 10]. In contrast to a flat metal surface, surface polarization in nanoparticles causes elastic repulsion forces which create the condition required for resonance behavior. Extensive studies have been made on the dephasing and decay mechanisms of the SP [5, 11].

However, little is known about the inelastic lifetime τ_{e-e} of a single excited electron in a nanoparticle (not the decay of a surface plasmon into a single electron–hole excitation). A standard technique for studying τ_{e-e} is time-resolved two-photon photoemission (TR-2PPE). The conventional method for investigating the electron dynamics of metallic nanoparticles is either to deposit the particles first on a substrate or to use nanolithographically designed particles out of a thin metallic film on top of a dielectric or conductive substrate [5, 11]. The observed inelastic lifetime τ_{e-e} in a TR-2PPE experiment would be strongly disturbed by substrate electrons and, in the case of a conductive substrate, by unknown particle–matrix interactions.

We investigated the electron dynamics of entirely free metallic nanoparticles suspended in a carrier gas at atmospheric pressure by means of time-resolved two-photon photoionization (TR-2PPI). Monodisperse nanoparticles in the size range from 10 to 80 nm pass through a photoionization tube, where they are irradiated by a pump and a probe fs laser pulse.

The pump pulse generates electron–hole pairs in the particle; the photon energy is chosen to be lower than the work function, so that no electrons are emitted. During the lifetime of the excitation, a second photon from the probe laser pulse can be absorbed. The excited electron can be photoemitted and, hence, the particles become ionized. The high carrier gas pressure does not allow any energy analysis of the photoelectrons, but it still permits us to count the number of ionized

particles as a function of the time delay between the pump and probe laser pulses.

1 Experiment

Combined with ultrafast laser techniques, time-resolved 2PPI can monitor the decay of the population of the intermediate states E_i in time domain. This is made possible by means of a pump-probe experiment: the first laser pulse ($h\nu_1$) pumps electrons into the intermediate state E_i , followed by a second laser pulse ($h\nu_2$) which subsequently photoemits the excited electrons (see Fig. 1a). By varying the time delay between the two pulses, the lifetime of the intermediate (normally unoccupied) states can be probed.

In contrast to the TR-2PPE method, which enables the kinetic energy of the photoexcited electron to be determined, the TR-2PPI process does not allow an exact determination of the intermediate state energy E_i . The extracted relaxation time is an average of the population decay times of all excited intermediate states, from where electrons can escape into the vacuum due to the probe laser pulse. The energy interval of possible intermediate states E_i is given by

$$\Phi - h\nu_2 < E_i < h\nu_1, \quad (1)$$

where Φ is the size-dependent work function of the nanoparticles and $h\nu_1$ and $h\nu_2$ the photon energy of the pump and probe laser pulse, respectively (see Fig. 1b). This energy range can be minimized by working in the two-color mode (pump pulse $h\nu_1$, probe pulse $h\nu_2$; $h\nu_1 \neq h\nu_2$) at the threshold limit ($h\nu_1 + h\nu_2 = \Phi$). By tuning $h\nu_1$ the inelastic lifetime of a single excited electronic state versus energy can be determined like in a normal TR-2PPE measurement. In this work, however, we will concentrate on the performance and potential of this novel method and present first data of Au and Pd nanoparticles obtained in the monochromatic mode ($h\nu_1 = h\nu_2$). The two metals have about the same work function, which allows a comparison of the obtained averaged relaxation times.

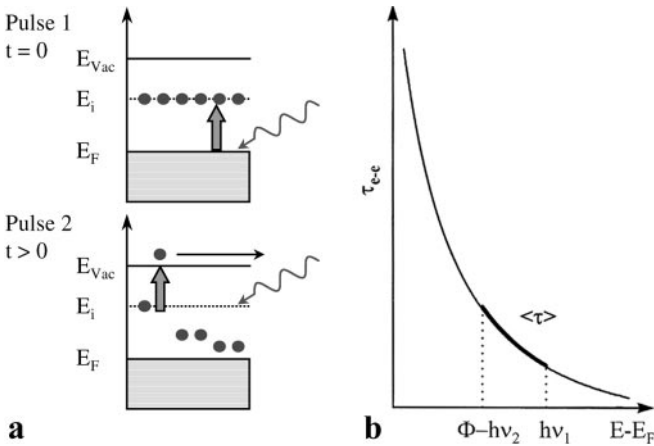


Fig. 1. **a** A schematic figure of the two-photon process, where Φ is the work function for the sample, E_i is the intermediate state, E_{vac} is the vacuum level and E_F is the Fermi level. **b** Lifetime τ_{e-e} of the intermediate state versus energy plus the energy interval of possible intermediate states E_i from where electrons can escape into the vacuum due to the probe laser pulse

Our initial investigations have shown that the signal-to-background ratio can be substantially increased by first charging all particles with one excess electron and photoemitting the excess electron by a 2PPI process. In this case, the 2PPI-excited particles become electrically neutral. The gas with the suspended particles is guided through an electrofilter where the few uncharged particles can be separated and counted. If we were to start with neutral particles and measure the accumulated charge of the ionized particles, a much higher laser intensity would be needed to get enough ionized particles for a current measurement. Taking into account that a nanoparticle already contains thousands of atoms, we do not expect a noticeable change of the band structure caused by the excess electron.

A schematic overview of the experimental set-up is shown in Fig. 2. Metallic nanoparticles are produced through condensation of a metal vapor. For gold, the vapor is produced through an electrical discharge between two gold electrodes. The heat generated by the spark vaporizes some material from the electrode. Palladium vapor is produced by heating a palladium wire. A carrier gas (nitrogen 5.0) at atmospheric pressure flows through the production unit and carries the particles through the experiment; the settling velocity of a nanoparticle under the influence of gravitation is negligible so the particles remain suspended in the carrier gas. The metal vapor cools rapidly in the carrier gas and condenses to particles and agglomerates in the size range 10–100 nm. Most of the particles will be electrically charged after production. In a diffusion charger the charge distribution on the particles is brought to an equilibrium: a radioactive source produces ionized gas molecules which attach to the charged particles. The result is that nearly all particles smaller than 100 nm are either neutral or receive a single negative or a single positive charge.

The particle size is selected in a differential mobility analyzer (DMA) [12], a device in which charged particles are attracted by a high voltage. The drag force acting on a par-

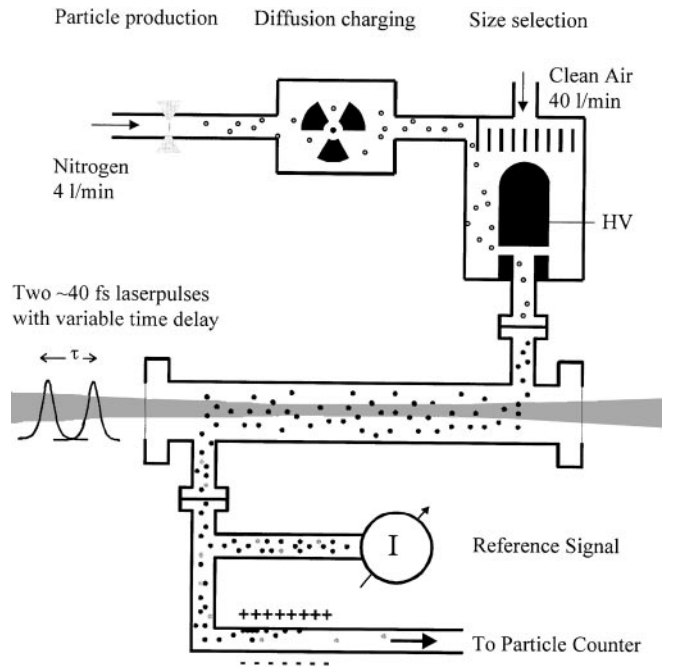


Fig. 2. A schematic overview of the experimental set-up

ticle in a gas is proportional to the particle diameter. Particles with a small diameter move faster in the electric field than particles of a large diameter as long as both carry the same charge. By varying the voltage one can select the particle size. Only the particles in the selected size range can exit the DMA through a narrow slit. Using a positive voltage in the DMA we select particles with one excess negative charge. Thereafter, the monodisperse negatively charged particles pass through the photoionization tube, where some of them are neutralized by the 2PPI process. The gas carrying the particles is passed through an electrostatic precipitator in which all charged particles are deposited. The remaining neutral particles are counted with a condensation nucleus counter (CNC), which is an optical single-particle counter. Submicron particles act as condensation nuclei in a saturated 1-butanol vapor. They grow through butanol condensation and can be counted optically by light scattering. We also monitor the output of the particle source with an electrometer in order to correct for fluctuations in the particle number.

The TR-2PPI experiments are performed with a femtosecond mode-locked Ti:sapphire laser, pumped by about 10 W from a cw Ar⁺ laser (see Fig. 3). The system delivers transform-limited and sech² temporal shaped pulses with up to 10 nJ/pulse and a duration of 40–50 fs at a repetition rate of 82 MHz. The linearly polarized output of the Ti:sapphire laser is frequency doubled in a 0.2-mm-thick beta-barium borate (BBO) crystal to produce UV pulses at $h\nu = 3.1$ eV. The UV beam is sent through a pair of fused silica prisms to pre-compensate for pulse broadening due to dispersive elements like lenses, beamsplitters and the photoionization tube window in the optical path. The pulses are divided by a beamsplitter into equal intensity (pump and probe) pulses, and one path is delayed with respect to the other by a computer-controlled delay stage. Both beams are combined collinearly and crosspolarized by a second beamsplitter and focused into the photoionization tube. The tube length is about 30 cm. We use laser pulses at low fluence and peak power to avoid space charge effects and highly excited electron distributions. Therefore, we measure the relaxation of single excited electronic states rather than the collective behavior of a transiently heated nonequilibrium electron gas.

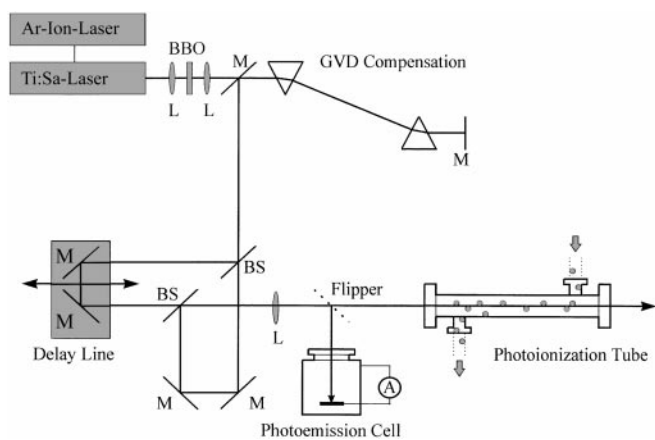


Fig. 3. Schematic diagram of the equal pulse correlation set-up for time-resolved 2PPI using ultrashort pump and probe laser pulses

2 Data analysis

The pump–probe experiments are carried out by monitoring the number of neutral nanoparticles as a function of the delay between pump and probe pulses (two-pulse correlation experiment). Raw data from scans obtained for Au and Pd nanoparticles (size 70 nm) are shown in Fig. 4. Actually we measure a background (see left and right sides of Fig. 4), that originates from neutral particles which lost their excess electron by two photons from the same laser pulse. The nonlinear character of the two-photon photoionization (2PPI is a second-order process) leads to an increase in the 2PPI yield when the pulses are spatially and temporally superimposed, as seen by $\Delta t = 0$ in Fig. 4. As long as the two laser pulses temporally overlap it is obvious that an electron can be emitted by absorbing one photon from each pulse. When the pulses are temporally separated, an excited electron from the first pulse is still able to absorb a photon from the second pulse as long as the inelastic lifetime of the intermediate state exceeds the delay.

In the experiment, the signal is affected by the finite pulse width of the laser pulse. Therefore, two-pulse correlation data are the result of a convolution of the actual signal (decay function) with the pump and probe pulse. The most plausible and straightforward method for comparing experimentally determined electron relaxation phenomena with theoretical hypotheses would be to compare experimental dynamic traces with simulated relaxation curves. This method is known as reconvolution and is in fact the inverse of deconvolution; by supposing a simplified mechanism prior to the numerical evaluation, calculated (convolved) points can be constructed. The sum of the squared differences from the measured points can then be minimized to obtain least-squares estimates for the dynamic parameters that are contained in the assumed mechanism. However, one should be careful in interpreting the experimental traces; the most simple mechanism (e.g. a monoexponential decay), which is convenient for describing the convoluted 2PPI traces in detail, is not necessarily the correct one. For some traces one can easily obtain a nearly perfect fit to the convoluted traces with an oversimplified mechanism. This also means that, unless independently obtained evidence would support a particular

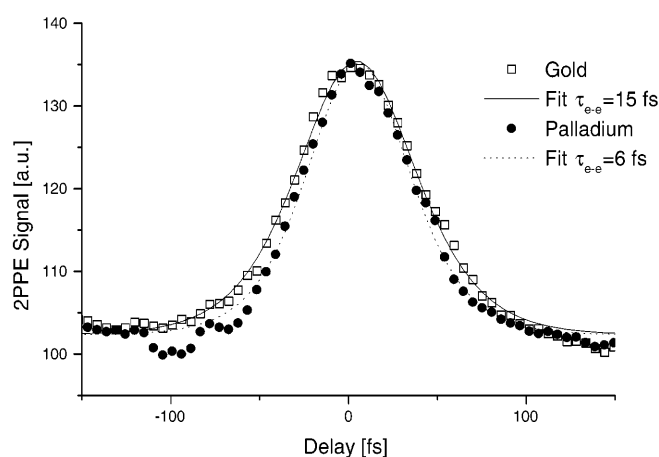


Fig. 4. 2PPI crosscorrelation traces obtained from Au and Pd nanoparticles. The *dashed lines* represent a fit to a sech² function with full width at half maximum (FWHM) of 78 fs and 68 fs

mechanism, parameters estimated from pump–probe results are to be regarded only within the framework of that particular mechanism. They are, however, a fingerprint of the fast and complicated electron relaxation process in metallic nanoparticles. For our reconvolution, a rate equation model has been used for the population of the intermediate state. This model is equivalent to the Bloch equations for a three-level system in the limit of rapid dephasing [13]. In this case, the evolution of the transient population $N(t)$ of the intermediate level is given by $dN(t)/dt = A(t) - N(t)/\tau_{e-e}$, where $A(t)$ is the excitation induced by the first (pump) laser pulse.

A further difficulty is finding the laser intensity cross-correlation curve $I_p(t) \otimes I_s(t)$ in the photoionization tube (underlying instrument-response function), because it is not possible to autocorrelate the frequency-doubled output of the laser system (390 nm) with a doubling crystal (BBO) to determine its full width at half maximum (FWHM). Instead, we crosscorrelate the output of the laser system by means of the nonlinear 2PPE process on a transition metal surface. In transition metals with a large number of unoccupied d orbitals, the inelastic lifetime τ_{e-e} is shorter than 2 fs at higher excitation energies ($E - E_F > 3$ eV, [14]). At those energies, electrons relax faster than can be observed within our time resolution. Hence, the FWHM of the two pulse correlation signals decreases to a nearly constant value at higher energies, and this value is (within < 2 fs) consistent with the electric field cross-correlation curve of the laser pulse. In fact this method is equivalent to second harmonic generation (SHG) in a thin nonlinear crystal, where we also do not expect pulse broadening caused by the SHG process within our time resolution.

We built a small photoemission cell to determine the underlying instrument-response function (see Fig. 4). Its entrance window is identical to that of the photoionization tube in order to create the same dispersion in the laser pulse duration. The transition metal photocathode is positively biased in order to avoid photoemission of electrons at lower intermediate state energies ($E - E_F < 3$ eV), which would broaden the instrument-response function. This set-up also allows us to optimize the pulse length in the photoionization tube with a pair of fused silica prisms which pre-compensate for pulse broadening due to dispersive elements in the beam path like lenses, beamsplitters and the tube entrance window.

Figure 4 shows how a time resolution of only a few fs can be obtained by using the equal pulse crosscorrelation technique. In spite of the fact that the FWHM of the crosscorrelation curve is about 65 fs (FWHM of the laser pulse is 46 fs), we are able to determine a change of only one or two fs in the FWHM, as long as the laser pulse width averaged over 10^8 pulses is sufficiently stable. With our set-up the correlation trace FWHM is stable within ~ 2 fs on a time scale of a few hours. Therefore, the relative uncertainty in determining the lifetime is less than a few fs for lower values ($\tau_{e-e} < 30$ fs). The absolute error, however, is estimated to be around 10 fs, because of the uncertainty in determining the laser intensity crosscorrelation curve and the work function of the metallic nanoparticles and the uncertainty related to the chosen simplified read-out model.

3 Results and discussion

The reconvolution using a rate equation model for the population of the intermediate state to fit the traces of Fig. 4 results in a mean lifetime $\langle \tau_{e-e} \rangle = 6$ fs and 15 fs for Pd and Au nanoparticles, respectively. Taking into account that the work functions of both metallic nanoparticles are nearly equivalent (5.0 ± 0.2 eV), the average lifetime of a single excited electron in a Au nanoparticle is roughly twice that of a Pd nanoparticle in the probed energy range (2.3 eV $< E - E_F < 3.1$ eV).

Gold has a much lower DOS around the Fermi energy than palladium does. A higher density of occupied and unoccupied states near the Fermi level is expected to lead to faster relaxation and hence to a shorter inelastic lifetime of excited electronic states. This prediction has been confirmed by TR-2PPE measurements on bulk states of transition metals [14]. The experimental values for transition metals are about a factor 10 smaller than those of noble metals.

4 Summary and conclusions

The present work shows that the time-resolved two-photon photoionization based on the equal pulse correlation technique can be used to investigate the relaxation processes of single excited electrons in free monodisperse metallic nanoparticles. The performance of the technique shown on Au and Pd nanoparticles is sufficient for obtaining a time resolution of only a few fs. This is necessary to study the dynamics in metallic systems, where the hot electrons relax directly to a thermal equilibrium with the whole electron gas. Better results would be possible by using a tunable light source (OPA), which allows us to work in the two-color mode and at the threshold limit and thus to probe a more restricted energy range.

Acknowledgements. We would like to thank L. Scherrer and P. Cohn for technical support and H.C. Siegmann for many stimulating discussions.

References

1. W.S. Fann, R. Storz, H.W. Tom, J. Bokor: *Phys. Rev. B* **46**, 13592 (1992)
2. C.A. Schmuttenmaer, M. Aeschlimann, H.E. Elsayed-Ali, R.J.D. Miller, D.A. Mantell, J. Cao, Y. Gao: *Phys. Rev. B* **50**, 8957 (1994)
3. N.W. Ashcroft, N.D. Mermin: *Solid State Physics* (Harcourt Brace, London 1976)
4. J.J. Quinn: *Phys. Rev.* **126**, 1453 (1962)
5. B. Lamprecht, A. Leitner, F.R. Aussenegg: *Appl. Phys. B* **64**, 269 (1997)
6. G. Giuliani, J.J. Quinn: *Phys. Rev. B* **26**, 4421 (1982)
7. M. Kaveh, N. Wiser: *Adv. Phys.* **33**, 257 (1984)
8. B. Schleicher, H. Burtscher, H.C. Siegmann: *Appl. Phys. Lett.* **63**, 1191 (1993)
9. C.F. Bohren, D.R. Huffman: *Absorption and Scattering of Light by Small Particles* (Wiley, New York 1983)
10. M. Born, E. Wolf: *Principles of Optics* (Pergamon, London 1959)
11. T. Klar, M. Perner, S. Grosse, G. von Plessen, W. Spirkel, J. Feldmann: *Phys. Rev. Lett.* **80**, 4249 (1998)
12. E.O. Knutson, K.T. Whitby: *J. Aerosol Sci.* **6**, 443 (1975)
13. E. Knösel, A. Hotzel, T. Hertel, M. Wolf, G. Ertl: *Surf. Sci.* **368**, 76 (1996)
14. M. Aeschlimann, M. Bauer, S. Pawlik: *Chem. Phys.* **205**, 127 (1996)